STUDIES OF YLIDES

Ross Wood Millar

A Thesis Submitted for the Degree of PhD
at the
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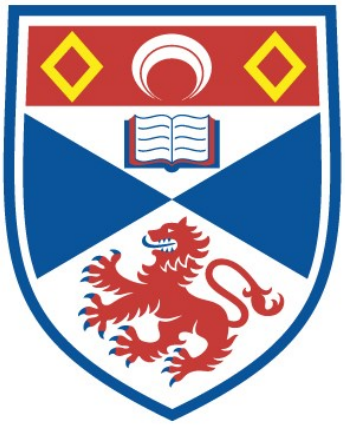

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STUDIES OF YLIDES

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ROSS WOOD MILLAR, B.Sc.

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ABSTRACT

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The preparation and attempted preparation of diaminomethylene-sulphuranes (thiouronium ylides) by various routes is described. The principal route chosen was by proton abstraction from the conjugate acid (thiouronium salt) using a suitable non-hydroxylic base, usually phenyl lithium or triethylamine. In the range of compounds examined where the carbanionic substituents contained electron withdrawing groups such as carbonyl, sulphonyl, nitrile and nitro groups, considerable difficulty was encountered in the preparation of the precursor salts. Of the few salts in this category that were obtainable, only one (disulphonyl substituted) gave rise to a stable ylide. On the other hand, many salts containing the cyclopentadiene ring gave rise to ylides. Some of these, notably the fluorenylides, could be isolated and characterised, while the properties of others could only be observed in solution and they decomposed or rearranged on attempted isolation. A second preparative route was briefly investigated, namely the thermal decomposition of 9-diazofluorene in the presence of arylthioureas, but in several cases this led to unexpected products.

Comparative studies of the reactivities of the fluorenylides towards carbonyl compounds and hydrolysis have been made, and some other reactions of these ylides are also described. The 2,3,4-triphenylcyclopentadienylides have been found to undergo novel cyclisation reactions with aldehydes and nitrosobenzene. A product from the former reaction was dehydrogenated to give a stable heterocycle with a 14 π electron periphery.

An attempt to prepare a selenium analogue of one of the thiouronium fluorenylides is described.

The attempted preparation of guanidinium fluorenylides by various methods is described, principally the 'salt' and 'diazo' methods.

The former method was more suitable for alkyl substituted guanidines, whereas the latter method was of benefit with aryl substituents. Proton abstraction from one of the alkylguanidinium salts gave rise to a product which showed some evidence for ylide character. On the other hand, the aryl substituted products appeared to show no ylide-like properties. A further point of interest arose in the diazo reaction, where the fluorene nucleus was shown to have substituted on the more sterically hindered position, which was verified later by synthesis.

DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is my own composition and has not previously been presented for a higher degree.

The work was carried out in the Department of Chemistry of the University of St. Andrews under the direction of Dr. D.M.G. Lloyd, B.Sc., D.Sc., F.R.I.C.

CERTIFICATE

I hereby certify that Mr. ROSS WOOD MILLAR, B.Sc., has spent eleven terms at research work under my supervision, has fulfilled the conditions of Resolution of the University Court 1967, no.1, and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews as an undergraduate in October 1968 and graduated B.Sc. with Second Class Honours (Division Two) in Chemistry in July 1972.

The research described in this thesis was carried out between October 1972 and August 1975, during which time I held a Research Studentship awarded by the University of St. Andrews.

ACKNOWLEDGEMENTS

I wish to thank Dr. Douglas Lloyd for providing this topic of research and for his advice and assistance throughout the last three years.

I am indebted to many members of the Chemistry Department for their cheerful help during the same period.

I am grateful to Mrs. Maureen Saunders, Mrs. Pat Cooper and others who have assisted in the production of this thesis.

Finally, I gratefully acknowledge a Research Studentship from the University of St. Andrews.

SUMMARY

The preparation and attempted preparation of diaminomethylene-sulphuranes (thiouronium ylides) by various routes is described. The principal route chosen was by proton abstraction from the conjugate acid (thiouronium salt) using a suitable non-hydroxylic base, usually phenyl lithium or triethylamine. In the range of compounds examined where the carbanionic substituents contained electron withdrawing groups such as carbonyl, sulphonyl, nitrile and nitro groups, considerable difficulty was encountered in the preparation of the precursor salts. Of the few salts in this category that were obtainable, only one (disulphonyl substituted) gave rise to a stable ylide. On the other hand, many salts containing the cyclopentadiene ring gave rise to ylides. Some of these, notably the fluorenylides, could be isolated and characterised, while the properties of others could only be observed in solution and they decomposed or rearranged on attempted isolation. A second preparative route was briefly investigated, namely the thermal decomposition of 9-diazofluorene in the presence of arylthioureas, but in several cases this led to unexpected products.

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CONTENTS

PART 3

EXPERIMENTAL

PUBLICATION

REFERENCES

APPENDIX

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

INTRODUCTION

1. YLIDES*

Ylides have been defined [1] as compounds in which a carbanionic centre is attached directly to a heteroatom that carries a high degree of positive charge, and can be represented by the general formula (1), although there may also be a contribution from a covalent structure (2).

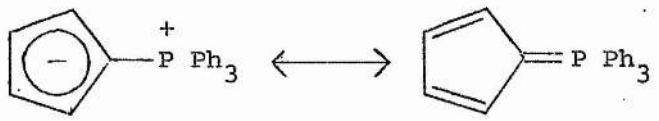
(1) (2)

The special feature of ylides that makes them worthy of study is the unique stabilisation of the potential carbanionic centre afforded by the adjacent heteronium group. Thus many ylides are isolable as crystalline solids whereas normal carbanions are very reactive towards atmospheric components. Ylides also have special chemical properties which are different from those of simple carbanions.

The fact that some ylides are sufficiently stable to be isolated has been attributed to the structural and electronic factors which may contribute to stabilisation of the ylidic carbanion. This stabilisation is thought to result from delocalisation of the non-bonded electrons of the carbanion, and is afforded by both the heteronium group (X) and the two carbanion substituents (R, R'). The nature and effects of these will be studied in turn.

* An alternative nomenclature has been developed whereby the term 'heteronium alkylides' which was formerly in use, is replaced by a name ending in 'ane', for instance triphenylphosphonium fluorenylide is renamed fluorenylidenetriphenylphosphorane. Likewise, sulphonium and arsonium ylides are renamed sulphuranes and arsenanes. Nitrogen ylides retain the old nomenclature.

The heteronium group (X) usually contains an atom belonging to groups V or VI of the Periodic Table, commonly nitrogen, phosphorus, arsenic or sulphur [1], although stable ylides have been prepared where the heteroatom is antimony [2], bismuth [3], selenium [4,5], tellurium [6] or iodine [7,8], and there is evidence for the transient existence of oxygen ylides [9]. The existence of a xenonium ylide has also been proposed [10]. In the case of elements of the second row (and below), stabilisation is generally believed to result from delocalisation of the non-bonded electrons on the carbanion into vacant low-lying orbitals of the heteroatom, in the case of phosphorus and sulphur the 3d orbitals. In this way the heteroatom can expand its valence shell to accommodate ten electrons, a phenomenon well known in phosphorus and sulphur chemistry, and this results in a contribution from the covalently bound canonical form (2). Thus ylides of elements of the second row (and below) can be regarded as resonance hybrids of the two canonical forms, (1) and (2), and the extent to which each of the canonical forms contributes to the resonance hybrid can be used to rationalise the observed physical and chemical properties. For instance, the dipole moment of 7.0 D for triphenylphosphoniumcyclopentadienylide

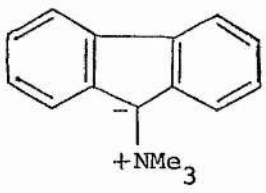


(3) (4)

(3) has been taken to show that the covalently bound canonical form (4) contributes approximately 50% to the resonance hybrid [11]. It should

be pointed out here that there are alternative descriptions to the one given above which do not invoke the use of d-orbitals, for instance the qualitative 3-centre-4-electron bonding theory as described by Musher [10], but discussion of these is beyond the scope of this thesis and for our purposes the use of d-orbitals, although not completely justified, provides a satisfactory basis for the experimental evidence.

In the case of the first row elements, valence shell expansion cannot occur because the 2d orbitals of nitrogen (and oxygen) are of too high an energy to interact with those of the carbanion, and stabilisation of the ylide, such as it is, is generally assumed to take place by electrostatic interaction of the opposite charges. That this gives rise to ylides of much lower stability compared to the phosphorus or sulphur analogues is demonstrated strikingly by a comparison of the pK_a's of the conjugate acids of two ylides in the fluorene series,



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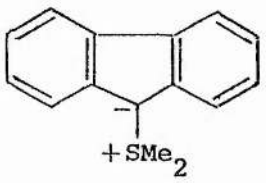

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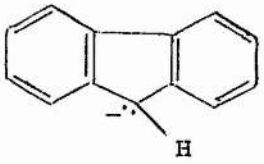
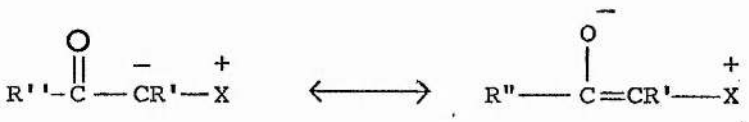


(7)

(5) and (6). The fluorenyl anion (7) can be formed from fluorene by treatment with a variety of bases such as butyllithium, and the pK_a of the conjugate acid, fluorene, is about 25[12]. By comparison, the conjugate acid of the nitrogen ylide (5)[13] has a pK_a only a little less than that of fluorene, showing that the inductive effect of the trimethylammonium group does not alter the stability

of the fluorenyl anion very much. In contrast, the pK_a of the conjugate acid of the sulphonium ylide (6) is 7.3[14]. This very low basicity of the ylide (6) reflects the ability of the dimethylsulphonium group to stabilise an adjacent carbanion by use of its vacant low-lying 3d orbitals, whereas the high basicity of the trimethylammonium ylide can be taken as strong evidence that this stabilisation is absent, which, as already stated, is because the 2d orbitals of the nitrogen are unable to interact with those of the carbanion. The nitrogen ylide (5) is also thermally much less stable than the sulphur ylide (6). Other types of nitrogen ylide of greater stability will be mentioned later.

The carbanion substituents R and R' also afford stabilisation by delocalisation of the electron pair on the carbanion and this can be achieved generally in two ways. First, attachment of electron withdrawing groups can afford stabilisation by inductive and/or conjugative effects. For instance the carbonyl group in ((1) R = R''CO) affords stabilisation by



(8)

a contribution from the enolate structure (8). Similar stabilisation results from use of cyano, sulphonyl or nitro groups, while groups with a purely inductive effect such as pentafluorophenyl are also of value. The second method entails the incorporation of the carbanion into an aromatic system such as the cyclopentadienide (9),

indenide or fluorenide

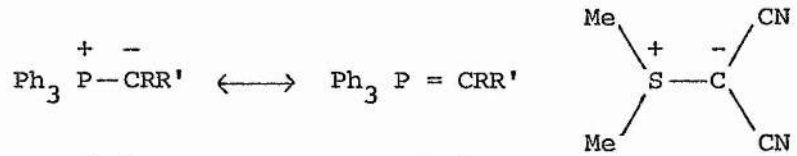
(9)

ring systems, which have stable sextets of Π electrons [15]. Stabilisation of ylides in this manner gives rise to a class of compounds with properties of non-benzenoid aromatic compounds, which will be described more fully later.

2. PHYSICAL PROPERTIES OF YLIDES

The structures of most of the ylides so far prepared have been determined on the basis of their chemical properties and also by physical means. Much important information about the nature of bonding in ylides, particularly the carbon to heteroatom bond, can be derived from an examination of the physical parameters. Those of principal importance include X-ray and dipole moment studies, and basicity (pK_a) measurements. Other techniques have also been used, such as ultra-violet and infra-red spectroscopy, nuclear magnetic resonance spectroscopy (both of ^{1}H and ^{13}C nuclei) and mass spectrometry. These will be mentioned in turn.

The bond lengths in several ylidenetriphenylphosphoranes (10) [16] and in one ylidenedimethylsulphurane (12) [17,18] have been



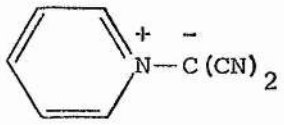
(10) (11)

(12)

reported. In the phosphorus ylides, the ylide carbon to phosphorus distance was found to lie in the range 1.66 to 1.74 Å, a distance intermediate between that expected for a fully covalent C = P bond of 1.66 Å, calculated [19] from the sum of double bond radii of carbon and phosphorus, and that expected for a C - P single bond of 1.85 Å, as found [20] in tertiary phosphines. This provides evidence for π bonding in the ylides. Interestingly, the compound methylene-triphenylphosphorane (R=R'=H) has the shortest ylide carbon to phosphorus bond length so far found in the ylidenetriphenylphosphorane series, and indicates an almost fully covalent C = P bond (structure (11)), consistent with the lack of stabilisation of dipolar forms (10). The overlap of a filled $2p_\pi$ orbital of the methylene carbon, which is believed to be sp^2 hybridised [16,21], with a vacant 3d orbital of the phosphorus is envisaged, and the value of the overlap integral has been shown [22] to be sufficient for formation of a $p_\pi - d_\pi$ bond. In compounds where stabilisation of the dipolar structure (10) is enhanced by attachment of electron-withdrawing groups (e.g. R=$SO_2C_6H_4Me$(p), R' =H; R=COPh, R' =Cl,I), the ylide carbon to phosphorus bond length is longer, showing increased contribution of the dipolar forms (10). This is consistent with other physical data. The ylide carbon to sulphur distance in the sulphurane (12) was found to be 1.73 Å, intermediate between the values known for C-S single bonds (1.81 Å) and those for C=S double bonds (1.55 Å), and similar considerations apply here.

In the case of the one nitrogen ylide on which X-ray measurements

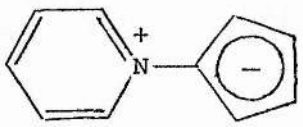
have been reported [23], namely



(13)

pyridinium dicyanomethylide (13), a different result would be expected owing to the inability of nitrogen to undergo valence shell expansion. This is indeed found, for the ylide carbon to nitrogen distance is 1.41 Å, which is only slightly shorter than the sum of the single bond radii [19] for carbon and nitrogen (1.47 Å) and much longer than the C=N double bond distance calculated in the same way (1.28 Å), including a Schomaker-Stevenson [24] correction. The slight shortening of the bond would appear to indicate a weak interaction between the carbanion and the pyridinium ring.

The dipolar nature of ylides is illustrated by dipole moment measurements, which for many ylides commonly lie in the range 5.0 to 7.0 D, but have been found to be as high as 13.5 D in the case of pyridinium cyclopentadienylide [25] (14), where extensive charge separation is

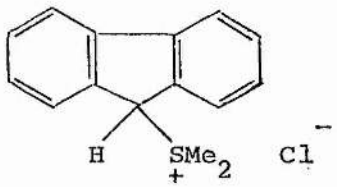


(14)

thought to occur. These values show that they are undoubtedly polar molecules. Dipole moment studies in the case where the heteroatoms belong to the second row (and below) have been used [26]

to assess the contribution made by dipolar forms, e.g. (4), (see sect. 1). These have been found to correlate quite well in most cases with other physical data, namely basicities, ultra-violet spectra, and ^{1}H nuclear magnetic resonance coupling constants.

The basicity of ylides is shown by the fact that many are soluble in dilute aqueous acid solution while they are commonly insoluble in water. The solubility is accounted for by formation of the conjugate acid e.g.

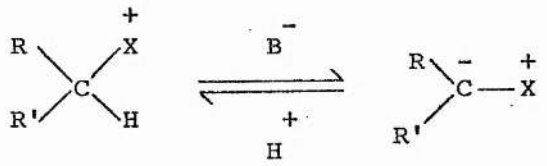


(15)

(15) in the case of fluorenylidenedimethylsulphurane (6) with dilute hydrochloric acid, and the reaction is the reverse of that used to prepare the ylide from its salt by basification. An initial indication of the basicity of a particular ylide can be obtained from the strength of the base required to generate the ylide from its conjugate acid (salt). For instance, in the case already quoted (see sect. 1), trimethylammoniumfluorenylide (5) requires a strong carbon base such as phenyl- or n-butyl-lithium, and hence is very basic ($pK_a \sim 25$), whereas fluorenylidenedimethylsulphurane (6) can be generated using aqueous ammonia and hence is very weakly basic (pK_a 7.3). The acid dissociation constants (pK_a values) have been measured accurately in many cases [27,28,29] using spectroscopic methods. The various

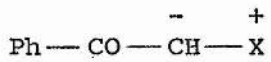
structural features affecting the basicity will now be briefly discussed.

As mentioned previously, stabilisation of the carbanionic carbon in a given ylide (1) is achieved in two main ways, either by orbital overlap with the heteroatom (X), or by attachment of groups (R, R') which can be electron withdrawing groups or form part of an aromatic system. The degree of acidity of the conjugate



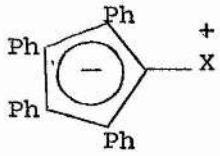
(16) (1)

acid (16) is believed to be primarily dependent on the degree of delocalisation of the carbanion electron pair in the resulting ylide (1). Thus highly stabilised ylides have a low pK_a and low basicity, while unstabilised ylides have a high pK_a and high basicity. Comparisons of the acidifying effects of various heteroatoms have been carried out in two series of ylides where the structures are identical except for alteration of the heteroatom, namely (17) [28] and (18) [29].



X = Ph_3P, Ph_3As, Ph_2S etc.

(17)



X = Ph_3P, Ph_3As, Ph_3Sb, (Ph_3Bi)
Ph_2S, Ph_2Se

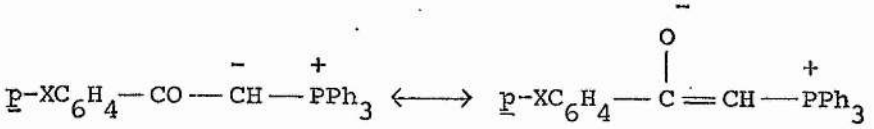
(18)

In each case the order of basicity of the ylides as established by pK_a measurements was found to be Sb > As > P >> Se ~ S. This is in agreement with the order established by other physical methods, notably dipole moment and ultra-violet spectroscopy (with the exception of antimony, where the ylide had an anomalously low dipole moment [26]). The low basicity of the sulphur ylides is attributed to highly effective $d_\pi - p_\pi$ overlap which can take place when the heteroatom is sulphur. This decreases progressively along the above series until the arsenic and antimony overlap is poor. This is believed to be due to the diffuse character and size of the d-orbitals, and in these cases the dipolar canonical form contributes more to the structure of the ylide. Arsenic ylides have considerably larger dipole moments than their phosphorus or sulphur counterparts.

The nature of the substituent groups on the heteroatom also has an important effect on the pK_a of the ylide. In the series (17) quoted above, the groups were phenyl but similar measurements were also made for X = Me_2S, Me_3P, Me_3As, MeSPh, Me_2PPh, Me_2AsPh, or Bu^n_3P, Bu^n_3As. In both cases a similar order is found with respect to change of heteroatom. On changing the substituent groups progressively from phenyl to methyl, a marked increase is found in the basicity of the ylide in each series. The dipole moment has also been found to increase on changing from triphenyl to tri-n-butyl phosphine in the fluorenylidenephosphoranes [30,31]. The explanation of these results follows from the proposal of Jaffe [32] and Craig [22,33] that π bonding with an atom carrying vacant d-orbitals is more efficient when the atom carries a positive charge. In the case

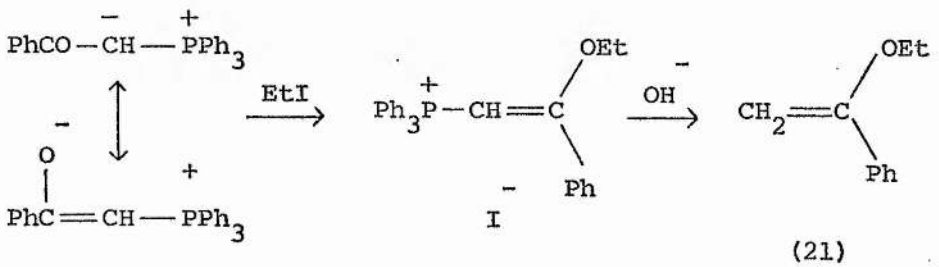
under study, bonding must be more effective between the filled 2p orbital of the carbanion and the 3d orbitals of the triphenylphosphonium group than it is with those of the trimethyl- or tri-n-butylphosphonium groups, as shown by the increased covalent character of the ylide bond in the former case. This implies, from the above proposal, that a lower electron density must be induced in the phosphorus atom by the phenyl substituents than by the methyl or n-butyl, and shows that the phenyl groups here are electron withdrawing in character. The electron withdrawing inductive effect of phenyl groups has been measured by Wepster [34] from an examination of the pK_a values for quinuclidine bases. In a series of fluorenylidene-tri(p-X-phenyl)phosphoranes, it was found [31] that where X was an electron withdrawing group the ylide was less basic than when X was hydrogen. These reports substantiate the foregoing account of the increased stability of arylphosphonium ylides over their alkyl counterparts, and presumably similar considerations apply to sulphur ylides.

The effect of carbanion substituents ((1), R, R') is somewhat simpler to evaluate. In the cases where stabilisation is not due to incorporation in an aromatic system, a study of the pK_a values of the conjugate acids of a series of acylated methylenetriphenylphosphoranes [35] (19) showed that the pK_a's of the salts lay in



(19) (20)

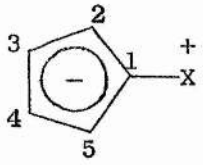
the order X = NO_2 < H < OMe, and consequently the nitro substituted ylide was the least basic. The electron withdrawing effects of a number of other groups have been examined [36] from the kinetic data of the ionisation rate constants for carbon acids, XCH_3 and X_2CH_2, and the strength of the electron withdrawing effect has been found to lie in the order X = NO_2 > CO > CN ≥ SO_2. Direct evidence for the delocalisation of charge in phenacyl ylides by enolate structures (e.g. 20) has come from an examination of the carbonyl absorption frequency in the infra-red spectrum, which is commonly found to lie in the region of 1500-1520 cm^{-1} (e.g. for $PhCO\bar{C}H\text{-}\overset{+}{P}Ph_3$) [37], but can lie as low as 1470-1505 cm^{-1} (for $PhCO\bar{C}H\text{-}\overset{+}{S}Me_2$) [38], whereas in the salt precursors the absorptions are in the 1700 cm^{-1} region. The increased single bond character of the ylide carbonyl group due to the canonical form (20) is illustrated by these data, and the delocalisation of negative charge on to the oxygen atom has also been shown in reactions which proceed via the enolate structure, for example O alkylation takes place on reaction of (19, X = H) with ethyl iodide to give the enol ether (21) [37].



(21)

In those ylides where the carbanion is incorporated into

an aromatic system, for instance the cyclopentadienylides (22),



$X = SMe_2$, PPh_3, $AsPh_3$

(22)

there is likewise good evidence from physical parameters for delocalisation of negative charge throughout the system. An examination [39] of the vicinal proton coupling constants of the 3 ylides (22) has shown that there is extensive delocalisation of the negative charge throughout the ring. A more detailed comparison of the differences in the bond orders of the C_2-C_3 and C_3-C_4 bonds has shown that the greatest charge delocalisation occurs where $X = AsPh_3$, which is in accord with dipole moment and chemical reactivity studies.

A technique often of utility in the study of ylides is ultraviolet spectroscopy, and a characteristic feature of many ylides is that they are coloured, which arises from a long wavelength absorption tailing into the visible region of the spectrum. This long wavelength absorption is believed to be associated with transitions of electrons involved in the ylide bond. In the unique series of tetraphenylcyclopentadienylides, (18), the absorption maxima shift to longer wavelengths as the group is descended (i.e. from P to Bi), indicating increased contribution from the dipolar form. This is also consistent with basicity (pK_a) data.

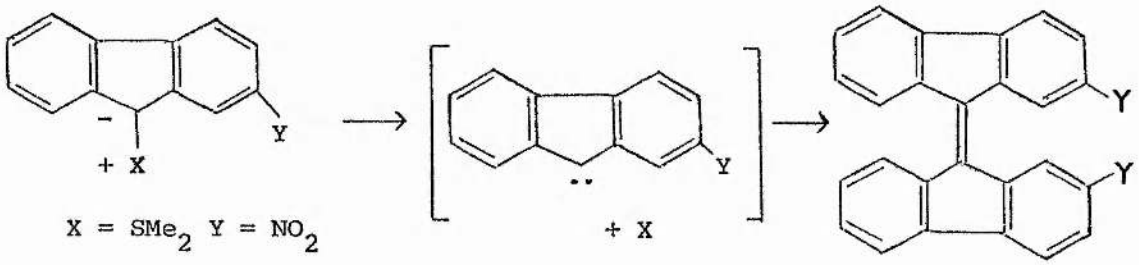
Solvent effects are sometimes evident, particularly in the case of more polar ylides, e.g. pyridinium and bismuthonium ylides (14), (18, X = Ph_3Bi).

Finally, other physical methods not mentioned so far include ^{13}C nuclear magnetic resonance spectroscopy and mass spectrometry. Very little has been reported on either of these techniques, and they will be described more fully in other sections of this thesis.

3. CHEMICAL PROPERTIES OF YLIDES

a) Chemical Stability

Phosphonium and arsonium ylides, in general, do not appear to be thermodynamically unstable, whereas, in comparison, sulphonium and ammonium ylides show a great tendency to decompose spontaneously. The mode of decomposition in many cases has been shown to proceed via the formation of a carbene, for example (23) [40,41], which is



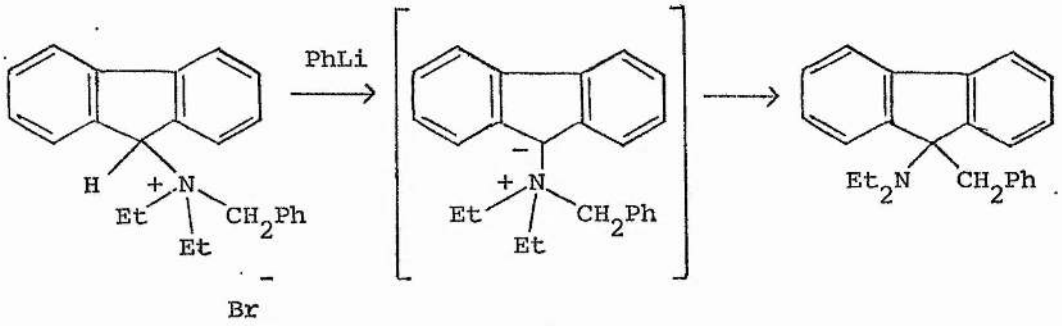
X = SMe_2 Y = NO_2

X = NMe_3 Y = H

(23)

believed to react with another molecule of ylide to give the isolated product, an olefin. An alternative mode of decomposition of ammonium

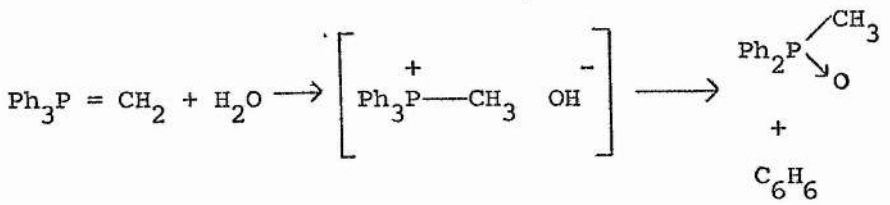
ylides involves a Stevens rearrangement, for example (24) [42],



(24)

where the initially formed unstable ylide immediately rearranges by migration of the benzyl group to give the observed product.

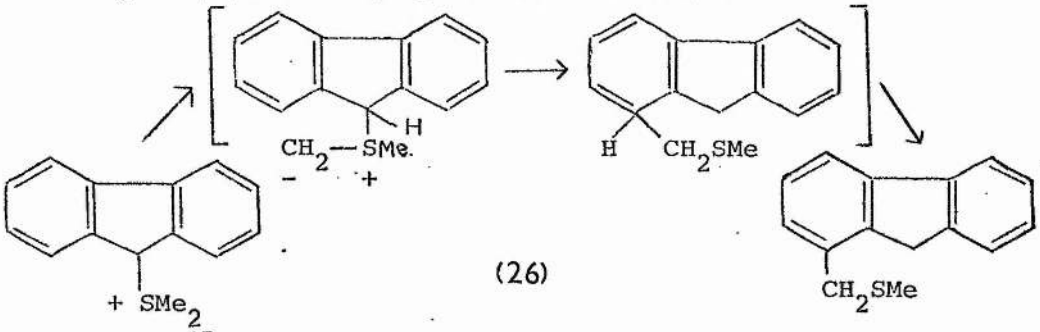
Many ylides are unaffected by atmospheric components, particularly oxygen and moisture. Phosphonium, arsonium and sulphonium ylides which can be isolated by virtue of stabilising groups attached to the carbanionic centre are usually inert to oxygen, whereas their nitrogen counterparts often decompose rapidly when kept in air and more slowly under nitrogen. Some of the less stabilised (i.e. more basic) phosphonium and arsonium ylides are susceptible to hydrolytic decomposition when stored in air, and initial attack is believed to proceed by formation of an unstable phosphonium (or arsonium) hydroxide e.g. (25) [43], which decomposes rapidly to give the phosphine oxide.



(25)

The more stabilised (and less basic) ylides do not undergo the first step.

Finally, the instability of some sulphonium ylides in the presence of excess base should be mentioned. Fluorenylidene-dimethylsulphurane has been shown [44] to undergo a Sommelet rearrangment, presumably by the intermediacy of a less stable



(26)

ylide (26) [45] which rearranges to give the observed product, a thioether.

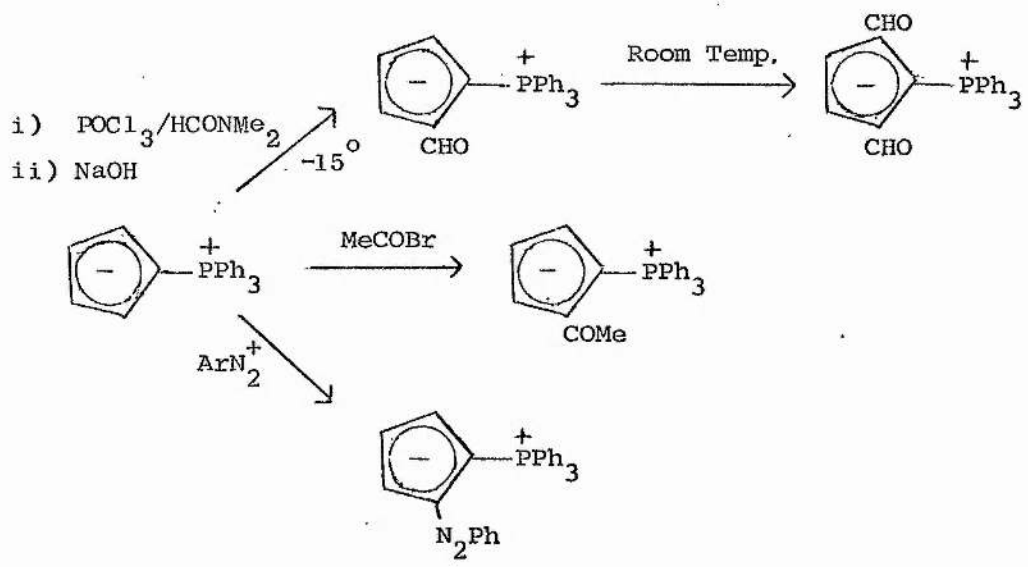
(b) Carbanionic reactions

The reactions of ylides can be classified generally into two groups : carbanionic and carbylidic reactions. In the first category the heteronium group plays no role other than the stabilisation of the carbanion, and is retained in the product. Reactions of this type include reactions with a wide variety of electrophiles, and an example is shown:

$$R_3\overset{+}{P}-\overset{-}{C}HR' \xrightarrow{(PhCO)_2O} R_3\overset{+}{P}-CH(COPh)R' \longrightarrow R_3\overset{+}{P}-\overset{-}{C}(COPh)R'$$

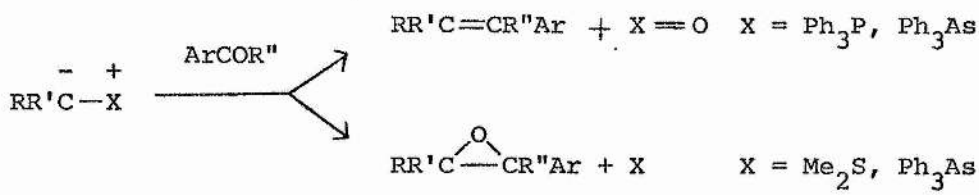
$$\overset{-}{O}COPh$$

Reaction can also take place on a carbon atom other than that next to the heteroatom as shown:



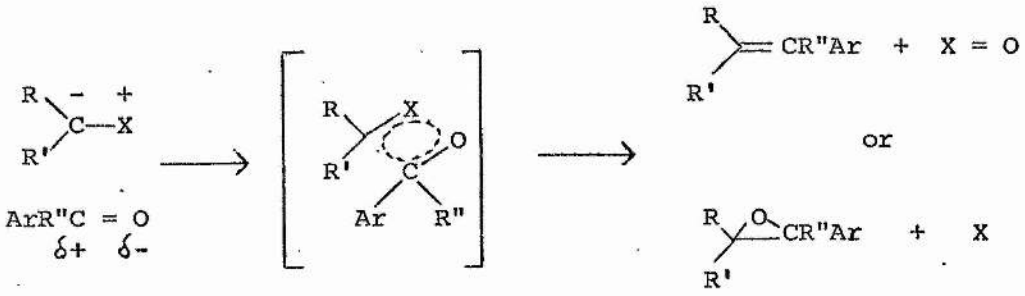
(c) Carbylidic reactions

Carbylidic reactions, on the other hand, entail loss of the heterogroup. For instance, with aldehydes and activated ketones, reaction can take place to give either an olefin or an epoxide dependent largely on the nature of the heteroatom (27).



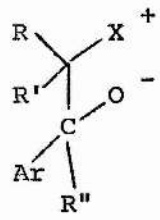
(27)

Phosphonium ylides generally give rise to olefins while sulphonium ylides give exclusively epoxides, and arsenic ylides can give either product. The reaction, which is of synthetic importance and is known as the Wittig reaction, is believed to proceed via a 4-membered cyclic transition stage (28).



(28)

The bonding in the cyclic transition stage may also be represented by a dipolar structure (28A). The nature of the products depends on

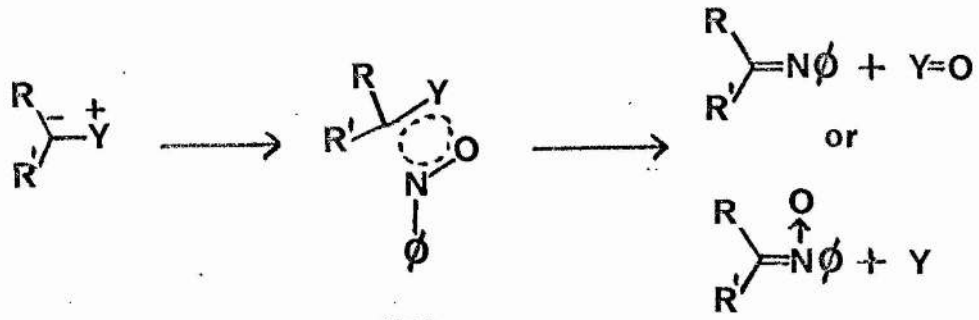


(28A)

the mode of collapse of this intermediate, and if the heteroatom to oxygen bond is strong, formation of the olefin would be expected, as is the case for phosphorus, but if the heteroatom to oxygen bond is weak, then formation of the epoxide is usually found, as is the case for sulphur. With arsenic, the arsenic-oxygen bond is intermediate in strength and either product may be obtained, other factors determining

which one predominates. Nitrogen ylides have not hitherto been found to undergo a Wittig reaction with aldehydes.

Reaction with nitrosobenzene follows a similar pathway (29) and phosphonium ylides normally give the anil while arsonium and



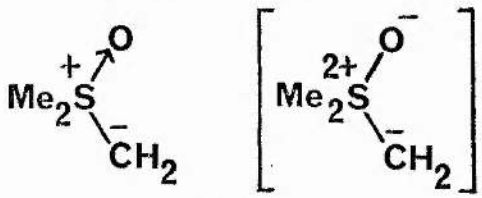
(29)

sulphonium ylides give the anil oxide. Nitrogen ylides, when they react, give the anil oxide.

In the unique series of tetraphenylcyclopentadienylides (18), the nucleophilicity of the ylides as indicated in the reaction with aldehydes and nitrosobenzene has been shown [29] to lie in the order Sb > As > Se > S > P, which does not exactly parallel the order of their basicities (see sect. 2). This illustrates the general principle that a precise correlation of these properties cannot be assumed for the good reason that basicities are concerned only with the measurement of a simple equilibrium involving a small electrophile (proton), whereas nucleophilic attack on reagents such as aldehydes involves a more complex series of events and is subject to greater steric effects.

4. SULPHUR AND SELENIUM YLIDES

While it is not intended to give here an exhaustive review of these compounds, as this information can be obtained readily from other sources [1,46], a short account follows of synthetic methods and some properties of sulphur ylides with particular reference to derivatives of the cyclopentadienyl system, and to a relatively unexplored branch of sulphur ylide chemistry, that of thiocarbonyl ylides. Although the above title would also include ylide systems where the sulphur is bonded directly to oxygen, for instance methylenedimethyloxysulphurane (30) [47], these compounds are of little



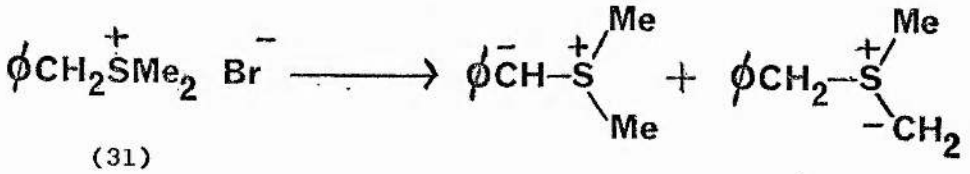
(30)

relevance here and attention will be focussed primarily on sulphonium ylides (and their selenium analogues).

a) Sulphonium Ylides

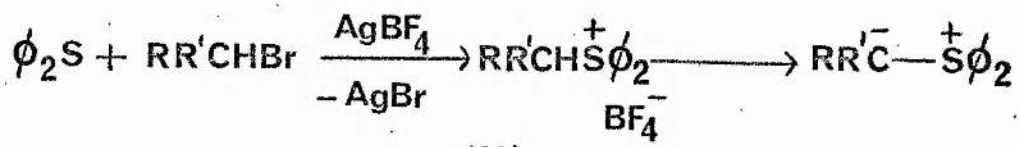
There have been reported, to date, eight different methods for the preparation of sulphonium ylides. The oldest and the one of most general application is the 'salt method', which was used by Ingold [48] to prepare the first sulphonium ylide, fluorenylidenedimethylsulphurane (6), from its conjugate acid, as already described (sect. 1). The only limitations to this method, which incidentally is of general application in the case of many other hetero groups, are i) the availability of the required salt, and ii) the salt should contain only one type of

acidic proton α to the hetero atom, and this must also be the most acidic proton in the molecule. The early development of sulphur ylide chemistry was held up for a long time because very few sulphonium salts were available that had only one type of acidic α proton. Fluorenyldimethylsulphonium bromide is such a salt, where the hydrogen on C-9 of the fluorenyl group is more acidic than the methyl hydrogens by at least 10 pK_a units. The conjugate acid of dimethylsulphonium cyclopentadienylide (22, X = SMe_2) [49] also falls into this category. A salt such as benzyldimethylsulphonium bromide (31), although easily obtainable, would lead to a mixture of



(31)

ylides on treatment with base. The answer obviously was to replace the acidic methyl groups by non-acidic groups such as phenyl, but diphenylsulphide was too weakly nucleophilic to be alkylated on sulphur by normal procedures, such as displacement of halide or tosylate. This difficulty was overcome by Franzen [50] and Johnson [51] who discovered that diphenylsulphide could be alkylated in good yield using silver ion assisted removal of halide (32).

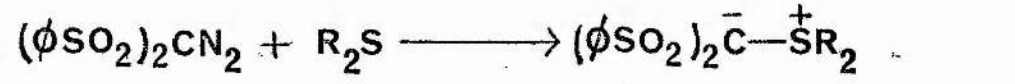


(32)

By this procedure the preparation of almost any given diphenylsulphonium

ylide should be possible, in principle, although the authors did not produce ylides of sufficient stability for isolation, and consequently few properties were reported.

The first example of a sulphonium ylide prepared by carbenic decomposition of a diazo compound in the presence of an alkyl sulphide was reported by Diekmann [52], with the thermally or photolytically induced decomposition of bis(phenylsulphonyl)diazomethane (33). The method was shortly thereafter applied by Lloyd and Singer [53] to the preparation of the cyclopentadienylidenesulphurane



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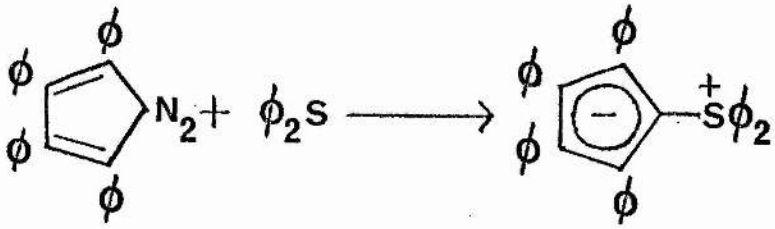
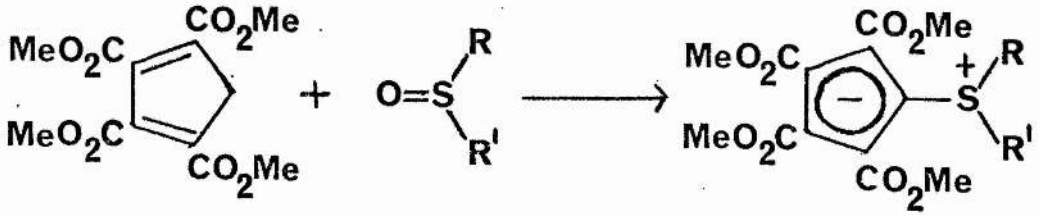


(34)

system (34), and its selenium analogue [4], and appears to be quite general for highly stabilised ylides.

Condensation reactions of reactive methylene compounds with alkyl or alkyl-aryl sulphoxides in the presence of an acid catalyst

were first reported in 1965 [54-58]. Diphenylsulphoxide was found to be ineffective [57]. Seitz [59] reported the preparation of a series of cyclopentadienylidenesulphuranes from tetra(carboxymethyl)cyclopentadiene and a series of acyclic and cyclic sulphoxides in the presence of acetic anhydride as dehydrating agent (35).



(35)

Triethylamine-phosphorus pentoxide or dicyclohexylcarbodi-imide-phosphoric acid [60] are also effective.

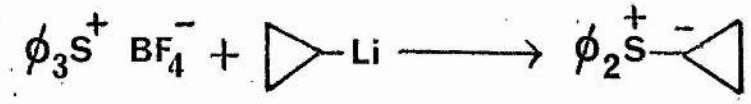
A recently reported [61] method involves the reaction of S,S disubstituted sulphimides with Grignard reagents (36) and gave the ylide in good yield. The sulphimide is easily prepared from

(36)

chloramine-T and the appropriate disubstituted sulphide, which may be alkyl or aryl substituted. The synthesis should be quite general but no further examples have been reported.

Other methods of generating sulphonium ylides are either refinements of the abovementioned methods or not of sufficiently

general application. For instance, the ligand exchange method of Trost et al [62] (37) still necessitates the availability of the



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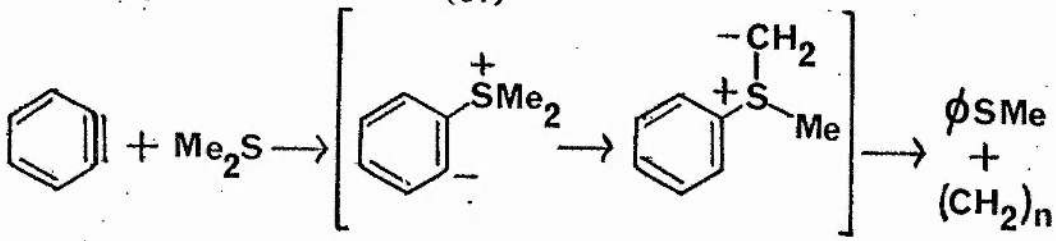

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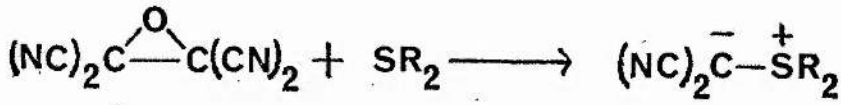
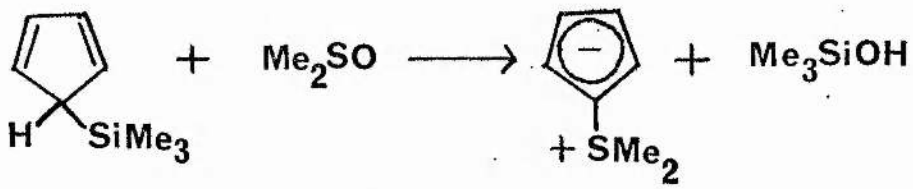


(39)

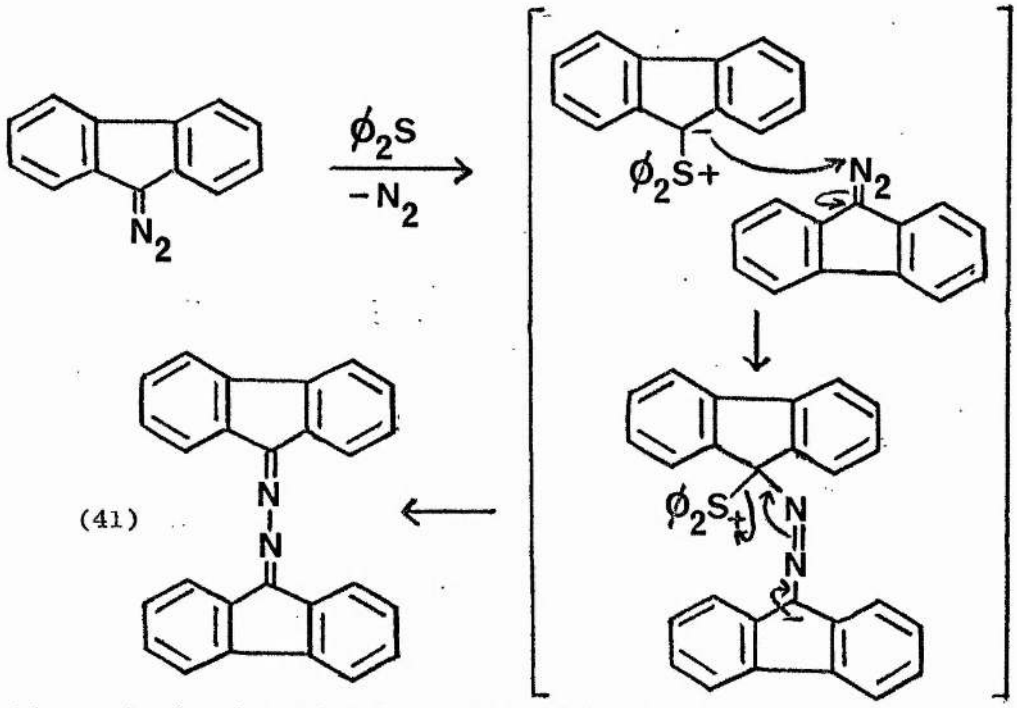
required sulphonium salt as starting material; the benzyne method reported by Franzen [63] (38) is not sufficiently versatile, while the reaction of sulphur nucleophiles with epoxides carrying strongly electron-withdrawing groups reported by Middleton [58] and Linn [64] (39) requires the availability of suitably substituted epoxides, which are difficult to prepare [64]. Finally, mention should be made of a novel synthesis of dimethylsulphonium cyclopentadienylide (22, X=SMe_2) reported by McLean and Reed [65] in which trimethylsilylcyclopentadiene was found to react with dimethylsulphoxide to give the ylide in good yield (40). No further examples of this interesting reaction have



(40)

been reported.

The utility of these synthetic methods in the preparation of sulphonium cyclopentadienylides is shown in Table I, where the annelated, phenylated and unsubstitutedcyclopentadienes shown are taken as representative examples of the series. The 'salt' and 'diazo' methods are of most widespread application, and the aforementioned limitation of availability of the salt is evident. No successful attempt has been reported of the use of silver ion assisted alkylation of diphenyl sulphide. The failure of the 'diazo' method in the reaction of 9-diazofluorene with diphenyl sulphide is particularly notable and illustrates a general tendency of fluorenylides of lower stability to react with a further molecule of diazofluorene to give fluorenone ketazine (41).



(41)

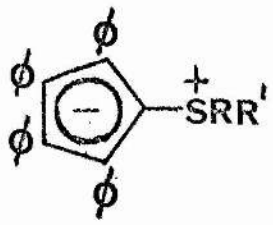
This mechanism has also been established in the reaction of triphenylarsine with 9-diazofluorene [69], and has been shown also in pyridinium [70] and phosphonium [70-72] ylide chemistry.

S-substituents	Dimethyl	Methylphenyl	Diphenyl
Fluorenylidene	Salt [48]	-	(Diazo gives ketazine) [66]
2,3,4,5-Tetraphenyl-cyclopentadienylidene	-	Diazo [67]	Diazo [53]
2,3,4-Triphenyl-cyclopentadienylidene	(Salt - 1-methylthio-2,3,4-triphenylcyclopentadiene was isolated) [66] (Condensation: no reaction) [66]	Diazo [66,68] (Salt: no reaction) [66]	-
Unsubstituted cyclopentadienylidene	Salt [49] Sulphoxide with trimethyl Silylcyclopentadiene [65]	-	-

Table I - Preparation of Sulphonium Cyclopentadienylides

Although a complete comparative study of the effect of the sulphur substituents on the basicity across a series SMe_2-SMePh-SPh_2 could not be made (see table I), it was evident from a study of the tetraphenylcyclopentadienylides that when both sulphur substituents are phenyl, the ylide is very weakly basic as shown by its complete insolubility indilute acid. When one methyl group is present, on the other hand, a perchlorate salt was isolated and characterised, showing that the ylide was more basic. S,S-Diphenylsulphonium ylides containing other stabilising groups have been reported [61,73-75] but only in one case, that of phenylsulphonyldiphenylsulphurane (36), has any mention been made of basicity. This ylide could be converted reversibly to the perchlorate. Diphenylselenoniumtetraphenyl-cyclopentadienylide (43) is also weakly basic. The low basicity of the two cyclopentadienylides, (34) and (43), is probably due to the high degree of stabilisation afforded by the carbanionic and heteroatom substituents. Both of the dimethylsulphonium ylides in table I were basic, as expected, and formed salts on treatment with acid. The effect of sulphur and carbanionic substituents on basicity in a series of phenacylides has been reviewed [76].

The chemical stability of the cyclopentadienylides in table I is diminished as progressively more phenyl groups are replaced by alkyl groups on the sulphur atom. Thus in (42, R=R'=Ph), the ylide is stable indefinitely in the dark and is recovered unchanged on attempted hydrolysis, whereas even (42, R=Me R'=Ph) was only



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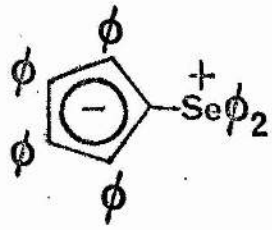

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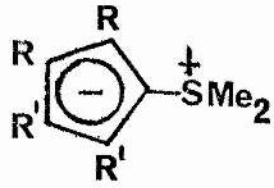
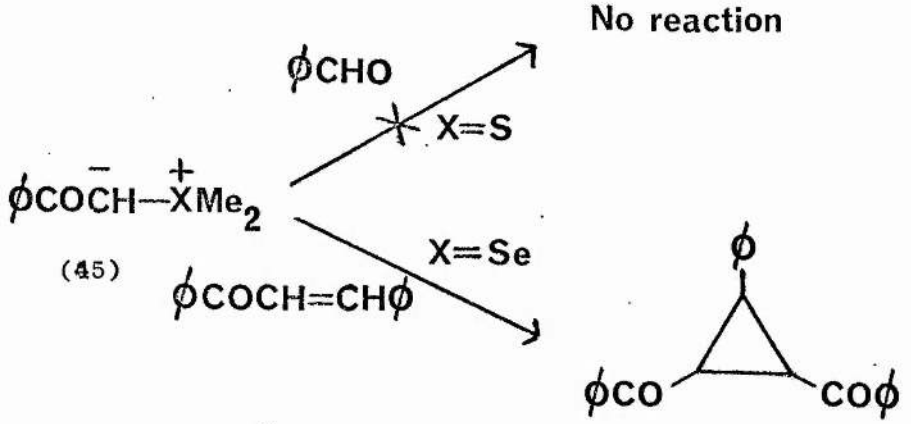
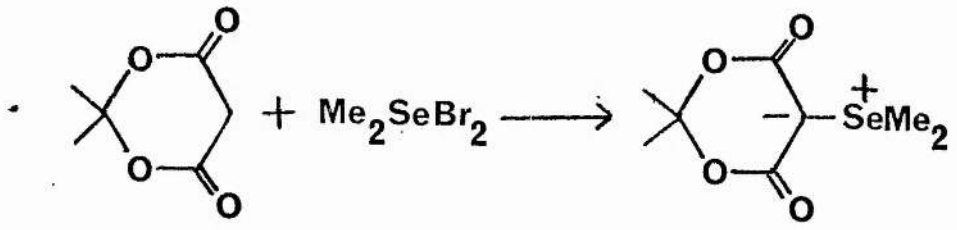


(44)

stable for a few weeks in the dark, and decomposed rapidly on exposure to light and on hydrolysis. The ylides (44, R=R'=H, and R,R=R',R'=-CH=CH-CH=CH-) were thermodynamically unstable and lost dimethylsulphide on standing. The ylides (42) did not react with p-nitrobenzaldehyde although (43) did, giving the epoxide as mentioned earlier (sect. 3). With nitrosobenzene both ylides (42) did react, and (42 R=Me,R'=Ph) gave the anil oxide in 80% yield while (42, R=R'=Ph) gave only a 5% yield of anil oxide under identical conditions, showing that it was less nucleophilic. However, the selenium analogue (43) of (42, R=R'=Ph) gave the anil oxide in 80% yield under the same conditions, a result which does not parallel the basicity results. Although the reactivity of other sulphonium ylides and their selenium counterparts with nitrosobenzene has not been sufficiently studied to permit a comparison, the reactivity trend noted above is observed in the reaction of the phenacyl ylides (45) with carbonyl compounds. Thus the sulphur ylide (45, X=S) does not react with benzaldehyde [77], whereas its selenium analogue (45, X=Se) reacts rapidly with benzalacetophenone to give a cyclopropane derivative [78]. The latter reaction is believed to proceed initially in a manner similar to the Wittig reaction. Thus it appears that selenium ylides are generally more reactive than their sulphur counterparts.



Finally, only three methods have been reported for the synthesis and isolation of selenium ylides: the salt method [78], the thermal decomposition of a diazo compound used by Lloyd and Singer [4] to prepare (43), and a reaction which has no analogue in sulphur chemistry, the reaction of a dihaloselenane with a reactive methylene compound in basic medium (46), which was first reported by Lloyd and Ernstbrunner [5]. This method, which was an



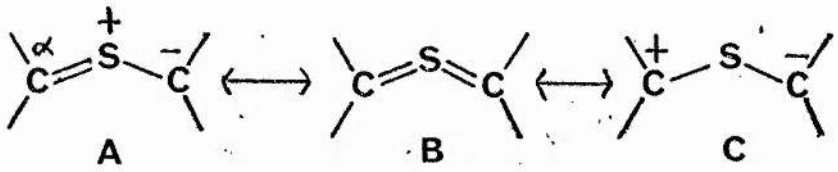
(46)

extension of the method developed by Horner [79] for the preparation of phosphonium ylides, has since been used by other workers [80,81] to prepare an extensive series of selenium ylides. The spectral properties of these ylides were found to closely resemble those of their sulphur counterparts, and an X-ray examination of one of these [81]

showed the selenium to carbon bond length in the ylide bond to be quite long (1.906 Å), indicating a greater contribution from dipolar forms in these ylides. Very few chemical properties of isolable selenium ylides have been reported.

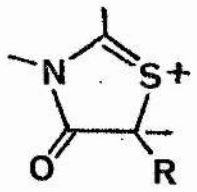
b) Thiocarbonyl Ylides

Thiocarbonyl ylides (47) can be formulated as conventional sulphur ylides (structures A and B) with an additional contribution from a 1,3 dipolar canonical form (structure C). Stabilisation of



(47)

the potential carbanionic centre is possible by the usual means (see Sect. 1) involving attachment of electron withdrawing groups or incorporation into an aromatic system. In addition, the partial positive charge on carbon α can also be delocalised by attachment of electron donating groups, for instance NR_2, SR etc., leading to a more stable ylide. The case for including the all-covalent canonical form (B), in which the valence shell of sulphur is expanded to hold ten electrons, seems justifiable in the light of recent work on the thienothiophenes [82] and related systems [83], and on the thiabenzenes [84,85]. Evidence will be presented to show that the 1,3-dipolar canonical form (C) also contributes to the overall structure.



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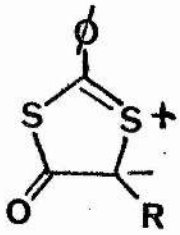
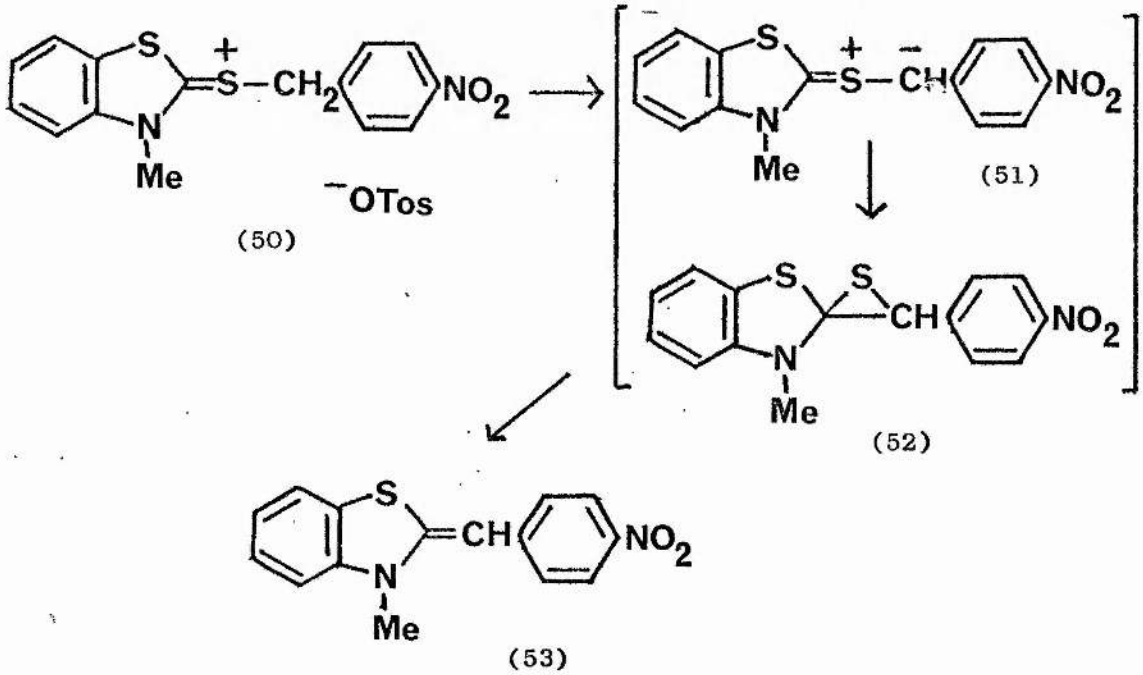


(49)

The consideration of cyclic structures such as (48) [86] and (49) [87] is not considered worthwhile in this discussion because the extent of charge delocalisation in these structures is such that they show very few ylide-like properties and are better considered as meso-ionic compounds [88].

The synthetic approaches so far adopted to the preparation of thiocarbonyl ylides can be classified according to whether or not the resulting ylide has stabilising groups attached to the carbanionic and α carbon atoms. The 'stabilised' ylides will be considered first. The earliest attempt to prepare a thiocarbonyl ylide was made by Knott [89] in 1955 when the salt (50), on treatment with aqueous triethylamine or pyridine, yielded the olefin (53) instead of the ylide (51). A rapid rearrangement of



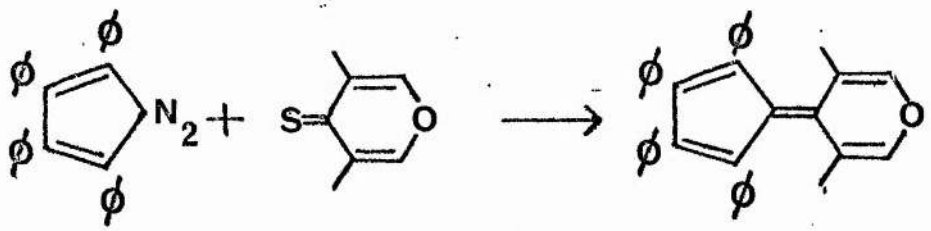
(50)

(51)

(52)

(53)

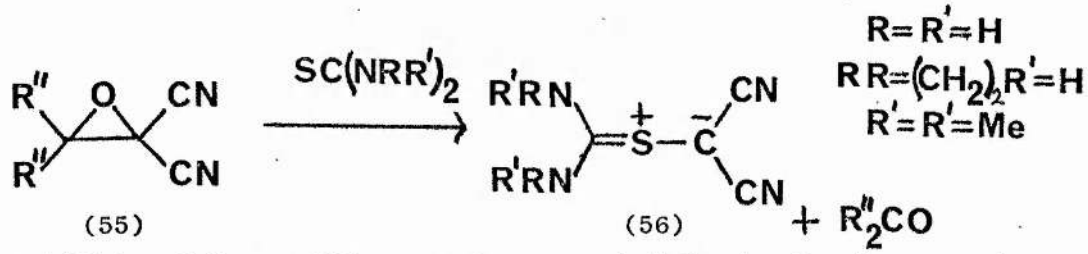
the ylide (51) via the thiirane (52) to give (53) with extrusion of sulphur was postulated. Further work (see below) verified the formation of the thiirane and the loss of sulphur from these is well established [90]. Lloyd and Wasson [91] utilised the collapse of an unstable thiocarbonyl ylide in this manner to prepare cyclopentadienylidenepyrans, by the thermal decomposition of diazotetraphenylcyclopentadiene in the presence of a thiopyran (54).



(54)

The similarity of the mechanism to that shown above (50) - (53) was shown by a kinetic study of the reaction [92].

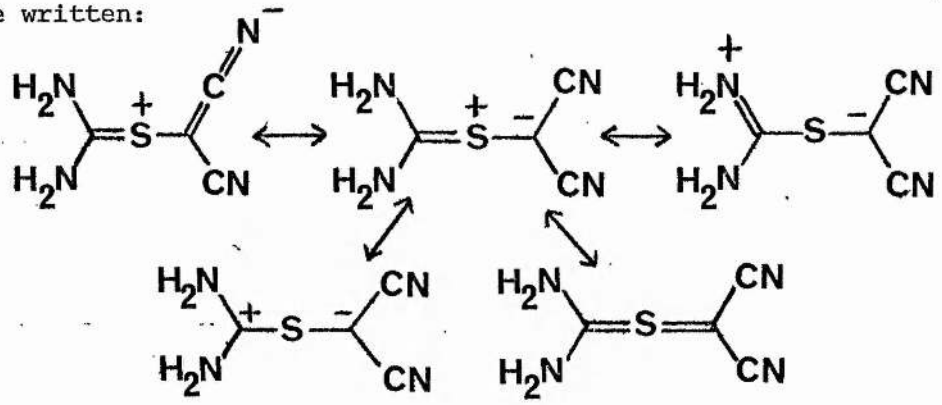
The first successful attempt to isolate a thiocarbonyl ylide was made by Middleton [93] who found that reaction of the oxirane (55, $R''=F_3C$) with thioureas gave rise to a series of stable thiouronium ylides (diaminomethylene sulphuranes) (56). The high



(55) (56)

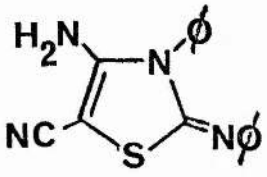
stability of these ylides can be accounted for by the large number of atoms over which both the positive and the negative charge can be delocalised. Thus for (56, R=R'=H) the following structures can

be written:

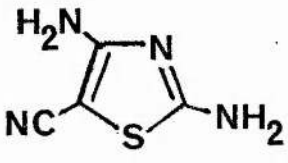


Evidence for the delocalisation of charge into the carbanionic substituents was obtained from the infra-red spectrum, where ν_{max} (C≡N) = 2180 cm^{-1}, consistent with the spectra of other dicyanomethylides [58]. The ylide (56, R=R'=Me) was only stable as a solid for a few hours at room temperature and decomposed rapidly in solution, whereas the other ylides (56) could be kept for several weeks at room temperature without significant decomposition.

When N,N'-diphenylthiourea was allowed to react with the oxirane (55, R''=F_3C), the iminothiazoline (57) was isolated instead of the expected ylide. This presumably arises through the intermediacy of the ylide (56, R=Ph, R'=H), which then cyclises. The



(57)



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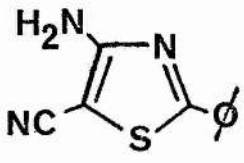
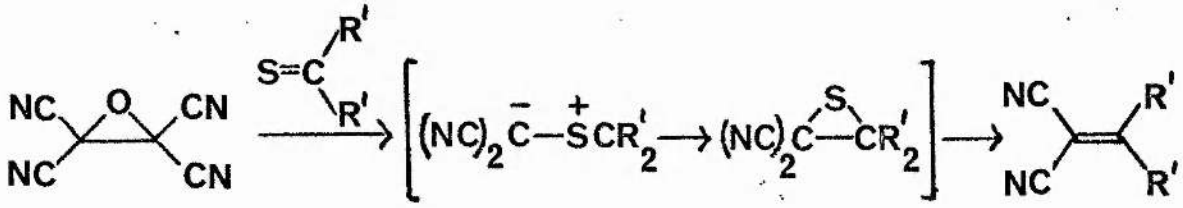


(59)

cyclisation of the ylide (56, R=R'=H) on heating to reflux in water for 2 hours to give the thiazole (58) supports this supposition, as does the formation of the thiazole (59) from the reaction of

thiobenzamide with the oxirane (55, $R''=F_3C$). The only mention of the reactions of these compounds with acids and bases was made for compound (56, $RR=(CH_2)_2$, $R'=H$), which was found to be soluble in dilute alkali and could be reprecipitated unchanged on addition of dilute acid. No explanation was made for this anomalous solubility behaviour.

Linn and Ciganek [94] extended Middleton's work by using the more readily available tetracyanoethylene oxide (55, $R''=CN$). They also confirmed the finding of Middleton and earlier workers that if groups which afforded less stabilisation to the resulting ylide (e.g. phenyl) were attached to the thiocarbonyl function, then an olefin was isolated instead of the ylide. For instance with thiobenzophenone and ethylene trithiocarbonate, the olefins

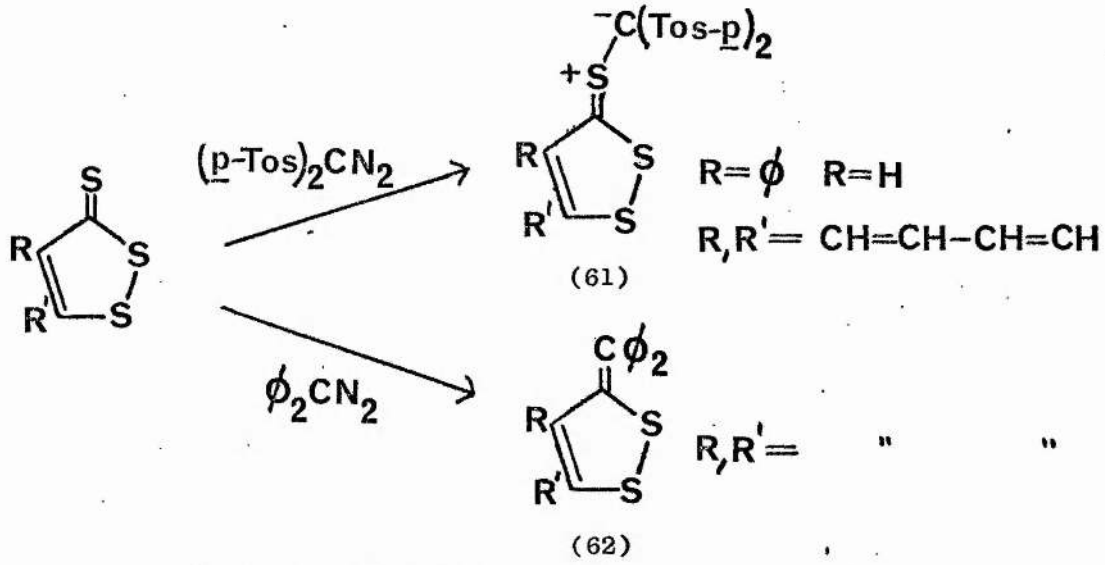


(60)

(60, R'=Ph and $RR'=(SCH_2)_2$) are isolated. The mechanism of the reaction was also discussed and correlated with other ring opening reactions which tetracyanoethylene oxide has been shown [95] to undergo, but for the present purposes it is sufficient to regard this reaction as a special case of the more general carbenic route (see Sect. 4(a)).

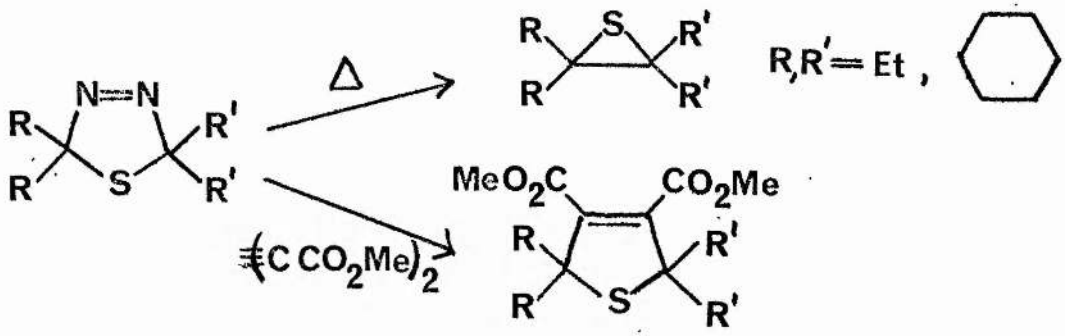
A recent report [96] showed that thermal decomposition of a diazo compound in the presence of thiocarbonyl compounds (and a

catalyst) could give rise to thiocarbonyl ylides (61). Stabilisation



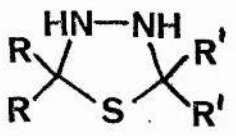
of the ylide (61) was considered to arise from the aromatic nature of the dithiole ring system and from the strong electron withdrawing effect of the carbanionic substituents. Even more recently, it was shown [97] that when the stabilisation on the carbanion was reduced by use of diphenyldiazomethane instead of bis(phenylsulphonyl)-diazomethane, then the olefin (62) was isolated, again presumably by collapse of the intermediate thiirane. Regrettably, no properties of the ylides (61) have yet been reported.

Thiocarbonyl ylides where the carbanionic and α carbon substituents are not strongly stabilising have been prepared by two methods, but because the resulting ylides were not characterisable the results will only be briefly mentioned here. 1,3,4-Thiadiazolines have been decomposed thermally [98, 99] in the presence or absence of dipolarophiles (63), and the presence of the thiocarbonyl ylide

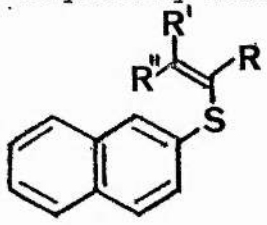


(63)

has been inferred only from the isolation of decomposition (e.g. the thiirane) or trapping (e.g. the dihydrothiophen) products. Other reactions of the transient ylide have also been reported, for instance with acids [99]. The decomposition could also be effected using diethylazidodicarboxylate with the thiadiazoline or with its dihydro derivative [100] (64). The second method utilised [101] the photolytically induced cyclisation



(64)

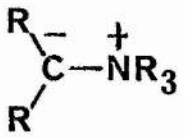


(65)

of a naphthyl vinyl sulphide (65), but the presence of the ylide was inferred only from its reactions, in this case with N-phenylmaleimide.

5. NITROGEN YLIDES

As in the case of sulphur ylides (section 4), these will only be discussed briefly in a more general sense and in greater detail with reference to cyclopentadiene derivatives. Nitrogen ylides fall generally into three groups, according to the nature of the groups attached to the nitrogen atom. Thus we have ammonium ylides (66), pyridinium ylides (67) and diazo compounds (69). The inclusion



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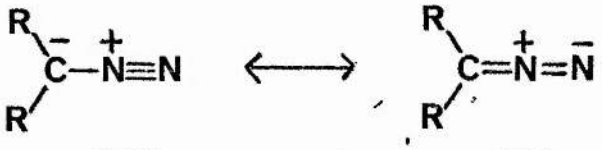
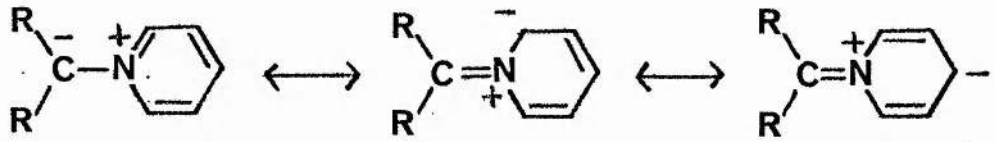


(69) (70)

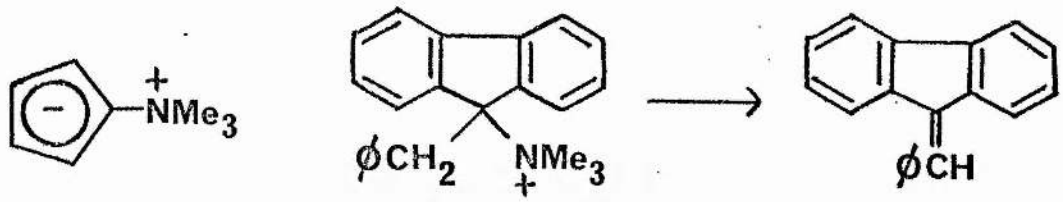


(67) (68)

of the latter class of compounds is open to question as they do undergo reactions which are not typical of ylides, but on the other hand, many of their reactions are closely analogous to those of ylides, which justifies their inclusion. The ammonium ylides are the least stable of the three types. This arises because delocalisation of charge on the carbanionic carbon cannot occur in the way that it is believed to occur in pyridinium ylides and diazo compounds (via canonical forms (68) and (70) respectively).

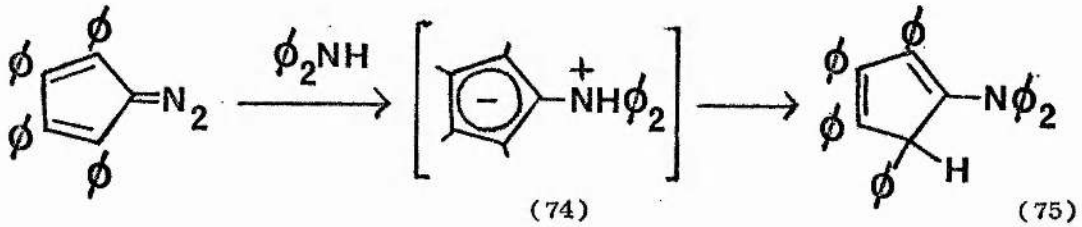
Some ammonium ylides and their chemistry have already been mentioned (sections 1 and 3). Trimethylammonium cyclopentadienylide (71) has been prepared [102] by the 'salt method', but, although it was reactive towards electrophiles, no identifiable products could

be isolated. Trimethylammonium fluorenylide, although unreactive



(71) (72) (73)

towards aldehydes, was reactive towards even weak electrophiles such as methyl iodide and benzyl bromide [13]. In the latter case the fulvene (73) was obtained on pyrolysis of the intermediate salt (72). When Lloyd and Singer [103] decomposed diazotetraphenylcyclopentadiene in the presence of diphenylamine in an attempt to prepare the ylide (74), they isolated instead the isomeric cyclopentadienyldiphenylamine

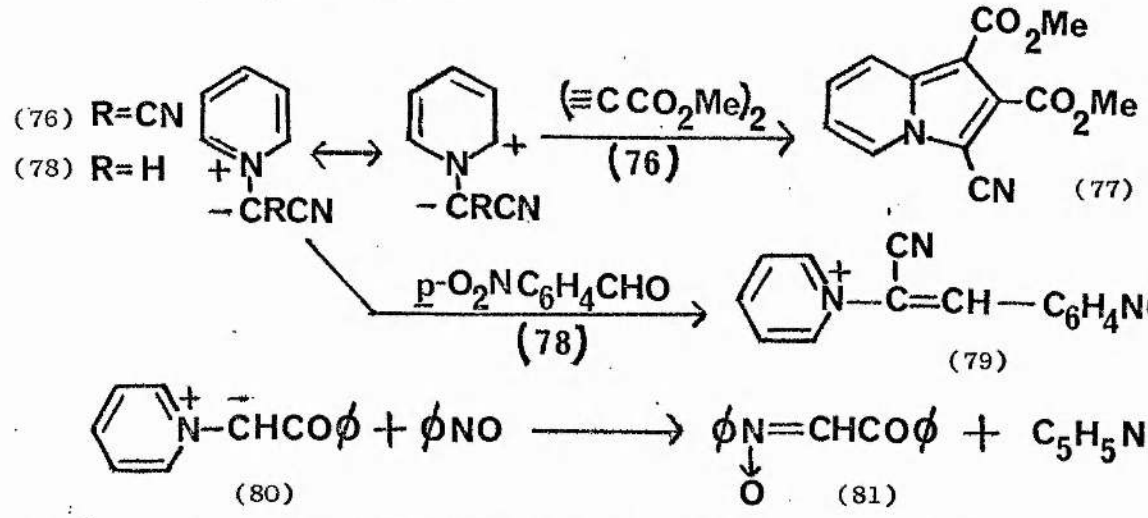


(74) (75)

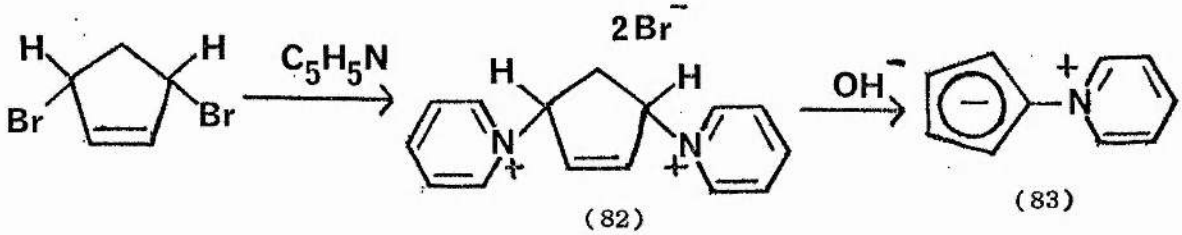
(75), presumably formed <u>via</u> the intermediacy of the ylide (74) which underwent a rapid prototropic shift. When triphenylamine replaced diphenylamine, no ylide could be isolated, and it was presumed that this was due to the low nucleophilicity and high steric hindrance of the amine.

Numerous pyridinium ylides not containing the cyclopentadienyl group have been prepared by the 'salt' method and characterised by Krohnke and co-workers [104, 105], and many more have been handled only in solution and used directly, often for the synthesis of heterocycles [106]. Pyridinium dicyanomethylide (76) was prepared

by Linn et al[64] by their standard method of reaction of a nucleophile (pyridine) with tetracyanoethylene oxide. The ylide, which was very stable, underwent a novel cyclisation with dimethylacetylenedicarboxylate to give a pyrrocoline derivative (77). Pyridinium cyanomethylide (78) was found [105, 107] to react with p-nitrobenzaldehyde to give an olefin (79), but the reaction is unlike that of phosphonium ylides in that the pyridinium group was retained.



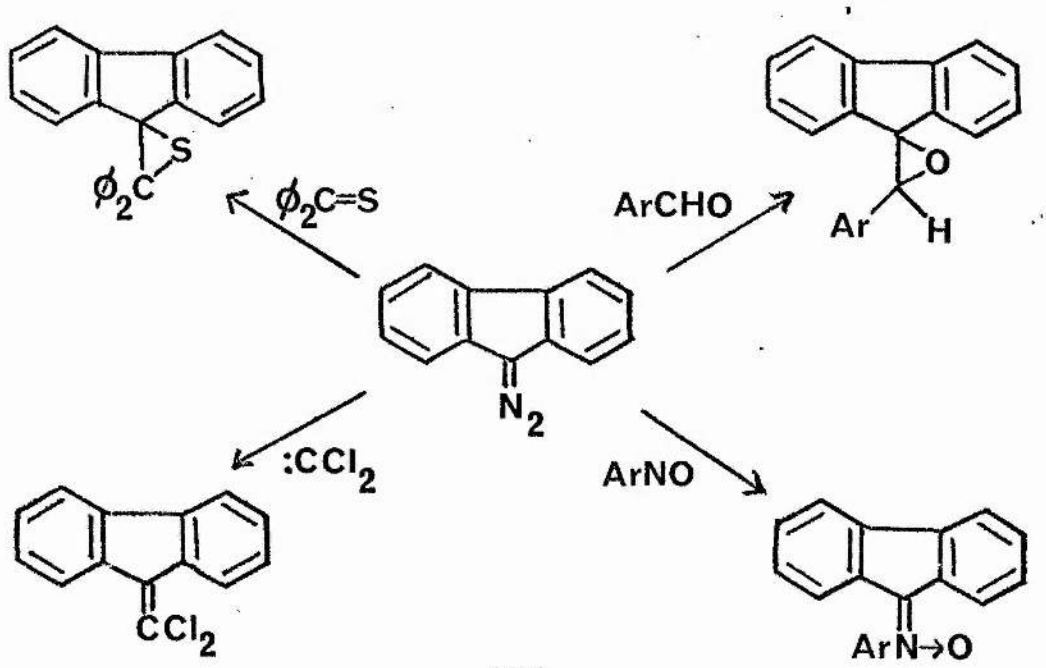
With nitrosobenzene, pyridinium phenacylide (80) gave the anil oxide (81) [108]. This behaviour is typical of pyridinium ylides in general [109]. Pyridinium cyclopentadienylide (83) was prepared by Lloyd and Sneezum [110] by basifying the bis-salt (82). The compound was interesting because of its high dipole moment and



solvatochromism (see section 2). It also reacted readily with bromine to give a tetrabromo derivative [111]. Pyridinium

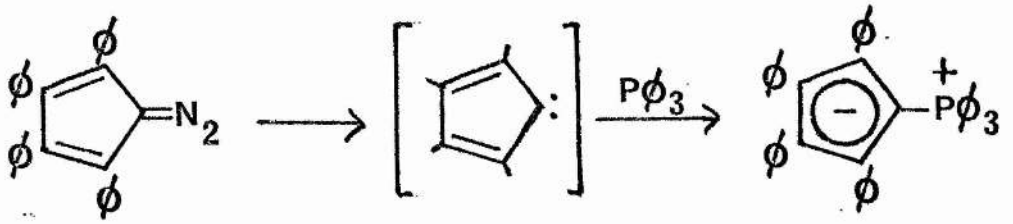
tetraphenylcyclopentadienylide was prepared by a similar route, and also later by the thermal decomposition of diazotetraphenylcyclopentadiene in pyridine solution [103]. Pyridinium fluorenylide was insufficiently stable for isolation [112].

Diazo compounds were the earliest known examples of nitrogen ylides. 9-Diazofluorene was prepared in 1911 by Staudinger [113], and other diazocyclopentadienes were prepared much later, for instance diazocyclopentadiene [114]. The reactions of diazo compounds, typefied by 9-diazofluorene, which are analogous to those of ylides are summarised in scheme (84).

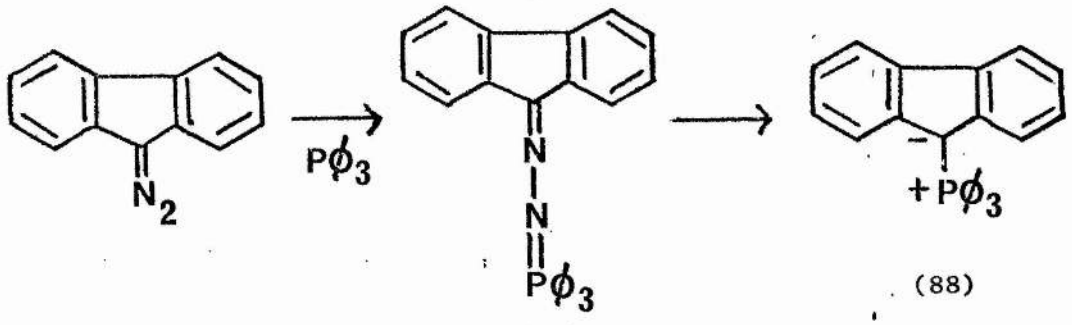


(84)

In addition, diazo compounds may undergo loss of nitrogen to give a carbene (85) which can react with a hetero group to give an ylide (see also section 4), for example (86). Some diazo compounds



(85) (86)



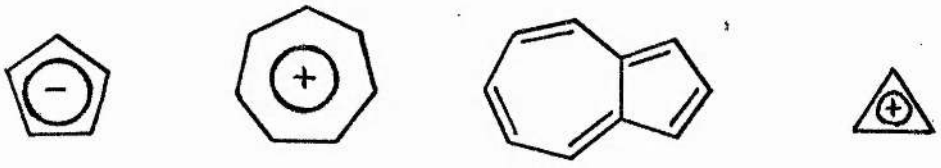
(87) (88)

react to give a stable phosphinazine (87) as an isolable intermediate, which can be decomposed to the ylide (88) on further heating. The formation of an azine (e.g. 87) as intermediate appears to depend on the nature of both the heteroatom and the diazo compound.

6. NON-BENZENOID AROMATIC COMPOUNDS AND ESPECIALLY DERIVATIVES OF CYCLOPENTADIENE

In 1931, Huckel introduced the basic rule underlying present day ideas on aromaticity [115]. It states that "amongst fully conjugated, planar, monocyclic olefins only those possessing (4n + 2) π electrons, where n is an integer, will have special aromatic stability". This expressed in a more general form the earlier concept of Armit and Robinson [116] that stability was conferred on a system which possessed an "aromatic sextet" of π electrons. The archetype of course is benzene

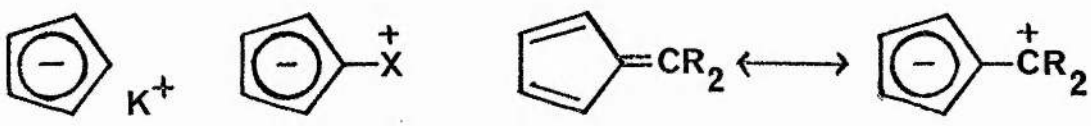
which, along with its more complex homologues, is considered to have physical properties, for instance a high resonance energy, and chemical properties, namely low reactivity with tendency to retain the type when it does react, which are typical of aromatic systems. It was recognised that not only could analogues of benzene such as pyridine and thiophen be included in this category, but also compounds with structures not directly related to that of benzene, for instance the cyclopentadienide anion (89)[117], the tropylium cation (90)[118], azulenes (91)[119], annulenes, and, recently, the cyclopropenium cation (92)[120]. In the first two cases six π electrons are involved,



(89) (90) (91) (92)

(91) and (92) involve 10 and 2 respectively, while annulenes have been prepared with, for example, 10, 14, 18 and 22 π electrons. The properties of compounds containing the cyclopentadienide anion will now be briefly discussed, and mention will be made later in this thesis of an analogue of azulene.

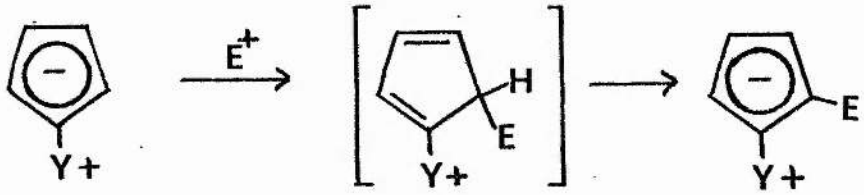
The alkali metal salts of cyclopentadiene, for example potassium cyclopentadienide (93)[117], are highly reactive and difficult to handle. (93) can be handled more easily in solution and it has been shown[121] to undergo, amongst other reactions, rapid deuterium exchange at all the ring positions. The cyclopentadienylides (94) and the fulvenes (95) are also compounds where the cyclopentadienide



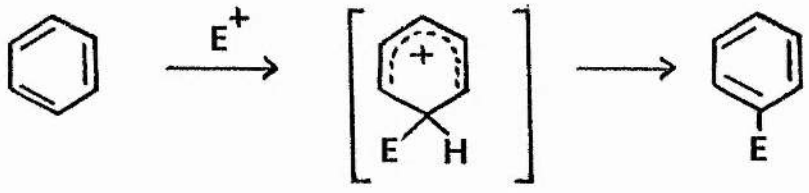
(93) (94) (95)

anion may contribute to the overall structure of the molecule. The extent to which the dipolar structure (94) contributes in the cyclopentadienylides has already been discussed (section 2, dipole moments). In the fulvenes, the dipolar structure generally contributes less than in the ylides (typical $\mu \simeq 1.5D$)[122], although attachment of electron-releasing groups at the 6-position enhances the dipole moment and hence the cyclopentadienide character. For example, 6,6-dimethylaminofulvene has μ=5.4D [123].

Owing to the electron rich nature of the cyclopentadienide ring, many ylides (and fulvenes) readily undergo reaction with electrophiles. This reaction has been the subject of a recent review [124]. The most notable feature of the reactivity of the ylides is that they react by a substitution mechanism (96) formally similar to that of compounds in the benzene series (97). The extent to which substitution occurs on the available ring



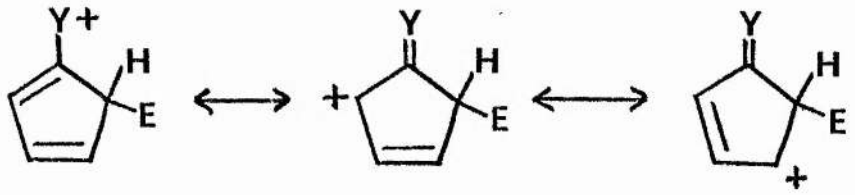
- - - (96)



- - - (97)

positions depends on whether the substituent is electron donating or electron accepting. In the former case (e.g. with bromine), the substitution of each hydrogen atom leads to increased

nucleophilic character of the cyclopentadiene ring and substitution will continue, in the presence of sufficient electrophile, to give a tetrasubstituted derivative. If the latter is the case, (e.g. with acetyl chloride), the substitution may only proceed to give a disubstituted, or, at the most, a trisubstituted derivative, even under forcing conditions. The second point of note relates to the position of substitution on the cyclopentadiene ring. This has been shown, for instance in the cases of diazocyclopentadiene [125] and triphenylphosphonium cyclopentadienylide [126], to take place preferentially at the 2-position on the ring because this involves a linearly conjugated transition state whereas attack at the 3-position would involve a cross-conjugated transition state. Thus in the former case charge delocalisation is more effective and three canonical forms can be drawn (98) whereas in the latter case only two canonical forms can be drawn (99), indicating that the reaction is more likely to proceed on the 2-position.



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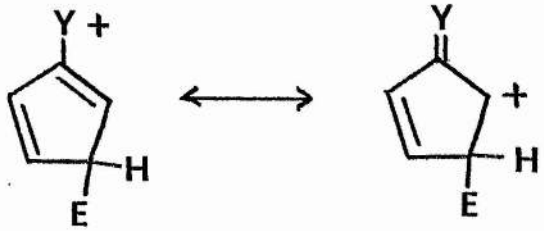


(99)

PART 2

DISCUSSION

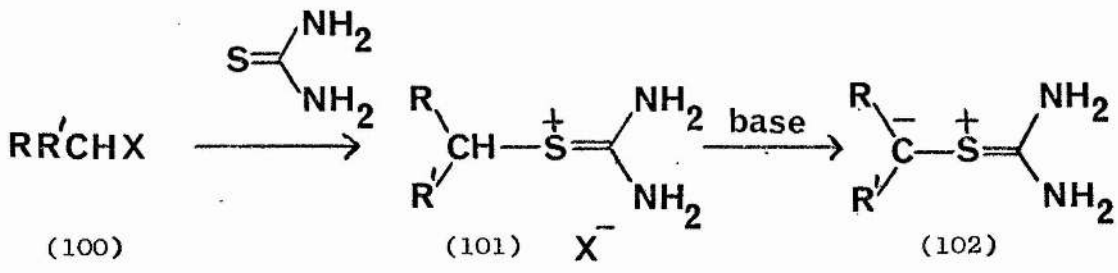
The aim of the work embodied in sections 1 - 4 of this discussion was the preparation and isolation of diaminomethylene sulphuranes (thiouronium ylides), prompted by the results of Middleton and Linn & Ciganek (see Introduction). In section 5 a selenium analogue is described. Sections 6 - 8 will be concerned with the preparation of guanidinium analogues of the ylides described in section 3 (i.e. the formal replacement of S by NH), and the title of section 9 is self-explanatory.

In the interests of brevity, some of the compounds discussed in this thesis are illustrated by formulae which in fact represent only one of the possible contributing canonical forms of the compound in question.

§1. PREPARATION (AND ATTEMPTED PREPARATION) OF THIOURONIUM SALTS

On consideration of the methods currently available for the preparation of sulphonium and thiocarbonyl ylides (see Introduction, sect. 4), it was considered that the two methods likely to be of most value in the present investigation were the 'salt' method and the diazo method. The reaction of thioureas with oxiranes, which had been successful in the hands of Middleton [93] and Linn & Ciganek [94], was rejected on account of the difficulties involved in preparing suitably substituted oxiranes [64]. Likewise the extrusion of nitrogen from thiadiazoles employed by Kellogg *et al* [98-100] was rejected owing to the difficulty of preparing the starting materials. The only other method of general utility in the preparation of sulphur ylides, namely the condensation of sulphoxides with reactive methylene compounds, was not feasible here because thiourea does not have a stable *S*-oxide.

On the other hand, the ability of thiourea to effect a nucleophilic displacement of halide ion is widely known and the resulting thiouronium salts (101) are readily isolable and characterisable owing to their high crystallinity. If groups R and R' are chosen such that stabilisation of the potential



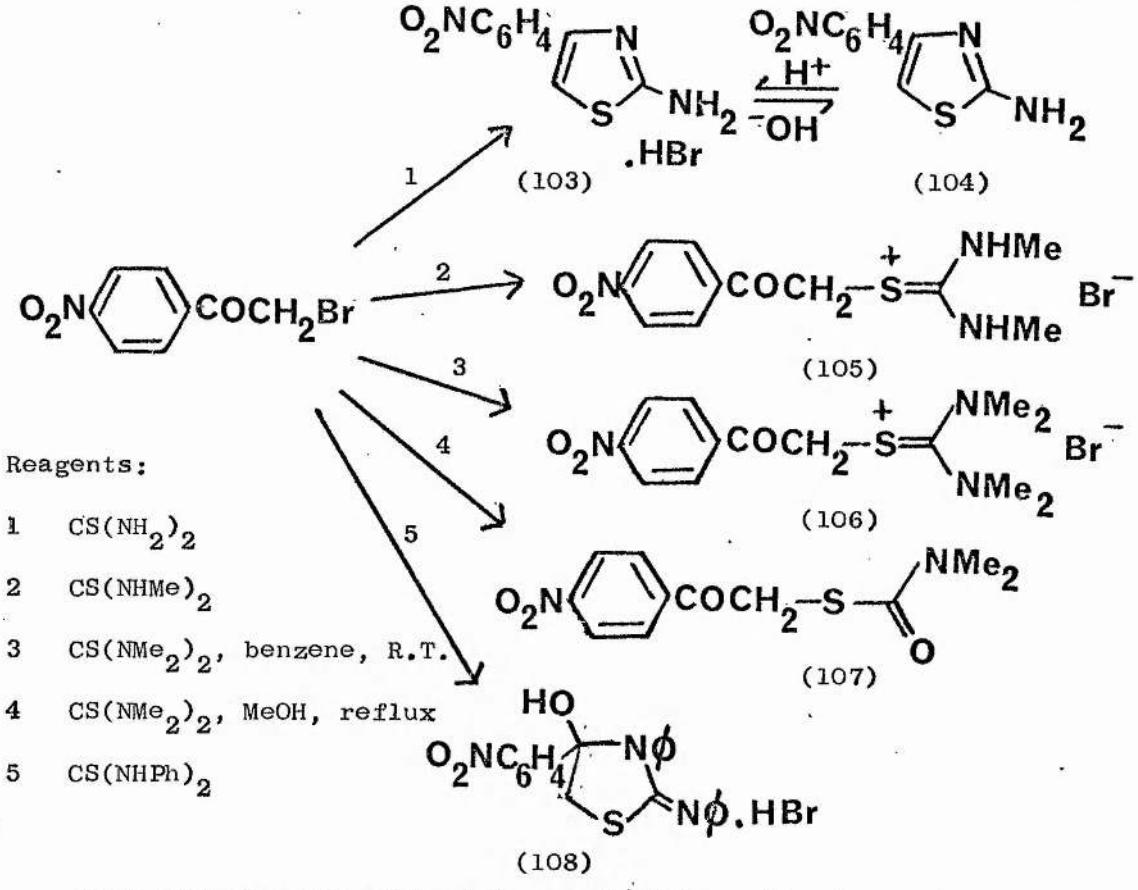
(100) (101) (102)

carbanion centre in the ylide (102) is achieved (see Introduction), or in other words if the α-proton is sufficiently acidic, then treatment with base should afford the ylide (102) by abstraction of the α-proton. The initial requirement, therefore, is that thiouronium salts be available with α carbon substituents (R & R') which are either strongly electron withdrawing or form part of a potentially aromatic cyclic system, for example cyclopentadiene or fluorene. The thermal decomposition of diazo compounds will be discussed in Section 4.

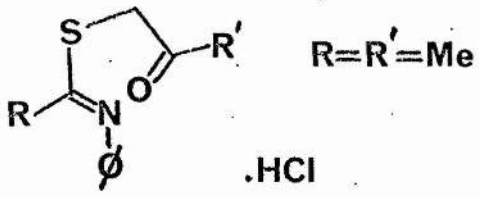
I Preparation and Attempted Preparation of Thiouronium Salts not Containing the Cyclopentadiene Ring

Appropriately substituted halomethanes (100), where the R, R' groups contained electron withdrawing substituents, namely carbonyl, nitrile, sulphonyl and nitro groups, were allowed to react in each case with a variety of substituted thioureas, generally thiourea, N,N'-dimethylthiourea and N,N,N',N'-tetramethylthiourea, although other thioureas, notably N,N'-diphenylthiourea and N,N'-ethylene-thiourea were used in some cases. The following halomethanes were used: p-nitrophenacyl bromide, dimethyl α-bromomalonate, ethyl chloroacetate, bromodibenzoylmethane, bromomalononitrile, bromobis-(phenylsulphonyl) methane, benzyl bromide and p-nitrobenzyl bromide, and the reactions of each will be described in turn.

(i) p-Nitrophenacyl bromide



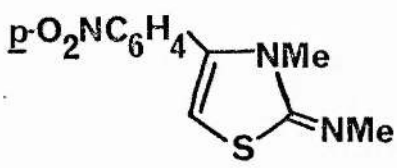
When thiourea was allowed to react with p-nitrophenacyl bromide, the 2-aminothiazole hydrobromide (103) was formed rapidly and quantitatively. Its structure was verified by reversible conversion to the free base (104) which could be diazotised and coupled to 2-naphthol. Phenacyl chloride reacts in a similar manner with thiourea [127], and these are examples of the well-known Hantzsch synthesis of thiazoles [128]. It has been shown that when certain thioamides, for example thioacetanilide, are used instead of thiourea then the intermediate salt (109) can be isolated and cyclised on heating [129]. The ring closure of the intermediate salts (109, R = NH_2) derived from thiourea therefore appears to



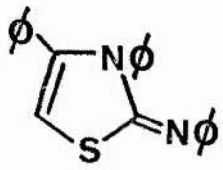
(109)

be very facile [130].

The reaction of N,N'-dimethylthiourea with p-nitrophenacyl bromide to give the thiouronium salt (105) is interesting, as it might have been expected to yield a 2-iminothiazoline (110), by analogy with the products from α-bromodimethylmalonate and



(110)



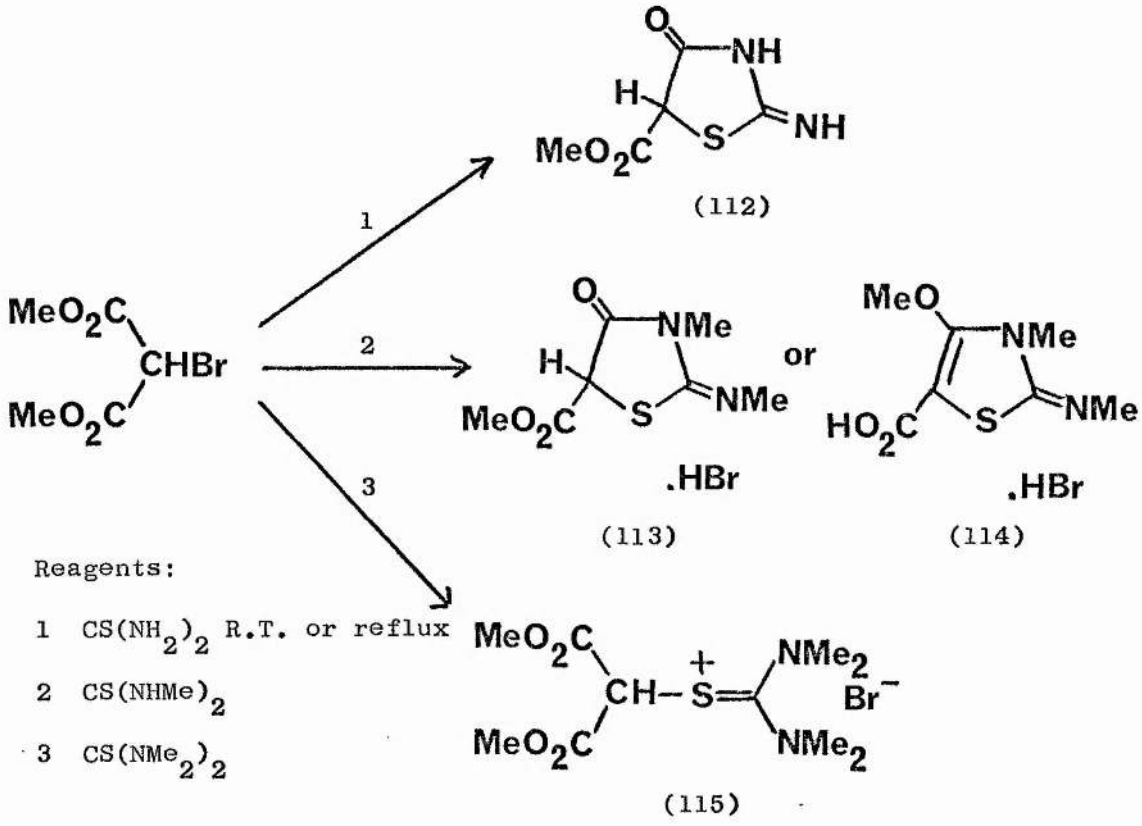
(111)

bromomalononitrile (see below). The structure (105) was established by analysis and by the infra-red spectrum where an absorption in the carbonyl region was present (ν_{max}^{nujol} (C=O) = 1655 cm^{-1}). N,N'-Diphenylthiourea, on the other hand, gave a cyclic product (108), established from its analysis and infra-red spectrum (no ν_{max} (C=O)). This is different from the product (111) reported [131] for the reaction of phenacyl bromide with N,N'-diphenylthiourea, but the conditions used were more severe than those used in the present investigation, and this could account for the isolation of the hydroxydihydrothiazoline (108) which is likely to lose water on further heating.

With N,N,N',N'-tetramethylthiourea, the reaction did not proceed very cleanly in boiling methanol, and the product which was

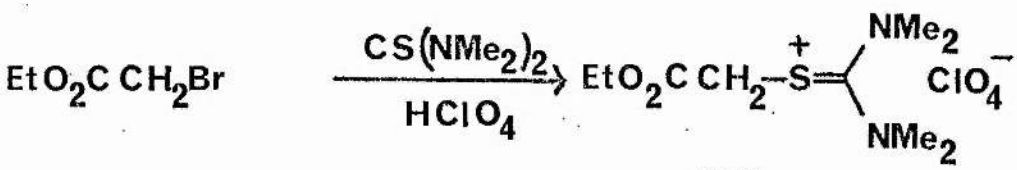
isolated in low yield was not the thiouronium salt (106) but the mercapto amide (107), formed presumably from hydrolysis of the salt (106). When the conditions were changed and the reaction was carried out in methanol at room temperature with addition of perchloric acid in an attempt to isolate the perchlorate of the salt (106), a high yield of an unidentified substance was obtained, which was shown to be neither the perchlorate of the salt (106) nor that of the amide (107). When the reaction was carried out in a non-polar solvent, benzene, at room temperature, however, rapid conversion to the thiouronium salt (106) did take place. Further examples of the effect of solvent and temperature on the reaction of N,N,N',N'-tetramethylthiourea with halomethanes will be given below.

(ii) Dimethyl α-bromomalonate



When thiourea was allowed to react with dimethyl α-bromomalonate, cyclisation took place to give the 2-iminothiazolidin-4-one (112), even when the reaction was performed at room temperature. This facile cyclisation had been observed before in the case of diethyl-α-bromomalonate [132]. Compound (112) was not basic and decomposed on warming with conc. hydrobromic acid. N,N'-Dimethylthiourea also gave a cyclic product as shown by the loss of one mole of water in the molecular formula of the product. Two formulations, (113) and (114), are possible here, the former by analogy with the product (112) from thiourea, but the latter seems more likely on the grounds of the increased basicity of the product, which formed a stable hydrobromide, and also from its infra-red spectrum which did not contain a strong carbonyl absorption at ν_{max} 1640 cm^{-1}, as had been the case with (112). N,N,N',N'-Tetramethylthiourea reacted when heated briefly in benzene to give the expected thiouronium salt (115), which could also be converted to the perchlorate salt.

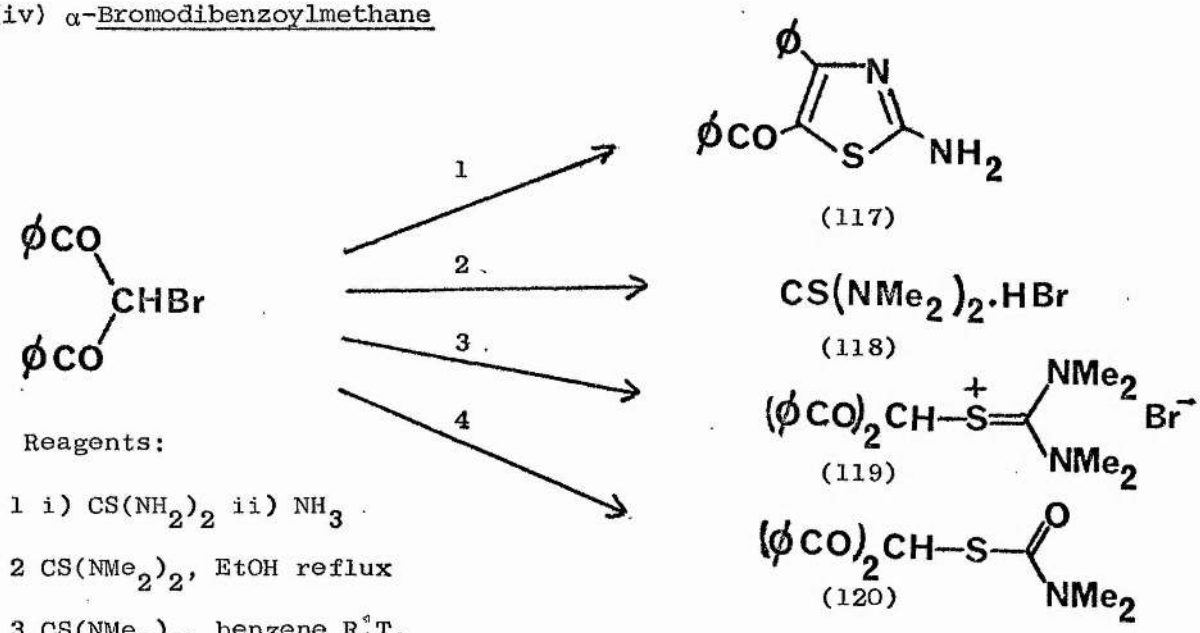
(iii) Ethyl chloroacetate



(116)

When the reactants were warmed briefly, the non-hygroscopic thiouronium perchlorate (116) was obtained in good yield.

(iv) α-Bromodibenzoylmethane



Reagents:

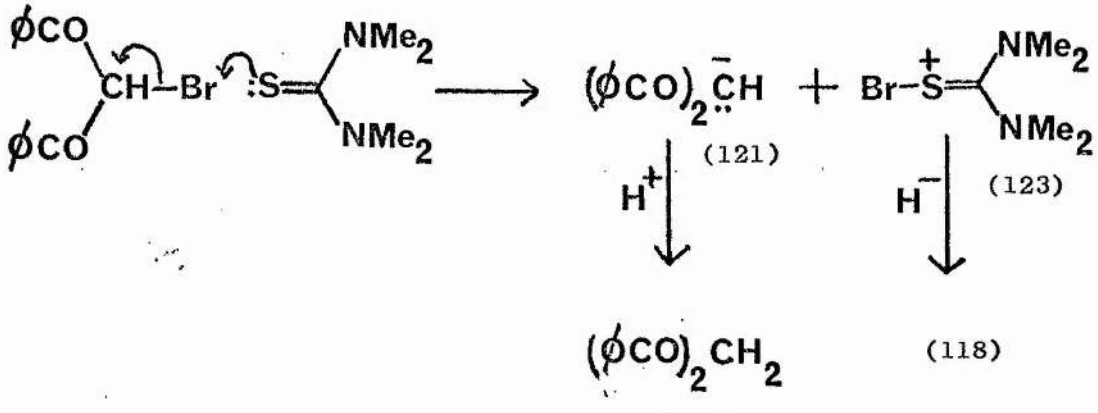
1 i) $CS(NH_2)_2$ ii) NH_3

2 $CS(NMe_2)_2$, EtOH reflux

3 $CS(NMe_2)_2$, benzene R.T.

4 $CS(NMe_2)_2$, MeOH R.T., $HClO_4$ or $NaClO_4$

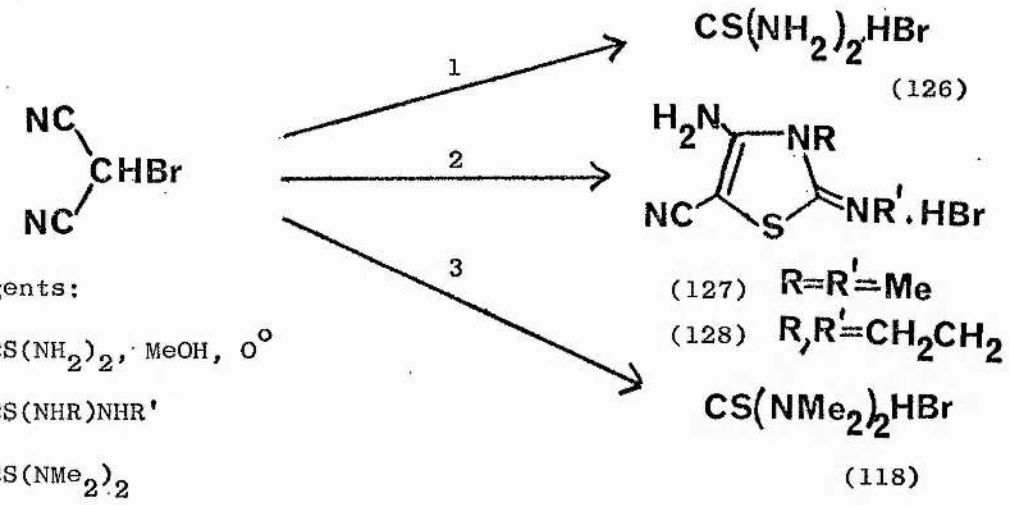
The reaction of α-bromodibenzoylmethane with thiourea to give the thiazole (117) has already been described in the literature [133]. With N,N,N',N'-tetramethylthiourea in a protic solvent, under reflux, protodehalogenation of the halomethane took place to give the thiourea hydrobromide (118) and reactive methylene compound (which was isolated in other examples, eg. (vi)). The mechanism of this reaction, which has already been discussed in the case of the reaction of organic halides with tertiary phosphines [134], is believed to involve initial attack of the nucleophile on the halogen atom:



The transient carbanion (121) then abstracts a proton from the solvent to give the reactive methylene compound (122), with concomitant oxidation of the S-bromothiouronium cation (123) to the observed product, the thiourea hydrobromide (118). The fact that α-bromodibenzoylmethane undergoes a protodehalogenation reaction in this manner, whereas p-nitrophenacyl bromide undergoes a substitution reaction under similar conditions, shows that in the former case the extra electron withdrawing effect of the second benzoyl group is sufficient to alter the course of the reaction, presumably because of the extra stability afforded to the transient carbanion (121).

When the reaction conditions were changed, however, and a non-polar solvent was used with reaction at room temperature, a highly deliquescent solid was obtained, the n.m.r. spectrum of which suggested that it might be the thiouronium salt (119). Unfortunately it was too deliquescent to handle satisfactorily, and on attempted conversion to a perchlorate or attempted isolation as the perchlorate from methanolic solution at room temperature, the mercapto amide (120) was always isolated, presumably from hydrolysis of the salt (119). A similar instance has been noted in the case of p-nitrophenacyl bromide (sect. (i)).

(v) Bromomalononitrile



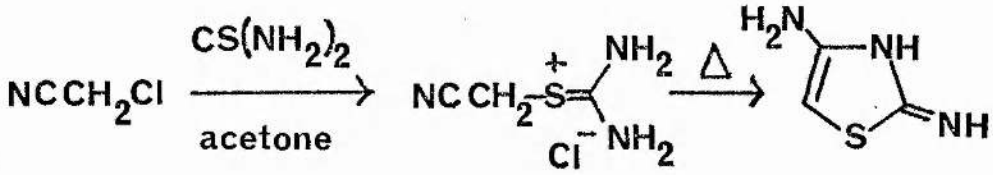
Reagents:

1 $CS(NH_2)_2$, MeOH, 0°

2 CS(NHR)NHR'

3 $CS(NMe_2)_2$

On reaction with thiourea at 0°, a solution of bromomalonitrile underwent rapid protodebromination to give thiouronium bromide (126). This behaviour is quite different from that reported [135] for chloroacetonitrile and thiourea, which gave the thiouronium salt (129) when kept at room temperature for 2 days, and is evidently due to

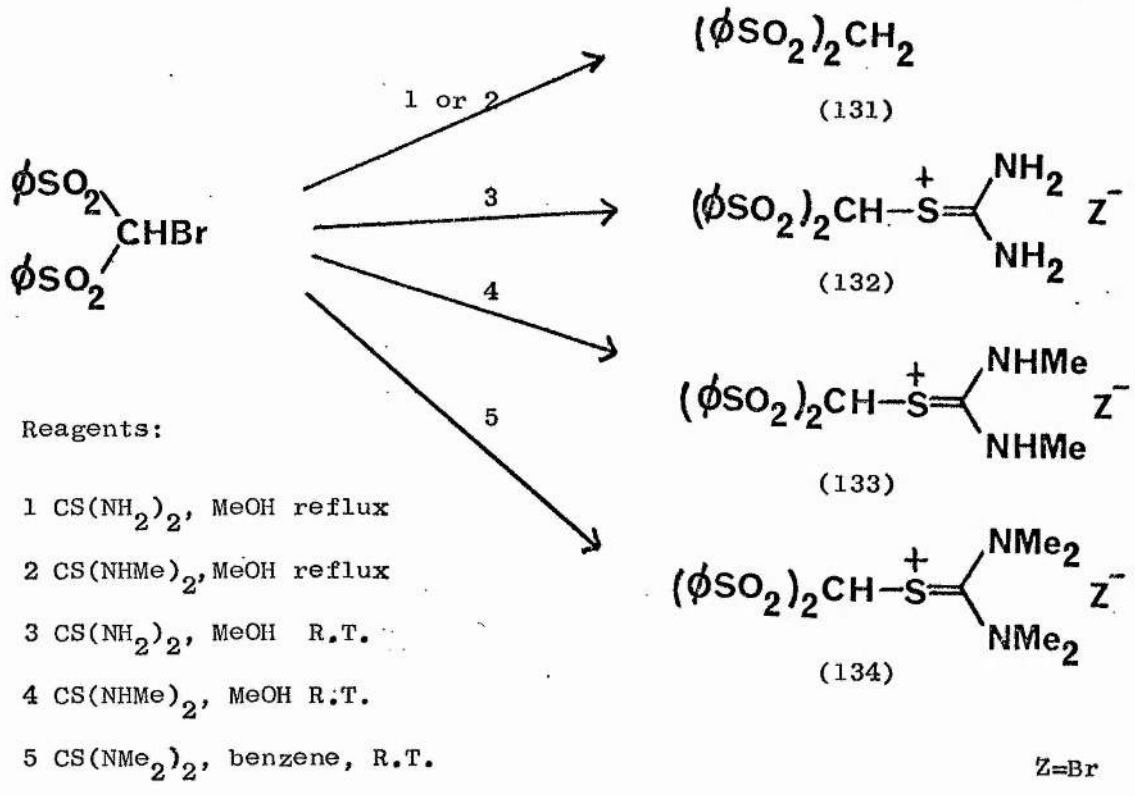


(129) (130)

the electron withdrawing effect of the extra cyano group which enhances the protodehalogenation route by stabilisation of the carbanion intermediate. The salt (129) was subsequently found to undergo a facile cyclisation to the 2-imino-4-aminothiazoline (130) [136]. N,N,N',N'-Tetramethylthiourea also underwent the protodebromination reaction under mild conditions, but with N,N'-dimethyl- and N,N'-ethylenethiourea, a new reaction pathway was observed, and the 2-imino-4-amino-5-cyanothiazolinium bromides (127) and (128) were isolated in good yield. (127) could not be diazo coupled,

behaviour typical of 4-aminothiazoles [130]. Presumably the cyclisation takes place by a route similar to that for compound (129), but the anomalous behaviour of thiourea, which does not undergo the cyclisation, remains to be explained. The protodehalogenation route has been found to prevail in the reaction of triphenylphosphine with bromomalononitrile [137].

(vi) α-Bromobis(phenylsulphonyl) methane



When thiourea and N,N'-dimethylthiourea were allowed to react withα-bromobis(phenylsulphonyl) methane in boiling methanol,

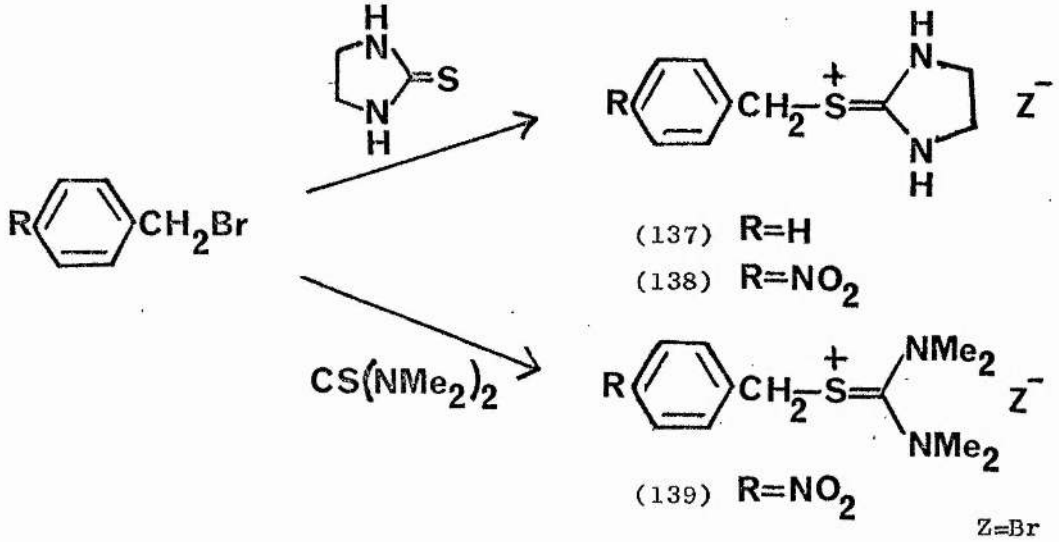
bis(phenylsulphonyl) methane (131) was obtained in good yield, showing that the strongly electron withdrawing sulphonyl groups favoured the protodebromination route (see above) over the substitution route (which gives the salts (132) and (133)). When the reaction was carried out at room temperature in methanol there was some evidence for formation of the salts (132) and 133), but bis(phenylsulphonyl)methane (131) still appeared to be the predominant product, and complete purification of (132) could not be achieved. The inertness of the halogen atom in α-bromosulphones towards nucleophilic substitution has been remarked upon [138, 139].

However, when α-bromobis(phenylsulphonyl) methane and N,N,N',N'-tetramethylthiourea in benzene were kept at room temperature for 10 days, a white precipitate separated which was shown by its subsequent reactions (§2)to be the thiouronium salt (134). Formation of an analogous phosphonium salt (135) which underwent spontaneous loss of hydrogen halide to give the ylide (136) was observed [134, 137] when triphenylphosphine

$$(\phi SO_2)_2CHBr + P\phi_3 \longrightarrow \underset{(135)}{\left[(\phi SO_2)_2CH-\overset{+}{P}\phi_3\ Br^-\right]} \longrightarrow \underset{(136)}{(\phi SO_2)_2\bar{C}-\overset{+}{P}\phi_3}$$

and α-bromobis(phenylsulphonyl) methane were allowed to react under similar conditions.

(vii) Benzyl bromide and p-nitrobenzyl bromide



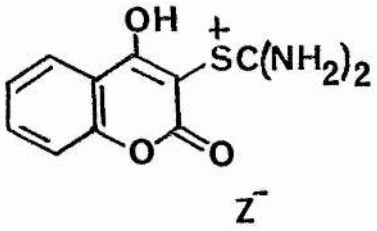
In all the cases so far examined, reaction took place rapidly and smoothly to give the S-alkylisothiouronium salts e.g. (137) - (139).

Conclusions

The reactions of the variously substituted thioureas with α-carbonyl halomethanes appear to follow a consistant trend. Thiourea itself invariably undergoes cyclisation, presumably after initial formation of the S-alkylisothiouronium salt, N,N,N',N'-tetramethylthiourea, if the correct conditions of aprotic solvent and low temperature are chosen, often provides the S-alkylisothiouronium salt owing to blocking of the cyclisation reaction by the N-substituents, while the behaviour of N,N'-dimethyl and N,N'-diphenylthiourea lies somewhere inbetween these two extremes. When the halomethane substituents are changed to nitrile or sulphonyl groups, the predominance of the protodehalogenation

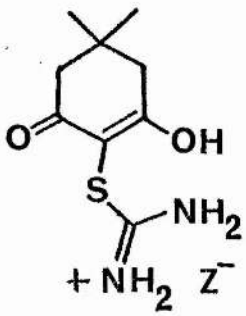
reaction is very noticeable, even under carefully chosen conditions. The exceptional reaction of N,N' disubstituted thioureas with bromomalononitrile is notable. The special nature of sulphonyl substituents, as exemplified in the work of Hoffmann [140] was not realised until a late stage in this work, and the reaction with thioureas still requires further investigation. The expedient of attaching stabilising groups remote from the α-carbon, for instance at the p-position on a phenyl ring, although only touched upon in this work, would appear to offer a convenient means of suppressing unwanted cyclisation reactions in many cases.

Finally, it was learned at a late stage in this investigation that S-alkylisothiouronium salts of two cyclic β-dicarbonyl compounds, 4-hydroxycoumarin (140) [141] and dimedone (141) [142, 143] had been

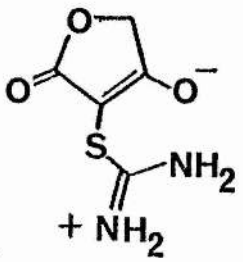


(140)

Z=Br



(141)

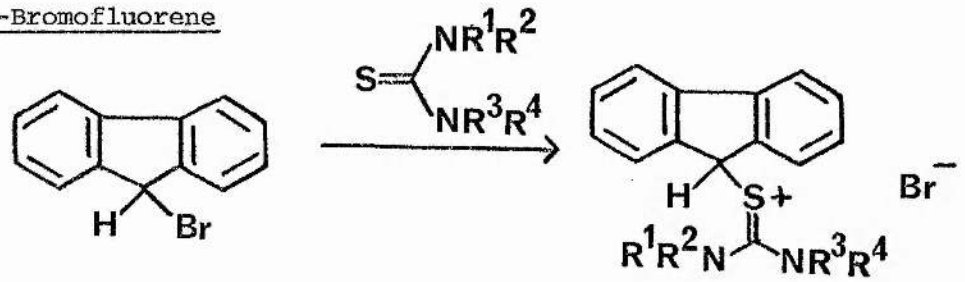


(142)

reported in the literature, and that a free isothioureido base of tetronic acid (142) [144] had been isolated as an intermediate in a thiazole synthesis. Further information on the reactions of these compounds will be presented in sections 2 and 3.

II Reactions of Thioureas with Halogenated Cyclopentadiene Derivatives

(i) 9-Bromofluorene



(143) $R^1=R^2=R^3=R^4=H$

(144) $R^1=R^3=Me$, $R^2=R^4=H$

(145) $R^1,R^3=CH_2CH_2$, $R^2=R^4=H$

(146) $R^1=R^3=Ph$, $R^2=R^4=H$

(147) $R^1=Ph$, $R^3=Me$, $R^2=R^4=H$

(148) $R^1=Ph$, $R^2=R^3=R^4=H$

(149) $R^1=R^2=R^3=R^4=Me$

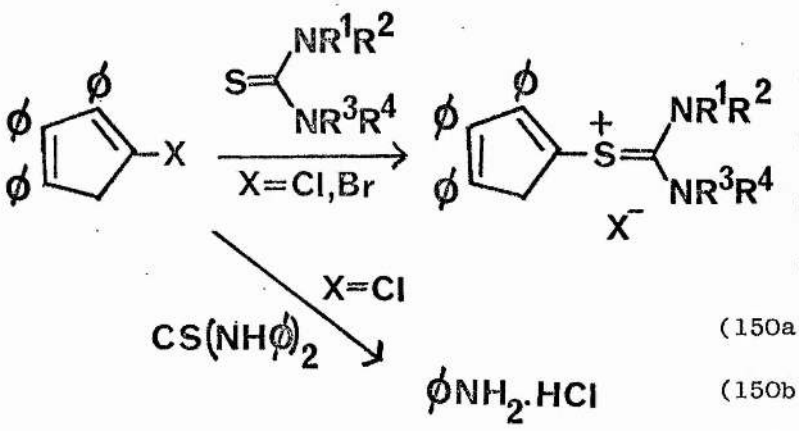
(143a - 149a) Perchlorates.

When 9-bromofluorene and the appropriately substituted thiourea were heated together under reflux in ethanol, the corresponding S-fluorenylisothiouronium salts were obtained in good yield, and isolated either as the bromide or the perchlorate.

(ii) 5-Chloro- and 5-Bromo-2,3,4-triphenylcyclopentadiene

5-Chloro or 5-bromo-2,3,4-triphenylcyclopentadiene (the former is easier to handle), when heated under reflux with the appropriately substituted thiourea in ethanol for a period of time varying according to the nature of X (X=Cl, typically 5 days; X=Br, typically ½-2 hr), gave good yields of the required S-(2,3,4-triphenylcyclopentadienyl)isothiouronium salts (150) - (153) except in the case of N,N'-diphenyl-

thiourea with 5-chloro-2,3,4-triphenylcyclopentadiene. In this



(154)

(150) $R^1=R^2=R^3=R^4=H$

(151) $R^1=R^3=Me, R^2=R^4=H$

(152) $R^1,R^3=CH_2CH_2, R^2=R^4=H$

(153) $R^1=R^2=R^3=R^4=Me$

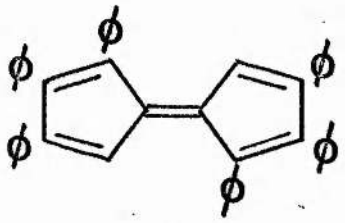
(150a - 153a) X=Cl

(150b - 153b) X=Br

(150c - 153c) $X=ClO_4$

(150d - 153d) X=Picrate

case, after a reflux period of 5 days, it was evident from the dark brown colour of the solution that decomposition had taken place and anilinium chloride (154) was isolated, presumably formed from breakdown of the initially formed isothiouronium salt. Also in the case of compounds (150a) - (153a), a small amount of a dark solid was isolated, the mass spectrum and colour of which suggested that it might be 2,3,4,2',3',4'-hexaphenylfulvalene (155). This might

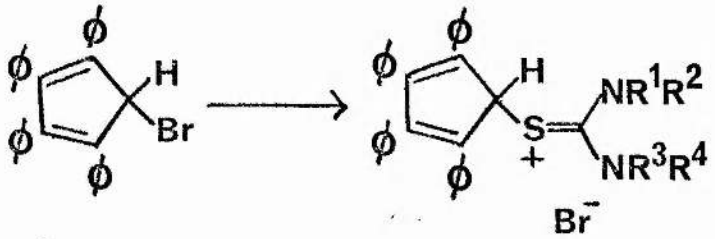


(155)

be formed by breakdown of the salts (150a)-(153a) under the harsh conditions employed. Characterisation of the salts (150a-c) - (152a-c) was difficult owing to either their hygroscopic nature or their adverse solubility characteristics. These problems were finally surmounted by preparation of the picrates (150d) - (152d). One

bromide salt (150b) was found to form a 1:1 complex with nitromethane. The fact that there was no sign of any protodebromination reaction, whereas this had been observed [67] in the reaction of triphenylphosphine with 5-bromo-2,3,4-triphenylcyclopentadiene, was particularly gratifying, and shows that thiourea acts as a better nucleophile than triphenylphosphine.

(iii) 5-Bromo-1,2,3,4-tetraphenylcyclopentadiene



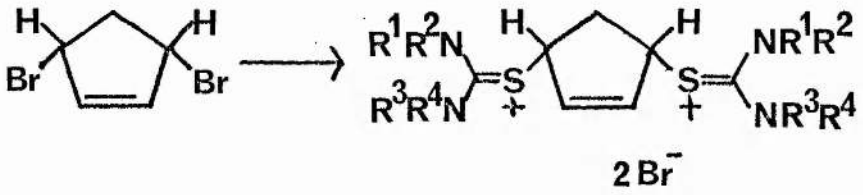
(156) $R^1=R^2=R^3=R^4=H$

(157) $R^1=R^3=Me, R^2=R^4=H$

(158) $R^1, R^3=CH_2CH_2, R^2=R^4=H$

Although the isothiouronium salts (156) - (158) were formed in high yield when the appropriate thiourea was heated to reflux with 5-bromo-1,2,3,4-tetraphenylcyclopentadiene, characterisation was very difficult owing to the high solubility of the salts (156) - (158) and their perchlorates in the usual recrystallisation solvents. Decomposition occurred on attempted formation of the picrates. However, from the reactions of the ylides generated from them (with aldehydes and nitrosobenzene), there can be little doubt that these were the required salts.

(iv) 3,5-Dibromocyclopentene



(159) $R^1=R^2=R^3=R^4=H$

(160) $R^1=R^3=Me, R^2=R^4=H$

(161) $R^1,R^3=CH_2CH_2, R^2=R^4=H$

(162) $R^1=R^2=R^3=R^4=Me$

Although not itself a cyclopentadiene, this material has been used [145] as a precursor for many cyclopentadienylides. When heated to reflux for a short time with the appropriate thiourea it gave the bis(isothiouronium) salts (159) - (162) in moderate yield, all of which except (162) were characterised as the bromide salts. (162) was too deliquescent to be handled satisfactorily and underwent decomposition on treatment with perchloric or picric acids.

Conclusion

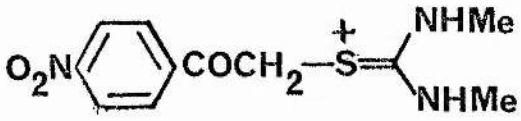
It is evident from the abovementioned reactions that the incorporation of a carbocyclic group, such as cyclopentadiene and its derivatives, into the ylide precursor overcomes many of the pitfalls encountered in the attempted use of other stabilising groups, as in sect. 1.I.

§ 2. REACTIONS OF THIOURONIUM SALTS

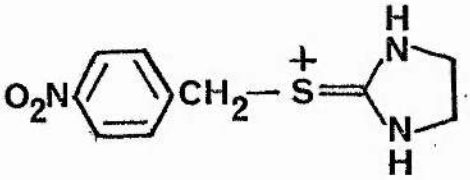
I. Thiouronium Salts not Containing the Cyclopentadiene Ring

In order to emphasise the similarity in behaviour of the various structural groupings, the thiouronium salts from sect. 1I will be classified according to the nature of the N,N'-substituents. This gives:

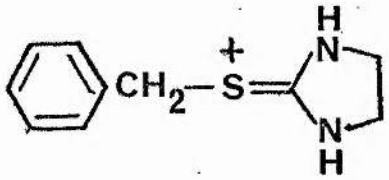
(a) N,N'-Disubstituted thiouronium salts



(105)

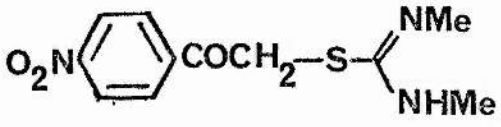


(138)

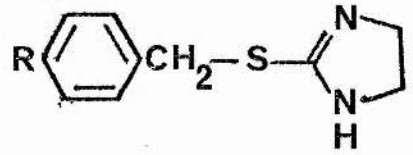


(137)

When S-(p-nitrophenacyl)-N,N'-dimethylisothiouronium bromide (105) was treated with aqueous sodium hydroxide, the S-alkylisothiourea (163) was isolated in high yield. Compounds (137) and (138)



(163)

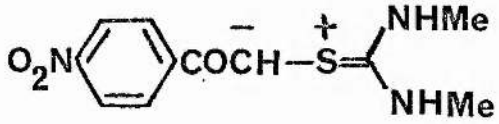


(164) R=NO_2

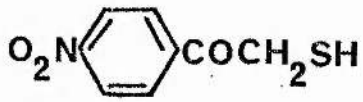
(165) R=H

reacted similarly with phenyl lithium to give (164) and (165).

This illustrates one of the limitations of the salt method which is that the proton attached to the α-carbon must be the most acidic proton in the molecule (see Introduction Sect. 4). Clearly this is not the case in compounds (105), (137) and (138), where the loss of an N-H proton shows that the protons of the thiourea moiety are relatively more acidic than those attached to the α-carbon. An alternative way of looking at this is to say that the ylide (166) is much more basic than the S-alkylisothiourea (163), and subsequent

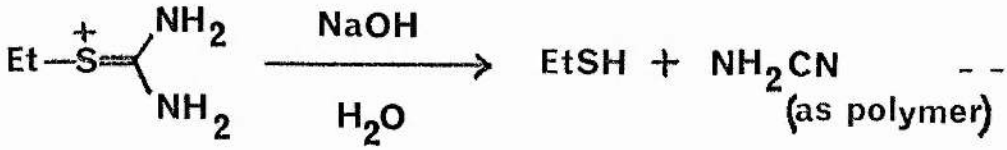


(166)



(167)

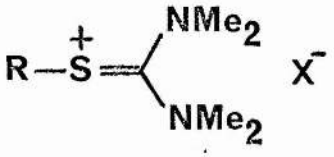
studies on fluorenylides (sect. 2II) confirm this. In any case, it appears that the remedy lies in the use of N,N'-tetrasubstituted thiouronium salts, and these are described below. A further point worthy of study is that the salt (163) on treatment with aqueous base does not give any of the mercaptan (167), which S-alkylisothiouronium salts not carrying any N substituents usually form. In this case the N-methyl substituents must prevent the normal mode of reaction, shown below [146], presumably in this case because the



(168)

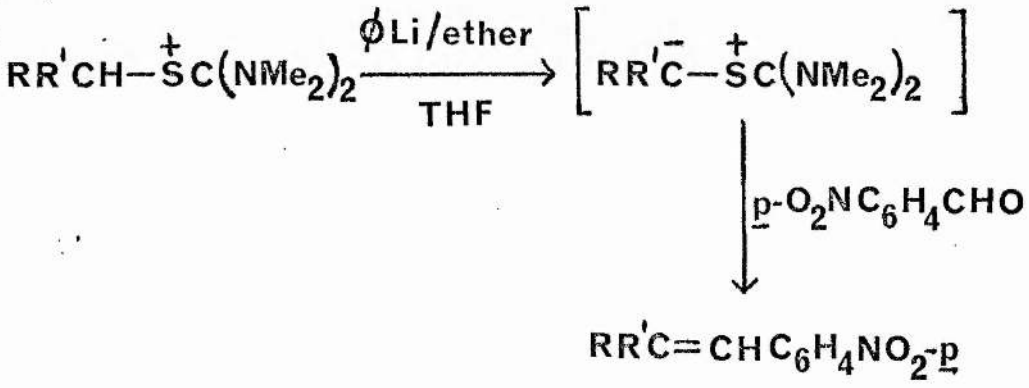
enamine (163) is stable whereas the imine intermediate in (168) rearranges immediately to the thiol and cyanamide.

(b) N,N,N',N'-Tetrasubstituted thiouronium salts



R	X	
p-$O_2NC_6H_4COCH_2$-	Br	(106)
EtO_2C-CH_2-	ClO_4	(116)
$(MeO_2C)_2CH$-	ClO_4	(115)
p-$O_2NC_6H_4CH_2$-	Br	(139)
$(PhSO_2)_2CH$ -	Br	(134)

Owing to the intractable nature of many of the products obtained when the N,N,N',N'-tetramethylisothiouronium salts were basified, it was decided initially to examine the reaction of the basified salt with p-nitrobenzaldehyde in situ, and this would eliminate the possibility of decomposition during workup. For reasons which will become apparent later (sect. 3II), the expected product from the aldehyde reaction is an olefin (169). This procedure was tried with

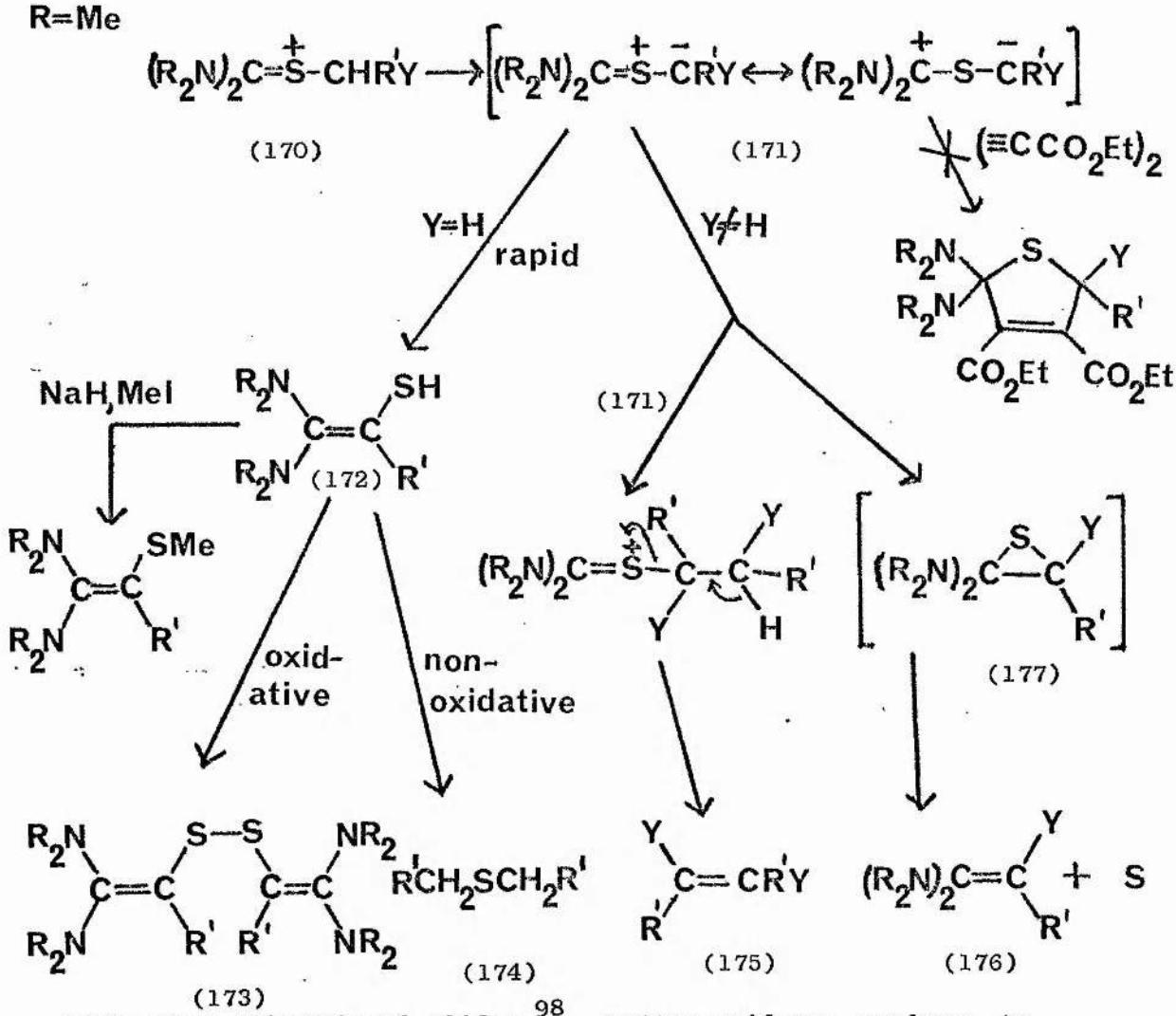


(169)

the salts from p-nitrophenacyl bromide (106), p-nitrobenzyl bromide (139) and dimethyl-α-bromomalonate (115). Although the salts obviously reacted on addition of phenyl lithium (1 mole), as shown by the development of colours or by solubility effects, in no case could any appreciable amount of olefin (or oxirane) be found. (In the case of (139), a small amount of p,p'-dinitro-trans-stilbene did precipitate out of solution after 3 days, but this is believed to have been formed by base-induced self-condensation of the aldehyde.) p-Nitrobenzaldehyde was recovered in substantial amount in the reaction with (115). If the ylides had been formed at all, then rapid reaction with the aldehyde would have been expected by analogy with the results obtained in section 3II.

The explanation of this lack of reactivity came when, during the course of this work, a paper was published by Nozaki et al [147] describing attempts to prepare some keto stabilised diaminomethylene sulphuranes very similar to those described already. Their findings will be discussed first in a more general form and later with regard to two particular compounds of great relevance here. Two distinct groups of products are obtained, according to the nature of the substituent Y on the potential carbanionic centre. When Y=H, either the disulphide bridged bis-enediamine (173) or the sulphide (174) is obtained according to the workup conditions. A rapid isomerisation of the ylide (171) to the enethiol (172) was postulated to account for this, and there was good evidence for the intermediacy of (172). No evidence could be found, however, for any more than a transient existence of the ylide (171), as it

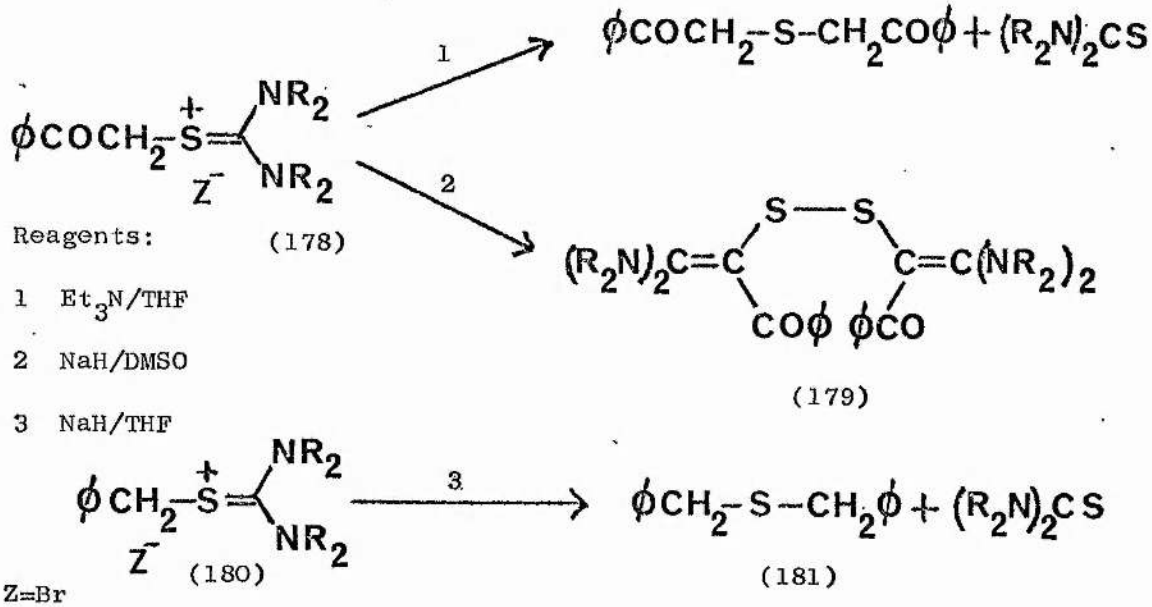
did not even undergo a cycloaddition reaction with dimethyl-acetylenedicarboxylate, which has been shown to proceed rapidly



with other thiocarbonyl ylides [98]. Better evidence, perhaps, to support the transient existence of the ylide (171) was obtained in the cases where Y≠H (e.g. Ph), for here the olefin (176) was isolated and this seems likely to be formed by a 1,3 ring closure of the ylide (171) to give the thiirane (177), which extrudes sulphur to give (176). Thiiranes [98,99] and olefins [89] have been isolated previously as decomposition products of thiocarbonyl

ylides (see Introduction, sect. 4). An alternative pathway when Y≠H involves reaction with a further mole of salt to give a symmetrical olefin (175) and the thiourea (also isolated).

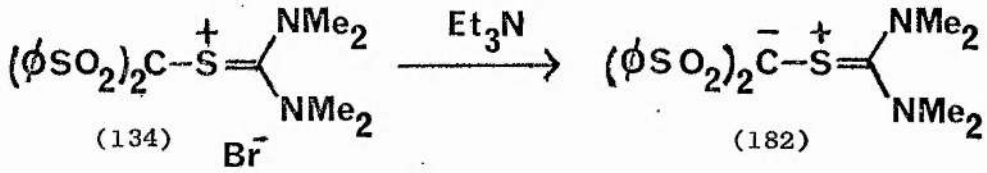
The two cases studied by Nozaki et al which are of relevance here are the salts of phenacyl bromide (178) and benzyl bromide (180). Under oxidative conditions these gave the disulphide-



bridged bis(enediamine) (179) and the sulphide (181) respectively. The reaction of the salt from p-nitrophenacyl bromide (106) with phenyl lithium was re-examined, and a product was found which appeared, from its mass spectrum, to correspond to the disulphide bridged bis(enediamine). Attempted purification of this compound by column chromatography failed. No p-nitrobenzyl sulphide could be detected (mass spectrum) in the product from the reaction of the salt from p-nitrobenzyl bromide (139) with base, but the yield quoted by Nozaki is much lower in this reaction and possibly

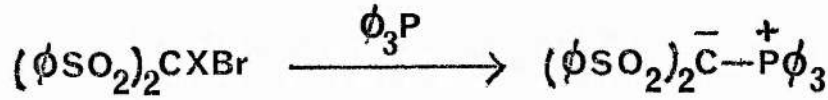
different conditions might have to be employed (e.g. longer reaction time).

The N,N,N',N'-tetramethylisothiouronium salt of bis(phenylsulphonyl) methane (134), on the other hand, exhibits a more predictable kind of behaviour and provided an ylide. When treated with triethylamine, it yielded the stable diaminomethylene sulphurane (182) which was protonated by perchloric acid (showing that it was basic) and showed evidence of delocalisation of negative charge from



(134) (182)

the carbanionic carbon into the sulphonyl substituents (by the shift of the sulphonyl absorption in the infra-red spectrum to lower frequency cf. salt). The chemical properties of (182) will be described in sect. 3II. It is notable that formation of the analogous triphenylphosphonium ylide (183) occurs even more readily [148]. In this case the excess triphenylphosphine acts as base, as the ylide

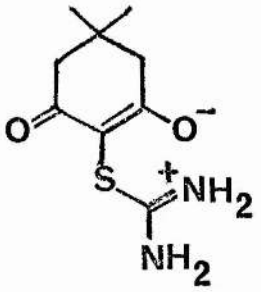


(183)

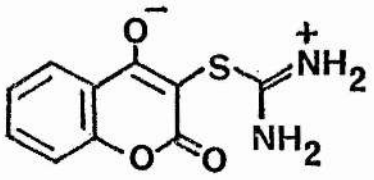
(183) is very weakly basic.

Some mention of the properties of the thiouronium salts from cyclic β-dicarbonyl compounds (140) and (141) (sect. II) is in order here. These were found [141,142] to lose hydrogen halide very readily. Thus the ylides (184) and (185) are very weakly basic,

presumably due to the extensive charge delocalisation within the planar



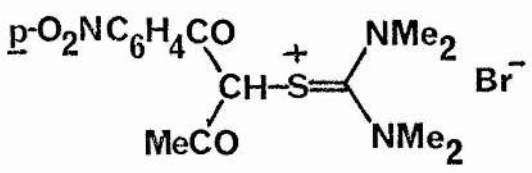
(185)



(184)

enolate system. Comment was made on the relative stability of these compounds towards cyclisation.

Finally, an unusual reaction of the salt from p-nitrophenacyl bromide (106) occurred when it was heated to reflux briefly with acetic anhydride or when heated in boiling acetyl chloride/acetic acid for 4 hours. The product, which was the same in both cases, was not the expected acetyl derivative (186), but a compound of empirical formula $C_{11}H_{12}N_2$. It formed a 2,4-dinitrophenylhydrazone, $C_{17}H_{16}N_2$, on treatment with Brady's reagent, showing that it contained a reactive carbonyl group. The structure of the product could not be elucidated further, but it appears likely that the tetramethylthiourea moiety is undergoing some obscure interaction, possibly akin to those found in sect. II.



(186)

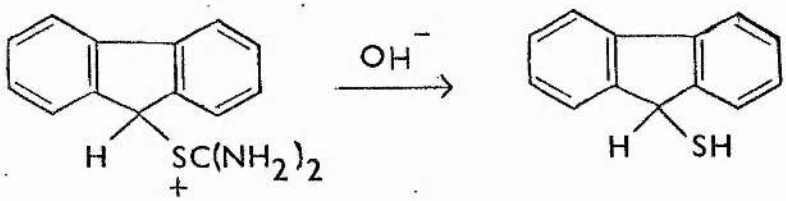
Conclusion

Therefore it appears that thiouronium ylides, $RR^1\bar{C}-\overset{+}{S}=C(NR^2R^3)_2$ stabilised by electron-withdrawing groups R and R^1, can only be isolated if R and R^1 are strongly electron-withdrawing in character, and at present only three classes of substituent have been found to be effective, namely disulphonyl, dicyano and trans-β-dicarbonyl groups. Because of this, attention was focussed on cyclopentadiene derivatives.

II. Thiouronium Salts Containing the Cyclopentadiene Ring

(i) Derivatives of fluorene

On treatment with one mole of aqueous base (or ethoxide), the unsubstituted thiouronium salt (143) yielded the thiol (187), which had been prepared previously [149] by a similar route, although the S-fluorenylisothiouronium salt (143) was not isolated. This method



(143) (187)

had given an ylide in the case of fluorenylidenedimethylsulphurane and other fluorenylides, but the alternative pathway to the thiol in the case of the thiouronium salt is not really surprising in view of the hydrolytic reactivity of this class of compounds (see sect. 2I). The method was not extended to the more highly substituted thiouronium salts for reasons which will become apparent in section 3 II.

When the series of substituted thiouronium salts (143) - (149) was treated with non-aqueous base, in the first instance phenyl lithium, the stable diaminomethylenesulphuranes (188) - (193) were isolated as highly crystalline colourless solids. These compounds form a series which is at present unique. The tetrasubstituted ylide (194) decomposed too rapidly to enable isolation, but its existence was inferred from its reactions in situ. It was

interesting in that it was the only ylide in the series which appeared to be coloured. Subsequently, it was found that

(188) $R^1=R^2=R^3=R^4=H$

(189) $R^1=R^3=Me;\ R^2=R^4=H$

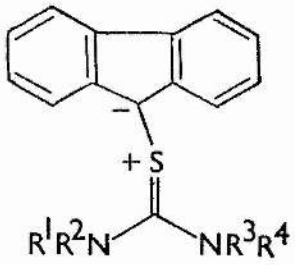
(190) $R^1,R^3=CH_2CH_2;\ R^2=R^4=H$

(191) $R^1=R^3=Ph;\ R^2=R^4=H$

(192) $R^1=Ph;\ R^2=R^3=R^4=H$

(193) $R^1=Ph,\ R^3=Me;\ R^2=R^4=H$

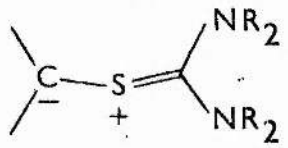
(194) $R^1=R^2=R^3=R^4=Me$



triethylamine was sufficiently basic to prepare the phenylated ylides (191) - (193), but the non-aryl ylides (188) - (190) could not be prepared using this reagent. Therefore the presence of aryl substituents in the heteronium group appears to enhance the acidity of the salts, a finding in line with that described previously for phosphonium ylides (see introduction, sect. 2). The aryl ylides (191) - (193) were nevertheless still sufficiently basic to be reconverted to their precursor salts on treatment with acid.

The increased basicity of the non-aryl ylides (188) - (190) compared with that of, for instance, fluorenylidenedimethylsulphurane (6) (pK_a of conjugate acid 7.8), is worthy of mention. Because the diaminomethylene sulphuranes (188) - (190) could not be generated in appreciable amount by the use of triethylamine, the pK_a of their conjugate acids (143) - (145) must be greater than that of triethylamine, i.e. greater than ~13. This indicates

that an alkyl substituted thiouronium group has a lesser acidifying effect than a dimethylsulphonium group on the α-carbon atom, and in turn suggests that the sulphur d orbitals in the thiouronium ylide (195) are able to interact less well with the potential



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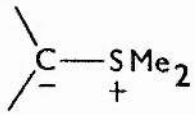
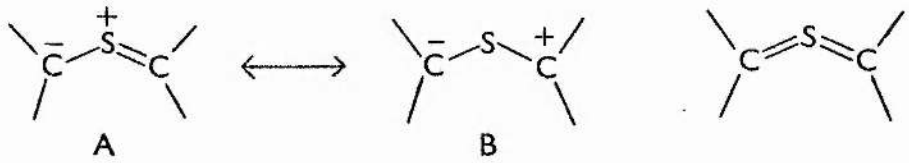


(196)

carbanionic centre than in the case of the sulphonium ylide (196). It has been shown that for effective d orbital overlap of an ylide heteroatom of the second row with an adjacent carbanionic centre, the heteroatom should bear a substantial degree of positive charge. Consideration of the canonical forms (197) contributing



A B

(197) (198)

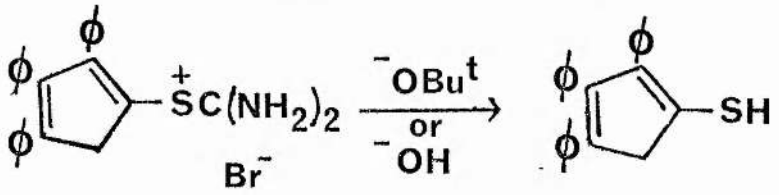
to thiocarbonyl ylides (excluding, for the moment, the tetracovalent form (198)) shows that if the 1,3-dipolar form, B, makes an appreciable contribution then the positive charge on the sulphur atom will indeed be diminished. This is likely to be the case in thiouronium ylides because the amino groups are also able to delocalise efficiently a positive charge on the adjacent carbon

atom. Therefore, from this simple explanation, they should be more basic than the corresponding sulphonium ylides. This is, of course, a gross simplification of what is probably a very complex phenomenon, but until more sophisticated bonding theories are developed which will enable an accurate estimation to be made of the contribution from the all-covalent canonical form (198), it appears to be sufficient in that it does explain the observed result.

The absorption maxima of the ylides (188) - (194) showed a shift to longer wavelength compared with the corresponding precursor salts, in line with the findings for other ylides. The N,N,N',N'-tetramethyl ylide (194), which showed absorption at 392 nm and was red, is the only coloured thiouronium ylide known at the present time. The ^{1}H n.m.r. spectra of the ylides (188)-(191) showed the absence of the signal due to the proton at the 9-position on the fluorene nucleus, as expected.

(ii) Derivatives of 1,2,3-triphenylcyclopentadiene

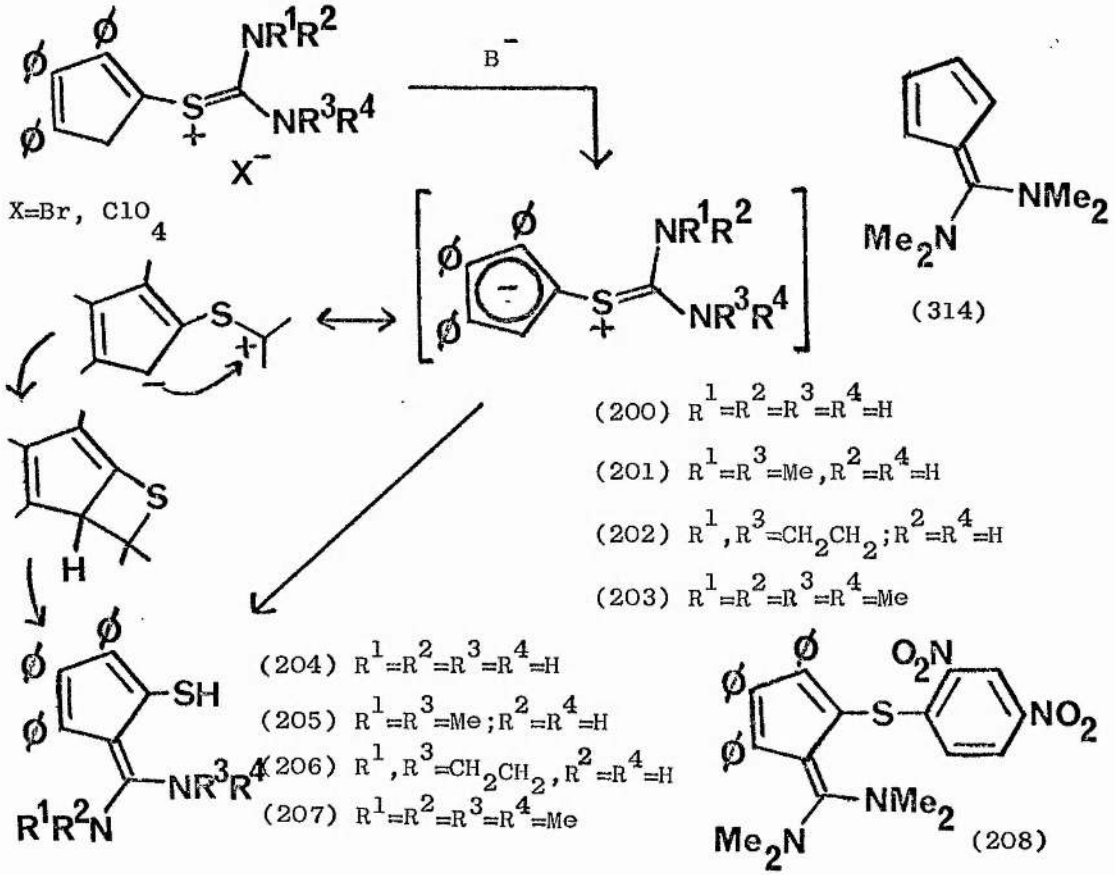
When t-butoxide (1 mol) was added to the unsubstituted thiouronium salt (150), the hitherto unreported thiol (199) was obtained in a reaction similar to that already described for fluorene.



(150) (199)

In the presence of aqueous hydroxide, the thiol (199) was again obtained but it was contaminated with an unidentified green compound, possibly a product from the aerial oxidation of the thiol.

With phenyl lithium in anhydrous conditions (or later with triethylamine in methanol) the behaviour appeared to be quite complex. It was shown, by reactions carried out on the freshly basified solution (see sect. 3II) that the ylides (201) - (202) were definitely present in the solution, but when isolation was attempted the solids which were obtained, although showing correct molecular-ion peaks in their mass spectra, did not in general possess the properties which the solutions had shown. In the case of the N,N,N',N'-tetramethyl substituted ylide (203), a rapid rearrangement appeared to have taken place involving a postulated

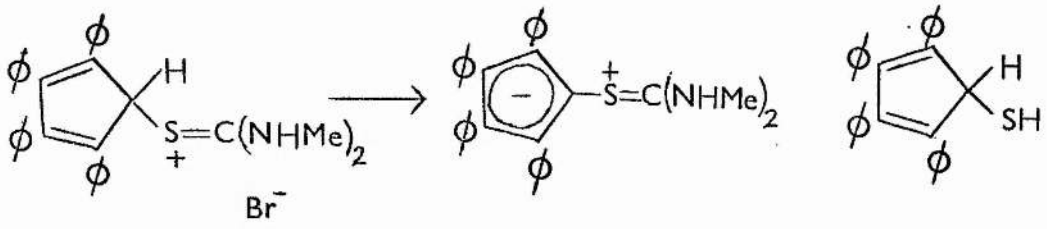


1,4 cyclisation mechanism to give the product, postulated as the mercaptofulvene (207), which was identified by comparison of its ultra-violet spectrum with that of 6,6-dimethylaminofulvene (314)[150]. Attempted characterisation as the 2,4-dinitrophenyl thioether (208) was not successful under the conditions employed. The postulated 1,4 cyclisation appears to be rapid because when the solution was allowed to react with p-nitrobenzaldehyde, none of the expected fulvene (252) was obtained. The products from the attempted isolation of the other three ylides could not be characterised but examination of their mass spectra suggested that some mercaptofulvene might be present in the case of (201) and (202). This 1,4 cyclisation is analogous to the 1,3 cyclisation observed in several thiocarbonyl ylides [89,93,94,98,99], and presumably occurs on the 5-carbon because of the reduced strain in the four-membered cyclic intermediate. The 5-position has also been shown to be more reactive (sect. 3II).

(iii) Derivatives of 1,2,3,4,-tetraphenylcyclopentadiene

The N,N'-dimethyl substituted salt (157) was the only salt in this series to be examined in detail, and its reactions are assumed to be representative of the class. When the salt (157) was treated with phenyl lithium in tetrahydrofuran or triethylamine in methanol, evidence was obtained which showed the existence of the ylide (209) in the solution (see §3II). Unfortunately, all attempts to isolate the ylide as a solid led to failure, and small amounts of the

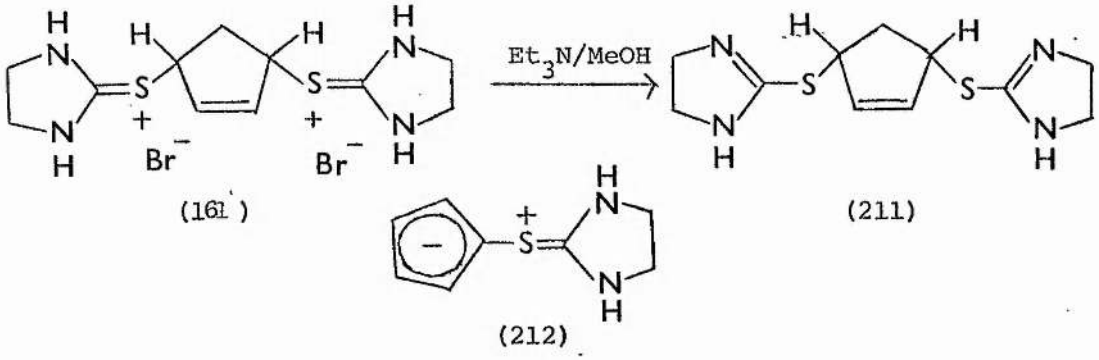
thiol (210) were isolated instead. Presumably this is formed, when



(157) (209) (210)

phenyl lithium is used as base, from hydrolysis of the salt (157) by small amounts of lithium hydroxide which is present in the phenyl lithium or may be generated in the aqueous workup.

(iv) Derivatives of unsubstituted cyclopentadiene

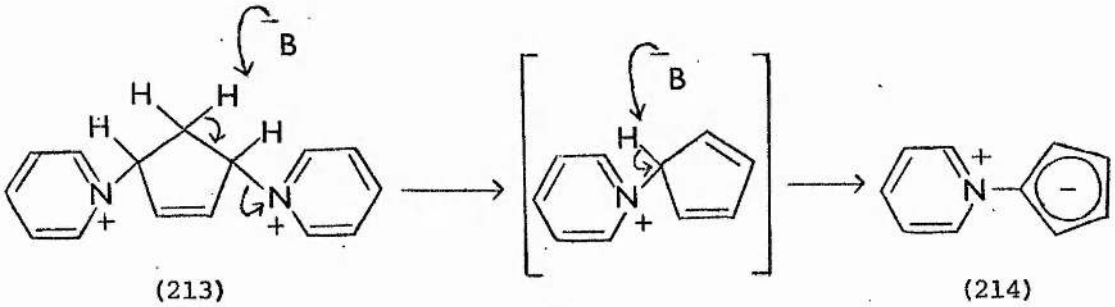


(161) (211)

(212)

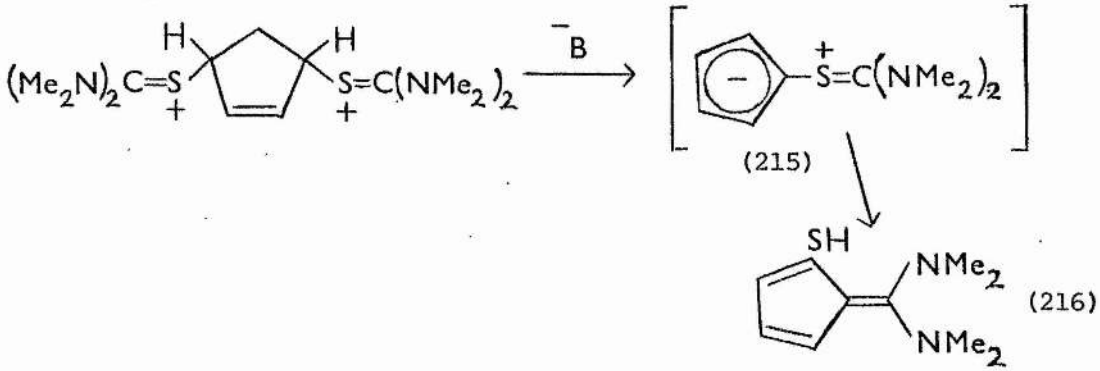
With the one salt which was examined (161), reaction with triethylamine afforded exclusively the bis(isothioureido) free base (211), identified by its analysis and spectra. No trace of the ylide (212) could be found, although (211) showed an intense peak in its mass spectrum at m/e 166 which had the molecular formula of the ylide. (211) did not give an azo dye with benzene diazonium chloride, which the ylide would be expected to give.

The fact that (161) gives the bis(isothioureido) free base (211) rather than the ylide (212) indicates that the protons on the 5-position of the cyclopentene ring are not sufficiently acidic compared with the protons on the thiouronium moiety. The initial attack of the base has been shown to take place at the 5-position in the case of other bis-salts (e.g. 213) which gave rise to ylides, for example pyridinium cyclopentadienylide (214). The remedy might



(213) (214)

be to use a tetrasubstituted thiouronium salt, but this does not appear to be readily available, and also the ylide (215), once formed, would be likely to undergo a rapid isomerisation to the mercaptofulvene (216), by analogy with the result described earlier (section (ii)). For these reasons, unsubstituted cyclopentadienylidene diaminomethylenesulphuranes were not studied further.



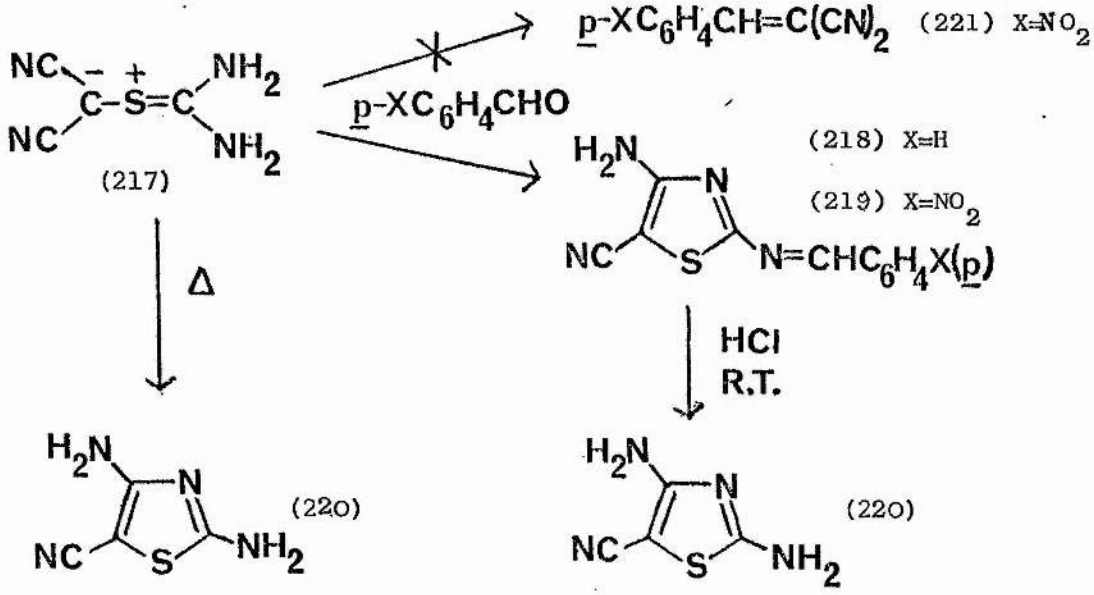
(215) (216)

§3. REACTIONS OF THIOURONIUM YLIDES

I. Ylides not Stabilised by the Cyclopentadiene Ring

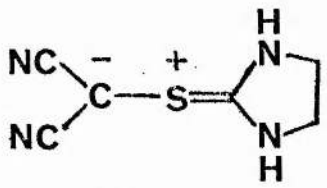
(i) Dicyanomethylenediaminomethylene sulphurane

Although the ylide (217) underwent reaction with aldehydes, none of the products expected from a Wittig reaction could be found. With the two aldehydes under investigation, benzaldehyde and p-nitrobenzaldehyde, the former reacted quite slowly whereas the latter reacted fairly rapidly with one mole of the aldehyde in boiling ethanol to give the corresponding Schiff's bases, (218) and (219). The structure of (218) was verified by its ready hydrolysis to



2,4-diamino-5-cyanothiazole and benzaldehyde. When 2 moles of aldehyde were used, in the case of p-nitrobenzaldehyde, a small

amount of a different product was found in addition to the Schiff's base (major product). This was not the expected fulvene (221), however. The formation of the Schiff's bases (218) and (219) indicates that the ylide (217) is undergoing cyclisation to the thiazole (220) faster than reaction with the aldehydes. The thiazole (220) has been shown[93] to result from the action of heat on (217) alone. The ylide (217) therefore appears to have a low nucleophilicity and this is explained by the extensive delocalisation of the charge on the potential carbanionic centre. The low basicity of these ylides also supports this (for instance, (222) is soluble in alkali).



(222)

(ii) Bis(phenylsulphonyl)methylenediaminomethylene sulphuranes

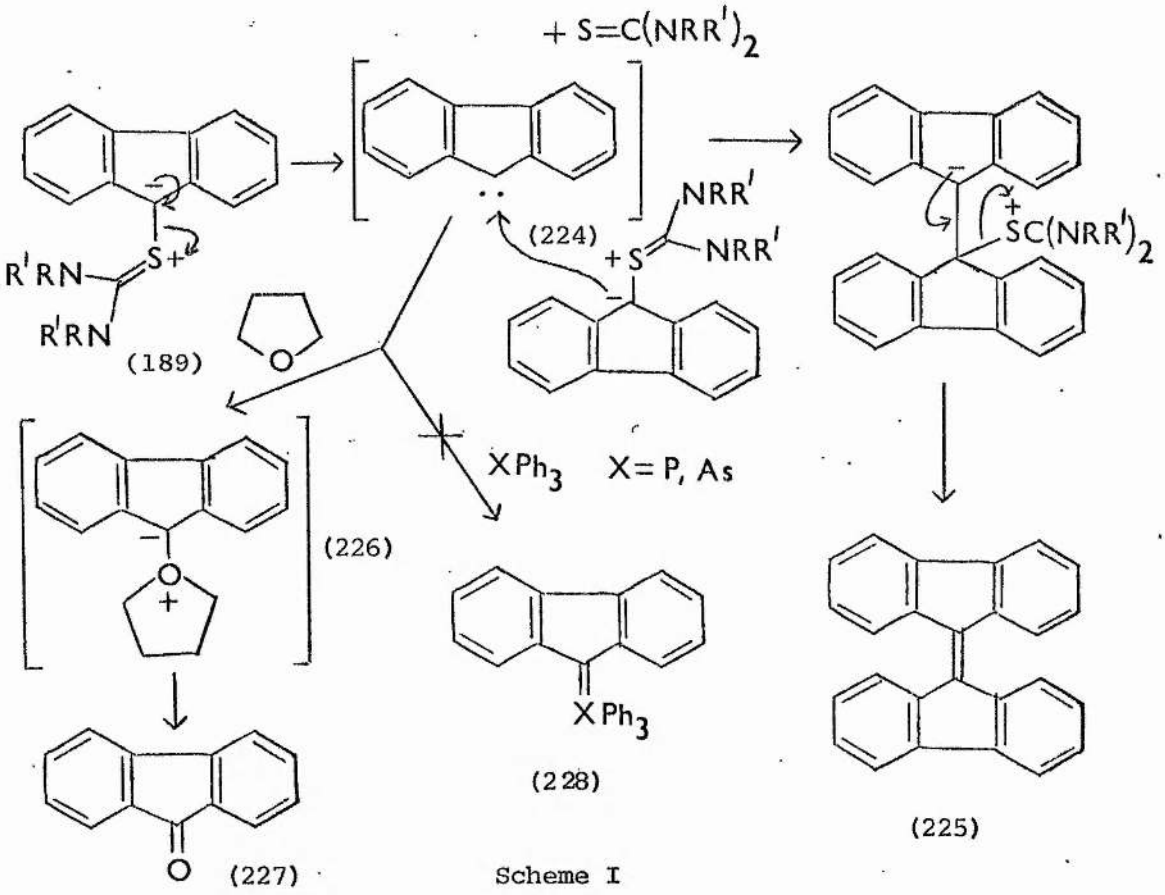
As the only member presently known in this series, the N,N,N',N'-tetramethyl ylide (182), was only discovered at a very late stage in this work, there has not been sufficient time to study its chemical reactions fully. However, the protonation which takes place in perchloric acid (see sect. 2I) shows that it is susceptible to some extent to electrophilic attack.

II. Ylides Stabilised by the Cyclopentadiene Ring

(i) Fluorenylides

(a) Thermal decomposition

The alkyl substituted fluorenylidenediaminomethylene sulphuranes (188) - (190) and (194) showed a tendency towards decreased thermal stability as the number of N-substituents was increased. Thus the unsubstituted ylide (188) was the most stable, and could be kept indefinitely at room temperature, the N,N'-disubstituted ylides (189) and (190) could only be kept for a few days at room temperature before signs of extensive decomposition were evident, and the N,N,N',N'-tetrasubstituted ylide (194) was too unstable in solution to enable isolation, even at low temperature. A similar stability trend has been observed in the dicyanomethylene-diaminomethylene sulphuranes [93], and the effect arises presumably as a result of steric crowding by the bulky N-methyl substituents. The principal breakdown product in the absence of air and in an inert solvent is bifluorenylidene (225), and the proposed mechanism is shown in scheme I. The ylide fragments spontaneously into the thiourea and the carbene (224), which is then attacked by another molecule of ylide to give the observed product. This mode of decomposition, by what is termed a biphilic mechanism (where the same compound is acting both as a nucleophile (ylide) and an electrophile (carbene)), has been well established in the case of other thermally unstable ylides, notably 2-nitro-fluorenylidenedimethylsulphurane and trimethylammonium fluorenylide (see introduction, sect. 3).



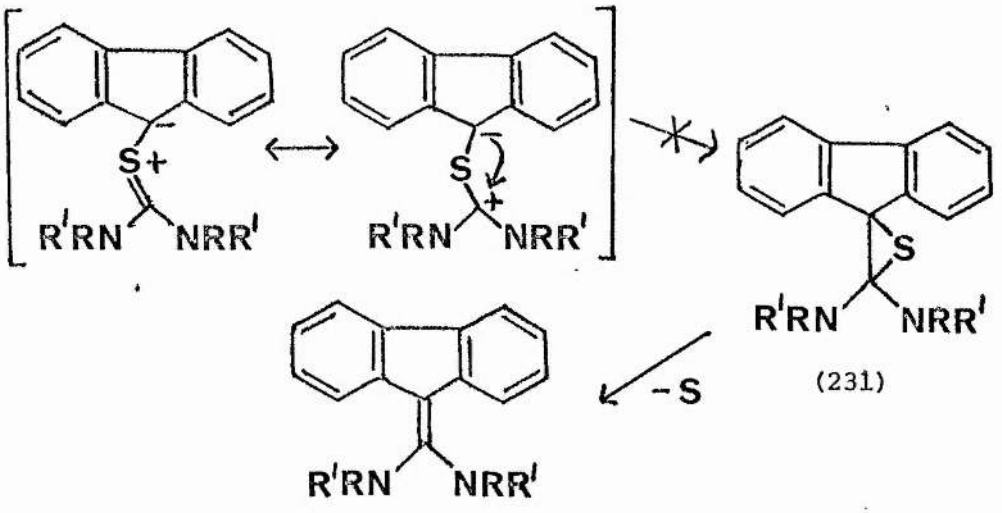
Scheme I

When decomposition of (189) was allowed to take place in tetrahydrofuran in the absence of air, fluorenone (227) was obtained exclusively instead of bifluorenylidene. It is believed that a molecule of the solvent attacks the carbene to form the unstable oxonium ylide (226), which decomposes to give fluorenone. An attempt to trap the carbene using a group V heteroatom, for instance with triphenylphosphine or triphenylarsine, and so effect a 'transylidation' reaction in a manner which has not been hitherto reported for fluorenylides, did not in fact

succeed and none of either ylide (228) could be detected. A substantial amount of triphenylphosphine oxide was isolated when the reaction with triphenylphosphine was carried out, under nitrogen, either in methylene chloride at room temperature or in a melt at 160°. Its mode of formation is uncertain, but as triphenylphosphine is known not to react with oxygen at similar temperatures even in air, then its presence might tend to suggest that some interaction with the ylide is taking place.

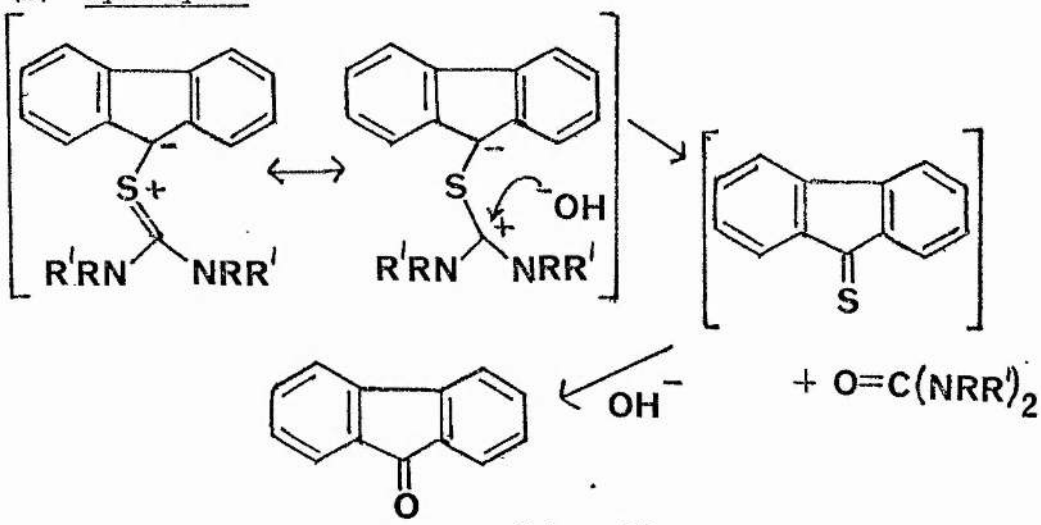
The N-arylated fluorenylidenediaminomethylenesulphuranes (191) - (193) are stable indefinitely at room temperature, but decompose rapidly above their melting points, again presumably by the same mechanism, for a high yield of fluorenone was isolated from the decomposition in air of the N,N'-diphenyl ylide (191). The carbene (224) reacts preferentially with oxygen in this instance.

Notably, the fluorenylides showed no tendency at all to undergo a 1,3 ring closure to give a thiirane (231) or its breakdown product, the fulvene (232), which has been quoted as a characteristic property of unstabilised thiocarbonyl ylides (see introduction, sect. 4). This reflects the greater stability conferred upon these ylides by the aromatic nature of the fluorene nucleus.



(232)

(b) Hydrolysis



Scheme II

When the non-aryl substituted fluorenylidenediamino-methylenesulphuranes (188) - (190) were treated with excess hydroxide in alcoholic solution, fluorenone was formed rapidly and in high yield. The postulated mechanism (scheme II) involves initial attack by the hydroxide ion on the carbon atom of the thiourea moiety as shown, to give the urea and the unstable fluorenone thione which is converted immediately

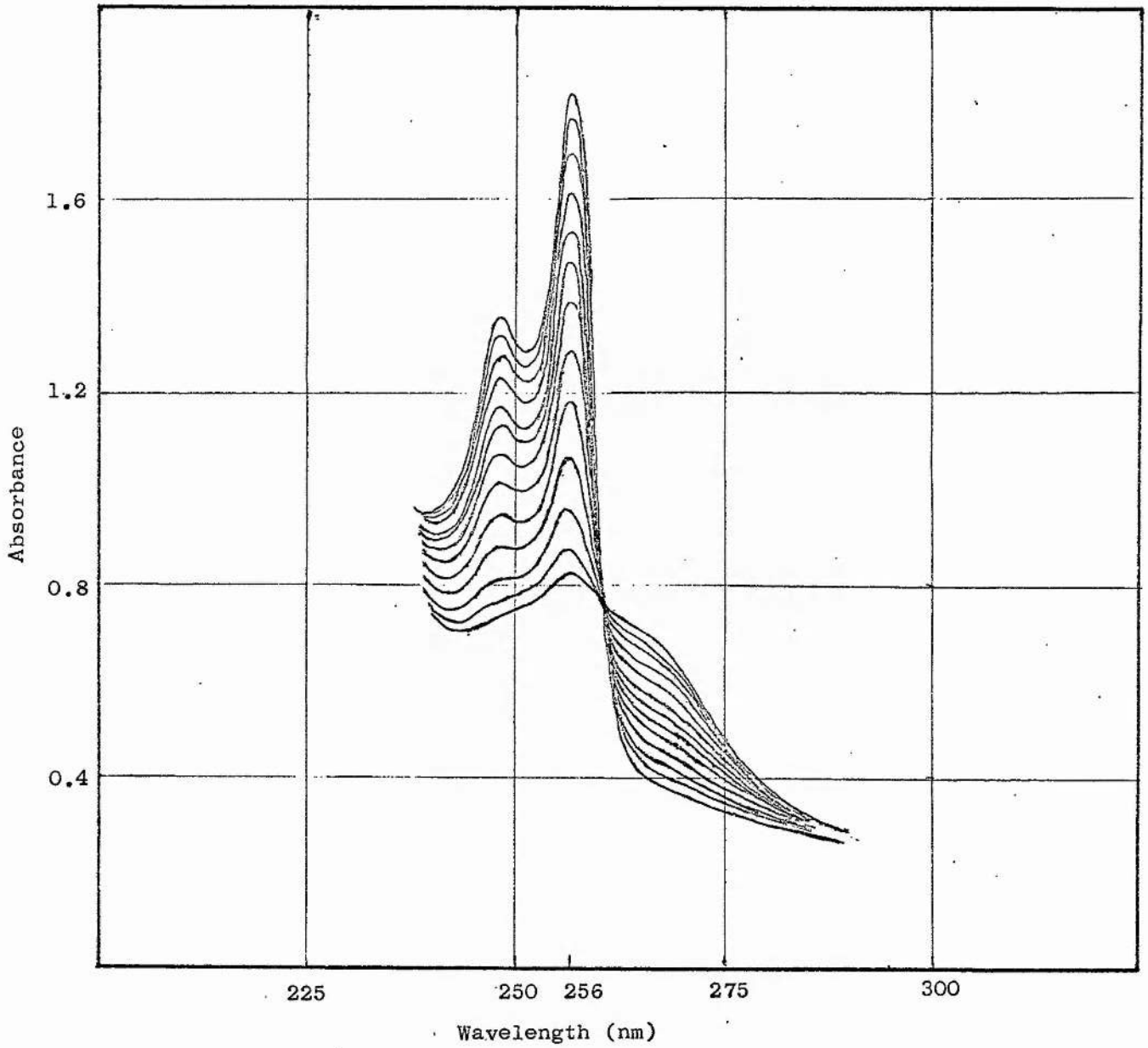
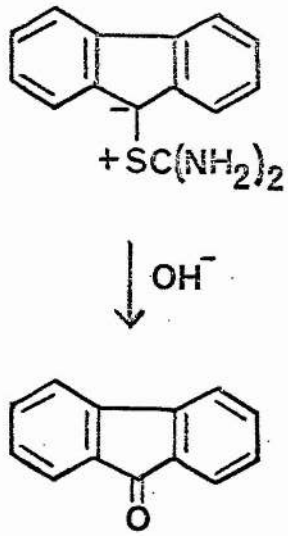


Figure 1

Hydrolysis of Fluorenylidene-diaminomethylenesulphurane



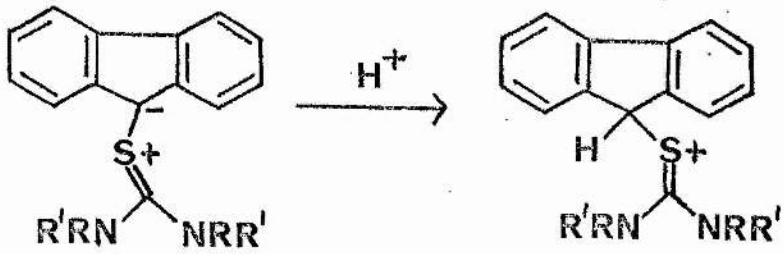
to fluorenone under the alkaline conditions. The instability of thiones to alkali has been reported [151]. The effect of the N-substituents on the rate of the reaction was of some interest. The formation of the product could be observed conveniently by monitoring the growth of the peak at 256 nm. in the ultra-violet spectrum (figure 1), when the reactions were carried out at 40°. The unsubstituted ylide (188) underwent hydrolysis most rapidly and the reaction was virtually complete after 45 min. The N,N'-ethylene bridged ylide (190) was slower, and the N,N'-dimethyl ylide (189) was the slowest of all and considerably slower than (190). Two points are of note. First, the effect of the N,N'-alkyl substituents is to reduce the rate of hydrolysis, and this can be explained by the increased steric hindrance around the reaction site. Second, the much greater rate of (190) vs. (189) appears to be due to decreased steric interaction of the alkyl substituents which are held rigidly in the ring, whereas the methyl substituents in (189) are free to rotate. The greater susceptibility of a thioureido carbon to nucleophilic attack when it is included in a ring will be observed again (sect. 6).

(c) Carbanionic reactions with electrophiles

1) Protonation

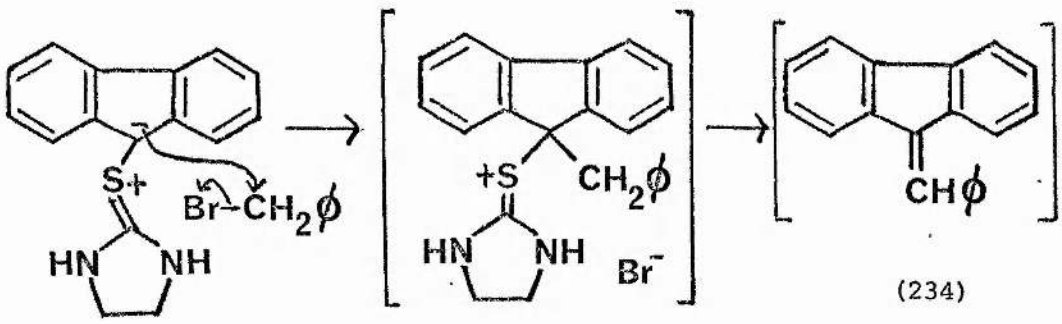
It has already been mentioned that the ylides (188) - (194)

are basic. Protonation was shown to take place in strong acid



at the 9-position on the fluorene nucleus in all cases including the N-aryl ylides (191) - (193).

2) With benzyl bromide



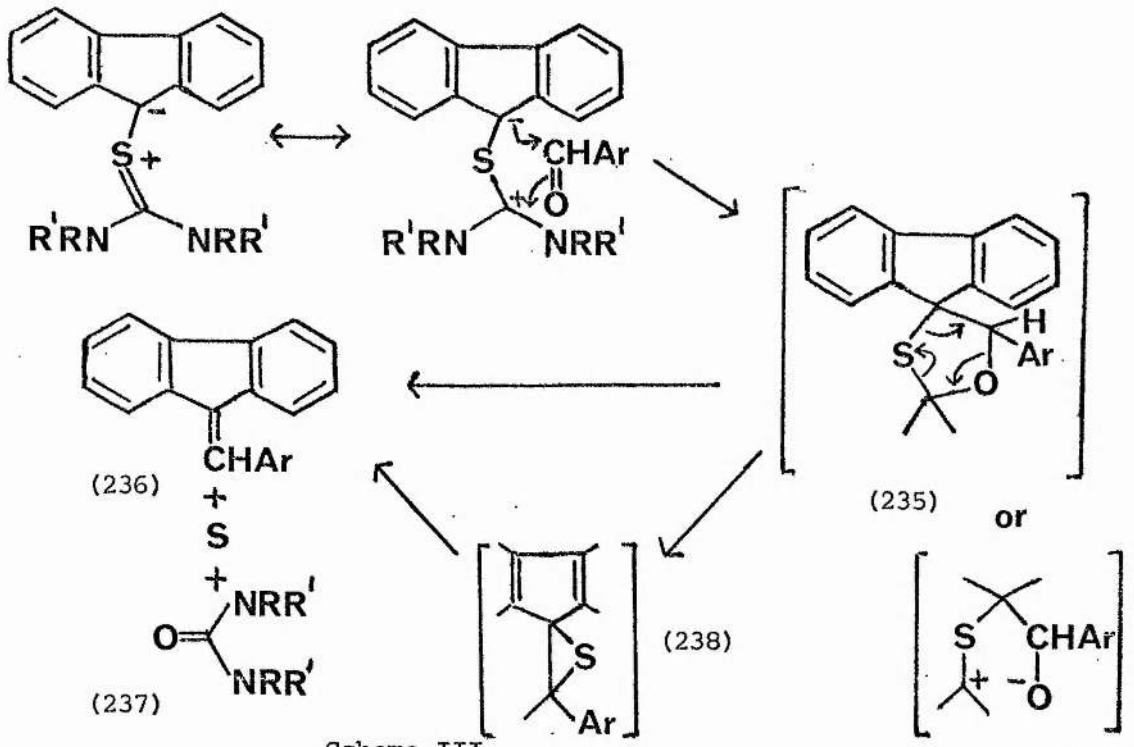
(233) (234)

Reaction took place at the 9-position of the fluorene nucleus as shown to give the postulated intermediate salt (233). All attempts to characterise this material failed. For instance, it underwent decomposition with perchloric and picric acids. Good evidence in favour of the proposed reaction was available, however, from the mass spectrum of (233), which showed an intense peak for the molecular ion of the fulvene (234) and

this could only arise if the reaction had followed the pathway shown. The fulvene could not be generated chemically on thermal decomposition of (233), even in the presence of base. An analogous reaction has been reported [152] for trimethylammonium fluorenylide, where the fulvene was isolated.

(d) Carbylidic reactions

1) With aldehydes



Scheme III

The fluorenylidenediaminomethylenesulphuranes (188) - (194) reacted readily with p-nitrobenzaldehyde and afforded in several cases almost quantitative yields of the fulvene (236) and the corresponding urea (237). As sulphonium ylides have hitherto been found to lead invariably to the formation of an oxirane, some

explanation of this apparently anomalous result is required. The mechanism proposed in scheme III accounts satisfactorily for the observed results, where the attack of the ylide on the aldehyde leads to a 5-membered cyclic transition stage (235), proposed by analogy with the 4-membered transition stage which is well established in phosphorus ylide chemistry (see introduction, sect.3). The collapse of (235) may proceed in the manner shown to give the olefin directly, or alternatively by way of an unstable thiirane (238) which extrudes sulphur immediately to give the observed products. In either case the major driving force appears to be the formation of the carbonyl bond at the expense of the thiocarbonyl bond, and examination of bond energy values [153] shows that the former is stronger than the latter by about 40 kcal mol^{-1}. On this basis, there is a stronger similarity to the chemistry of phosphorus ylides than to sulphonium ylides, where formation of the strong phosphorus-oxygen bond is the major driving force of the conventional Wittig reaction. By analogy, the term 'homo-Wittig' has been coined to describe this novel behaviour of thiouronium ylides, as the transition stage (235) contains one more carbon atom than that of the usual Wittig reaction. It should also be pointed out that the dipolar structure (239) could be used equally well to describe the transition stage.

The unsubstituted and dialkyl diaminomethylenesulphuranes (see table 2) showed complete reaction with p-nitrobenzaldehyde within 20 hr. at room temperature, and a substantial amount of product appeared to have been formed after only one hour. This

Ylide	R^1	R^3	R^2,R^4	Reaction time	Reaction temp	Yield of fulvene (%)	mpt. (°)*
(188)	H	H	H	16 hr	R.T.	90	146-58
(189)	Me	Me	H	20 hr	R.T.	85	130-45
(189)	Me	Me	H †	1 hr	R.T.	40	150-7
(190)	CH_2CH_2		H	20 hr	R.T.	87	128-40
(191)	Ph	Ph	H	3 days	61°	1.5	160-66
(194)	Me	Me	Me†	1 hr	R.T.	40	158-62

* lit.[197] mpt. of fulvene 167-8°

† Ylide reacted *in situ*

Table 2. Reactions of fluorenylidenediaminomethylenesulphuranes with *p*-nitrobenzaldehyde

Ylide	R^1	R^3	R^2,R^4	Aldehyde/ketone	Reaction time*	Yield of fulvene (%)	mpt. (°) (lit.°)
(190)	CH_2CH_2		H	*p*-nitrobenzaldehyde	20 hr	87	128-40 (167-8)
(189)	Me	Me	H†	cinnamaldehyde	2 days	28	105-40 (154-5)
(190)	CH_2CH_2		H	*p*-anisaldehyde	19 days	30	112-8 (128-9)
(190)	CH_2CH_2		H	*p*-nitroacetophenone	28 days	0	-
(189)	Me	Me	H†	cyclohexanone	13 days	0	-

* All reactions were carried out at room temperature.

† Ylide reacted *in situ*

Table 3. Comparative reactivity study of reactions of *N*,*N*'-disubstituted fluorenylidenediaminomethylenesulphuranes with carbonyl compounds

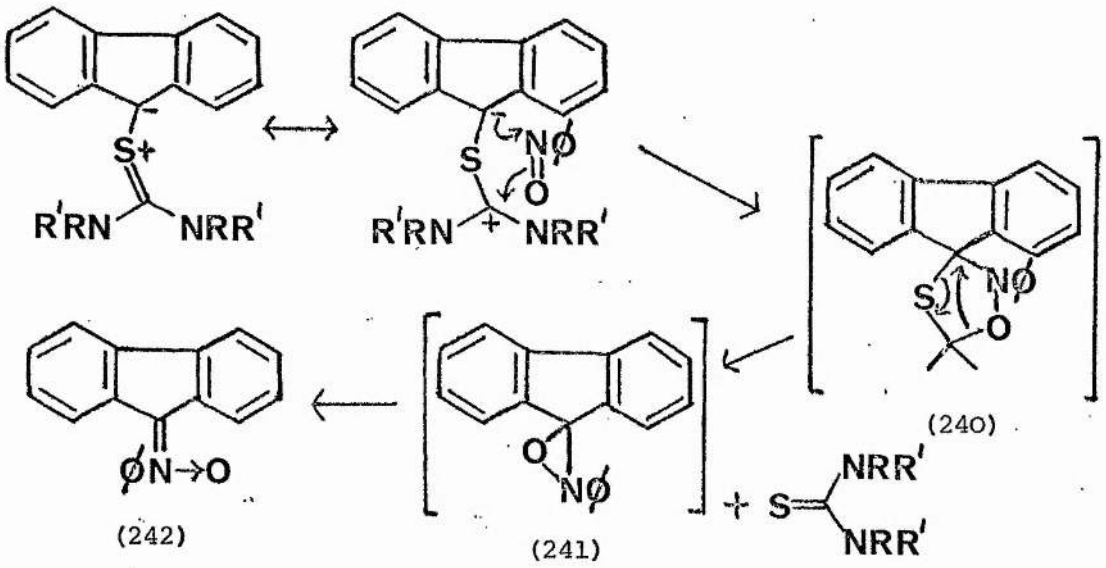
indicates that the ylides (188) - (194) are quite reactive towards carbonyl compounds. The N,N;N',N'-tetramethyl ylide (194), although it was not isolated, appeared to show a similar degree of reactivity (by comparison with (189) in situ). The N,N'-diphenyl ylide (191), on the other hand, was very much less reactive, and this is believed to result primarily from steric considerations. This is in keeping with results obtained from ^{13}C n.m.r. spectroscopy (see appendix).

The results of a comparative reactivity study of the N,N'-dialkylfluorenylidenediaminomethylenesulphuranes (189) and (190) with various aldehydes and activated ketones are shown in table 3. The least reactive aldehyde was p-anisaldehyde (p-$MeOC_6H_4CHO$), as expected owing to the fact that the electron donating p-substituent reduces the partial positive charge on the carbonyl carbon atom, which is therefore less susceptible to attack by the nucleophilic ylide. The ylides did not react with the two activated ketones, in line with the results observed for other stabilised ylides.

2) With nitrosobenzene

A transition stage (240) analogous to that proposed in the reaction with aldehydes (235) is envisaged in this reaction, but collapse of the transition stage (240) appears to proceed in a different manner in this instance to afford the anil oxide (242) and the thiourea. The anil oxide is believed to result from

spontaneous fragmentation of the oxazirane (241), as reported [154] in the reaction of sulphonium ylides, and substantiated by reports

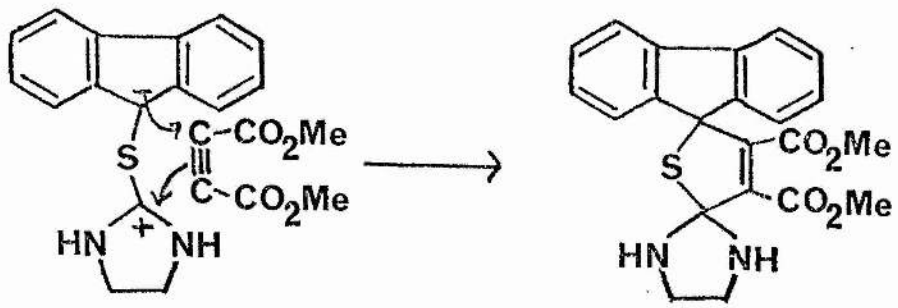


from other work [155,156] where N-phenyloxaziranes have been shown to isomerise very readily in this way. The fact that the overall reaction proceeds analogously to that of other sulphonium ylides, whereas the reaction with aldehydes proceeds differently, is difficult to rationalise. Evidence to be presented from the reaction of tetraphenylcyclopentadienylides will show that the problem is even more complex, and further discussion will be deferred until then.

Reaction of the N,N'-dialkyl ylide (190) with nitrosobenzene was complete within 10 min. at room temperature. The N,N'-diphenyl ylide (191) reacted much more slowly, similarly to the result found with aldehydes, but after 20 hr. at room temperature it too gave a high yield of the anil oxide.

(e) 1,3 Dipolar cycloaddition reaction

A number of the foregoing reactions have involved the use of a 1,3 dipolar structure to explain the position of attack of a nucleophile (for example in hydrolysis and carbylidic reactions) and from this point of view, as well as to provide a comparison with the reactions of other thiocarbonyl ylides, it appeared desirable to investigate whether fluorenylidenediaminomethylenesulphuranes would also undergo such a reaction. This indeed proved to be the case, for the ylide (190) underwent reaction with dimethylacetylene-dicarboxylate in boiling chloroform to afford the substituted dihydrothiophen (243).



(190) (243)

ii) 2,3,4-Triphenylcyclopentadienylides

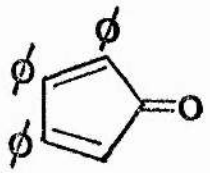
As mentioned earlier, the tendency of these ylides towards rearrangement or decomposition made it necessary that the reactions be carried out in situ, and this will be the case in this and the following subsection except where otherwise stated.

(a) Thermal decomposition

The ready tendency of at least one of these ylides (203) to undergo rearrangement to the mercaptofulvene (207) has been discussed already (sect. 2II(ii)). This mode of reaction evidently replaces the carbenic mode of decomposition which is prevalent in the fluorenylides, and demonstrates the advantages which accrue in the latter case from the presence of an annelated cyclopentadiene.

(b) Hydrolysis

Owing to the unstable nature of the ylides, this was not carried out. Furthermore, the expected product, 2,3,4-triphenylcyclopentadien-1-one (244), is known to be unstable [157].

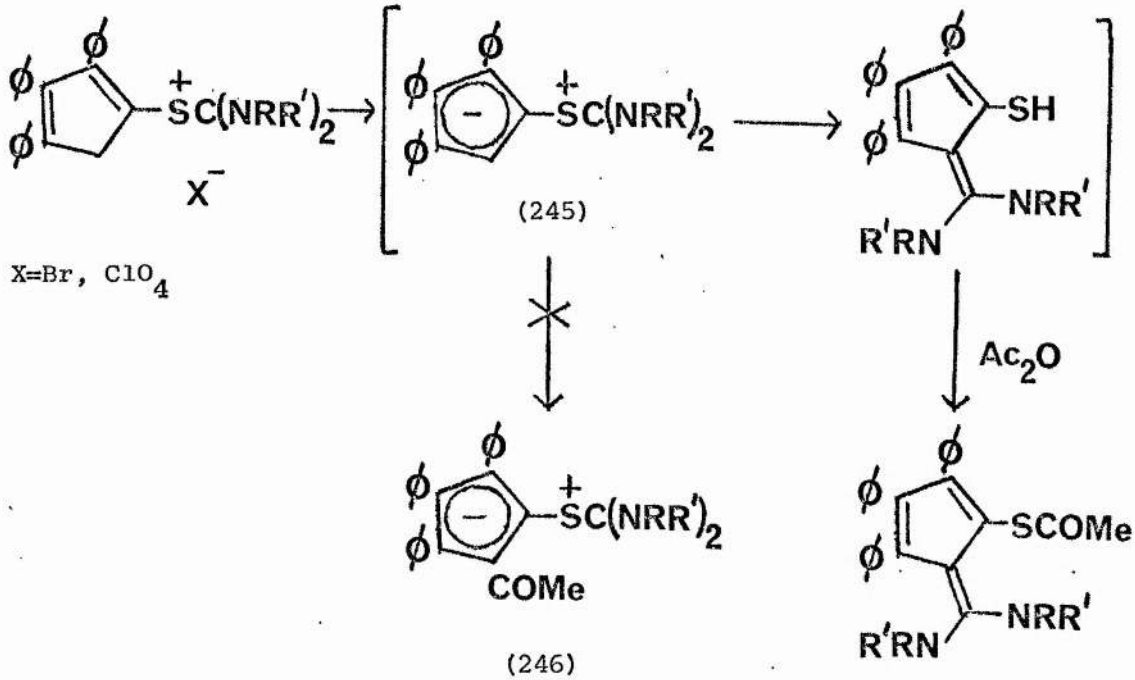


(244)

(c) Carbanionic reactions with electrophiles

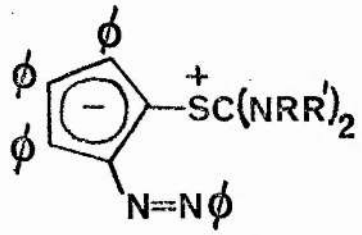
Two representative reactions were chosen to illustrate the reactivity of these ylides towards electrophiles, namely acetylation and the azo coupling reaction. When the former reaction was carried out using acetic anhydride at an elevated temperature, the products which were isolated were not the 5-acyl ylides (246) which would be expected if electrophilic aromatic substitution were

taking place on the vacant 5-position of the cyclopentadiene ring (cf. introduction, sect. 3), but instead appeared to be the S-acetyldiaminofulvenes (247) and (248), resulting from the acetylation of the rearrangement products of the ylides. The



fulvene structures (247) and (248) are supported by the relatively high carbonyl absorption frequencies (ν_{max} 1675 and 1710 cm^{-1}, respectively) whereas the ylides (246) would be expected to show a carbonyl absorption around or below 1600 cm^{-1}. Mercaptans are known to undergo S-acetylation under these conditions [158]. With benzene diazonium chloride solution, reaction took place in high yield in the case of the N,N'-tetrasubstituted ylide (245, R=R'=Me) and in lower yields with other ylides to give products of uncertain

identity, but from their mass spectra and low basicity they did not appear to be the 5-phenylazo ylides (249). Whereas 5-phenylazo ylides derived from phosphorus and arsenic ylides



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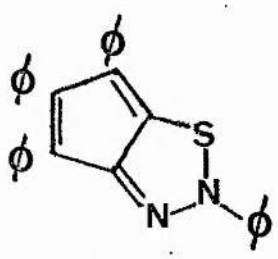


(250)

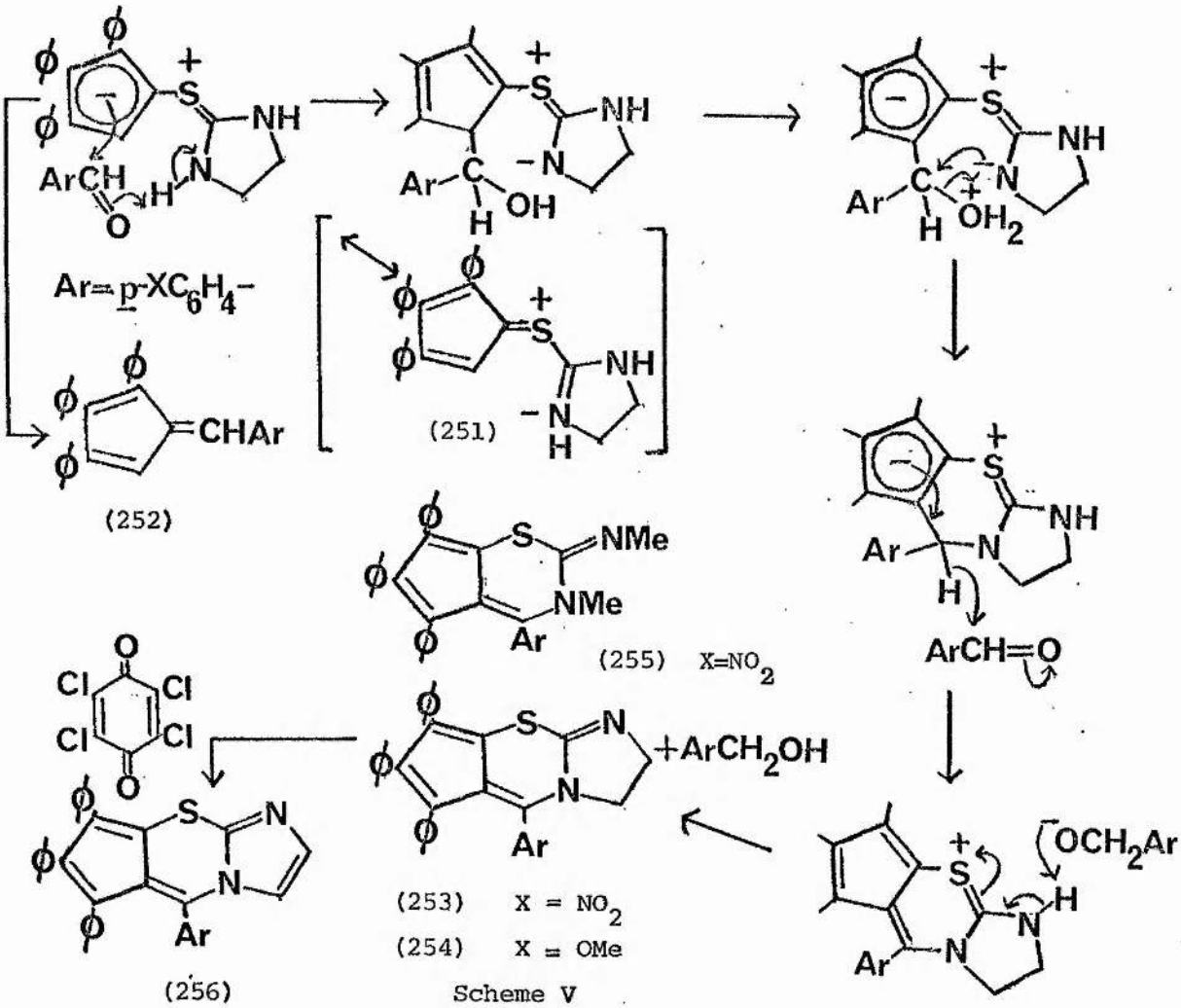
have been shown to give strong parent ion peaks, these compounds, on the other hand, all gave no peak at the m/e value expected for (249) but instead they all gave an intense peak at m/e 428, which is consistent with the possible structure (250).

(d) Carbylidic reactions

1) Aldehydes

When the N,N'-disubstituted ylides (201) and (202) were allowed to react with an equimolar amount of p-nitrobenzaldehyde, a small amount of the expected fulvene (252) was obtained, presumably by a mechanism similar to that already described for the fluorenylidenediaminomethylenesulphuranes. However, the major product, which was obtained in each case in yields of about ten times that of the fulvene, was the novel heterocycle (253), ((255) in the case of ylide (201)), which is a member of the pseudoazulene family. A possible scheme to explain the formation of the heterocycles is suggested above, and involves initial

attack of the ylide carbanion at position 5 of the cyclopentadiene ring instead of the usual position 1 (which gives the fulvene),



Scheme V

followed by ring closure by nucleophilic attack of the thioureido nitrogen on the exocyclic carbon atom. The required oxidation level of the observed product is accounted for by a proposed hydride transfer mechanism, and is consistent with the observation that the greatest yield of (253) obtainable was 32%, because half of the aldehyde is necessarily reduced to benzyl alcohol. An

alternative mechanism (not shown) is for the thioureido nitrogen initially to attack the aldehyde (through a canonical form such as (251)). p-Anisaldehyde reacted similarly to give the pseudoazulene (254) in substantially lower yield under the same conditions.

The reactions of the ethylene bridged pseudoazulene (253) with a variety of oxidising agents were studied, partially to confirm its structure and partially to investigate the properties of the resulting heterocyclic system (256), which contains 14 π electrons in its periphery and should therefore show aromatic properties. Attempted reaction with a weak oxidising agent such as benzoquinone led to the recovery of the starting material in high yield. With chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), the dehydrogenated heterocycle (256) was isolated in yields of 15% and 6% respectively under the same conditions. The structure of (256) was inferred from its n.m.r. spectrum, which showed that the signals of the aliphatic protons in the starting material were no longer present, suggesting that the remaining two protons on the ethylene bridge were aromatic in nature, and its ultra-violet spectrum, which showed a new absorption band at long wavelength (515 nm.). The high stability of the compound was shown by its lack of decomposition in air at the melting point (~300°), and also by the absence of any significant breakdown in the mass spectrum (70 ev.), where a single peak at $M^{+\cdot}$ 523 was obtained. The major product in the reaction of (253) with DDQ was an unidentified product (9%) of

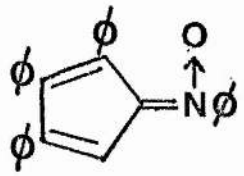
lower melting point than (256) and molecular weight 557.

The heterocycle (256) underwent reaction with bromine to give an intensely coloured solution, the contents of which decomposed on attempted isolation to give unchanged starting material. This is further evidence of the stability of (256), for it appears to be forming a molecular complex with the bromine instead of undergoing electrophilic aromatic substitution, a characteristic of other stable heterocyclic systems.

When the N,N'-tetrasubstituted ylide (203), generated *in situ*, was allowed to react with p-nitrobenzaldehyde, a variety of unidentified products of high molecular weight was obtained, but no trace of the expected fulvene (252) could be detected. This would tend to shed doubt on the existence of the ylide (203) as anything more than a transient intermediate.

2) Nitrosobenzene (with ylide (202)).

The reaction proceeded rapidly at room temperature, but no trace of the expected anil oxide (257), or even the anil (258),



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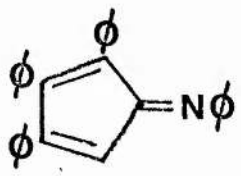

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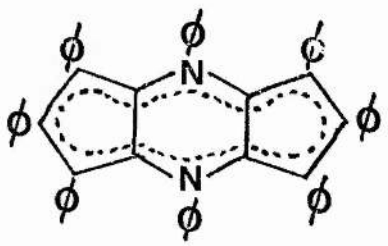


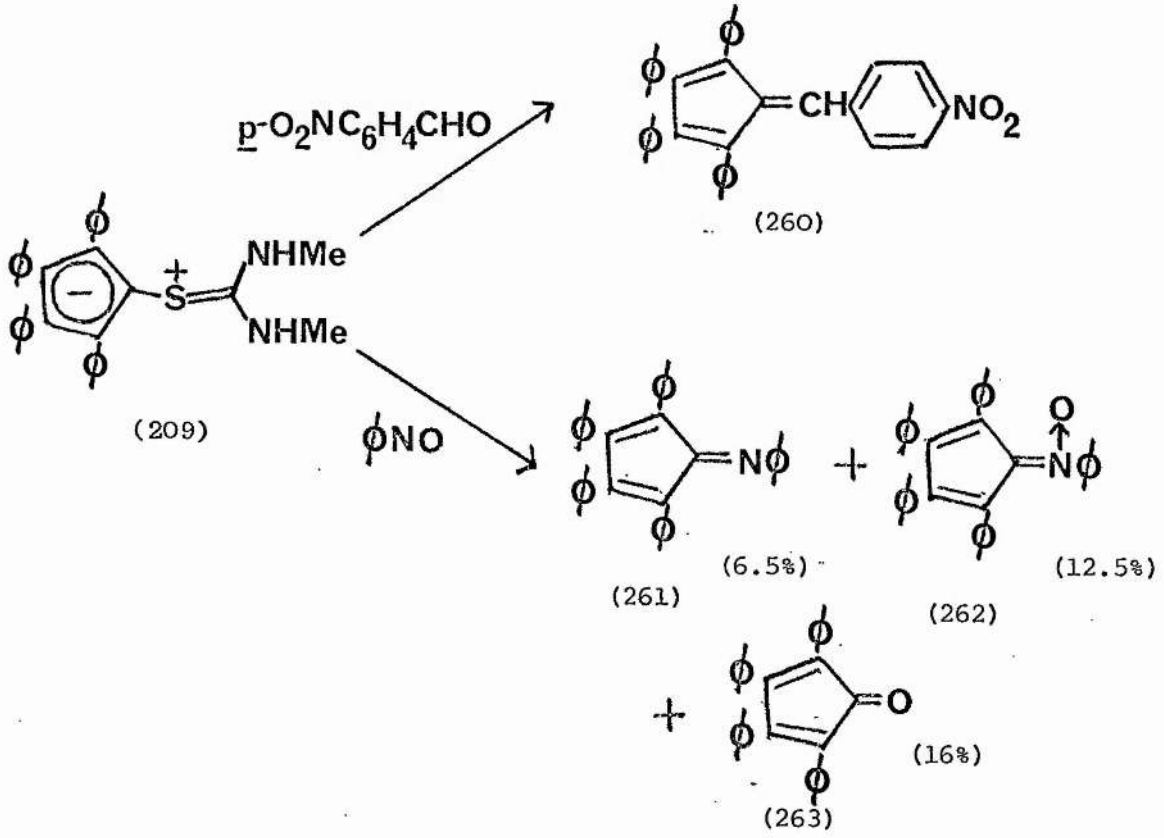
(259)

could be detected. Instead, a dark blue compound (259) was

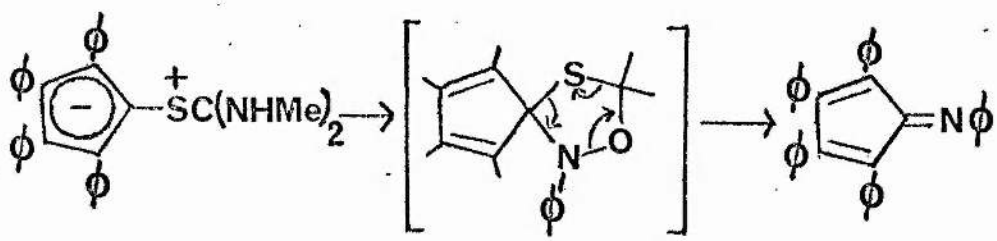
isolated and its mass spectrum showed a parent peak at $M^{+\cdot}$ 764.317 ($C_{58}H_{40}N_2$), which is the molecular weight of a dimer of (258). Its mode of formation remains obscure, but a possibility of initial attack at the 5-position on the cyclopentadiene ring of the ylide would appear to be indicated, on the strength of the results observed with the aldehydes.

(iii) 2,3,4,5-Tetraphenylcyclopentadienylides

The only work undertaken with these compounds was a study of the reactions of the N,N'-dimethyl ylide (209), *in situ*, with p-nitrobenzaldehyde and nitrosobenzene, the main purpose of which was to verify that the anomalous reactions observed in these cases with the 2,3,4-triphenylcyclopentadienylides were due to the interaction of the vacant 5-position on the ring. The results are summarised as shown.



With p-nitrobenzaldehyde, reaction took place to give the expected fulvene (260). It did not appear to be the sole product of the reaction, but no attempt was made to identify the other products. With nitrosobenzene, the reaction did not appear to run exactly parallel with the reaction observed with the fluorenylides. Although the anil oxide (262) was obtained in reasonable yield, indicating that collapse of the postulated 5-membered ring intermediate (264) had taken place analogously to that of the fluorenylides, a substantial amount of the anil (261) was also isolated, which would appear to indicate a competing mode of collapse of (264), as shown. A possible explanation of this different behaviour from the fluorenylides

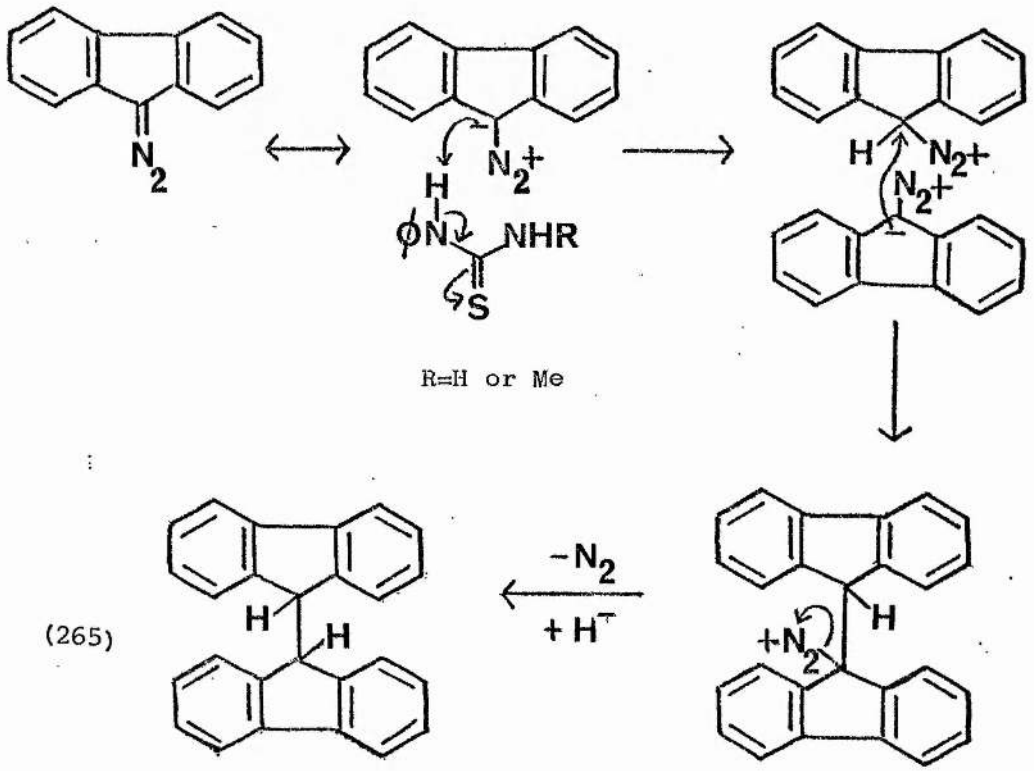


(264)

might be that the increased steric hindrance of the phenyl groups in the 2- and 5-positions on the cyclopentadiene ring makes it more difficult for the oxygen atom to approach the 1-position, as required for formation of the oxazirane which gives the anil oxide, and hence the anil is formed instead.

§4. REACTIONS OF DIAZOFLUORENE WITH ARYLTHIOUREAS

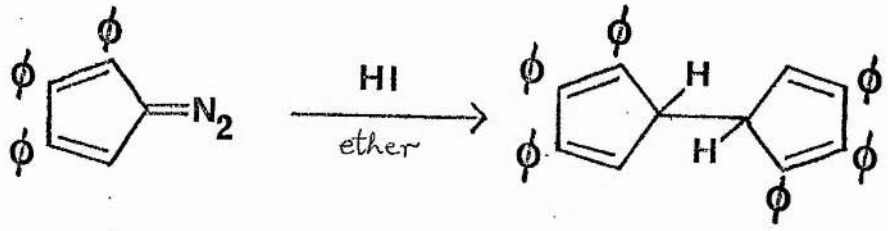
The thermal decomposition of diazo compounds in the presence of carbene acceptors has been used for the preparation of some thiocarbonyl ylides [96]. However, when 9-diazofluorene was decomposed in a melt in the presence of N-phenyl-N'-methyl thiourea and copper bronze, although the reaction proceeded cleanly, a high yield of bifluorenyl (265) was obtained instead of the expected



(265)

ylide (193). This result, although at first sight somewhat surprising, is consistent with the fact that diazocyclopentadienes are known to react with acids whose conjugate bases are of low nucleophilicity to give dihydrofulvalenes, for instance, diazo-2,3,4-triphenyl-cyclopentadiene (266) reacts with hydrogen iodide to give (267).

Owing to the relative acidity of their N-H protons, arylthioureas belong to this category of compound.



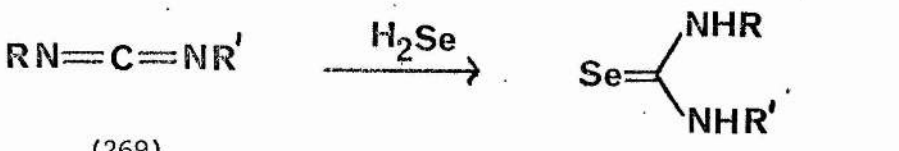
(266) (267)

Under similar conditions, N-phenylthiourea gave approximately equal amounts of bifluorenyl and bifluorenylidene, while N,N'-diphenylthiourea gave almost exclusively bifluorenylidene, with a trace of the expected ylide (191) and fluorenone ketazine. Further work is clearly necessary to establish the significance of these results, and in particular the course followed by the reaction without copper bronze could be profitably studied. In any event, it is apparent that the method is of little or no practical value for the preparation of thiouronium ylides.

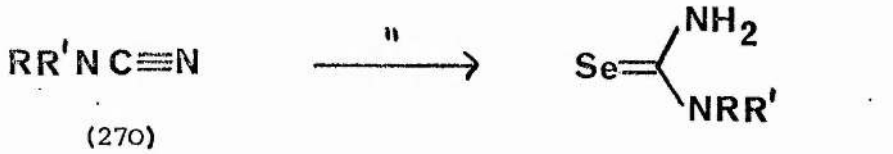
§5. ATTEMPTED PREPARATION OF A SELENOURONIUM FLUORENYLIDE

Selenoureas (268) have been known for some time and although few are commercially available, they can be readily prepared from the corresponding di-imides (269) [159] (in the case of N,N'-substituents) or cyanamides (270) [160] (in the case of

N,N substituents) by reaction with hydrogen selenide. The aryl



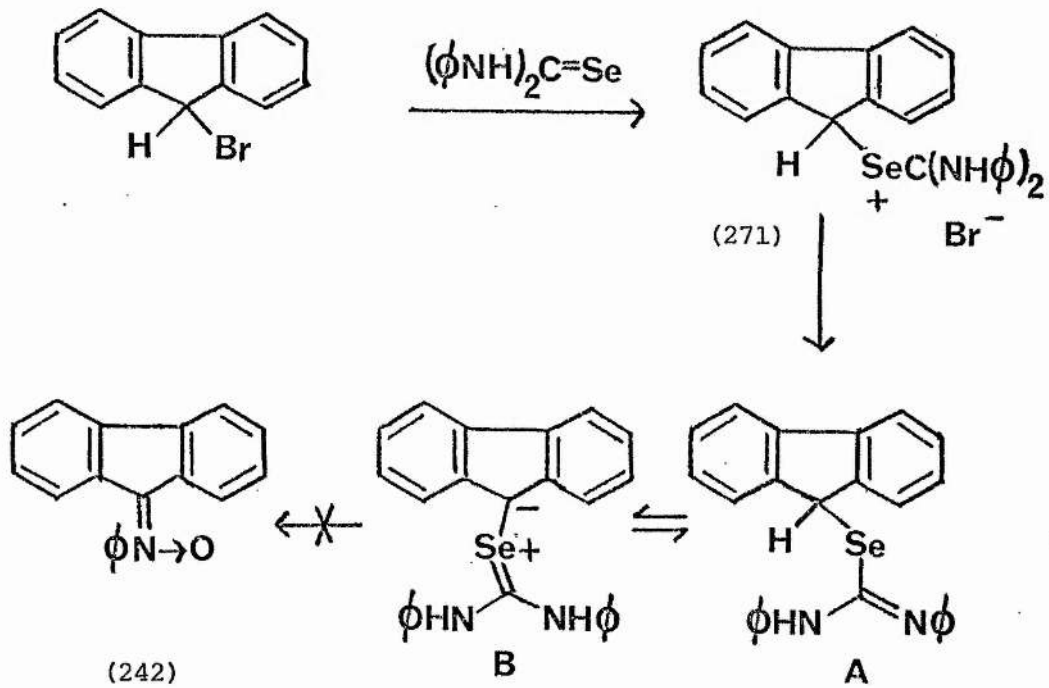
(269) (268)



(270)

substituted selenoureas are the most stable and would also be expected to give rise to the most stable ylides (by analogy with the series of thiouronium ylides already prepared, sect. 2 & 3), and accordingly N,N'-diphenylselenourea was selected for study.

When N,N'-diphenylselenourea and 9-bromofluorene were heated under reflux in ethanol, formation of the Se-alkylselenouronium salt (271) took place rapidly and in high yield. When the salt



(271)

(242) (272)

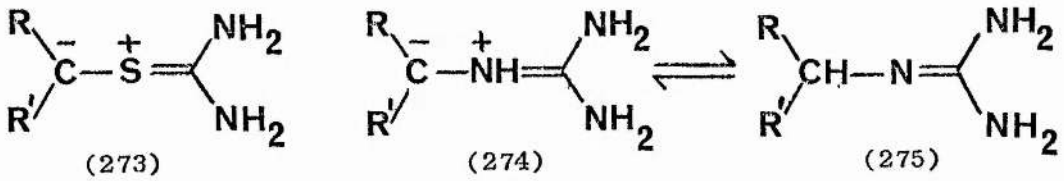
(271) was treated with triethylamine, the free base (272) was liberated. This compound can be formulated either as a selenouronium fluorenylide (272B) or as a Se-fluorenyliso-selenourea (272A). The available evidence from spectra and chemical reactivity suggests that the ylide form (272B) makes a negligible contribution, if any. The ultra-violet spectrum of (272) shows the absence of a long wavelength absorption such as was found in the thiouronium analogue (sect. 2), and in fact the u.v. spectrum of (272) is unchanged from that of the precursor salt (271). The ^{1}H n.m.r. spectrum cannot be interpreted unequivocally, owing to the difficulty in distinguishing the signals due to the N-H protons from that due to the C-9 proton on the fluorene nucleus. The ^{13}C n.m.r. spectrum will be discussed more fully later, but was not found to give conclusive evidence for one structure or the other. However, the unreactivity of (272) towards nitrosobenzene suggested that there must be a negligible contribution from the ylide form (272B), because none of the anil oxide (242) (or fluorenone anil) could be detected even after a prolonged reaction period. This supposition can be justified on the grounds that it has been shown (see introduction, sect. 4) that selenonium ylides are generally more reactive than the corresponding sulphonium compounds, and furthermore N,N'-diphenylthiouronium fluorenylide (191) is known to react readily with nitrosobenzene to afford the anil oxide (242).

Hence the free base (272) must exist as a Se-fluorenyliso-selenourea (272A), and in some respects the situation is analogous

to that found for N-fluorenyl-N',N"-diphenylguanidine (see sect 8). As a continuation of this work, it would be interesting to see if an ylide could be obtained from an alkyl substituted selenourea. This might be more likely because of the lower acidity of the N-H protons, which might lead to the removal of the proton α to the selenium atom by base rather than the N-H proton, as is found to prevail in the aryl substituted case.

§§ 6 - 8 GUANIDINES

In view of the fact that stable thiouronium ylides (273) can be prepared, as described in § 3 of this discussion, it was of interest to investigate the possibility that nitrogen analogues (274) might be capable of preparation and isolation. Stabilisation



(273) (274) (275)

(276) (277)

in such an ylide (274), a guanidinium ylide, would arise from extensive delocalisation of the positive charge within the hetero group, as occurs in the stable guanidinium cation (276) [161].

The result of this stabilisation in guanidine itself (277) is that it is one of the strongest organic bases and is comparable in strength to the hydroxide ion. An ylide such as (274) might be expected to show lower stability than its sulphur analogue (273) owing to the inability of the nitrogen atom to undergo valence shell expansion, a feature which has already been noted in nitrogen ylides (introduction, sect. 5). The ylide (274) may also undergo a proton shift to give a non-dipolar tautomer (275), the contribution of which will be discussed more fully in the light of the results to be described. It was decided to use fluorene once again as the stabilising group for the carbanionic moiety in order to suppress unwanted cyclisation reactions and also in view of the ready availability of the starting materials.

The line of attack adopted in the first instance was to prepare variously substituted fluorenyl guanidinium salts (278) (§6), and then to use base to generate the corresponding free base (279) (§7), in a manner similar to that employed for the

(278)

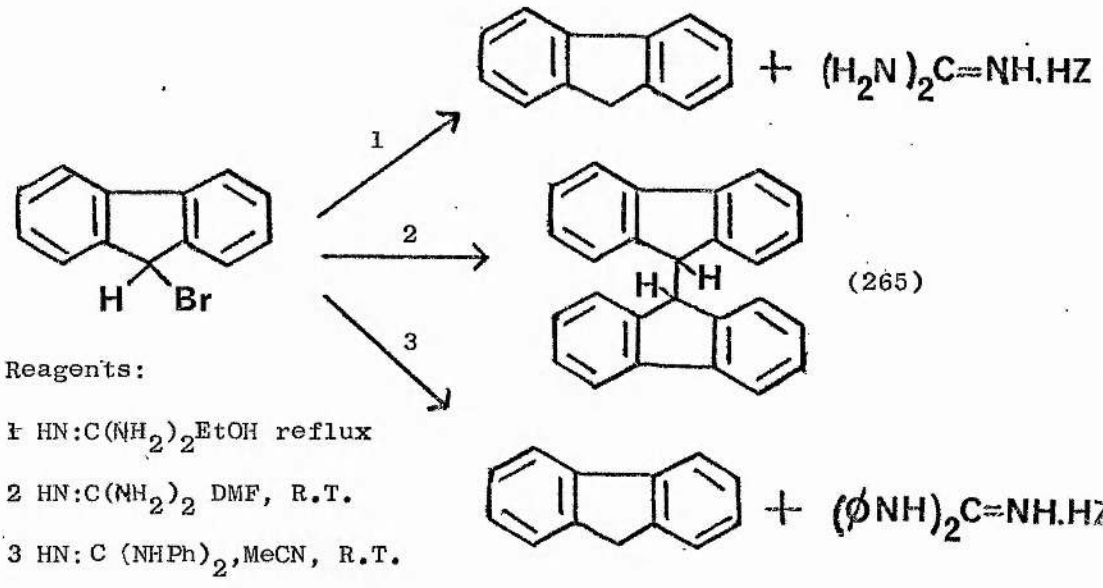
(279)

thiouronium ylides. However, at an early stage it became apparent that several of the more highly substituted salts were not available by any simple known procedure and accordingly a new route involving the thermal decomposition of diazofluorene with guanidines was investigated (§ 8). The results of these studies will now be presented.

§6. PREPARATION AND ATTEMPTED PREPARATION OF GUANIDINIUM SALTS

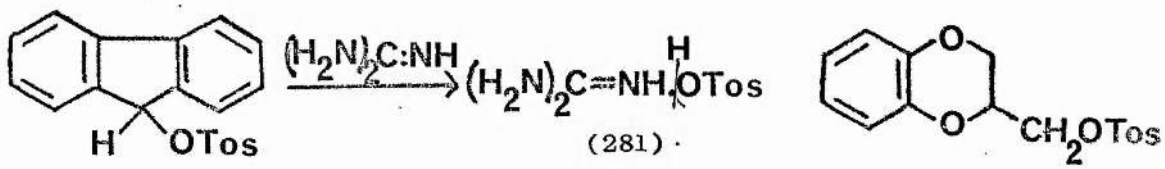
1) By nucleophilic substitution of halide or tosylate

Owing to the low nucleophilicity and high basicity of guanidine, reaction of guanidine and N,N'-diphenylguanidine with 9-bromofluorene led instead to the isolation of proto-debromination products when the reactants were heated under reflux or kept at room temperature in various solvents, as shown below. The formation of bifluorenyl (265) on reaction of



guanidine with 9-bromofluorene in dimethylformamide at room temperature was unexpected, but is similar to the result obtained by Wittig and Laib [162] when they treated 9-bromofluorene with trimethylstibine under similar conditions. The melting point of (265) was appreciably higher than previously reported values[162,163], despite correct analytical and spectral data, and is probably due to the isolation of a different crystal form.

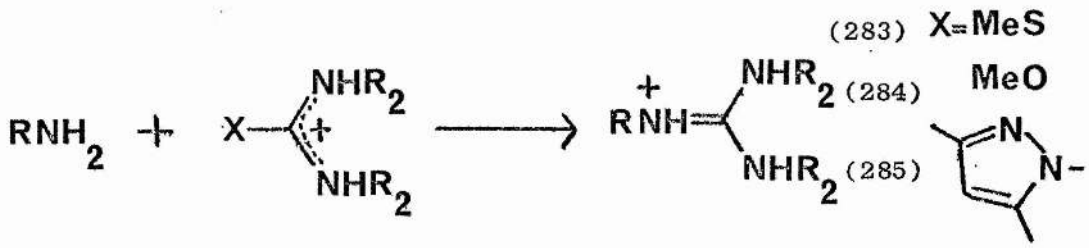
A report [164] that a nucleophilic substitution could be effected if the tosylate anion was used as the leaving group instead of the bromide ion was investigated. The reaction of 9-fluorenyl-p-tosylate (280) with guanidine in boiling ethanol was studied, but in this case guanidinium p-tosylate (281) was isolated in high yield, showing that protodetosylation was the prevalent reaction. The difference in behaviour of (280)



(280) (281) (+ fluorene) (282)

compared with the example quoted in the literature, a 2-methyl-1,4-benzodioxan derivative (282), probably arises largely as a result of the enhanced stability of the fluorenide anion, compared with the anion derived from (282), as the former is an intermediate in this pathway.

2) By displacement reactions using amines

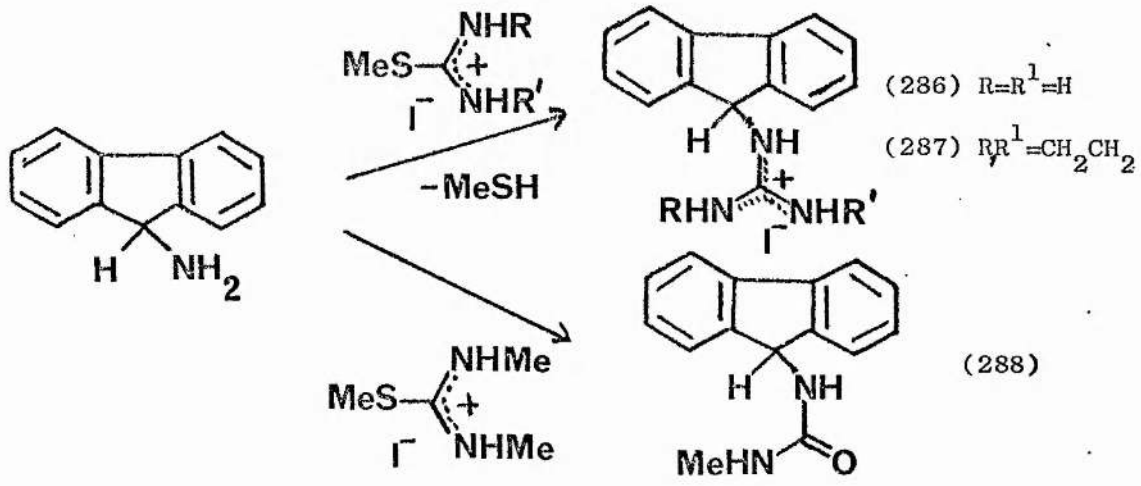


Scheme VI

The reaction scheme shown in scheme VI appears to be one of

the most general routes for the preparation of substituted guanidines, and the reactions of a wide variety of amines, both primary and secondary, with S-methylisothiouronium salts (283)[165-168], O-methylisouronium salts (284) [169,170] and 3,5-dimethylguanylpyrazolium salts (285)[171] have been reported. In several cases N-substituted-N',N"-dialkyl guanidines have been prepared (i.e. R=alkyl).

The reaction of 9-aminofluorene with S-methylisothiouronium iodide and S-methyl-N,N'-ethyleneisothiouronium iodide yielded the required guanidinium salts, (286) and (287), in yields of 46% and



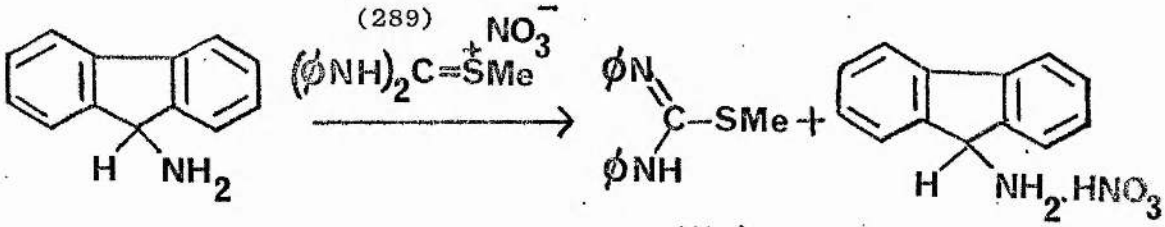
(286) $R=R^1=H$

(287) $RR^1=CH_2CH_2$

(288)

16-20% respectively, under considerably longer reflux periods than those reported [168] for simple amines. When N,N',S-trimethylisothiouronium iodide was allowed to react under the same conditions, none of the expected guanidinium salt was isolated, and instead the N-fluorenyl urea (288) was obtained in very low yield (ca.2%). Presumably the formation of the desired salt occurs much more slowly in this case than in the case of the N,N'-ethylene substituted compound (287) owing to the increased steric effect of the N,N'-dimethyl groups around the site of nucleophilic attack, leading to predominance of competing reactions. The formation of the urea

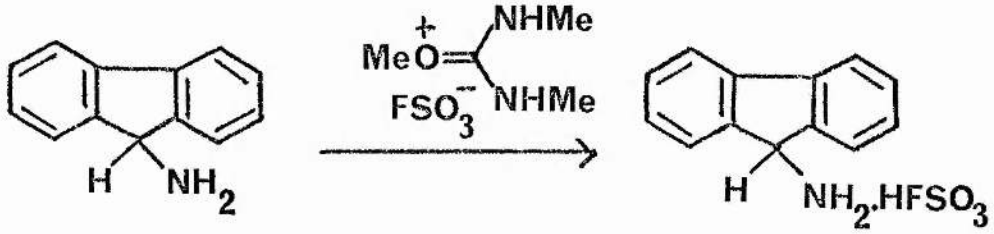
(288) may take place by hydrolysis of the initially-formed guanidinium salt. Guanidines are known [172] to undergo hydrolysis to ureas in the presence of water. S-Methyl-N,N'-diphenylisothiouronium nitrate (289) did not give any of the desired guanidinium salt, but instead reaction with aminofluorene gave the isothiourea (290) and aminofluorene nitrate, presumably arising from a combination of steric hindrance and the greater acidity of



(290)

the N-H protons in this case. The latter effect is illustrated by the fact that the free base (290) can be generated from the salt (289) merely by addition of ammonia.

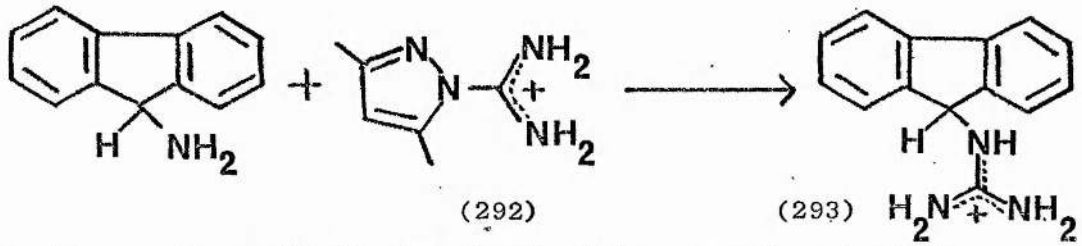
The O-methylisourea salts (284), although readily obtainable from the appropriate urea and methyl fluorosulphate [173], were difficult to handle on account of their ready hydrolytic decomposition, and when N,N',O-trimethylisouronium fluorosulphate was allowed to react with 9-aminofluorene in boiling ethanol, the only product isolated was 9-aminofluorene fluorosulphate (291). A similar reaction appeared to take place when benzylamine was used instead



(291)

of 9-aminofluorene, so the method was abandoned as it appeared to be less efficient than the reaction with S-methylisothiourea salts.

Finally, reaction of guanylpyrazolium salt (292) with 9-aminofluorene was studied, and resulted in the isolation of the guanidinium salt (293) in a yield very similar to that observed

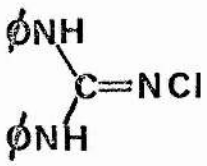


(292) (293)

in the reaction with the S-methylisothiourea salt. For this reason, and because of the more tedious preparation of starting materials, the method was not employed further.

It appears from the above results that the preparation of more highly substituted fluorenyl guanidines than those obtained above will require different methods of synthesis, and several were considered but not employed for various reasons. Alkylation of guanidines by reaction of N-nitrosoguanidines with amines has been described [174], but the highly explosive nature of the nitroso compounds precluded their use. Likewise the reaction of amines with chloroformamidinium chloride [175] was not used because of the need to use phosgene to generate the amidinium salt. A report [176] of the condensation of aromatic amines with substituted ureas in the presence of phosphoryl chloride appeared promising, but would be unlikely to work with an amine such as 9-amino-fluorene, which is not an aromatic amine and is also sterically

hindered. Finally, a completely novel method involving the condensation reaction of a chloroguanidine with fluorene, somewhat analogous to the condensation of chloroselenanes with active methylene compounds to give selenium ylides[5,80-1], failed owing to the fact that the required chloroguanidines, for instance (294), could not be prepared by the method reported[177] for analogous compounds, e.g. (295), or because those which could



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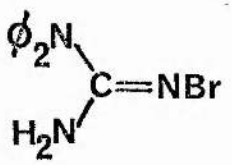

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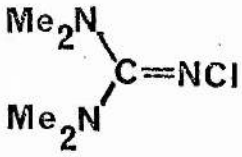


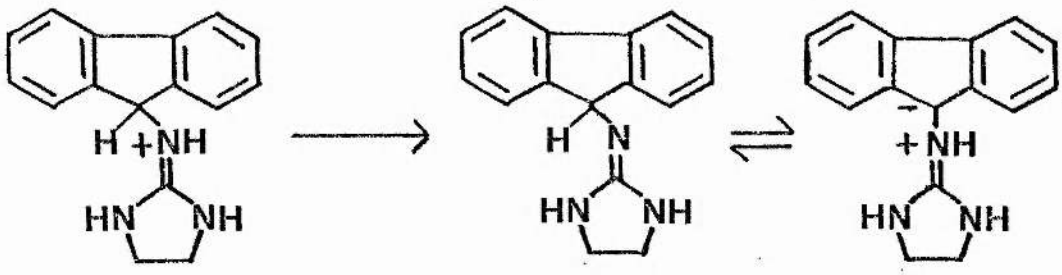
(296)

be prepared, for instance (296), were explosive[178].

§ 7. REACTIONS OF GUANIDINIUM SALTS

Of the two salts available for study (see §6.2), N-fluorenyl-N',N"-ethyleneguanidinium iodide (297) was chosen to facilitate the study of reactions, since the N,N'-substituents can suppress unwanted side reactions (e.g. condensation on to a free $-NH_2$ group) and also because it can be readily monitored in the n.m.r. spectrometer.

The addition of one mole of phenyl lithium to (297) in dry tetrahydrofuran, followed by aqueous workup gave the free base (298). Reaction of (297) with concentrated sodium hydroxide also gave (298), but in greatly reduced yield. The compound (298) is interesting because it can be formulated either as an



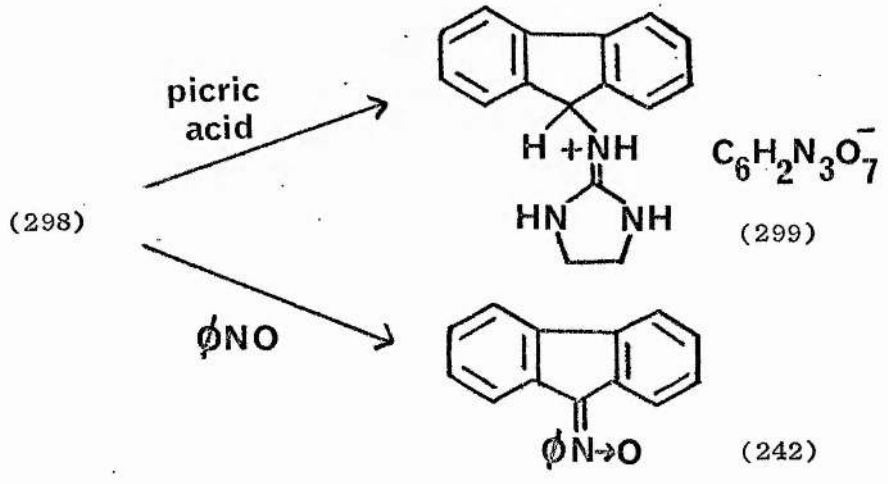
(297) A (298) B

N-fluorenylguanidine (298A), or as the isomeric guanidinium fluorenylide (298B). As will become evident, contributions from both structures are required to account for the properties of the compound.

The spectra of the free base (298) appeared to indicate prevalence of the fluorenylguanidine structure (298A). For instance, the longest wavelength absorption in the ultra-violet spectrum remained unchanged, compared with the salt, at 305 nm.

The ^{1}H n.m.r. spectrum showed a slight upfield shift of the protons in the ethylene bridge relative to the salt spectrum, which can be accounted for by the diminution of the positive charge in the guanidinium residue, although either structure could account for this. More importantly, the ^{13}C n.m.r. spectrum showed no appreciable upfield shift of the C-9 carbon of the fluorene moiety as has been observed [179] in other fluorenylides, and would have been expected if this carbon atom bore appreciable negative charge as required by the ylide structure (298B).

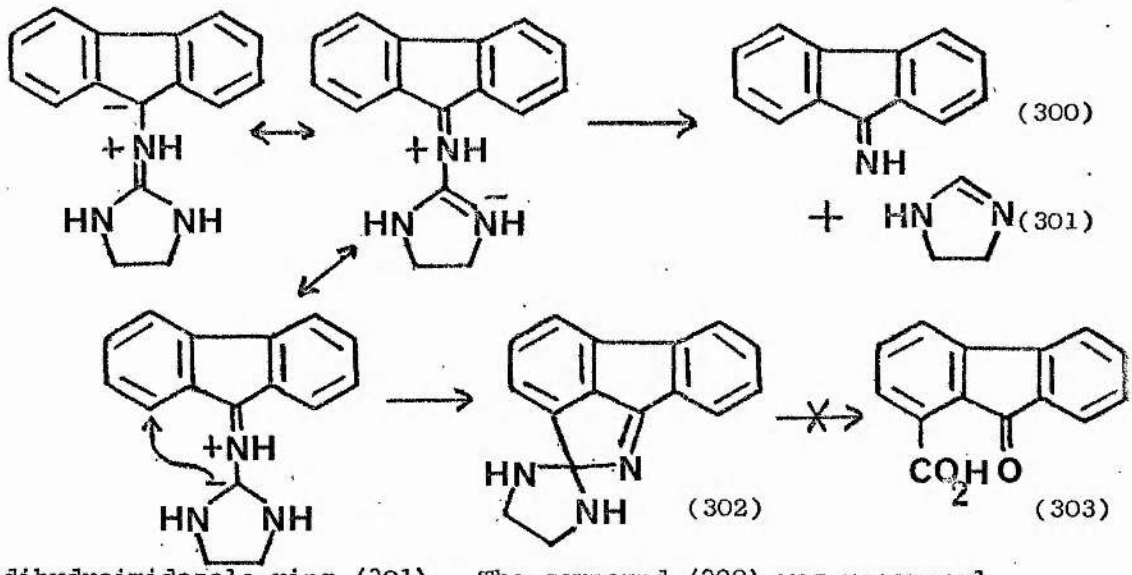
However, the chemical behaviour of (298) was such that the fluorenyl guanidine structure (298A) did not account satisfactorily for some of its properties. Thus although it reacted with picric acid to give the picrate (299), which is essentially the reverse reaction to that employed in the preparation of (298), this can be accounted for by either structure A or structure B. However, it reacted rapidly with nitrosobenzene to give the anil oxide (242).



The formation of this compound necessitates a degree of carbanionic

character on the 9-carbon of the fluorene nucleus, and this fact alone indicates that there must be a contribution from the ylide structure (298B). Reaction with nitrosobenzene to give an anil oxide is a feature displayed by many nitrogen ylides (see introduction).

The chemical behaviour of (298) in other respects was more complicated. It was thermally labile and underwent extensive decomposition on storage at room temperature for a week, even under nitrogen, although it could be kept for longer periods at -40°. Fluorenone imine (300) appeared to be one of the breakdown products, presumably arising from loss of the stable



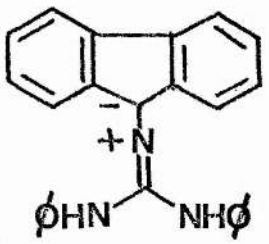
dihydroimidazole ring (301). The compound (298) was recovered unchanged after 6 hr. in boiling methanolic sodium hydroxide, showing that it was resistant to hydrolysis, but on attempted recrystallisation from hot ethanol it yielded a substantial amount of an unidentified solid, which showed a shift to long wavelength in the ultra-violet spectrum (λ_{max} 310 nm.) and a much lower

melting point. Largely on the basis of an intense peak in the mass spectrum at m/e 190 ($C_{14}H_8N$), the structure (302) was considered, which might arise by a Sommelet rearrangement of the ylide form (298B) as shown to give (302). Oxidative degradation of the rearranged product gave only fluorenone, however, whereas (302) might have been expected to give fluorenone-1-carboxylic acid (303), which is known [180] to be stable under the conditions of the oxidation. The problem has not yet been resolved. Finally, the free base (298) was found to react rapidly with p-nitrobenzaldehyde at room temperature, but the product was too labile to be characterised fully. Ethylene guanidine did not appear to be lost in the reaction, however, as might have been expected from a Wittig-type mechanism, and in this respect the reaction of (298) is comparable to that of other nitrogen ylides, for example pyridinium cyanomethylide [105,107].

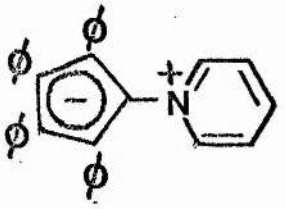
§8. REACTIONS OF DIAZOFLUORENE WITH GUANIDINES

1) With Arylguanidines

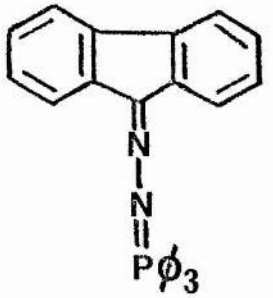
Because of the fact that N-fluorenyl-N',N"-diarylguanidines, e.g. (304), and related compounds were not available by the methods described in §6, it was decided to investigate the possibility that they might be prepared by the thermal decomposition of 9-diazofluorene in the presence of the appropriate guanidine, since it has been shown[66,67] that other ylides can be prepared in this manner, for example pyridinium tetraphenylcyclopentadienylide (305) and, especially, numerous tetraphenylcyclopentadienylides containing aryl substituted heteroatoms of groups V and VI. One feature noted



(304)



(305)



(306)

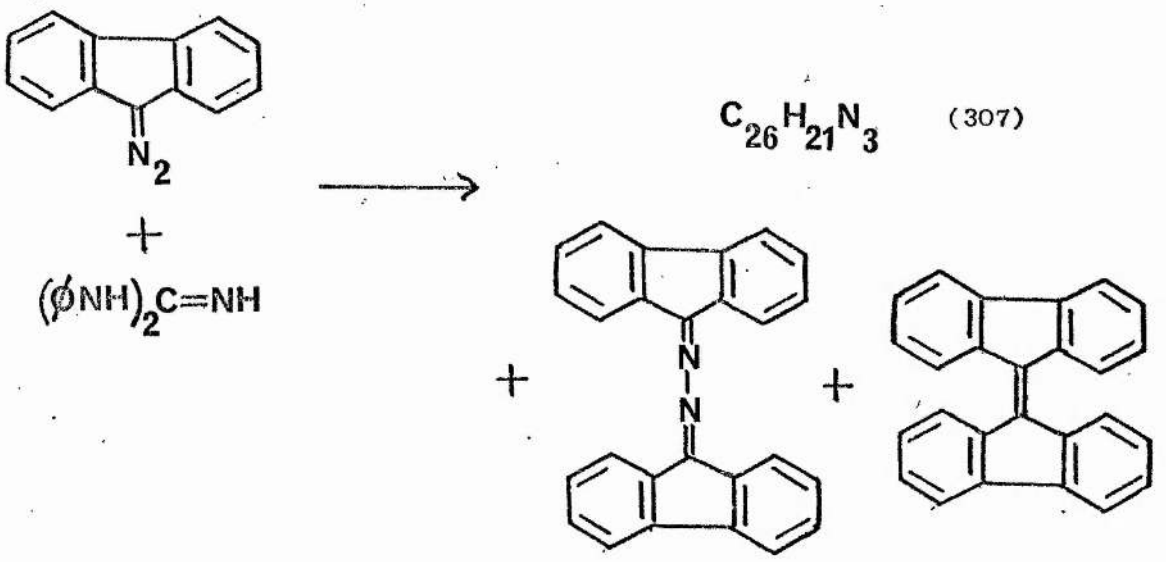
with 9-diazofluorene is the tendency to form azines. Thus with triphenylphosphine, 9-diazofluorene gives fluorenylidenetriphenylphosphinazine (306) in high yield[181]. It has also been noted[66] that if the decomposition reactions are carried out in the presence of a catalyst, for instance copper bronze, then in many cases improved yields of the ylides are obtainable. This is believed to arise as a result of interaction between the filled d orbitals of the transition metal and the vacant p_z orbital of

the carbene which is generated from the diazo compound, and gives stability to the carbene which is often described as a 'carbenoid' species. This is also believed to enhance the ability of the carbene to react with the desired substrate, namely the donor atom of group V and VI, which may also undergo some form of complex formation with the transition metal and further assist the formation of the ylide, although the latter effect is believed to be less likely with nitrogen where the d orbitals are not of a suitable energy to interact.

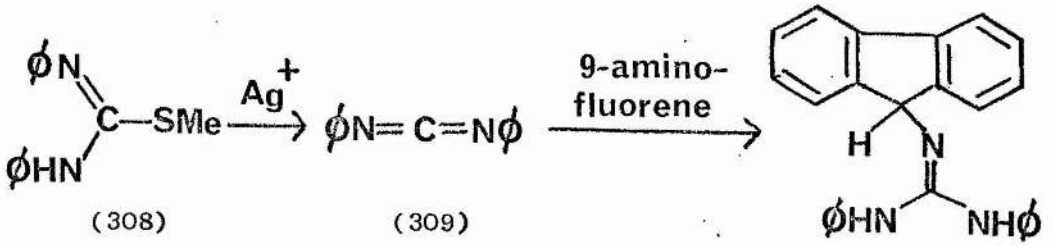
When 9-diazofluorene was decomposed in molten N,N'-diphenyl-guanidine without copper bronze, a high yield of fluorenone ketazine was obtained. The mechanism is believed to be similar to that already described for diphenyl sulphide with 9-diazofluorene (see introduction, sect. 4), where the ylide, as soon as it is formed, attacks another molecule of diazo compound to give the observed product. However, when 9-diazofluorene was decomposed under similar conditions but in the presence of copper bronze, a compound with the correct composition for the ylide (307) was obtained, along with lesser amounts of fluorenone ketazine and bifluorenylidene, the latter probably arising from slight decomposition of the product (307). The intermediacy of (307) in the formation of the ketazine was demonstrated since the latter was formed when (307) and 9-diazofluorene were mixed and kept at room temperature for several weeks.

Owing to the low yield of the product (307) obtained and the difficulty of separation from by-products, a more practical route

for its preparation was sought. The reaction of carbodi-imides

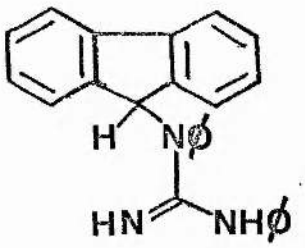


with amines has been known for a long time, and results in the formation of guanidines [182,183]. Furthermore, a convenient and reliable method for the preparation of carbodi-imides was reported [184] in 1963 whereby a heavy metal ion, usually silver or mercury, is used to assist the removal of methyl mercaptan from an S-methylisothiourea, for example (308), and the resulting di-imide (309) is allowed to react in situ with the amine. When the reaction was carried out using 9-aminofluorene and the S-methylisothiourea mentioned above, a good yield of the N-fluorenyl-N',N"-diphenylguanidine (310) was obtained.

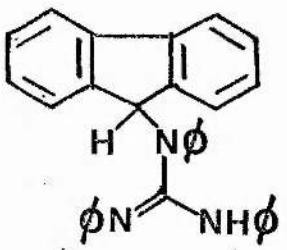


(308) (309) (310)

Suprisingly, though, this compound was different from the product (307) obtained from the diazo decomposition reaction, and therefore it seemed likely that (307) had the structure shown below,



(307)



(311)

or in other words that the reaction had taken place on a nitrogen atom bearing a phenyl group. Some evidence to support this view came from a re-examination of the mass spectrum of (307), which showed a fragment peak at m/e 257, the molecular weight of N-phenyl-9-aminofluorene, which was absent in the spectrum of (310). More evidence came from the reaction of 9-diazofluorene with sym-triphenylguanidine, where reaction took place to give the fluorenylguanidine (311), and here the reaction can only take place on a nitrogen atom bearing a phenyl group, thus substantiating the previous suggestion that reaction had taken place on an N-phenyl group. It is not clear why the reaction should proceed on this site, especially in the case of N,N'-diphenylguanidine, where there is much less hindrance at the non-aryl substituted nitrogen atom. Finally, attempts to prepare the fluorenylguanidine (307) using the thermal decomposition of 9-diazofluorene under different conditions (either a large excess of the guanidine or in boiling ethanol) were unsuccessful. The latter set of conditions have

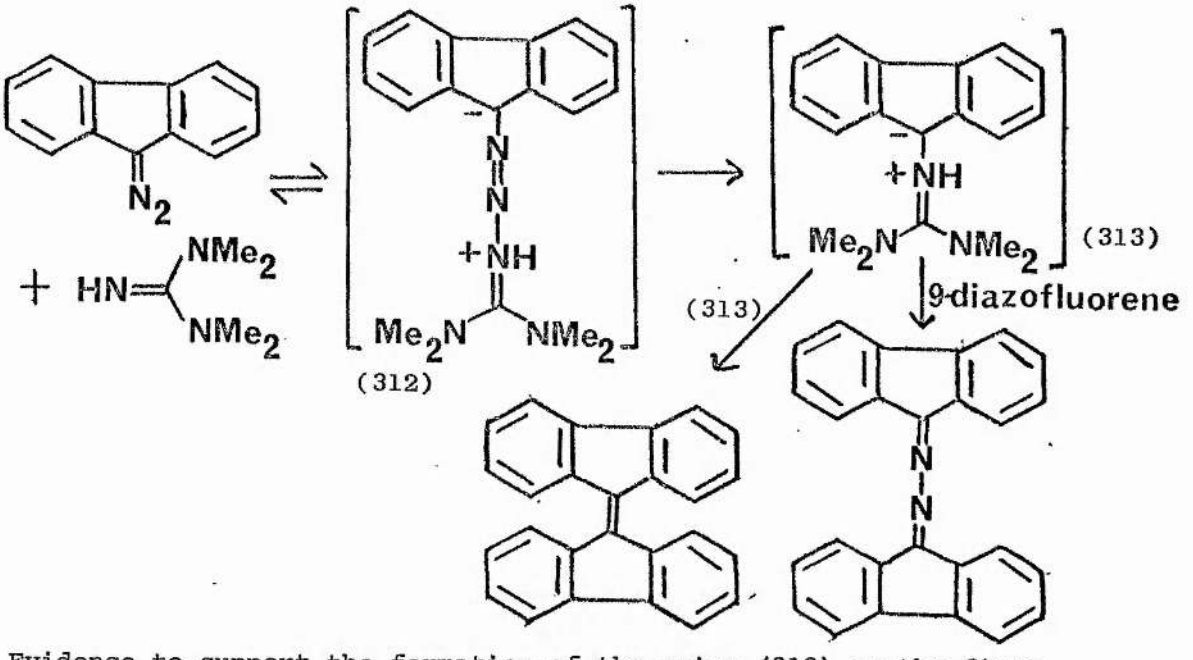
been successfully employed to prepare other ylides [66].

The properties of the symmetrically N,N'-disubstituted compound (310) did not appear to show any ylide-like characteristics. For instance, it appeared to undergo decomposition on treatment with strong acid, and with nitrosobenzene none of the anil oxide (242) could be detected. Instead, an unidentified yellow compound was obtained in good yield. The high resolution mass spectrum indicated a high oxygen content, which might suggest that some form of nitrosation of the free N-H groups had occurred. N,N'-Diphenylguanidine itself has been found to undergo N-nitrosation on treatment with nitrous fumes [185].

2) With Alkylguanidines

In the absence of copper bronze, no tractable products resulted from the reaction of guanidine with 9-diazofluorene. With copper bronze at 120°, fluorenone ketazine was isolated in 24% yield, presumably formed by a mechanism similar to that described previously (§8.1). N,N,N',N'-Tetramethylguanidine differed in its behaviour in that it underwent reaction with 9-diazofluorene in the presence of copper bronze at temperatures as low as -20°. The ultimate product was the same, fluorenone ketazine, which was formed in almost quantitative yield at -20°, and contamination with the by-product, bifluorenylidene, increased as the reaction temperature was raised. The reaction at low temperature is interesting and may indicate that the first step of the reaction is the formation of an unstable triazine such as

(312), which then loses nitrogen to give the unstable ylide (313), which, in turn, either reacts with further diazofluorene to give the ketazine or decomposes biphilically to give bifluorenylidene.

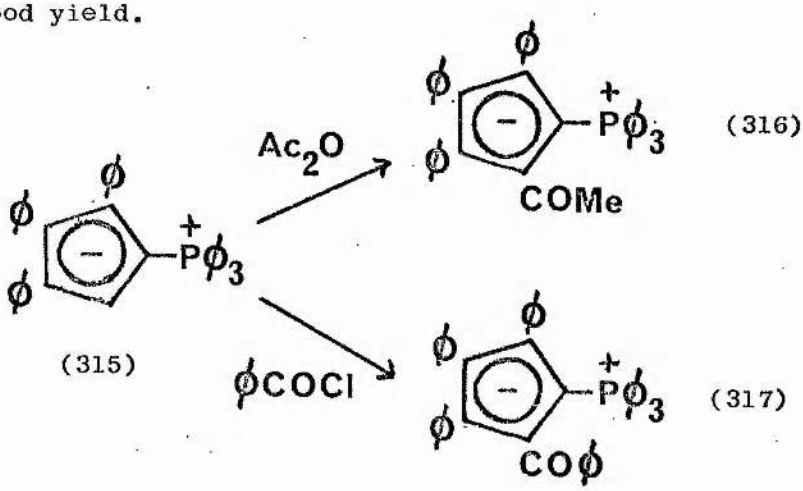


Evidence to support the formation of the azine (312) as the first step is observed in the reaction of triphenylphosphine with 9-diazofluorene at room temperature, where the phosphinazine (306) has been isolated [181]. The scheme shown above also explains the greater amount of bifluorenylidene formed at higher temperatures, as the ylide will show a greater tendency to undergo biphilic decomposition at these temperatures. In any event, it appears that the ylide (313) is much too unstable to be isolable, and in this respect resembles its thiouronium counterpart.

§9 MISCELLANEOUS REACTIONS

1. Benzoylation of 2,3,4-Triphenylcyclopentadienylidenetriphenylphosphorane

The ylide (315) has been found[67] to undergo acetylation to give the 5-acetyl derivative (316). The corresponding benzoylation reaction has now also been shown to take place with benzoyl chloride under prolonged heating in benzene to give the 5-benzoyl derivative (317) in good yield.

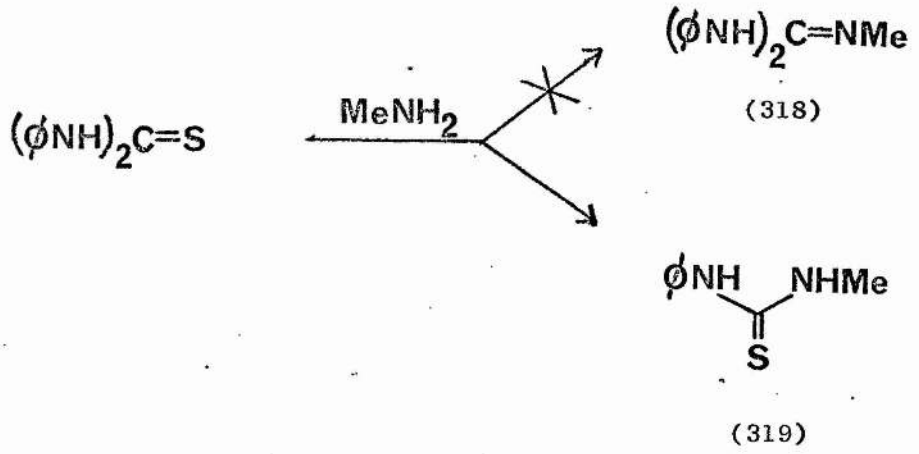


(315) (316) (317)

2. Reaction of N,N'-Diphenylthiourea with methylamine

Although an earlier report[185a] suggested that this reaction could be used to prepare N-methyl-N',N''-diphenylguanidine (318) by displacement of hydrogen sulphide, the results of the present study show that, under the conditions chosen, N-methyl-N'-phenylthiourea (319) is obtained instead, and in high yield. Presumably this occurs because aniline is a better leaving group than hydrogen sulphide. The method constitutes a simple procedure for the preparation of N-alkyl-N'-arylthioureas, and further reactions with a variety of alkylamines are being studied to

establish the generality of the method.



PART 3

EXPERIMENTAL

General

Ultra-violet and visible spectra were measured with Unicam S.P.800 and Perkin-Elmer 402 instruments.

Infra-red spectra were obtained with a Perkin-Elmer 257 instrument.

^{1}H n.m.r. spectra were carried out on a Varian HA 100 spectrometer operating at 100 MHz or a Varian EM360 spectrometer operating at 60 MHz. ^{13}C n.m.r. spectra were recorded on a Varian CFT20 spectrometer operating at 20 MHz.

Mass spectra were recorded and molecular weights determined on an A.E.I. MS 902 instrument.

Microanalyses were carried out by Mr. J. Bews in the Department of Chemistry, University of St. Andrews.

Column chromatography was carried out on either activated alumina, Type H 100/200 mesh or silica gel, grade M60 .

Thin layer chromatograms were run on silica (M.N. Kieselgel G) coated plates.

Samples analysed by means of molecular weight determinations were pure (t.l.c., spectra) unless otherwise indicated.

Light petroleum had bpt. 40-60°.

All melting points are uncorrected.

EXPERIMENTAL

§1. PREPARATION (AND ATTEMPTED PREPARATION) OF THIOURONIUM SALTS.

I. REACTIONS OF THIOUREAS WITH HALOGENATED REACTIVE METHYLENE COMPOUNDS NOT CONTAINING THE CYCLOPENTADIENE RING.

1. p-Nitrophenacyl Bromide

(a) Preparation of p-nitrophenacyl bromide

The method used for p-bromophenacyl bromide[188] was adapted. p-Nitroacetophenone (41g, 0.25mol) was dissolved as completely as possible in glacial acetic acid and the solution was filtered. Bromine (40g, 12.5ml, 0.25mol) was added slowly with vigorous stirring, and the temperature of the solution was not allowed to exceed 20°. (Addition was complete in 30 min.) The solution was allowed to stand overnight when decolorisation of the bromine had taken place and an off-white precipitate had formed, which was filtered off and washed with 50% ethanol. Yield 49.3g (81%), mpt. 96-99° (lit.[187] 98°). The material was used without further purification.

(b) Reaction of p-nitrophenacyl bromide with thiourea.

p-Nitrophenacyl bromide (980mg, 4mmol) and thiourea (304mg, 4mmol) were dissolved in ethanol (25ml). On heating to reflux, the mixture solidified and when it was cooled, a fine crystalline precipitate was filtered off and washed with ether to give the pale yellow 2-amino thiazole hydrobromide (103), (1.20g, 94%), which turned brown on prolonged suction. A portion recrystallised from ethanol had mpt. 251-6°.

Treatment with base in the following manner gave the free 2-amino thiazole:- The salt (480mg) was dissolved in warm ethanol

(40 ml) and aqueous sodium hydroxide (2 M, 12 drops) was added. A fine yellow precipitate formed and, when cool, was filtered off and washed with ethanol followed by ether to give the free base (104), (240 mg, 68%), mpt. 284-8°. (Found: C, 48.5; H, 3.1; N, 18.9. $C_9H_7N_3O_2S$ requires C, 48.9; H, 3.2; N, 19.0%.)

Diazotisation of 2-amino-4-(p-nitrobenzoyl)thiazole and reaction with 2-naphthol.

Sodium nitrite (ca. 70 mg) was dissolved in conc. sulphuric acid (1 ml) and the 2-aminothiazole (ca. 30 mg) was added, giving a pale yellow solution. Excess sulphamic acid (ca. 100 mg) was added to decompose the excess nitrite. A solution of 2-naphthol (ca. 100 mg) in aqueous sodium hydroxide (2 M, 1 ml) was spotted on a filter paper alongside a spot of the diazo solution, diluted 1 part in 10 parts water, and a deep purple colour developed at the interface showing the presence of an azo dye.

As a check for formation of the dye, the reaction was carried out in solution as follows:- half of the 2-naphthol solution was cooled on ice and a few drops of the diazo solution were added (effervescence). The solution was made alkaline (2 M, NaOH) and extracted into chloroform (2 ml) in a test-tube. This was washed with water and extracted again, then addition of conc. sulphuric acid (ca. 0.25 ml) with shaking gave a deep blue colour, showing the presence of an azo dye.

Reaction of 2-amino-4-(p-nitrobenzoyl)thiazole with aqueous hydrogen bromide.

To a solution of the thiazole (55 mg) in methanol (5 ml) was added aqueous hydrogen bromide solution (48%, 5 drops). The solution was warmed to 60° (orange colour disappears) and when cooled, pale yellow needles separated which were filtered off and washed with methanol and ether to give the hydrobromide of the

2-aminothiazole (103). mpt. 246° (dec.). It did not depress the melting point of an authentic sample.

(c) Reaction of p-nitrophenacyl bromide with N,N'-dimethylthiourea.

p-Nitrophenacyl bromide (980 mg, 4 mmol) and N,N'-dimethylthiourea (416 mg, 4 mmol) were dissolved in ethanol (25 ml), and the mixture was warmed. A white precipitate formed which was filtered off from the cooled solution, and washed with ethanol followed by ether to give the dimethylthiouronium salt (105), (1.30 g, 92%), mpt. 250° (dec.). (Found: C, 37.7; H, 3.9; N, 12.0. $C_{11}H_{14}BrN_3O_3S$ requires C, 37.9; H, 4.0; N, 12.1%).

(d) Reaction of p-nitrophenacyl bromide with N,N,N',N'-tetramethylthiourea.

(i) In methanol.

p-Nitrophenacyl bromide (980 mg, 4 mmol) and N,N,N',N'-tetramethylthiourea (528 mg, 4 mmol) were suspended in methanol (10 ml). The mixture was heated under reflux for 5 min., then cooled, and the solvent was removed under reduced pressure. Addition of further methanol (ca. 5 ml) gave a brown precipitate which was filtered off and washed with methanol followed by ether to give the amide (107), (85 mg, 8%). (Found: C, 49.1; H, 4.5; N, 10.0. $C_{11}H_{12}N_2O_4S$ requires C, 49.3; H, 4.5; N, 10.4%).

(ii) In benzene.

p-Nitrophenacyl bromide (980 mg, 4 mmol) was dissolved in benzene (8 ml). A solution of finely-ground N,N,N',N'-tetramethylthiourea (528 mg, 4 mmol) dissolved in benzene (4 ml) was added dropwise with stirring and a precipitate began to form. After 1 hour pale yellow microcrystals were filtered off and washed with ether to give the tetramethylthiouronium salt (106), (1.40 g, 93%), mpt. 125°. (Found: C, 41.3; H, 5.0; N, 10.9. $C_{13}H_{18}BrN_3O_3S$ requires C, 41.5; H, 4.8; N, 11.2%).

(iii) In methanol, perchlorate workup.

p-Nitrophenacyl bromide (490 mg, 2 mmol) and N,N,N',N'-tetramethylthiourea (264 mg, 2 mmol) were stirred in methanol (8 ml) at room temp. for 10 min. The solution turned yellow-brown. Perchloric acid (70%, 0.3 ml, ca. 2 mmol) was added and the mixture was shaken and scratched. Yellow crystals separated after 10 min. and were filtered off and washed with methanol followed by ether to give an unidentified substance (400 mg), mpt. 135-7°. A portion was recrystallised from benzene/acetonitrile. (Found: C, 38.2; H, 3.7; N, 8.5%. Closest empirical formula $C_{11}H_{12}N_2$.)

(e) Reaction of p-nitrophenacyl bromide with N,N'-diphenylthiourea.

p-Nitrophenacyl bromide (980 mg, 4 mmol) was dissolved in warm ethanol (10 ml) and the solution was added to a warm solution of N,N'-diphenylthiourea (912 mg, 4 mmol) in ethanol (25 ml). Crystals began to form almost immediately, and the solution was cooled on ice. After half an hour, pale yellow crystals were filtered off and washed with ether to give the 2-amino-4-hydroxythiazolidinium salt (108), (1.55 g, 82%). A portion was recrystallised from methanol, mpt. 270° (dec.). (Found: C, 53.0; H, 3.9; N, 8.5. $C_{21}H_{18}BrN_3O_3S$ requires C, 53.3; H, 3.8; N, 8.9%).

2. Dimethyl α-Bromomalonate

(a) Reaction of dimethyl-α-bromomalonate with thiourea.

(i) In a preliminary attempt, dimethyl-α-bromomalonate (1.05 g, 5 mmol) and thiourea (380 mg, 5 mmol) were dissolved in ethanol (20 ml), and the mixture was heated under reflux for 5 min. Removal of solvent under reduced pressure followed by trituration of the glassy residue with ether and a mixture of ether-light petrol resulted in each case in the formation of an oil.

(ii) Dimethyl-α-bromomalonate (3.15 g, 0.015 mol) was mixed neat with thiourea (1.14 g, 0.015 mol) and the mixture was allowed to stand for 10 min. (Heat was evolved.) Acetone (50 ml) was added to the glassy residue and a white precipitate was filtered off (100 mg). This was discarded. The bulk of the filtrate was then reduced as far as possible in vacuo, and the glassy residue was allowed to stand overnight, when crystallisation took place. The sticky white solid was triturated with further acetone, filtered off, and washed with ether to give the 2-iminothiazolidone (112), (2.1 g, 81%). A portion was recrystallised from ethanol, mpt. 250° (dec., black). Found: C, 34.4; H, 3.6; N, 15.8. $C_5H_6N_2O_3S$ requires C, 34.5; H, 3.4; N, 16.1%).

(iii) Dimethyl-α-bromomalonate (1.05 g, 5 mmol) and thiourea (380 mg, 5 mmol) were dissolved in methanol (10 ml) and set aside. After 3 weeks, a fine white precipitate had separated which was filtered off, and washed with a small volume of methanol and ether to give the 2-iminothiazolidone (160 mg, 19%), mpt. 250° (black).

(b) Reaction of dimethyl-α-bromomalonate with N,N'-dimethylthiourea.

Dimethyl-α-bromomalonate (1.05 g, 5 mmol) and N,N'-dimethylthiourea (520 mg, 5 mmol) were dissolved in ethanol (9 ml), and the mixture was heated under reflux for 30 min. The solution was cooled on ice and a white precipitate appeared which was filtered off and washed with a small volume of cold ethanol followed by ether. Addition of ether (50 ml) to the filtrate brought down a second crop of crystals, and the combined yield of 2-iminothiazoline hydrobromide (114) was 980 mg (69%). A portion was recrystallised from ethanol, mpt. 158° (dec.). (Found: C, 30.0; H, 3.8; N, 9.6. $C_7H_{11}BrN_2O_3S$ requires C, 29.8; H, 3.9; N, 9.9%).

(c) Reaction of dimethyl-α-bromomalonate with N,N,N',N'-tetramethylthiourea.

Dimethyl-α-bromomalonate (1.05 g, 5 mmol) and N,N,N',N'-tetramethylthiourea (660 mg, 5 mmol) were dissolved in benzene (5 ml). The mixture was heated under reflux for 2 min., cooled, and the viscous residue was stirred with ether (15 ml). Crystallisation was complete after ca. 2 hr., and the pale yellow precipitate was filtered off and washed with ether to give the tetramethylthiouronium bromide (115), (1.10 g, 64%). Perchloric acid (70%, 0.4 ml) was added to a solution of the bromide (0.76 g) in ethanol (5 ml). Addition of ether (ca. 10 ml) with scratching brought down colourless crystals of the perchlorate (0.65 g, 52% overall yield), mpt. 92-5° (Found C, 33.5; H, 5.6; N, 7.7. $C_{10}H_{19}ClN_2O_8S$ requires C, 33.1; H, 5.2; N, 7.7%).

3. Bromomalononitrile.

(a) Preparation of bromomalononitrile (in solution).

Malononitrile (6.84 g, 0.105 mol) was dissolved in methanol (75 ml) and a solution of bromine (1.44 g, 0.09 mol) in methanol (30 ml) was added dropwise, with stirring, on an ice-bath. (Addition took ca. 20 min.) Stirring was continued for a further 1½-2 hr. while the solution was allowed to reach room temperature. During this period the colour of the solution changed from brown to pale yellow.

(b) Reaction of bromomalononitrile with thiourea.

To one-third of the above solution of bromomalononitrile (0.03 mol) a solution of thiourea (2.28 g, 0.03 mol) in methanol (25 ml) was added, and the mixture was kept at 0° for 1 hour. After the first 5 min., colourless crystals began to precipitate. The precipitate was filtered off and was ed with a small volume of methanol followed by ether to give thiouronium bromide (126), (1.15 g, 24%), mpt. 200-5°

(dec.) (Found: C, 7.8; H, 2.8; N, 18.4. CH_5BrN_2S requires C, 7.7; H, 3.2; N, 17.9%).

(c) Reaction of bromomalononitrile with N,N'-dimethylthiourea.

To one-third of the above solution of bromomalononitrile (0.03 mol) a solution of N,N'-dimethylthiourea (3.12 g, 0.03 mol) in methanol was added. The mixture was warmed to 60° and crystals began to appear after 5 min. The solution was then cooled on ice for ca. 30 min., and the colourless crystals which had separated were filtered off and washed with a small volume of methanol followed by ether to give a first crop of the 2-iminothiazoline hydrobromide (127), (1.2 g). Addition of ether (ca. 100 ml) to the filtrate brought down a second crop (3.1 g). Total yield was 4.3 g (58%). A portion was recrystallised from methanol, mpt. 270° (dec.) (Found: C, 28.8; H, 3.8; N, 22.7. $C_6H_{10}BrN_4S$ requires C, 28.8; H, 4.0; N, 22.4%). Diazotisation was attempted as described in expt. 1(b).

(d) Reaction of bromomalononitrile with ethylenethiourea.

To one-twelfth of the above solution of bromomalononitrile (7.5 mmol) a solution of ethylene thiourea (765 mg, 7.5 mmol) dissolved in methanol (20 ml) was added. The mixture was heated under reflux for 5 min., during which time a white precipitate appeared. The solution was cooled on ice and the precipitate was filtered off and washed with ether to give the 2-iminothiazoline hydrobromide (350 mg (20%), mpt. 170° (dec.) identified by its n.m.r. and i.r. spectra.

(e) Reaction of bromomalononitrile with N,N,N',N'-tetramethylthiourea.

To one-twelfth of the above solution of bromomalononitrile (7.5 mmol) a solution of N,N,N',N'-tetramethylthiourea (0.99 g, 7.5 mmol) in methanol (5 ml) was added. The solution was warmed to 50° for 5 min., then cooled on an ice-bath. A small amount of

colourless crystals formed which was filtered off (ca. 5 mg) and discarded. The bulk of the solvent was then reduced in vacuo and trituration with chloroform afforded colourless crystals which from their i.r. and n.m.r. spectra consisted of N,N,N',N'-tetramethylthiourea hydrobromide (125 mg, 8%).

(f) Reaction of bromomalononitrile with N,N'-diphenylthiourea.

To one-twelfth of the above solution of bromomalononitrile (7.5 mmol) a solution of N,N'- diphenylthiourea (1.70 g, 7.5 mmol) dissolved in ethanol (50 ml) was added, and the mixture was heated under reflux for 50 min. Solvent was removed under reduced pressure from one half of the solution, and addition of methanol (5 ml) followed by ether brought down white crystals of unknown identity (350 mg) mpt. dec.>200°. Thin layer chromatography using chloroform as eluant showed one component. (Found: C, 26.5; H, 4.3; N, 12.3%. Closest empirical formula $C_5H_{10}N_2$). When the experiment was repeated using a different solution of bromomalononitrile, the product described above could not be obtained.

4. α-Bromobis(phenylsulphonyl)methane.

(a) Preparation of α-bromobis(phenylsulphonyl)methane.

Methylene diphenyl disulphide was prepared from thiophenol and dibromomethane by the method of Shriner, Struck and Jorison[188]. Bis(phenylsulphonyl)methane was prepared by oxidation of methylene diphenyl disulphide using hydrogen peroxide in glacial acetic acid, according to the method of Kohler and Tishler[189]. This was then dibrominated using bromine in aqueous sodium hydroxide solution and subsequently allowed to react with further bis(phenylsulphonyl)-methane to give monobromobis(phenylsulphonyl)methane, as described by Kohler and Tishler[189].

(b) Reaction of α-bromobis(phenylsulphonyl)methane with thiourea.

(i) To a solution of α-bromobis(phenylsulphonyl)methane (562 mg, 1.5 mmol) in methanol (10 ml) was added a solution of thiourea (114 mg, 1.5 mmol) in methanol (2 ml), and the mixture was heated under reflux for 10 min. The bulk of the solvent was reduced *in vacuo* to *ca.* 2 ml and the concentrated solution was cooled on ice and scratched. Colourless needles appeared which were filtered off and washed with a little cold methanol to give bis(phenylsulphonyl)-methane (280 mg, 63 %), mpt. 118-9° (lit[187] 119-20°). It did not depress the melting point on admixture with an authentic sample.

(ii) α-Bromobis(phenylsulphonyl)methane (1.50 g, 4 mmol) and thiourea (304 mg, 4 mmol) were dissolved in methanol (55 ml) and set aside for 16 days at room temperature. Removal of the solvent under reduced pressure gave colourless crystals which were washed well with ether (950 mg). Purification was attempted as follows:

(1) A portion was dissolved in the minimum volume of methanol at room temperature and then cooled to -70° in an acetone-cardice bath. The colourless crystals were rapidly filtered on a pre-cooled sinter funnel and washed with ether to give bis(phenylsulphonyl) methane. (Found, C, 52.8, H, 4.1, N, 0.0. $C_{13}H_{12}O_4S_2$ requires C, 52.7; H, 4.1; N, 0.0%).

(2) A portion was washed thoroughly with benzene and dried. Its n.m.r. spectrum showed reduction in magnitude of peaks due to bis(phenylsulphonyl)methane compared with the spectrum of crude material, but since complete purification of the salt by this means was not possible, further study of the compound was abandoned.

(c) Reaction of bromobis(phenylsulphonyl)methane with N,N'-dimethylthiourea.

N,N'-Dimethylthiourea was reacted under reflux and also at room temperature under identical conditions to those used in (b) and gave similar results.

(d) Reaction of bromobis(phenylsulphonyl)methane with N,N,N',N'-tetramethylthiourea.

α-Bromobis(phenylsulphonyl)methane (500 mg, 1.33 mol) and N,N,N',N'-tetramethylthiourea (175 mg, 1.33 mmol) were stirred in benzene (40 ml) until a clear solution was obtained (ca. 1 hr.). The solution was set aside for 10 days at room temperature, during which time a white precipitate formed. This was filtered off and washed with benzene followed by ether to give the thiouronium salt (134) (300 mg, 58%), mpt. 101-5°. It was characterised as the free base (ylide) (see § 2).

5. α-Bromodibenzoylmethane.

(a) Preparation of α-bromodibenzoylmethane.[190]

Dibenzoylmethane (11.2 g, 0.05 mol) was dissolved in chloroform (20 ml) and a solution of bromine (8 g, 0.05 mol) in chloroform (20 ml) was added dropwise with stirring (hydrogen bromide was evolved). The solution was kept overnight, and the bulk of the solvent was then reduced to ca. 10 ml in vacuo. The mixture was cooled on ice and solidified when scratched. The precipitate was filtered off and washed with ether to give off-white crystals of α-bromodibenzoylmethane (10.65 g, 69%) mpt. 89-90° (lit.[190] 93°). The material was used without further purification.

(b) Reaction of α-bromodibenzoylmethane with N,N,N', N'-tetramethylthiourea.

(i) α-Bromodibenzoylmethane (760 mg, 2.5 mmol) and N,N,N',N'- tetramethylthiourea (310 mg, 2.35 mmol) were heated under reflux in ethanol (25 ml)

for 10 min. The solvent was removed under reduced pressure giving an oil which crystallised on addition of ether, and pale yellow deliquescent crystals were filtered off (150 mg, 28%), the n.m.r. spectrum of which suggested that they were N,N,N',N'-tetramethylthiouronium bromide.

(ii) α-Bromodibenzoylmethane (456 mg, 1.5 mmol) and N,N,N',N'-tetramethylthiourea (198 mg, 1.5 mmol) were added to benzene (5 ml) and the mixture was stirred for 10 min., during which time an oil separated. Excess benzene was decanted and ether (50 ml) was added giving an oil which crystallised when kept for one week. The yellow solid was filtered off and washed with ether to give the highly deliquescent thiouronium salt (119) (170 mg, 26%).

(iii) α-Bromodibenzoylmethane (1.82 g, 6 mmol) was made into a slurry with methanol (10 ml), and finely ground N,N,N',N'-tetramethylthiourea (792 mg, 6 mmol) was added. The mixture was stirred at room temperature for 5 min. providing a yellow solution. A methanolic solution of sodium perchlorate (1.66 M, 3.4 ml,~6 mmol) was added and colourless crystals separated in 5 min. These were filtered off and washed with methanol and ether to give a colourless solid (650 mg), mpt. 184-6° identified as the mercaptoamide (120) by its n.m.r. and i.r. spectra.

6. Other Halogenated Reactive Methylenes.

Ethyl chloroacetate and N,N,N',N'-tetramethylthiourea.

(i) Ethyl chloroacetate (490 mg, 4 mmol) and N,N,N',N'-tetramethylthiourea (528 mg, 4 mmol) were dissolved in benzene (15 ml) and the mixture was refluxed for 3 hrs. Solvent was removed under reduced pressure giving an oil which crystallised when scratched. The colourless crystals were filtered off but had deliquesced before isolation was possible.

(ii) Ethyl chloroacetate (2.45 g, 20 mmol) and N,N,N',N'-tetramethylthiourea (2.64 g, 20 mmol) were mixed neat and warmed for 5 min. at 50°. Methanol (12 ml) was added, followed by perchloric acid (70%, 2.1 ml) and finally ether (60 ml). On scratching, colourless crystals separated and were filtered off and washed with ether to give the thiouronium perchlorate (116), (1.78 g, 28%). A portion was recrystallised from methanol/ether, mpt 71-4°. (Found: C, 33.8; H, 6.3; N, 8.7. $C_9H_{19}N_2O_6SCl$ requires C, 34.0; H, 6.0; N, 8.8%).

(b) p-Nitrobenzyl bromide

(i) With N,N'-ethylenethiourea

p-Nitrobenzyl bromide (6.47 g, 30 mmol) and N,N'-ethylenethiourea (3.06 g, 30 mmol) in ethanol (20 ml) were heated under reflux for 30 min. The solution was cooled and off-white crystals of S-(p-nitrobenzyl)-N,N'-ethylenethiouronium bromide separated (8.5 g, 89%), mpt. 146-8°, which was characterised as the free base (see section 2, experiment 4(a)).

(ii) With N,N,N',N'-tetramethylthiourea.

p-Nitrobenzyl bromide (6.47 g, 30 mmol) and N,N,N',N'-tetramethylthiourea (3.96 g, 30 mmol) were reacted under identical conditions to (i) to give S-(p-nitrobenzyl)-N,N,N',N'- tetramethylthiouronium bromide (9.9g, 95%), which crystallised on addition of ether. The bromide, (5.21 g, 15 mmol) dissolved in ethanol (25 ml), was treated with perchloric acid (70%, 2.2 ml, ca. 15 mmol) resulting in the separation of the perchlorate (4.52 g, 81%), mpt. (from methanol) 89-91° (Found: C, 39.2; H, 5.1; N, 11.4. $C_{12}H_{18}N_3O_6SCl$ requires C, 39.2; H, 4.9; N, 11.4%).

(c) Benzyl bromide with N,N'-ethylenethiourea.

Benzyl bromide (11.8 ml, 0.1 mol) and N,N'-ethylenethiourea (10.2 g, 0.1 mol) were reacted under similar conditions to those used in (b)(i) to give S-benzyl-N,N'-ethylenethiouronium bromide

(25.6 g, 94%), mpt. (from ethanol) 175-8°, which was characterised as the free base (see section 2, experiment 5).

II. Reactions of Thioureas with Halogenated Cyclopentadienes.

1. 9-Bromofluorene

Equimolar amounts of 9-bromofluorene and the thiourea in ethanol (ca. 15 ml solvent/0.01 mol of reactant) were heated under reflux for the specified period of time (see table 4). If the thiouronium salt did not precipitate on cooling, the solution was concentrated in vacuo and the precipitated bromide was filtered off, and washed well with ether. Recrystallisation from methanol or ethanol afforded analytical samples. Where applicable, the perchlorates were prepared as follows. An equimolar amount of perchloric acid (70%) was added to a slurry of the bromide in methanol and the mixture was warmed until the solid had dissolved. If the perchlorate did not separate on cooling, a small amount of water was added to assist precipitation. The perchlorates were recrystallised from methanol.

2. 5-Chloro- (and 5-Bromo-) 2,3,4-triphenylcyclopentadiene.

Equimolar amounts of 5-chloro- (or 5-bromo-) 2,3,4-triphenylcyclopentadiene and the thiourea were heated under reflux in ethanol (60-70 ml solvent/0.01 mol of reactant) for the specified time (see table 5). The hot solution was filtered from insoluble material and if the thiouronium salt did not precipitate on cooling, the solution was concentrated in vacuo and stirred with ether, resulting in the separation of the chloride (or bromide). These were purified further, where necessary, by reprecipitation from ethanolic solution using ether. The picrates were prepared by addition of a hot

Table 4. Preparation of S-Fluorenylthiouronium Salts

Cpd. No.	Thiourea $S=C(NR^1R^2)(NR^3R^4)$ R^1	R^3	R^2	R^4	Counter ion	Rn. time	Yield[4] (%)	Mpt.(°)	Formula	Elemental Analysis % Calculated C	H	N	Found C	H	N
(143)	H	H	H	H	Br	15 min	90	216-9	$C_{14}H_{13}N_2SBr$	52.3	4.0	8.7	52.3	4.0	8.7
(143a)	"	"	"	"	ClO_4	-	47	144-7	$C_{14}H_{13}N_2O_4SCl$	49.3	3.8	8.2	49.0	3.9	8.2
(144)	Me	Me	H	H	Br	1 hr.	86	95-108	-		-			-	
(144a)	"	"	"	"	ClO_4	-	56	65-72	$C_{16}H_{17}N_2O_4SCl$	52.1	4.6	7.6	51.6	4.8	7.5
(145)	CH_2CH_2		H		Br	15 min.	96	232-8	-[3]		-			-	
(145a)	"	"	"	"	ClO_4	-	86	202-4	-		-			-	
(146)	Ph	Ph	H	H	Br	30 min.	89[1]	167-9	$C_{26}H_{21}N_2SBr$	65.9	4.4	5.9	65.5	4.7	5.7
(147)	Ph	H	H	H	Br	"	78.5	164-8	-[3]		-			-	
(148)	Ph	Me	H	H	Br	"	94.5	197-200	$C_{21}H_{19}N_2SBr$	61.3	4.7	6.8	61.2	4.9	6.9
(149)	Me	Me	Me	Me	Br	1½ hr.	-[2]	-	-		-			-	
					ClO_4	-	64	167-9	$C_{18}H_{21}N_2O_4SCl$	54.5	5.3	7.1	54.3	5.4	7.2

[1] Precipitated using excess ether

[2] Bromide not isolated (converted to perchlorate *in situ*)

[3] Satisfactory analysis results were obtained for the corresponding ylides.

[4] Yields quoted for perchlorates are overall yields.

Table 5. Preparation of S-(2,3,4-Triphenylcyclopentadienyl)thiouronium Salts

Cpd. No.	Thiourea S=C(NR¹R²)(NR³R⁴)				Counter ion	Rn. time	Yield (%)	Mpt. (°)	Formula	Elemental Analysis %					
										Calculated			Found		
	R^1	R^3	R^2	R^4						C	H	N	C	H	N
(150a)	H	H	H	H	Cl	6 days	74	155 (dec.)	–		–			–	
(150b)	"	"	"	"	Br	30 min.	71	170-85	$C_{24}H_{21}N_2SBr$	64.1	4.7	6.2	63.7	4.8	6.1
(150d)	"	"	"	"	Picrate	-	-	198-201	$C_{30}H_{23}N_5O_7S$	60.3	3.8	11.7	59.9	3.7	11.5
(151a)	Me	Me	H	H	Cl	6 days	70	204-7	-		-			-	
(151d)	"	"	"	"	Picrate	-	-	155-8	$C_{32}H_{27}N_5O_7S$[3]	61.4	4.3	11.2	60.3	4.5	10.7
(152a)	CH_2CH_2		H		Cl	3 days	96	218-24	-		-			-	
(152d)	"	"	"	"	Picrate	-	-	182-4	$C_{32}H_{25}N_5O_7S$	61.6	4.0	11.2	61.3	4.0	10.9
-	Ph	Ph	H	H	Cl	5 days	0[1]	-	-		-			-	
(153a)	Me	Me	Me	Me	Cl	5 days	64	163-9	-		-			-	
					ClO_4	-	54[2]	220-3	$C_{28}H_{29}N_2O_4SCl$	64.1	5.5	5.3	63.8	5.6	5.2

[1] Decomposition to anilinium chloride occurred

[2] Overall yield

[3] Light sensitive

saturated solution of picric acid (1 mmol) to a hot saturated solution of the chloride (1 mmol) in methanol. The picrates separated when the solution was cooled and were recrystallised from methanol. The perchlorate (153) was prepared in a similar manner using 70% perchloric acid (1 mmol). N,N'-Diphenylthiourea (20 mmol), when treated as described above, gave anilinium chloride (1.95 g, 15 mmol), mpt. 194-8° (lit.[191] 198°).

3. 5-Bromo-1,2,3,4-tetraphenylcyclopentadiene.

5-Bromo-1,2,3,4-tetraphenylcyclopentadiene and N,N'-dimethylthiourea were treated as described in expt. 2 to give the thiouronium bromide (157) (93%) as a pale yellow solid, mpt. 157-70° (after two recrystallisations from methanol-ether). The compound was too soluble in the usual recrystallisation solvents to enable further purification, and gave a brown tar on treatment with picric acid in methanol.

4. 3,5-Dibromocyclopentene.[192]

(a) Preparation of 3,5-dibromocyclopentene.

Bromine (17 ml) was added rapidly with stirring to a solution of freshly distilled cyclopentadiene (22 g, 25 ml) dissolved in chloroform (35 ml) at -30 to -40° (addition took ca. 5-10 min.) The solution, which was pale brown, was kept at -10 to -20° for 1 hour before use.

(b) With N,N'-ethylenethiourea.

The dibromocyclopentene solution (21 ml, 0.1 mol $C_5H_6Br_2$) was added to a suspension of N,N'-ethylenethiourea (20.4 g, 0.2 mol) in methanol (200 ml). The mixture was heated under reflux for 1 hour and allowed to cool. Removal of the solvent under reduced pressure (care-bumping) left a viscous brown oil with white solid matter suspended in it. The whole was dissolved in cold water (250 ml)

and washed with methylene chloride (2 x 150 ml). The solvent was removed under reduced pressure and the viscous residue was stirred with acetone. Crystallisation was complete in 1 hour, and the off-white crystals were filtered off, dissolved in the minimum volume of methanol and reprecipitated with excess ether. The colourless precipitate was filtered off and washed with methanol followed by ether to give 3,5-(bis(N,N'-ethylene)isothiouronium)cyclopentene dibromide (18.0 g, 42%). A portion recrystallised from methanol had mpt. 197-9°. (Found: C, 30.6; H, 4.2; N, 12.9. $C_{11}H_{18}N_4S_2Br_2$ requires C, 30.7; H, 4.2; N, 13.0%). N,N'-Dimethylthiourea reacted similarly.

(c) With thiourea.

3,5-Dibromocyclopentene and thiourea were treated in a similar manner to that described in (b) to give 3,5-bis(isothiouronium)-cyclopentene dibromide (43%), mpt. (from methanol) 192-4° (Found: C, 22.2; H, 3.9; N, 14.8. $C_7H_{14}N_4S_2Br_2$ requires C, 22.2; H, 3.7; N, 14.8%).

(d) With N,N,N',N'-tetramethylthiourea.

The dibromocyclopentene solution (1.05 ml, 5 mmol $C_5H_6Br_2$) was added to a solution of N,N,N',N'-tetramethylthiourea (1.32 g, 10 mmol) in chloroform (15 ml) and the mixture was stirred for 30 min. at room temperature. Solvent was removed under reduced pressure and addition of ether (50 ml) to the resultant brown oil produced off-white crystals after 12 hours. On attempted filtration these deliquesced within 30 seconds of exposure to the atmosphere. Addition of aqueous perchloric acid (70%) or saturated ethanolic picric acid solutions to an ethanolic solution of the crystals gave tarry precipitates.

§2. REACTIONS OF THIOURONIUM SALTS.

I. Thiouronium salts not stabilised by the cyclopentadienyl ring.

1. Salts from p-nitrophenacyl bromide.

(a) S-(p-Nitrophenacyl)-N,N'-dimethylisothiouronium bromide (105).

Aqueous Base. To a solution of the salt (522 mg, 1.5 mmol) dissolved in warm ethanol (100 ml) was added aqueous sodium hydroxide (2M, 0.5 ml). The mixture was allowed to stand for 30 min. with occasional shaking. The bulk of the solvent was reduced to ca. 10 ml in vacuo, and when cooled on ice pale yellow crystals separated which were filtered off, and washed with ethanol and ether to give the free base (350 mg, 87%). A portion recrystallised from ethanol had mpt. 185° (dec.). (Found: C, 49.1; H, 4.9; N, 15.6. $C_{11}H_{13}N_3O_3S$ requires C, 49.4; H, 4.9; N, 15.7%).

(b) S-(p-Nitrophenacyl)-N,N,N',N'-tetramethylisothiouronium bromide (106).

(i) Aqueous base. The salt (295 mg) was dissolved in methanol (4 ml) and aqueous sodium hydroxide (2M, 8 drops) was added with shaking. A black, tarry precipitate was formed which was not treated further.

(ii) Triethylamine. The salt (50 mg) was added to triethylamine (3 ml) in the cold and very little dissolved (no colour change was observed). When heated, the solution darkened resulting in a brown oily precipitate which was not treated further.

(iii) Phenyl lithium followed by p-nitrobenzaldehyde in situ. The salt (1.50 g, 4 mmol) was made into a slurry with dry tetrahydrofuran (120 ml) and a solution of phenyl lithium in ether (0.8M, 5.5 ml, 4.4 mmol) was added with stirring under a stream of dry nitrogen. The solid dissolved giving a dark brown turbid solution. After 15 min. p-nitrobenzaldehyde (604 mg, 4 mmol) was added. The solution initially darkened then the turbidity gradually disappeared to give a clear, burgundy-red solution. Stirring was continued for 2½ hr. at room temperature. The solvent was then removed under reduced pressure and

the viscous red residue was taken up in chloroform (80 ml), washed with water (3 x 80 ml), and dried over magnesium sulphate. Removal of solvent under reduced pressure gave a viscous red oil which did not crystallise on addition of the usual solvents, nor would it crystallise on treatment with decolourising charcoal. Thin-layer chromatography using chloroform as eluant showed three major components.

The oil was dissolved in methylene chloride (ca. 6 ml) and applied to a silica gel column prepared with methylene chloride. Elution with this solvent brought off a red band, which gave a red oil when evaporated to dryness in vacuo. Trituration of the oil with hot methanol (2 x 25 ml) brought down an orange-brown solid which was filtered and washed with methanol to give an unidentified solid (130 mg) mpt. 110-125°. (The expected olefin, 4,4'-dinitro-trans-chalcone, exists as a pale yellow solid, mpt.[193] 202-5°.)

(iv) Acetic anhydride and acetyl chloride.

(1) A suspension of the salt (376 mg, 1 mmol) in acetic anhydride (50 ml) was refluxed for 30 min. The solution was cooled on ice, and off-white crystals were filtered off and washed with ether to give an unidentified substance (180 mg), mpt. 240-4° (dec.), ν_{max} (C=O) 1665 cm^{-1}.

(2) The salt (3.59 g, ca. 10 mmol) was dissolved in a mixture of acetyl chloride (10 ml) and acetic acid (5 ml), and refluxed for 4 hours. Acetic acid (7.5 ml) was added in 2.5 ml aliquots at hourly intervals. Finally, after dilution with further acetic acid (5 ml) the solution was cooled and scratched; this brought down colourless crystals which were filtered and washed with ether to give the unidentified substance (1.95 g). A portion recrystallised from ethanol had mpt. 230-5°.

(Found: C, 41.3; H, 3.7; N, 8.3% Closest empirical formula $C_{11}H_{12}N_2$).

(3) The 2,4-dinitrophenylhydrazone of the unidentified substance was prepared as follows:- The unidentified substance from (2) (250 mg) was dissolved in the minimum volume of cold methanol and a solution of Brady's reagent (10 ml) was added. The mixture was heated under reflux for $1\frac{3}{4}$ hours, during which time an orange precipitate developed. The solution was cooled and the orange precipitate was filtered off and washed with cold methanol to give the dinitrophenylhydrazone of the unidentified substance (90 mg). A portion was recrystallised from nitromethane, mpt. 234-7°. (Found: C, 45.0; H, 3.7; N, 18.3%. Closest empirical formula $C_{17}H_{16}N_6$).

2. Salts from ethyl chloroacetate.

S-(Ethoxycarbonylmethyl)-N,N,N',N'-tetramethylthiouronium perchlorate with acetic anhydride.

The salt (637 mg) was dissolved in acetic anhydride (10 ml) and heated under reflux for 15 min. (Solution turned pale brown.) Addition of ethanol (50 ml) to the cooled solution, followed by ether (250 ml) precipitated off-white crystals of the starting material (330 mg, 50%), mpt. 72-5° (authentic mpt. 71-4°).

3. Salts from dimethyl-α-bromomalonate

S-Bis(methoxycarbonylmethyl)-N,N,N',N'-tetramethylthiouronium perchlorate with phenyl lithium followed by p-nitrobenzaldehyde in situ.

The salt (1.45 g, 4 mmol) was made into a slurry with dry tetrahydrofuran (100 ml) and a solution of phenyl lithium (1.07 M, 4.3 ml, 4 mmol) was added at 0° with stirring under a stream of dry nitrogen. A yellow colour developed and the solid dissolved. Stirring was continued for 20 min., then p-nitrobenzaldehyde (604 mg, 4 mmol) was added. (The colour of the solution became deeper orange). Stirring

was continued for a further 1 hr., then the solution was allowed to stand for 16 hr. Colourless needles had precipitated. The solution and precipitate were treated as follows. Solvent was removed under reduced pressure and the residue was taken up in methylene chloride (50 ml), washed with water (4 x 50 ml) and dried over magnesium sulphate. Removal of solvent under reduced pressure gave colourless plates which were filtered off and washed with ether to give p-nitrobenzaldehyde (250 mg, 41%), identified by its n.m.r. spectrum.

4. Salts from p-nitrobenzyl bromide

(a) S-(p-Nitrobenzyl)-N,N'-ethylenethiouronium bromide with phenyl lithium.

The salt (2.1 g, 6.6 mmol), in dry tetrahydrofuran (50 ml), was treated with ethereal phenyl lithium solution (0.96 M, 6.85 ml, 6.6 mmol), and after stirring 20 min., the solvent was removed in vacuo from the pale red solution. The yellow-brown residue was dissolved in ether (300 ml), washed with water (4 x 75 ml), and dried over magnesium sulphate. When the solvent was removed in vacuo, trituration of the pale yellow residue with ether gave S-(p-nitrobenzyl)-N,N'-ethylene isothiourea (860 mg, 55%) mpt. 151-3°. (Found: C, 51.0; H, 4.8; N, 17.5. $C_{10}H_{11}N_3O_2S$ requires C, 50.6; H, 4.6; N, 17.7%.)

(b) S-p-Nitrobenzyl-N,N,N',N'-tetramethylthiouronium perchlorate.

(i) With phenyl lithium

The salt (1.97 g, 4 mmol) was treated with ethereal phenyl lithium solution (4 mmol) as described in (a). A deep crimson colour appeared instantly. Workup using methylene chloride gave a deep red oil which solidified on trituration with acetone-ether to give a deep purple unidentified substance (130 mg), mpt. 60-150°. Further attempts at purification were not successful.

(ii) With phenyl lithium and p-nitrobenzaldehyde in situ.

The salt (1.97 g, 4 mmol) was treated as described in (b)(i),

p-nitrobenzaldehyde (604 mg, 4 mmol) was added to the tetrahydrofuran solution, and the mixture was kept for 3 days. The red colour did not disappear. Yellow needles had separated and these were filtered off to give p,p'-dinitro-trans-stilbene (20 mg), mpt. 288-95° (lit.[191] 303-4° (294-5°)), mpt. undepressed on admixture with an authentic sample.

5. S-Benzyl-N,N'-ethylenethiouronium bromide

With phenyl lithium

The salt (2.05 g, 7.5 mmol) was treated with ethereal phenyl lithium (8.25 mmol) as described in (a)(i) to give S-benzyl-N,N'-ethyleneisothiourea (710 mg, 49%), mpt. 50-4°. (Found: C, 62.4; H, 6.3; N, 14.5. $C_{10}H_{12}N_2S$ requires C, 62.5; H, 6.2; N, 14.6%).

6. S-Bis(phenylsulphonyl)methyl-N,N,N',N'-tetramethylthiouronium bromide (134)

With triethylamine

The salt (ca. 100 mg) was suspended in methanol (2 ml) and triethylamine (2 drops) was added. A transient solution resulted, from which colourless crystals separated which were filtered off and washed with methanol to give the ylide (182), (ca. 50 mg, 60%), mpt. 170-3° (Found: C, 50.3; H, 5.0; N, 6.7. $C_{18}H_{22}N_2O_4S_3$ requires C, 51.1; H, 5.2; N, 6.6%).

II. Thiouronium salts containing the cyclopentadienyl ring.

1. Salts from 9-Bromofluorene

(a) S-Fluorenylthiouronium bromide and its perchlorate.

(i) With aqueous sodium hydroxide.

S-Fluorenylthiouronium bromide (161 mg, 0.5 mmol) was dissolved in ethanol (ca. 3 ml) and aqueous sodium hydroxide (2M, 0.25 ml, 0.5 mmol) was added. The solution was shaken and after

5-10 min. fine colourless needles began to separate. After 30 min. the precipitate was filtered off and washed with a small volume of cold ethanol followed by ether to give fluorene-9-thiol, (25 mg, 25%), mpt. 155-60° (lit.[194], 105-6°). A portion was washed with ether (5 x 1 ml) and the washings were evaporated to dryness and recrystallised from ethanol, mpt. 162-3°. (Found: C, 77.6; H, 4.2; N, 0.0. $C_{13}H_{10}S$ requires C, 78.8; H, 5.0; N, 0.0%). The high mpt. may be due to isolation of a different crystal form.

(ii) With phenyl lithium

S-Fluorenylthiouronium perchlorate (8.18 g, 24 mmol) was dissolved in dry tetrahydrofuran (80 ml). A freshly prepared ethereal solution of phenyl lithium (0.90 M, 26.6 ml, 24 mmol) was added with stirring under a stream of dry nitrogen. A transient yellow colour was observed. The solution was stirred for 20 min., then solvent was removed under reduced pressure and the residue was taken up in methylene chloride (100 ml) and washed with water (5 x 100 ml). The organic layer was dried over magnesium sulphate and removal of solvent under reduced pressure precipitated colourless needles which were filtered off and washed with ether to give fluorenylidenediaminomethylenesulphurane (1.16 g). Removal of solvent from the mother liquor followed by trituration with ether yielded a second crop which was filtered off and washed with light petrol followed by ether/light petrol (1.12 g). Combined yield 2.28 g (40%), mpt. 120-2°. (Found: C, 69.8; H, 4.9; N, 11.8. $C_{14}H_{12}N_2S$ requires C, 70.0; H, 5.0; N, 11.7%).

(b) S-Fluorenyl-(N,N'-dimethyl)thiouronium perchlorate.

With phenyl lithium.

S-Fluorenyl-N,N'-dimethylthiouronium perchlorate (12.9 g, 35 mmol) was treated in a similar manner to that described in (a) to give fluorenylidene-N,N'-dimethyldiaminomethylenesulphurane (7.6 g, 83%), mpt. (from methylene chloride/light petrol) 111-2°. (Found: C, 71.5; H, 6.1;

N, 10.4. $C_{16}H_{14}N_2S$ requires C, 71.6; H, 6.0; N, 10.4%). It was stored at -40°

(c) S-Fluorenyl-N,N'-ethylenethiouronium perchlorate.

(i) With phenyl lithium

S-Fluorenyl-N,N'-ethylenethiouronium perchlorate (12.4 g, 34 mmol) was treated in a similar manner to that described in (a) to yield the ylide (6.1 g, 68 %), mpt. 101-4°. (Found: C, 71.5; H, 5.0; N, 10.9. $C_{16}H_{14}N_2S$ requires C, 72.1; H, 5.2; N, 10.5%.) It was stored at -40°.

(ii) With triethylamine.

S-Fluorenyl-N,N'-ethylenethiouronium bromide (695 mg, 2 mmol) was dissolved in warm methanol (10 ml) and triethylamine (1.5 ml, 11 mmol) was added. Addition of ether (50 ml) brought down colourless needles of triethylamine hydrobromide, mpt. 248-50°, which were filtered off. The filtrate was evaporated in vacuo and the sticky residue was triturated with ether (ca. 10 ml) and kept overnight. A pale yellow solid separated (90 mg), mpt. 126-34° (red), which was identified as the ylide contaminated with some triethylamine hydrobromide (from its ultra-violet spectrum and the fact that it gave a precipitate with ethanolic silver nitrate solution).

(d) S-Fluorenyl-N,N'-diphenylthiouronium bromide

(i) With phenyl lithium.

S-Fluorenyl-N,N'-diphenylthiouronium bromide (14.2 g, 30 mmol) was treated in an identical manner to S-fluorenyl-N,N'-dimethyl-thiouronium perchlorate and the product crystallised as a colourless solid (9.8 g, 83%) mpt. 125-8°. (Found: C, 79.3; H, 5.0; N, 7.3. $C_{26}H_{20}N_2S$ requires C, 79.6; H, 5.1; N, 7.1%). Storage in a deep freeze was not necessary.

(ii) With triethylamine.

S-Fluorenyl-N,N'-diphenylthiouronium bromide (950 mg, 2 mmol) was dissolved in methanol (7 ml) and triethylamine (0.3 ml, 2.2 mmol)

was added. A white solid separated immediately and this was filtered off and washed with methanol to give the ylide (730 mg, 93.5%), mpt. 128-30°.

(e) S-Fluorenyl-N,N,N',N'-tetramethylthiouronium perchlorate.

(i) Phenyl lithium.

S-Fluorenyl-N,N,N',N'-tetramethylthiouronium perchlorate (1.19 g, 3 mmol) was made into a slurry with dry tetrahydrofuran (30 ml) on an ice bath. An ethereal solution of phenyl lithium (1.07 M, 5 ml, 5.35 mmol) was added with stirring under a stream of dry nitrogen. A deep red colour developed and the solution was stirred for 15 min. Removal of solvent from one half of the solution under reduced pressure gave a red oil which was taken up in methylene chloride (30 ml) and washed with water (4 x 30 ml). The organic extract was dried over magnesium sulphate and removal of the solvent gave a red oil which dissolved in ether and gave a sticky precipitate on trituration with light petrol. Removal of solvent from the other half of the solution under reduced pressure gave the red oil which was taken up in ether (25 ml) and washed with water (5 x 40 ml). The organic extract was dried over magnesium sulphate and slow evaporation of the solvent from one portion overnight gave a red tarry residue. Light petrol was added to a second portion but no precipitate appeared when it was kept for 2 days.

(ii) With sodium hydride.

The perchlorate (400 mg, 1 mmol) was made into a slurry with dry tetrahydrofuran (15 ml), and a suspension of sodium hydride in mineral oil (80%, 250 mg) was added under a stream of dry nitrogen and the mixture was stirred for 3 hours. The solution turned deep orange. It was filtered, and removal of solvent from the filtrate under reduced pressure, followed by addition of ether (3 ml) produced brilliant orange crystals which were filtered off and washed with methanol to give bifluorenylidene (50 mg, 15%). A portion was recrystallised from methanol, mpt. 189° (lit.[195] 187-8°). (Found: C, 94.1; H, 5.0; N, 0.0. $C_{26}H_{16}$ requires C, 95%; H, 4.8; N, 0.0%).

(f) S-Fluorenyl-N-phenylthiouronium bromide.

With triethylamine.

S-Fluorenyl-N-phenylthiouronium bromide (3.97 g, 10 mmol) was

slurried in methanol (10 ml) and triethylamine (1.5 ml, ca. 11 mmol) was added. The solid dissolved giving a clear transient solution followed by a thick white precipitate. This was filtered off and washed with a small volume of methanol to give fluorenylidene-N-phenyl-diaminomethylene sulphurane (2.9 g, 92%), mpt. 88-97°. A portion recrystallised from methanol had mpt. 120-4°. (Found: C, 75.8; H, 5.3; N, 9.0. $C_{20}H_{16}N_2S$ requires C, 76.0; H, 5.1; N, 8.8%.)

(g) S-Fluorenyl-N-methyl-N'-phenylthiouronium bromide.

With triethylamine.

S-Fluorenyl-N-methyl-N'-phenylthiouronium bromide (4.11 g, 10 mmol) was dissolved in warm methanol (30 ml) and triethylamine (1.5 ml, ca. 11 mmol) was added. Colourless needles separated on cooling and these were filtered off and washed with methanol to give fluorenylidene-N-methyl-N'-phenyldiaminomethylene sulphurane (2.8 g, 85%), mpt. 145-7°. (Found: C, 76.4; H, 5.7; N, 8.4. $C_{21}H_{18}N_2S$ requires C, 76.3; H, 5.5; N, 8.5%.)

2. Salts from 2,3,4-Triphenylcyclopentadiene

(a) S-(2,3,4-Triphenylcyclopentadienyl)thiouronium bromide and chloride

(i) With aqueous sodium hydroxide

When sodium hydroxide solution (2M, 0.3 ml, 0.6 mmol) was added to a solution of the bromide (110 mg, 0.25 mmol), in ethanol (2 ml), impure 2,3,4-triphenyl-cyclopentadiene-1-thiol separated as a green solid (35 mg, 44%), mpt. 160-85°. Further attempts at purification were unsuccessful.

(ii) With potassium t-butoxide

To the bromide (400 mg, 1 mmol) dissolved in t-butanol (70 ml), 1 ml of a solution of potassium t-butoxide (prepared by heating under reflux potassium (1 g) in dry t-butanol (20 ml) for 2 hr.) was added. 2,3,4-Triphenylcyclopentadiene-1-thiol separated as a yellow solid (90 mg, 28%). A portion was recrystallised from benzene-petrol (bpt. 60-80°) (1:1), mpt. 193-6° (dec.) (Found: C, 83.5; H, 5.4; N, 0.0.

$C_{23}H_{18}S$ requires C, 84.6; H, 5.5; N, 0.0%).

(iii) With phenyl lithium

An ethereal solution of phenyl lithium (0.84 M, 4.5 ml, 3.85 mmol) was added to a suspension of the chloride (1.40 g, 3.5 mmol) in dry tetrahydrofuran. A pale green solution resulted, and after this had been stirred for 20 min. the solvent was removed in vacuo. The residue was dissolved in methylene chloride (40 ml), washed with water (5 x 40 ml) and dried over magnesium sulphate. When the solvent was removed and the viscous brown residue was triturated with ether-light petrol (1:6), (80 ml), a light yellow solid, believed to be the mercaptofulvene (204), was isolated (950 mg, 71%), mpt. 153-63° (dec.) (Mol. wt. 366.118. $C_{24}H_{18}N_2S$ requires 366.119).

(b) S-(2,3,4-Triphenylcyclopentadienyl)-N,N'-dimethylthiouronium chloride

(i) With phenyl lithium

When the chloride (1.52 g, 3.5 mmol) was treated with ethereal phenyl lithium solution (0.94 M, 4.1 ml, 3.85 mmol) in an identical manner to that described in expt. 2(a)(iii) above, a green-brown solid, believed to be the mercaptofulvene (205), was isolated (780 mg, 56%), mpt. 118-130° (dec.) (Mol. wt. 394.150. $C_{26}H_{22}N_2S$ requires 394.150). A portion of the solid (70 mg) was dissolved in the minimum volume of hot methanol and, to this, a solution of picric acid (50 mg) dissolved in the minimum volume of hot methanol was added. Yellow crystals of unchanged picric acid, mpt. 118-21° (lit.[191] 122°), were filtered off from the cooled solution. Addition of ether to the filtrate resulted in the separation of a brown tar.

(ii) With triethylamine

The chloride (865 mg, 2 mmol) was dissolved in methanol (8 ml) and triethylamine (200 mg, 0.27 ml, 2 mmol) was added. The green-brown solution was diluted with ether (80 ml), and colourless crystals of triethylamine hydrochloride (230 mg, 86%) were filtered off. When

the solvent was removed from the filtrate *in vacuo* and the resulting green oil was triturated with methanol, a green solid, believed to be the mercaptofulvene (205), was isolated (530 mg, 67%), mpt. 130-40° (dec.). Attempted conversion to the picrate as described in (i) also failed.

(c) S-(2,3,4-Triphenylcyclopentadienyl)-N,N'-ethylenethiouronium chloride

The chloride (860 mg, 2 mmol) was treated with ethereal phenyl lithium solution (1.06 M, 2.05 ml, 2.2 mmol) in an identical manner to that described in expt. 2(a)(iii). A khaki coloured solid, believed to be the mercaptofulvene (206), was isolated (530 mg, 67%), mpt. 115-35° (dec.). It was reprecipitated from methylene chloride solution using ether-light petrol, mpt. 134-45° (dec.). It did not show a parent-ion peak at the expected value ($M^{+\cdot}$ 392) in its mass spectrum.

(d) S-(2,3,4-Triphenylcyclopentadienyl)-N,N,N',N'-tetramethylthiouronium perchlorate

The perchlorate (1.05 g, 2 mmol) was treated with ethereal phenyl lithium solution (1.06 M, 2.05 ml, 2.2 mmol) in an identical manner to that described in expt. 2(a)(iii), resulting in an instant red coloration in the tetrahydrofuran solution. A red solid was obtained on trituration with ether and was washed with ether to give the mercaptofulvene (207), (220 mg, 26%), mpt. 105-20° (dec.). A portion was reprecipitated from methylene chloride solution using ether, mpt. 146-55° (dec.) (Mol.wt. 422.181. $C_{28}H_{26}N_2S$ requires 422.182). The solid gave a poorly-resolved ultra-violet spectrum in tetrahydrofuran solution which failed to revert to the salt spectrum on addition of perchloric acid, as the freshly basified solution had done. $\lambda_{max}^{CHCl_3}$=355 nm(sh

1-Chloro-2,4-dinitrobenzene (50 mg) was added to a solution of the mercaptofulvene (50 mg) in a mixture of ethanol (3 ml) and aqueous sodium

hydroxide solution (5%, 1.5 ml). The mixture was heated under reflux for 10 min. and an unidentified brown solid (25 mg) separated, which, although it showed an absorption attributable to a nitro group in its infra-red spectrum (ν_{max} 1525, 1375 cm^{-1}), did not show a parent ion peak at the value expected for the 2,4-dinitrophenyl thioether (208) in its mass spectrum.

3. Salts from 1,2,3,4-Tetraphenylcyclopentadiene

S-(2,3,4,5-Tetraphenylcyclopentadienyl)-N,N'-dimethylthiouronium perchlorate

The perchlorate (855 mg, 1.5 mmol) was treated with etheral phenyl lithium solution (1.3 M, 1.25 ml, 1.65 mmol) in an identical manner to that described in expt. 2(a)(iii). A pale yellow solid was isolated (170 mg, 28%), mpt. 122-30°, whose n.m.r. spectrum suggested that it was 2,3,4,5-tetraphenylcyclopentadiene-1-thiol.

4. Salts from Unsubstituted Cyclopentadiene

3,5-Bis(N,N'-Ethylenethiouronium)cyclopentene dibromide (161).

The salt (1.92 g, 4 mmol) was dissolved in warm methanol (10 ml) and triethylamine (1.1 ml, 8 mmol) was added dropwise. The solution was cooled and the white precipitate was filtered off and washed with methanol and ether to give the free base (211) (710 mg, 66%), mpt. 146-8° (dec.). It was recrystallised from a large volume of ethanol, mpt. 154-5° (dec.) (Found: C, 48.9; H, 6.3; N, 20.7 $C_{11}H_{16}N_4S_2$ requires C, 49.2; H, 6.0; N, 20.9 %) Mol. wt. of base peak in mass spectrum 166.056. $C_8H_{10}N_2S$ requires 166.056). The compound was virtually insoluble in all of the commonly available solvents which were tried.

§3. REACTIONS OF THIOURONIUM YLIDES.

I. Ylides not stabilised by the cyclopentadienyl Ring.

1. Dicyanomethylenediaminomethylenesulphurane.

(a) With p-nitrobenzaldehyde.

The ylide (350 mg, 2.5 mmol) and p-nitrobenzaldehyde (375 mg, 2.5 mmol) were dissolved in ethanol (25 ml) and heated under reflux for 1 hr. The solution turned red. Solvent was removed under reduced pressure and the red glossy residue recrystallised on scratching. The lustrous orange-red crystals were filtered off and washed with a small volume of ethanol to give the Schiff's base (219) (165 mg, 25%). A portion was recrystallised from ethanol, mpt. 249° (dec.) (Found: C, 48.2; H, 2.6; N, 25.5. $C_{11}H_7N_5O_2S$ requires C, 48.4; H, 2.6; N, 25.6%). Increased reflux time did not improve the yield.

(b) With p-nitrobenzaldehyde (2 mol).

The ylide (700 mg, 5 mmol) and p-nitrobenzaldehyde (1.51 g, 10 mmol) dissolved in ethanol (25 ml) were heated under reflux for 40 hr. The solvent was removed under reduced pressure and trituration of the residue with methanol (ca. 5 ml) afforded orange crystals of the Schiff's base (219) (270 mg, 20%). The filtrate was applied to an alumina column prepared with chloroform/methanol 5:1 and elution with this solvent brought off an orange band (Schiff's base) which was discarded. Further elution with chloroform/methanol (1:1) brought off a colourless band which crystallised on removal of solvent in vacuo to give an unidentified solid (100 mg), τ (DMSO-D_6) 2.25 (brs.), 3.45 (brs.) peak heights 1:1; ν_{max} 2190 cm^{-1} (C≡N).

(c) With benzaldehyde (1 mol).

Commercial benzaldehyde (5 ml) was dissolved in ether (20 ml) and the ethereal solution was washed with saturated aqueous sodium bicarbonate solution followed by water (2 x 30 ml) and then dried over

sodium sulphate. The ether was removed under reduced pressure to give the starting material.

The ylide (350 mg, 2.5 mmol) and benzaldehyde (265 mg, 2.5 mmol) were dissolved in ethanol (20 ml) and refluxed for 16 hr. The solvent was removed under reduced pressure giving yellow crystals, which were filtered off and washed with a small volume of cold ethanol, followed by ether, to give the Schiff's base (218), (120 mg, 21%), mpt. 192-6°. A portion recrystallised from acetonitrile had mpt. 198-200°. (Found: C, 57.5; H, 3.7; N, 24.0. $C_{11}H_8N_4S$ requires C, 57.9; H, 3.5; N, 24.5%). The material showed signs of decomposition on further recrystallisation.

With benzaldehyde (2 mol).

The ylide (700 mg, 5 mmol) and benzaldehyde prepared as above (1.06 g, 10 mmol) were dissolved in ethanol (25 ml) and heated under reflux for 5 days. The solvent was removed under reduced pressure and the resulting yellow solid was filtered off and washed with ethanol to give the Schiff's base (218), (630 mg). Thin layer chromatography of the mother liquor using chloroform/methanol 5:1 as eluant showed the presence of at least 5 components. On standing for a further 2 days, the mother liquor gave a further yellow precipitate of Schiff's base (218), (300 mg). Total yield was 930 mg (81%).

Hydrolysis of benzylidene-2,4-diamino-5-cyanothiazole (218).

Methanolic hydrogen chloride solution (10% w/v, ca. 4 ml) was added to the Schiff's base (230 mg, 1 mmol), resulting in a clear transient solution from which crystals were beginning to separate. The reaction was completed by warming to 60° for 1 min., then the mixture was cooled and colourless needles of 2,4-diamino-5-cyano-thiazole hydrochloride (70 mg, 40%) were filtered off, mpt. 220° (dec.).

It was characterised as the free base as follows. The hydrochloride (35 mg) was dissolved in water (ca. 0.5 ml) and conc. ammonia solution (2 drops) was added. The free base (221) precipitated as colourless needles (15 mg), mpt 178-83° (lit.[93] 190-2°). Mpt. after one recrystallisation from water was 181-4°. 2,4-Dinitrophenylhydrazine reagent was added to the methanolic filtrate from the hydrolysis, resulting in precipitation of benzaldehyde-2,4-dinitrophenylhydrazone (60 mg, 21%) mpt. 196-205° (dec.), (lit.[196] 237°).

II Ylides stabilised by the cyclopentadienyl ring.

Fluorenylides.

General

(i) Reactions with aldehydes (or ketones)

Equimolar amounts of the ylide and the appropriate aldehyde (or ketone) were allowed to react for the specified period of time (see tables 2 and 3, discussion, sect. 3 II) in a similar manner to the typical example described below.

Fluorenylidene-N,N'-ethylenediaminomethylenesulphurane (1·06 g, 4 mmol) and p-nitrobenzaldehyde (604 mg, 4 mmol) were dissolved in methylene chloride (30 ml) and kept at room temperature for 20 hr. The solution was washed with water (3 x 30 ml) and dried over magnesium sulphate. The aqueous washings were evaporated to dryness in vacuo to give N,N'-ethylene urea (290 mg, 84%), mpt. 98-110° (lit.[191] 131°). Removal of solvent in vacuo from the methylene chloride extract gave yellow crystals of p-nitrobenzylidenefluorene (1.05 g, 89%), mpt. 128-40° (lit.[197] 167-8°). A portion recrystallised from ethanol had mpt. 166-8° and did not depress the mpt. on admixture with an authentic sample (prepared[197] by the condensation of fluorene with p-nitrobenzaldehyde). An insoluble pale yellow residue remaining from this recrystallisation

was washed well with hot ethanol to give elemental sulphur (10 mg, 8%) (Mol. wt. 255.781. S_8 requires 255.777; shows correct breakdown pattern).

In those cases where the ylide was generated *in situ*, the aldehyde (or ketone) was added to a solution of the ylide in tetrahydrofuran, prepared as described in section 2 II. Workup was carried out in a similar manner to that described above.

(ii) Comparative kinetic hydrolysis study of ylides (188), (189) and (190).

A saturated solution of sodium hydroxide in methanol (at *ca.* 40°) (*ca.* 0.5 ml) was added to a methanolic solution of the ylide (*ca.* 0.03 mM, 2.5 ml) and after the mixture had been shaken thoroughly, readings were taken on the ultra-violet spectrometer at suitable time intervals (3-15 min.) until the reaction was approximately 90% complete (1-2 hr.). All the reactions were carried out at 40°.

1. Fluorenylidenediaminomethylenesulphurane with p-nitrobenzaldehyde

See table 2.

2. Fluorenylidene-N,N'-dimethyldiaminomethylenesulphurane

(a) Hydrolysis.

The ylide (536 mg, 2 mmol) was dissolved in ethanol (25 ml) and an aqueous solution of sodium hydroxide (5 M, 2 ml, 10 mmol) was added. After 2 days at room temperature, the solvent was removed under reduced pressure leaving a brown tar. This was taken up in methylene chloride (20 ml), washed with water (4 x 30 ml) and dried over magnesium sulphate. The organic extract was concentrated *in vacuo* to *ca.* 3 ml and applied to a silica gel column prepared with a chloroform/methanol mixture (9:1). Elution with this solvent brought off a red band which, on removal of solvent *in vacuo*, followed by trituration with methanol, gave orange crystals of fluorenone (100 mg, 27%), mpt. (from methanol) 75-8° (lit.[191] 83-4°), undepressed on admixture with an authentic sample.

(b) With p-nitrobenzaldehyde* and cinnamaldehyde

See tables 2 and 3. *N,N'-Dimethylurea (29%) was also isolated in this reaction mpt. 84-95° (lit.[191] 108°), undepressed on admixture with an authentic sample.

(c) With p-anisaldehyde

Removal of solvent from the methylene chloride extract gave an orange oil which was dissolved in benzene and applied to an alumina columm prepared with benzene. Elution with this solvent brought off an orange band, which, after removal of the solvent in vacuo, crystallised from methanol. Mpt. of fulvene (from glacial acetic acid) 125-8° (lit.[198] 128-9°). See table 2.

(d) With cyclohexanone

The solution was worked up as described in (c) to give a small amount of an orange solid, identified by t.l.c. as a mixture of fluorenone and bifluorenylidene.

(e) Thermal decomposition in presence of triphenylphosphine.

(i) The ylide (803 mg, 3 mmol) and triphenylphosphine (3.8 g, 15 mmol) were dissolved in methylene chloride (20 ml). The solution was flushed with nitrogen and kept stoppered at room temperature for 10 days. The solution, which had turned brown, was washed with water (2 x 25 ml) and dried over magnesium sulphate. Removal of solvent under reduced pressure gave a brown oil, which was triturated with light petrol (70 ml). Buff coloured plates separated, which were filtered off and washed with light petrol to give triphenylphosphine oxide (750 mg, 2.65 mmol. 89%) mpt. 140-9° (lit.[191] 156-7°). It did not depress the melting point on admixture with an authentic sample. The aqueous extracts were combined, washed with methylene chloride (30 ml), and evaporated to dryness in vacuo. The resultant yellow oil was triturated with acetone and an unidentified flesh-coloured solid separated which was filtered off (10 mg).

(ii) The ylide (540 mg, 2 mmol) and triphenylphosphine (1.3 g, 5 mmol) were ground together to a fine powder, placed in a flask which was flushed well with nitrogen and then plunged into a bath at 160-5° and kept at that temperature for 1½hr. The mixture, which had darkened, was cooled and ether (10 ml) was added, resulting in the separation of triphenylphosphine oxide (300 mg, 21%), mpt. 139-42° (lit.[191] 156-7°) undepressed on admixture with an authentic sample. The solvent was removed from the filtrate and addition of methanol precipitated triphenylphosphine (570 mg, 44%), mpt. 61-4° (lit.[191] 80°). A pale yellow solid separated when the methanolic solution was kept overnight, but it was established that this was not fluorenylidenetriphenylphosphorane by examination of its ultra-violet spectrum.

(f) Thermal decomposition in methylene chloride

The ylide (803 mg, 3 mmol) was dissolved in methylene chloride (20 ml) and the flask was flushed with nitrogen, sealed and kept for 9 months at room temperature. The solution was filtered, the solvent was removed *in vacuo* and the residue was triturated with methanol to give bifluorenylidene (115 mg, 23%), mpt. 65-120° (lit.[195] 187-8°), identified also by its ultra-violet spectrum. A portion washed with glacial acetic acid had mpt. 145-65°.

(g) Thermal decomposition in tetrahydrofuran

The ylide (535 mg, 2 mmol) was dissolved in dry tetrahydrofuran (15 ml) and treated as described in (f). The residue was dissolved in chloroform (30 ml), washed with water and dried over magnesium sulphate. When the solvent was removed *in vacuo* a yellow oil was obtained which crystallised from methanol to give fluorenone (90 mg, 25%), mpt. 65-73° (lit.[191] 82-5°), undepressed on admixture with an authentic sample.

3. Fluorenylidene-N,N'-ethylenediaminomethylenesulphurane

(a) With p-nitrobenzaldehyde

See table 2.

(b) With p-nitroacetophenone

The aqueous extracts were combined, washed with methylene chloride, and solvent was removed in vacuo to give colourless crystals of ethylenethiourea (23%), mpt. 178-85° (lit.[191] 200-3°). The methylene chloride extract was treated as follows. Solvent was removed in vacuo and the resulting brown oil was triturated with methanol (5 ml) to give yellow crystals of bifluorenylidene (22%), mpt. 85-110° (lit.[195] 189°). A portion recrystallised from chloroform-methanol had mpt. 178-82°.

(c) With nitrosobenzene.

The ylide (800 mg, 3 mmol) was dissolved in ether (30 ml) and a solution of nitrosobenzene (320 mg, 3 mmol) in ether-benzene (1:1) mixture (25 ml) was added. After 10 min (solution yellow) solvent was removed in vacuo and the residue was dissolved in methylene chloride (50 ml), washed with water (2 x 30 ml) and dried over magnesium sulphate. Removal of solvent in vacuo gave an orange-yellow oil which crystallised on cooling to give yellow crystals of the anil oxide (580 mg, 71.5%). A portion recrystallised from ethanol had mpt. 193-5° (lit.[199] 189-91°).

The reaction was also carried out in benzene (50 ml) using the quantities stated above, and after 3 weeks fine crystals of ethylene thiourea (130 mg, 61%) had separated, which did not depress the mpt. on admixture with an authentic sample. The anil oxide was isolated in 78% yield.

(d) With dimethylacetylenedicarboxylate (DMAD)

The ylide (800 mg, 3 mmol) and DMAD (470 mg, 0.41 ml, 3.3 mmol) in chloroform (15 ml) were heated under reflux for 14 hr. The solvent

was removed *in vacuo* and the residue was dissolved in the minimum volume of benzene and applied to an alumina column prepared with benzene-petrol (60-80). Elution with this solvent brought off a yellow band which gave an unidentified pale orange solid (35 mg), mpt. 97-100°, on removal of solvent. The solvent was changed to tetrahydrofuran and a brown band was collected which gave the 2,3-dihydrothiophen derivative (243) as a buff-coloured solid (80 mg, 6.3%), mpt. 110° (dec.) (Mol. wt. 408.114. $C_{22}H_{20}N_2O_4$ requires 408.114).

(e) With benzyl bromide (and benzyl iodide)

The ylide (1.60 g, 6 mmol) was dissolved in ether (50 ml), benzyl bromide (1.13 g, 0.80 ml, 6.6 mmol) was added and the mixture was kept for 16 days at room temperature. (A precipitate had begun to form after *ca.* 1 hr.) An off-white solid was filtered off (400 mg, 14%), mpt. 150° (dec.) whose mass spectrum suggested that it was the 9-benzyl-*S*-fluorenylthiouronium bromide (233) (intense fragment peak at m/e 254.110; the expected fulvene (234) ($C_{20}H_{14}$) requires 254.110). Attempted conversion to the perchlorate or picrate led to decomposition. After a further 2 months, the ethereal filtrate yielded a second crop of the salt (233) (670 mg, 24%).

Under similar conditions, benzyl iodide gave a pale orange solid, presumed to be the corresponding iodide salt, in yields of 7.5% after 4 days and 50% after 4 weeks.

The iodide (400 mg, *ca.* 1 mmol) and triethylamine (0.15 ml) in ethanol (5 ml) were heated under reflux for 5 hr. When the solution was cooled, an unidentified pale orange solid separated (50 mg), mpt. (from ethanol) 133-8°, which was not the expected fulvene (mpt.[197] 76°).

4. Fluorenylidene-N,N'-diphenyldiaminomethylene sulphurane.

(a) With p-nitrobenzaldehyde

The ylide (980 mg, 2.5 mmol) and p-nitrobenzaldehyde (378 mg, 2.5 mmol) were heated under reflux in carbon tetrachloride (25 ml) for 3 days. The solvent was removed from the filtrate under reduced pressure and the yellow residue was dissolved in benzene (3 ml) and applied to an alumina column prepared with benzene-petrol (bpt. 60-80°) (1:1). Elution with this solvent brought off an orange band, which, on removal of solvent and trituration with methanol gave orange crystals of bifluorenylidene (8 mg, ca. 1%), identified by its u.v. spectrum. Elution was continued with the same solvent and a yellow band was brought off. Removal of solvent under reduced pressure followed by trituration with ethanol gave yellow crystals of p-nitrobenzylidenefluorene (10 mg, 1.5%), mpt. 160-66° (lit.[197] 167-8°). It did not depress the melting point on admixture with an authentic sample.

(b) With nitrosobenzene.

The ylide (980 mg, 2.5 mmol) and nitrosobenzene (270 mg, 2.5 mmol) dissolved in methylene chloride (20 ml) were kept at room temperature for 24 hr. The solution, which had turned yellow-green, was concentrated in vacuo and applied to an alumina column prepared with methylene chloride. Elution with this solvent brought off a pale green band and removal of solvent in vacuo followed by trituration with ether-petrol gave colourless crystals of unchanged ylide (30 mg, 3%), mpt. 100-7° (authentic mpt. 125-8°). Further elution with the same solvent brought off a yellow band and evaporation to dryness in vacuo gave yellow crystals of the anil oxide (460 mg, 69%), mpt. 177-81° (lit.[199] 189-91°). Elution was continued with a large volume of methylene chloride which brought off an incomplete band, which, on evaporation to dryness in vacuo, gave colourless crystals of

N,N'-diphenylthiourea (260 mg, 44%), mpt. 134-8° (lit.[191] 154°).

5. Fluorenylidene-N,N,N',N'-tetramethyldiaminomethylenesulphurane

With p-nitrobenzaldehyde

See table 1. The fulvene did not depress the mpt. on admixture with an authentic sample.

6. 2,3,4-Triphenylcyclopentadienylidene-N,N'-dimethyldiaminomethylenesulphurane

(a) With p-nitrobenzaldehyde

A solution of the ylide in tetrahydrofuran was prepared from the chloride salt (151a) (3.02 g, 7 mmol) and an ethereal solution of phenyl lithium (1.20 M, 7.0 ml, 8.4 mmol) as described in §2, expt. 2(b)(i). p-Nitrobenzaldehyde (1.06 g, 7 mmol) was added with stirring, and a deep red coloration appeared immediately. The stirring was continued for a further 2 hr. and the solution was kept overnight. The solvent was removed in vacuo and the viscous red residue was dissolved in methylene chloride (50 ml), washed with water (4 x 75 ml) and dried over magnesium sulphate. The solvent was removed and the residue was dissolved in the minimum volume of benzene and applied to an alumina column prepared with benzene-petrol (bpt. 60-80°) (1:2) mixture. Elution with this solvent brought off a green band and when the solvent was removed and the residue was triturated with light petrol, an unidentified green solid (50 mg) was isolated. It was insoluble in common solvents and gave a purple solution in trifluoroacetic acid (Mol. wt. 614.212. $C_{35}H_{32}N_7S_2$ requires 614.215). Further elution with the same solvent brought off a brown band, and when the solvent was removed and the residue was triturated with methanol, 6-(p-nitrophenyl)-2,3,4-triphenylfulvene (20 mg, 0.7%) was obtained as a brown solid, mpt. 145-51° (lit.[67] 163-4°), undepressed on admixture with an authentic sample. The solvent was changed to benzene-petrol (bpt. 60-80°) (3:1), and elution with this solvent brought off

an orange band. When the solvent was removed and the residue was crystallised from benzene (ca. 2 ml), orange crystals of the pseudoazulene (255) (140 mg, 3.7%) were obtained, mpt. 253-62°. Mpt. after two recrystallisations from nitromethane was 263-4° (Found, N, 7.9. $C_{33}H_{25}N_3O_2S$ requires N, 8.0; Mol. wt. 527.166. $C_{33}H_{25}N_3O_2S$ requires 527.167).

(b) With benzene diazonium chloride

A solution of benzene diazonium chloride was prepared in the usual manner from aniline (2.0 g) dissolved in conc. hydrochloric acid (6 ml) and water (10 ml), and sodium nitrite (1.6 g) dissolved in water (20 ml). Sodium acetate (10 g) was added and the volume was made up to 40 ml with water.

The ylide was generated in situ by addition of triethylamine (0.07 ml, 0.55 mmol) to a solution of the perchlorate (151 c) (250 mg, 0.5 mmol) in chloroform (10 ml), and the solution was cooled to below 10°. The solution of diazonium salt (2 ml, ca. 1 mmol) was added rapidly with swirling. The mixture, which had darkened, was shaken vigorously for 1 min., then set aside for 30 min. with occasional shaking. Aqueous sodium hydroxide solution (5 M, ca. 2 ml) was then added and the organic layer was extracted from the alkaline solution, washed twice with water and dried over magnesium sulphate. Removal of solvent in vacuo gave a dark red viscous residue which gave a red-brown solid, believed to be the heterocycle (250) (30 mg, 14%), mpt. 145-57° (dec.), on trituration with ether. A portion dissolved in chloroform gave an intense blue coloration with conc. sulphuric acid. (Mol. wt. 428.134. $C_{29}H_{20}N_2S$ requires 428.134).

The green solid isolated from §2, expt. 2(b)(ii) (10 mg) was dissolved in chloroform (ca. 0.5 ml) and an equal volume of the benzene diazonium chloride solution was added with shaking. Although the

solution darkened, when the organic layer was treated with conc. sulphuric acid a brown tar was formed, showing that the compound described above had not been formed.

(c) Acetylation

S-(2,3,4-Triphenylcyclopentadienyl)-N,N'-dimethylthiouronium chloride (865 mg, 2 mmol) was suspended in acetic anhydride (10 ml) and triethylamine (0.28 ml, 2 mmol) was added. The mixture was heated on the steam bath for 2-3 min. (solution turns red). It was cooled and poured into water (120 ml) with stirring. A light-brown solid separated after 30 min. which was collected by filtration through a glass wool plug, washed with water and dried to give S-acetyl-2,3,4-triphenyl-6,6-bis(methylamino)fulvene-1-thiol (80 mg, 9 %), mpt. 90-105° (dec.) (Mol. wt. 438.176. $C_{28}H_{26}N_2OS$ requires 438.176).

7. 2,3,4-Triphenylcyclopentadienylidene-N,N'-ethylenediaminomethylene-sulphurane

(a) With p-nitrobenzaldehyde

A solution of the ylide (2 mmol) in tetrahydrofuran, prepared as described in §2, expt. 2(c), was treated with p-nitrobenzaldehyde (302 mg, 2 mmol) as described in expt. 6(a) above. Chromatography on an alumina column prepared with methylene chloride and eluted with this solvent brought off a red band. When the solvent was removed *in vacuo* and the residue was triturated with methanol, red-brown crystals of the pseudoazulene (253) (135 mg, 13%) were obtained, mpt. 279-86°. (Mol. wt. 525.150. $C_{33}H_{23}N_3O_2S$ requires 525.151). Further elution with the same solvent brought off a brown band, and when the solvent was removed and the residue was triturated with ether, 6-(p-nitrophenyl)-2,3,4-triphenylfulvene was obtained as a brown solid (20 mg, 2.5%), mpt. 165-72° (lit.[67] 163-4°), undepressed on

admixture with an authentic sample.

When the experiment was repeated under the same conditions using a reaction period of 3 days, the pseudoazulene was obtained in 32% yield and furthermore could be isolated without employing a chromatographic separation. It sufficed to evaporate the methylene chloride extract to dryness in vacuo and triturate the viscous brown residue with acetone, whereupon the pseudoazulene separated.

When the khaki-coloured solid isolated from §2, expt. 2(c) and p-nitrobenzaldehyde were allowed to react in methylene chloride solution for 5 days, no trace of the pseudoazulene (253) or the fulvene (252) could be detected (t.l.c., chloroform eluant), even in the presence of excess phenyl lithium. A similar result was obtained when the reactants were heated in boiling chloroform for 16 hr.

Dehydrogenation of the pseudoazulene (253)

(i) With chloranil

A solution of the pseudoazulene (790 mg, 1.5 mmol) and chloranil (738 mg, 3 mmol) in toluene (25 ml) was heated under reflux for 16 hr. The solution was filtered whilst warm, the residue was washed with benzene until the washings were colourless and the combined filtrate and washings were evaporated to dryness in vacuo. The residue was dissolved in the minimum volume of methylene chloride and applied to an alumina column prepared with methylene chloride. Elution with this solvent brought off a purple band and when the solvent was removed in vacuo, the dehydrogenated heterocycle (256) was obtained as a purple solid (120 mg, 15%), mpt. 289-94°. A portion recrystallised from nitromethane had mpt. 299-301°. (Found: N, 8.0. $C_{33}H_{21}N_3O_2S$ requires N, 8.0; Mol. wt. 523.136. $C_{33}H_{21}N_3O_2S$ requires 523.135).

(ii) With 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

The pseudoazulene (1.18 g, 2.25 mmol) and DDQ (1.02 g, 4.5 mmol) in toluene (30 ml) were treated as described for chloranil (see above).

Elution with methylene chloride brought off a purple band and when the solvent was removed in vacuo, an unidentified purple solid (105 mg, 9%), mpt. 270-6° was obtained (Mol. wt. 557. There was only one fragment peak at m/e 523, suggesting that the compound is possibly a dioxide derivative of the pseudoazulene (253)). Further elution brought off a purple-brown band and when the solvent was removed in vacuo, the dehydrogenated heterocycle (256) was obtained (70 mg, 6%), mpt. and mixed mpt. with an authentic sample 296-9°, (authentic mpt. 299-301°).

(iii) With benzoquinone

The pseudoazulene (261 mg, 0.5 mmol) and freshly sublimed benzoquinone (108 mg, 1.0 mmol) in toluene (20 ml) were heated under reflux for 24 hr. Examination of the dark solution (t.l.c., methylene chloride eluant) showed that it contained largely unchanged pseudoazulene together with a trace of the dehydrogenated heterocycle (256).

Bromination of the dehydrogenated heterocycle (256)

A 2 ml portion of a solution of bromine (80 mg) in methylene chloride (20 ml) (0.05 mmol Br_2) was added to a solution of the dehydrogenated heterocycle (256) (25 mg, ca. 0.05 mmol) in methylene chloride (3 ml). The solution immediately turned deep purple, and examination by t.l.c. using chloroform-methanol (5%) as eluant showed that an unstable product had been formed, as the purple spot initially lagged behind a spot of authentic starting material on a comparative run, but once the development of the plate was complete, the purple colour had disappeared and the two spots had the the same R_f value. After 2 hr. the solvent was removed in vacuo, keeping the temperature below 40°, and the sticky residue crystallised after some time to give a dark brown solid (25 mg), mpt. 90° (dec.), the mass spectrum of which suggested that it was unchanged starting material.

(b) With p-anisaldehyde

A solution of the ylide (7.5 mmol) in tetrahydrofuran, prepared as described in §2, expt. 2(c), was treated with p-anisaldehyde (1.02 g, 7.5 mmol) as described in expt. 7(a), with a reaction period of 5 weeks. Chromatography on an alumina column using benzene-petrol (bpt. 60-80°) (1:2) as eluant yielded 6-(p-methoxyphenyl)-2,3,4-triphenylfulvene (10 mg, 0.3%), mpt. 136-50° (Mol. wt. 412.182. $C_{31}H_{24}O$ requires 412.183). Further elution using benzene-ether (5%) brought off a red band which gave a red solid from methanol which was identified as the pseudoazulene (254) (140 mg, 3.7%), mpt. 259-65° (Mol. wt. 510.176. $C_{34}H_{26}N_2OS$ requires 510.176).

(c) With nitrosobenzene

A solution of the ylide in chloroform was prepared from the perchlorate (152c) (495 mg, 1 mmol) by addition of triethylamine (1.4 ml, 1 mmol). Nitrosobenzene (110 mg, 1 mmol) was added, and the solution immediately turned deep crimson and went progressively darker over several minutes. Examination of the solution by t.l.c. using methylene chloride as eluant showed that no trace of the expected anil oxide (or anil) was present. After $1\frac{1}{4}$ hr., the solution was applied to an alumina column prepared with methylene chloride. Elution with this solvent brought off an intense blue-violet band, and removal of the solvent in vacuo followed by trituration with methanol gave the anil dimer (259) as a deep blue solid (55 mg, 14.5%), mpt. 132-47° (Mol. wt. 764.317. $C_{58}H_{40}N_2$ requires 764.319).

(d) With benzene diazonium chloride

A solution of the perchlorate (152c) (1.5 g, 3 mmol) was treated in a manner similar to that already described (expt. 6(b)), to give a red-brown solid (200 mg, 16%), mpt. 140° (dec.), believed to be the heterocycle (250) (Mol. wt. 428.134. $C_{29}H_{20}N_2S$ requires 428.134).

8. 2,3,4-Triphenylcyclopentadienylidene-N,N,N',N'-tetramethyldiaminomethylenesulphurane

(a) With p-nitrobenzaldehyde

A solution of the ylide in tetrahydrofuran was prepared from the perchlorate salt (2.10 g, 4 mmol) and an ethereal solution of phenyl lithium (1.30 M, 3.4 ml, 4.4 mmol) as described in §2, expt. 2(d). Addition of p-nitrobenzaldehyde (604 mg, 4 mmol) followed by workup after 3 days as described in expt. 6(a) gave a green-brown residue which was purified by chromatography on an alumina column. 6 bands were brought off, described as follows:

Band no.	(elution solvent)	colour	(trituration solvent)	yield
1	(benzene-petrol (60-80°) 1:1)	green	(methanol)	10 mg
2	(" " " ")	yellow	(")	50 mg
3	(" " " ")	pale green	(")	75 mg
4	(" " " ")	dark green	(ether-light petrol)	145 mg, mpt. 290-8°
5	(benzene-ether (5%))	brown	(" ")	180 mg, mpt. 190°(dec.
6	(" " (1:1))	"	(" ")	80 mg

Characterisation was only attempted on the major products, namely bands 4 and 5, and a comparative t.l.c. carried out on band 6, the only other band that could possibly contain the expected fulvene, using benzene-petrol (bpt. 60-80°) (1:1) as eluant, showed no trace of fulvene. Band 4, which contained a nitro group from its infra-red spectrum (ν_{max}^{nujol} 1520 and 1350 cm^{-1}) had mol. wt. 749.233 ($C_{44}H_{53}N_4O_5S$ requires 749.232). Band 5, which showed a peak in its mass spectrum with the correct m/e value for the expected fulvene (mol. wt. 427), was shown by t.l.c. using benzene-petrol (bpt. 60-80°) (1:1) as eluant to contain no trace of the fulvene.

The red solid (suspected to be the mercaptofulvene (202) isolated from §2, expt. 2(d)) and p-nitrobenzaldehyde in methylene chloride were

allowed to react for 1 week. Examination of the solution by t.l.c. using benzene-petrol (bpt. 60-80°) as eluant showed that only components 1 and 5 described above were formed under these conditions.

(b) With benzene diazonium chloride

A solution of the perchlorate (153c) (3.15 g, 6 mmol) was treated in a manner similar to that already described (expt. 6(b)) to give a brown solid (2.65 g, 100%), mpt. 125-40° (dec.), believed to be the heterocycle (250) (Mol. wt. 428.134. $C_{29}H_{20}N_2S$ requires 428.134). Treatment with an equivalent of picric acid in methanol resulted in an intractable black tar. A portion dissolved in chloroform gave an intense blue coloration on addition of conc. sulphuric acid. When the compound (800 mg) in methanol (5 ml) was treated with perchloric acid (70%, 0.25 ml), it was recovered unchanged (500 mg, 63%), as established by its infra-red spectrum.

(c) With acetic anhydride

The perchlorate (153c) (2.1 g, 4 mmol) was treated in a similar manner to that described in expt. 6(c) to give S-acetyl-2,3,4-triphenyl-6,6-bis(dimethylamino)fulvene-1-thiol (140 mg, 7.5%), mpt. 80-95° (dec.) (Mol. wt. 466.207. $C_{30}H_{30}N_2OS$ requires 466.208). The compound had completely decomposed after storage for one month at room temperature.

9. 2,3,4,5-Tetraphenylcyclopentadienylidene-N,N'-dimethyldiaminomethylene sulphurane

(a) With p-nitrobenzaldehyde

A solution of the ylide (3 mmol) in tetrahydrofuran, prepared as described in §2, expt. 3., was treated with p-nitrobenzaldehyde (453 mg, 3 mmol) in an identical manner to that described for the 2,3,4-triphenyl compound (196) in expt. 6(a). Examination of the solution (after 16 hr.) by t.l.c., using benzene-petrol (bpt. 60-80°) as eluant, showed the presence of at least 6 components. Chromatography

on a silica gel column prepared with benzene-petrol (bpt. 60-80°) (1:1) and eluted with this solvent brought off a red-brown band which, on workup in the usual manner, gave purple crystals of 6-(p-nitrophenyl)-1,2,3,4-tetraphenylfulvene (5 mg, 0.3%). mpt. 180-205° (lit.[67] 232-4°) mpt. undepressed on admixture with an authentic sample. (Mol. wt. 503.189. $C_{36}H_{25}NO_2$ requires 503.188).

(b) With nitrosobenzene

A solution of the ylide (0.5 mmol) in chloroform was prepared and treated with nitrosobenzene in an identical manner to that described for the 2,3,4-triphenyl analogue (expt. 7(c)). The solution darkened rapidly. Chromatography on an alumina column prepared with benzene-petrol (bpt. 60-80°) and eluted with this solvent yielded three components after workup in the usual manner. The first, a red-brown band, crystallised from methanol to give N-phenyl-2,3,4,5-tetraphenylcyclopentadienone anil (15 mg, 6.5%), mpt. 223-7° (lit.[67] 235°), mpt. undepressed on admixture with an authentic sample. The second, a purple band, crystallised from methanol to give 2,3,4,5-tetraphenylcyclopentadienone (30 mg, 16%), mpt. 215-9° (lit.[200] 223-4°), undepressed on admixture with an authentic sample. The third, eluted with benzene, was a green-brown band and crystallised from methanol to give N-phenyl-2,3,4,5-tetraphenylcyclopentadienone ketoxime as a green solid (30 mg, 12.5%), mpt. 206-8° (lit.[67] 224-6°). A portion recrystallised from n-propanol had mpt. 219-21°, undepressed on admixture with an authentic sample.

§4 REACTIONS OF DIAZOFLUORENE WITH ARYL THIOUREAS

1. General procedure

9-Diazofluorene, copper bronze and the arylthiourea were ground together to a fine powder and placed in a thin-walled flask which was flushed with oxygen-free nitrogen. It was then plunged into an oil bath

at the stated temperature and kept there for a period, normally 3-4 min. after the evolution of nitrogen had ceased, before the flask was cooled. The mixture was dissolved in chloroform and filtered.

Products which had been previously reported in the literature had correct ultra-violet spectra.

2. With N,N'-diphenylthiourea.

9-Diazofluorene (576 mg, 3 mmol), copper bronze (250 mg) and N,N'-diphenylthiourea (1.37g, 6 mmol). Oil bath temperature 142°, reaction time 10 min. Nitrogen was evolved vigorously over a period of 2-3 min. Examination of the chloroform solution by thin layer chromatography using benzene-petrol (bpt. 60-80°) (1:1) as eluant showed the presence, in order of increasing polarity, of bifluorenylidene (major) fluorenone ketazine (trace), the expected ylide (trace) and N,N'-diphenylthiourea (major). Removal of chloroform in vacuo gave a red residue, which was washed with ether to give N,N'-diphenylthiourea (350 mg, 24%) as a colourless solid. Removal of solvent in vacuo from the washings followed by trituration of the viscous residue with methanol gave bifluorenylidene (140 mg) as a red solid, mpt. 147-65° (lit.[195] 187-8°). A second crop (50 mg) separated from the mother liquor when it was kept overnight. Total yield of bifluorenylidene was 190 mg (38%).

3. With N-phenylthiourea

9-Diazofluorene (1.15 g, 6 mmol), copper bronze (500 mg) and N-phenylthiourea (1.83 g, 12 mmol). Oil bath temperature was 145°, reaction time 5 min. Nitrogen was evolved vigorously with much effervescence. Examination of the chloroform solution by thin-layer chromatography as described in 2 showed corresponding components with the exceptions that presence of the ylide was not definitely established, and that a major colourless component was present with polarity similar

to that of bifluorenylidene. Removal of chloroform *in vacuo* followed by trituration of the residue with methanol gave a light brown solid which was washed with methanol to give bifluorenyl (250 mg, 25.5%), mpt. 208-14° (lit.[163] 240°), identified also by its ultra violet spectrum. A portion recrystallised from chloroform had mpt. 232-5°, and did not depress the mpt. on admixture with an authentic sample. The methanolic filtrate was cooled to give bifluorenylidene as a red solid, (190 mg), mpt. 108-135° (lit.[195] 187-8°). When the mother liquor was kept overnight a second crop separated, (105 mg), mpt. 110-150°. Total yield of bifluorenylidene was 295 mg (29%).

4. *With N-methyl-N'-phenylthiourea*

9-Diazofluorene (770 mg, 4 mmol), copper bronze (330 mg) and *N*-methyl-*N*'-phenylthiourea (1.88 g, 11.3 mmol). Oil bath temperature was 138-40°, reaction time 5 min. Nitrogen was evolved vigorously over a period of 2 min. Removal of chloroform *in vacuo* followed by trituration of the viscous red residue with methanol gave bifluorenyl (250 mg, 38%) as a pale orange solid, mpt. 209-20° (lit.[163], 239-40°). Recrystallisation from chloroform afforded a colourless product, mpt. 244-5°. The methanolic filtrate was evaporated to dryness *in vacuo* and the residue was taken up in ether and filtered. Removal of solvent from the red ethereal solution gave a sticky solid which crystallised on trituration with glacial acetic acid to give bifluorenylidene (120 mg, 18%) as an orange-red solid, mpt. 85-110° (lit.[195] 187-8°). The coloured contaminant in the bifluorenyl was shown to be fluorenone ketazine (trace), when it was examined by thin layer chromatography using benzene-petrol (bpt. 60-80°) (1:1) as eluant.

§5. ATTEMPTED PREPARATION OF A SELENOURONIUM FLUORENYLIDE.

1. Preparation of N,N'-diphenylselenourea

A solution of diphenylcarbodi-imide was prepared as follows. S-Methyl-N,N'-diphenylisothiourea (24.4 g, 0.1 mol) was dissolved in dimethylformamide (80 ml) containing triethylamine (10 g, 13.7 ml, 0.1 mol) and Hyflo supercel (8 g). A solution of silver nitrate (16.8 g, 0.1 mol) in dimethylformamide (60 ml) was added with stirring, and after 10-15 min. the brown precipitate of silver methyl mercaptide was filtered off and washed thoroughly with further dimethylformamide (4 x 25 ml). One-quarter of the above solution was treated with a stream of dry hydrogen selenide, generated from freshly-ground aluminium selenide (5 g) and strong (ca. 10 M) hydrochloric acid and dried by passing through a calcium chloride tower. After 1 hr., the solution, which had turned black, was poured into water (200 ml) and an orange-brown precipitate of crude N,N'-diphenylselenourea (2.8 g, 40%), mpt. 176-85° (lit.[201] 190-2°) was filtered off, washed with water and dried. It was recrystallised from a large volume of methanol to give pale pink plates, mpt. 182-5°.

2. Reaction of N,N'-diphenylselenourea with 9-bromofluorene

The selenourea (825 mg, 3 mmol) and 9-bromofluorene (735 mg, 3 mmol) in ethanol (10 ml) were heated under reflux for 15 min. The pale yellow-green solution was filtered and the solvent was removed in vacuo. Ether (15 ml) was added to the resulting viscous glass, which crystallised when kept overnight to give the fluorenylselenouronium bromide (271) as a slightly hygroscopic pale yellow solid (1.05 g, 67.5%), mpt. 60° (dec.). A portion recrystallised from ethanol had mpt. 135-40°. Addition of picric acid to a portion of the bromide dissolved in ethanol, followed by addition of ether, precipitated the pale yellow

picrate, mpt. 144-7°, identified by its infra-red spectrum. It decomposed to give the free base, mpt. and mixed mpt. with an authentic sample 115-20°, on attempted recrystallisation from acetonitrile.

The free base was also prepared as follows. Triethylamine (1 ml) was added to a solution of the bromide (ca. 700 mg) dissolved in the minimum volume of ethanol, and the free base separated as an off-white mass (230 mg, 40%), mpt. 118-22°. A portion was recrystallised from ethanol, mpt. 130-2° (Found: C, 70.8; H, 4.8; N, 6.4. $C_{26}H_{20}N_2Se$ requires C, 71.1; H, 4.6; N, 6.4%).

The free base (ca. 30 mg) and nitrosobenzene (ca. 30 mg) in chloroform (ca. 2 ml) were kept at room temperature for 4 weeks. Examination by t.l.c. using chloroform as eluant showed that none of the expected anil oxide had been formed, and the dark colour of the solution showed that extensive decomposition had occurred.

§6. PREPARATION (AND ATTEMPTED PREPARATION) OF GUANIDINIUM SALTS.

I. REACTIONS OF GUANIDINES WITH HALOGENATED (AND TOSYLATED) REACTIVE METHYLENE COMPOUNDS CONTAINING THE CYCLOPENTADIENE RING.

1. 9-Bromofluorene

(a) Reaction of 9-bromofluorene with guanidine

(i) Preparation of guanidine from guanidinium carbonate.

Guanidinium carbonate (4.5 g, 25 mmol) was dissolved in water (20 ml) and dil. sulphuric acid (5 M, 5 ml) was added (effervescence). Addition of a further few drops of acid gave no further reaction, showing that conversion into the sulphate was complete. The solution was warmed to drive off carbon dioxide, then treated with a solution of barium hydroxide (4.27 g) in water (70 ml), which resulted in the formation of a fine white precipitate. The solution was filtered, and removal of solvent in vacuo gave a yellow oil. Trituration with ethanol (40 ml) brought down barium hydroxide which was filtered off

and discarded, and the filtrate was retained for further use. (Titration with 0.5 M HCl:- a 5 ml portion of the ethanolic filtrate required 3.0 ml of 0.5 M HCl for neutralisation using phenolphthalein as indicator. Molarity of the guanidine solution was therefore 0.3, showing a conversion from carbonate of ca. 50%.)

(ii) Reaction under reflux.

The guanidine solution (15 ml = 4.5 mmol guanidine) and 9-bromofluorene (1.1 g, 4.5 mmol) were heated under reflux for 10 min. The solution, which was pale orange, was cooled, and removal of solvent in vacuo gave a sticky red mass which was beginning to crystallise. Trituration with ether afforded a nearly colourless solid (400 mg), which from its infra-red spectrum appeared to consist of guanidinium bromide. Conversion to the nitrate was carried out as follows:- the solid was dissolved in water (5 ml) and filtered to remove a small amount of insoluble material. A solution of silver nitrate (320 mg) in water (2 ml) was added, and after the thick white precipitate had been removed by centrifugation, removal of solvent in vacuo afforded colourless crystals of guanidinium nitrate (120 mg, 22%), mixed mpt. with authentic sample 206-9° (lit.[191] 214°).

The ether washings from above were treated as follows:- solvent was removed in vacuo to give a pale orange solid (100 mg), which was washed with methanol. It was identified as fluorene by its mixed mpt. of 104-7° (lit.[191] 115-6°) with an authentic sample. Concentration of the mother liquor afforded a second crop (40 mg) which was washed with ethanol. Total yield was 140 mg (19%).

(iii) Reaction at room temperature.

A solution of guanidine in dimethylformamide was prepared using the method and quantities described in (i), with the exception that dimethylformamide (40 ml) was used in the final trituration stage instead of ethanol. The guanidine solution (17.5 ml, ca. 11 mmol)

was added to a solution of 9-bromofluorene (2.45 g, 10 mmol) in dimethylformamide (10 ml). The solution darkened immediately. After 19 days, the solution, which was dark brown and opaque, was scratched and fine pale yellow crystals began to separate. These were filtered off after ca. 30 min and washed with ether to give bifluorenyl (1.25 g, 76%) mpt. 277-84° (lit.[163] 240° *). A portion was recrystallised from ether, mpt. 288-92°. (Found: C, 94.6; H, 5.4. $C_{26}H_{18}$ requires C, 94.5; H, 5.5%). *See discussion.

(b) Reaction of 9-bromofluorene with N,N'-diphenylguanidine.

N,N'-Diphenylguanidine (2.11 g, 10 mmol) was dissolved as far as possible in acetonitrile (20 ml) and the solution was filtered. A solution of 9-bromofluorene (2.45 g, 10 mmol) in acetonitrile (10 ml) was added, and the mixture was set aside for 3 weeks. (It had darkened after a few hours, but addition of excess ether to a small sample withdrawn after 5 days did not result in a precipitate.) The bulk of the solvent was reduced in vacuo to ca. 10 ml, and when ether (30 ml) was added, fine colourless crystals separated. These were filtered off and washed with ether to give N,N'-diphenylguanidine hydrobromide (1.1 g, 37%), mpt. 145-50°, identified by its u.v. spectrum, and also gave a white precipitate with ethanolic silver nitrate solution.

The mother liquor was treated as follows:- excess ether (150 ml) was added and the mixture was kept overnight. The ethereal solution was decanted from sticky insoluble material, and concentrated in vacuo to give a brown sticky residue which was beginning to crystallise. Trituration with methanol afforded colourless crystals which were filtered off and washed with further methanol to give fluorene (400 mg, 24%), mpt. 85-92° (lit.[191] 115-6°). A portion recrystallised from ethanol had mpt. 105-9°, undepressed on admixture with an authentic sample.

2. 9-Fluorenyl-p-Tosylate.

(a) Reaction of 9-fluorenyl-p-tosylate with guanidine.

(i) Preparation of 9-fluorenyl-p-tosylate.

The method reported[202] for benzhydryl-p-tosylate was adapted. Silver p-tosylate (5.6 g, 0.02 mol; prepared by the metathetic reaction of silver nitrate and p-toluenesulphonic acid) was added to a solution of 9-bromofluorene (4.9 g, 0.02 mol) in dry ether (100 ml). The mixture, which formed a suspension, was heated under reflux with occasional swirling for 1½ hr. The grey suspension of silver bromide was filtered off and the bulk of the filtrate was reduced *in vacuo* to *ca.* 20 ml to give a white crystalline precipitate of 9-fluorenyl-p-tosylate (1.8 g) mpt. 47°dec. (lit.[203] 51°), which was washed with ether. Concentration of the mother liquor afforded a second crop (1.6 g). Total yield was 3.4 g (49%). The compound was characterised also by the sulphonyl bands in the infra-red spectrum at 1180 and 1360 cm^{-1} (lit.[203] 1176 and 1359 cm^{-1}). It was stored at -40°.

(ii) Reaction under reflux.

Guanidine was prepared as an oil by following the procedure outlined in 1(i) and evaporating the ethanolic solution as far as possible *in vacuo* to give a yellow basic oil. The oil (180 mg, 3 mmol) was added to a suspension of the tosylate ester (1.06 g, 3 mmol) in ethanol, and the mixture was heated under reflux for 2 hr. (A white precipitate appeared after this time.) The solution was cooled on ice and filtered to give a white solid (330 mg), mpt. 265° (dec.), which from its i.r. and n.m.r. spectra consisted of guanidinium p-tosylate. Concentration of the mother liquor, followed by trituration of the sticky residue with ether, afforded a second crop (280 mg). Total yield 610 mg (84%).

II. REACTIONS OF GUANYLPYRAZOLIUM, O-METHYLISOURONIUM AND S-METHYLISOTHIOURONIUM SALTS WITH AMINES.

1. Guanylpyrazolium Salts.

1.1 3,5-Dimethylguanylpyrazolium Nitrate.

(a) Preparation.

The compound was prepared from aminoguanidinium nitrate and acetylacetone as described in the literature[171]. A solution of aminoguanidinium nitrate was obtained as follows:- Aminoguanidinium bicarbonate (68 g, 0.5 mol) was slurried in water (200 ml) and a slight excess of dil. nitric acid (5 M, 104 ml) was added (effervescence).

(b) Reaction of 3,5-dimethylguanylpyrazolium nitrate with 9-aminofluorene.

(i) Preparation of 9-aminofluorene.

9-Aminofluorene was prepared as the hydrochloride salt by the method of Ingold[204]. The free amine was liberated as follows:- 9-aminofluorene hydrochloride (16.3 g, 75 mmol) was dissolved in hot water (750 ml), the solution was filtered, and allowed to cool to 50°. Excess of dil. ammonia solution was added resulting in an immediate white precipitate which solidified fully on cooling on ice. The crystals of 9-aminofluorene were filtered off, washed with water and dried over P_2O_5 before use. Yield was 12.5 g (92%), mpt. 55-8° (lit.[204] 62-3°). A small portion dissolved in aqueous ethanol (50%) gave no cloudiness on treatment with dil. silver nitrate solution. The material was stored at -40° and had a useful life of 2-3 weeks.

(ii) Reaction with excess amine.

3,5-Dimethylguanylpyrazolium nitrate (3.01 g, 15 mmol) and 9-aminofluorene (4.07 g, 22.5 mmol) were heated together under reflux in ethanol (100 ml). After 20 hr., the solution was cooled and the bulk of the solvent was reduced in vacuo to ca. 25 ml. Colourless plates separated when the solution was cooled on ice, and these were filtered off and washed with ether to give 9-aminofluorene nitrate

(1.2 g, 33%), mpt. 158° (dec.), identified by its infra-red and ultra-violet spectra.

Treatment of the mother liquor as follows yielded the guanidinium salt. Ether (250 ml) was added and fine white crystals separated, which appeared from their i.r. spectrum to be fluorenylguanidinium nitrate (1.8 g, 42%). A portion recrystallised from acetonitrile had mpt. 192-6° (dec.). (Found: C, 59.6; H, 5.1; N, 17.9. $C_{14}H_{14}N_4O_3$ requires C, 58.8; H, 4.9; N, 19.5%). The compound decomposed on treatment with picric acid in methanol.

2. O-Methylisouronium Salts.

(a) Preparation of N,N', O-trimethylisouronium fluorosulphate.

N,N'-Dimethylurea (1.76 g, 20 mmol) was dissolved in methylene chloride (10 ml) and methyl fluorosulphate ('Magic Methyl') (20 mmol) was added. The mixture was allowed to stand for 16 hr. at room temperature. When ether (30 ml) was added, an oil separated which did not crystallise on scratching at 0° (1 hr). The ether was decanted and the residual oil was triturated with acetone (5 ml). Fine white crystals separated which were filtered off and washed with ether to give the hygroscopic O-methylisouronium fluorosulphate (840 mg, 21 %) mpt. 90° (dec.) (Found: C, 22.9; H, 5.9; N, 13.4. $C_4H_{11}N_2FO_4S$ requires C, 23.7; H, 5.4; N, 13.8%. Gained ca. 3% in weight during weighing).

The experiment was also carried out using chloroform as solvent with similar results but lower yield.

(b) Reaction with 9-aminofluorene.

N,N',O-Trimethylisouronium fluorosulphate (404 mg, 2 mmol) and 9-aminofluorene (452 mg, 2.5 mmol) in ethanol (15 ml) were heated under reflux for 18 hr. The solution was cooled and after the solvent had been removed in vacuo, the resulting pale yellow oil was

triturated with acetone. Colourless crystals separated slowly, and these were filtered off and washed with ether to give 9-aminofluorene fluorosulphate (150 mg, 27%), which was characterised as the picrate, mpt. 176° (dec.). It did not depress the mpt. on admixture with an authentic sample (prepared from 9-aminofluorene hydrochloride and picric acid).

(c) Reaction with benzylamine.

N,N',O-Trimethylisouronium fluorosulphate (404 mg, 2 mmol) and benzylamine (268 mg, 2.5 mmol) were heated under reflux in ethanol (15 ml) for 6 hr. When the solution was cooled on ice, colourless plates separated, which were washed with ethanol to give a colourless compound (25 mg), mpt. 285-9°, which appeared from its mass spectrum to consist of benzylamine fluorosulphate.

3. S-Methylisothiouronium salts.

3.1 S-Methyl-N,N'-ethyleneisothiouronium iodide.

(a) Reaction with 9-aminofluorene.

(i) Reaction in ethanol.

S-Methyl-N,N'-ethyleneisothiouronium iodide (4.88 g, 20 mmol) and 9-aminofluorene (5.43 g, 30 mmol) in ethanol (100 ml) were heated under reflux for 30 hr. The solution, which was green, was concentrated *in vacuo* to *ca.* 50 ml. Ether (250 ml) was added to the cooled, mercaptan-free solution, and a sticky off-white solid was deposited on the walls of the flask. The ether was decanted off and trituration with acetone (10 ml) afforded fine white crystals of the guanidinium iodide (287) (1.25 g, 16.6%), mpt. 239-46°. A portion recrystallised from methanol had mpt. 258-65°. The crude iodide (377 mg, 1 mmol) was dissolved in the minimum volume of hot methanol and a solution of picric acid (230 mg, 1 mmol) dissolved in the minimum volume of hot methanol was added. Yellow crystals of the picrate separated, which were recrystallised from methanol, mpt. 204-7°. (Found: C, 55.0;

H, 3.8; N, 17.7. $C_{22}H_{18}N_6O_7$ requires C, 55.2; H, 3.8; N, 17.5%).

The experiment was repeated under identical conditions using a 4 day reflux period and 20% excess amine. The yield of the guanidinium iodide (287) was 19.5%, mpt. 233-41°.

(ii) Reaction in acetone.

S-Methyl-N,N'-ethyleneisothiouronium iodide (7.80 g, 32 mmol) and 9-aminofluorene (7.35 g, 41 mmol) in acetone (250 ml) were heated under reflux for 2½ days. The solution was cooled and the bulk of solvent was reduced to ca. 75 ml. The solution was worked up in identical manner to that in sect. 3.1(a) (i) to give the guanidinium iodide (1.00 g, 8.3%).

3.2 N,N',S-Trimethylisothiouronium iodide with 9-aminofluorene

The reactants (0.26 mol iodid e and 0.32 mol amine) were treated in identical manner to that described in 3.1(i), with a reaction period of 5 days. Trituration with acetone afforded N-fluorenyl-N'-methylurea (1.38 g, 2.2%), mpt. 110-5° (from dimethylformamide) (Found: C, 75.0; H, 6.0; N, 11.5. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.9; N, 11.7%). No further solid could be isolated on attempted trituration with common solvents (ether, acetone, methanol).

3.3 S-Methylisothiouronium iodide with 9-aminofluorene.

S-methylisothiouronium iodide (21.8 g, 0.10 mol) and 9-aminofluorene (21.7 g, 0.12 mol) in ethanol (140 ml) were treated as described in 3.1 (i) with a reflux period of 40 hr. to give fluorenylguanidinium iodide (16.0 g, 46%), mpt. 195-215°, identified by its infra-red and ultra-violet spectra. Attempted characterisation as the iodide, picrate or sulphate failed.

3.4 S-Methyl-N,N'-diphenylisothiouronium nitrate with 9-aminofluorene.

S-Methyl-N,N'-diphenylisothiouronium nitrate (6.1 g, 20 mmol) and 9-aminofluorene (5.43 g, 30 mmol) in ethanol (120 ml) were heated under reflux for 16 hr. The solution was concentrated and excess ether was added. 9-Aminofluorene nitrate separated as fine needles (3.0 g, 61 %),

mpt. and mixed mpt. with an authentic sample 166° (dec.) (mpt. of authentic sample 158°). The solvent was removed from the filtrate *in vacuo* and the viscous residue was triturated with ethanol to give *S*-methyl-*N*,*N*'-diphenylisothiourea (1.05 g, 22%) mpt. 94-100° (lit.[205] 109°). Mpt. (from ethanol) 102°.

4. Attempted Preparation of N-Chloro-N,N"-diphenylguanidine.

(a) From N,N'-diphenylguanidinium chloride and sodium hypochlorite solution

(i) Under alkaline conditions

Sodium hypochlorite solution (2 *M*, 8 ml), in which sodium hydroxide (*ca*. 100 mg) had been dissolved, was added dropwise to a solution of *N*,*N*'-diphenylguanidinium chloride (1.98 g, 8 mmol) in water (50 ml) with vigorous stirring (Temperature kept below 10°; addition took 5 min.). The brown precipitate which had appeared instantly was filtered off, washed with water until the washings were alkaline-free (litmus test), and dried to give impure *N*-chloro-*N*',*N*"-diphenylguanidine (1.3 g, 66%) mpt. 60° (dec.), identified by its mass spectrum. Attempted purification by reprecipitation from benzene solution using light petrol gave a brown solid, mpt. 75° (dec.). It underwent decomposition on attempted chromatography using silica gel with chloroform as eluant.

(ii) Under neutral conditions

When sodium hypochlorite solution (2 *M*, 8 ml) and *N*,*N*'-diphenylguanidinium chloride (3.96 g, 16 mmol) were allowed to react under similar conditions to (i) in the absence of alkali, separation of a fine white solid was observed. This turned into a sticky dark purple tar on attempted filtration, and the method was abandoned.

The experiment was repeated using 8 mmol of *N*,*N*'-diphenylguanidinium chloride under the same conditions, and the dark purple material was isolated as a non-hygroscopic solid (600 mg), mpt 50° (dec.).

(b) From N,N'-diphenylguanidine and N-chlorosuccinimide.

A solution of N-chlorosuccinimide (1.33 g, 10 mmol) in methylene chloride (30 ml) was added to a solution of N,N'-diphenylguanidine (2.11 g, 10 mmol) in methylene chloride (30 ml) with vigorous stirring in an ice-bath. (Temperature was kept below 10°; addition took 10 min). The brown solution was concentrated to ca. 10 ml in vacuo, and when it was cooled, colourless crystals were filtered off and washed with hot carbon tetrachloride to give succinimide (390 mg, 40%), mpt. 105-115° (lit.[191] 125-6°), undepressed on admixture with an authentic sample. The filtrate, when kept overnight, turned into a black tar and the method was abandoned.

§7 REACTIONS OF GUANIDINIUM SALTS

1. N-Fluorenyl-N',N"-ethyleneguanidinium iodide

(a) With phenyl lithium

N-Fluorenyl-N',N"-ethyleneguanidinium iodide (12.8 g, 34 mmol) was suspended in dry tetrahydrofuran (200 ml) and a freshly prepared ethereal solution of phenyl lithium (1.10 M, 31 ml, 34 mmol) was added with stirring, resulting in a clear solution. After 10 min, the solvent was removed in vacuo and the residue was dissolved in chloroform (250 ml), washed with water (4 x 250 ml) and dried over magnesium sulphate. When the solvent was removed in vacuo, a white solid was obtained, and it was washed with ether to give N-fluorenyl-N',N"-ethyleneguanidine (4.35 g, 53%), mpt. 225-30° (dec.) (sealed tube). (Mol. wt. 249.126. $C_{16}H_{15}N_3$ requires 249.126). The compound showed extensive decomposition after storage for one week at room temperature in vacuo, but it could be stored successfully at -40° over much longer periods. It also appeared to be labile towards acetone (the n.m.r. spectrum in D_6-acetone showed decomposition), but not towards chloroform or methanol.

(b) With aqueous sodium hydroxide

Excess sodium hydroxide solution (40%, ca. 1 ml) was added to a solution of N-fluorenyl-N',N"-ethyleneguanidinium iodide (1.13 g, 3 mmol) dissolved in methanol (ca. 3 ml). Addition of water (15 ml) precipitated the free base as fine white microcrystals (100 mg, 13.5%), mpt. 211-5° (dec.) (sealed tube).

1.1 N-Fluorenyl-N',N"-ethyleneguanidine

(i) Reaction with picric acid

To N-fluorenyl-N',N"-ethyleneguanidine (250 mg, 1 mmol) and picric acid (230 mg, 1 mmol), methanol (10 ml) was added with stirring. Heat was evolved initially, and the mixture was boiled for 2 min. to

complete the reaction. When it was cooled, bright yellow crystals formed which were filtered off and washed with ether to give N-fluorenyl-N',N"-ethyleneguanidinium picrate (295 mg, 62%), mpt. 195-9° (authentic mpt. 204-7°), mpt. undepressed on admixture with an authentic sample.

(ii) Attempted hydrolysis

N-Fluorenyl-N',N"-ethyleneguanidine (375 mg, 1.5 mmol) and powdered sodium hydroxide (400 mg, 10 mmol) in methanol (10 ml) were heated under reflux for 5 hr. The solution was cooled, and addition of water (20 ml) precipitated the unreacted starting material (175 mg, 47%), mpt. 213-20° (dec.) (sealed tube) (authentic mpt. 225-30°).

(iii) Reaction with nitrosobenzene

N-Fluorenyl-N',N"-ethyleneguanidine (250 mg, 1 mmol) was dissolved in dry benzene (50 ml) and nitrosobenzene (108 mg, 1 mmol) was added with stirring. The solution, initially green, had turned yellow in 10 min. After 30 min, the solvent was removed *in vacuo* and the viscous residue crystallised on addition of ether to give bright yellow crystals of N-phenylfluorenone ketoxime (15 mg, 5.5%), mpt. 163-70° (lit.[181] 189-91°), undepressed on admixture with an authentic sample.

(iv) Reaction with p-nitrobenzaldehyde

N-Fluorenyl-N',N"-ethyleneguanidine (500 mg, 2 mmol) and p-nitrobenzaldehyde (300 mg, 2 mmol) were dissolved in chloroform (40 ml) and kept for 30 hr. under nitrogen at room temperature. Examination by thin-layer chromatography, using chloroform as eluant, showed that no aldehyde remained. The solution was washed with water (2 x 25 ml) and dried over magnesium sulphate. (The washings, by titration with 0.5 M hydrochloric acid using phenolphthalein as indicator, were found to contain less than 0.05 mmol of basic material). When the solvent was removed *in vacuo* and the pale brown viscous residue was triturated

with ether, an unidentified substance was isolated (420 mg), mpt. 85° (dec.), which decomposed on attempted recrystallisation or on storage at room temperature for more than a few days. When the substance was mixed with an equal amount of picric acid in methanol, a yellow solid precipitated. It was recrystallised twice from glacial acetic acid, mpt. 242-4° (Found: C, 54.3; H, 3.8; N, 16.7. Closest empirical formula $C_{23}H_{19}N_6O_7$).

(v) Thermal decomposition in ethanol

N-Fluorenyl-N',N"-ethyleneguanidine (1.0 g, 4 mmol) in ethanol (20 ml) was heated under reflux for 2 hr. The solvent was removed in vacuo, and trituration of the dark solid residue with ethanol gave an off-white solid which was washed with ether to give unchanged N-fluorenyl-N',N"-ethyleneguanidine (340 mg, 34%), identified by its ultra-violet spectrum. The ether washings were concentrated in vacuo and an unidentified white solid separated (30 mg), mpt. 94-6°. Excess ether was added to the ethanolic filtrate and the solution was filtered. Concentration in vacuo afforded a second crop of the unidentified substance (70 mg) as a fine white solid mpt. 86-94°.

Oxidative degradation of the unidentified substance[180]:
The solid (70 mg) was dissolved in hot glacial acetic acid (5 ml) and sodium dichromate (400 mg) was added slowly. (Addition took 5 min). The mixture was heated under reflux for 2 hr., cooled, and water (20 ml) was added. Fluorenone separated as pale yellow crystals (25 mg, 32%), mpt. 78-81°, (lit.[191] 83-85°), mpt. undepressed on admixture with an authentic sample.

§8. REACTIONS OF 9-DIAZOFLUORENE WITH GUANIDINES

General

If the guanidine was a solid, the guanidine (6 mmol), copper bronze (250 mg) (where applicable) and 9-diazofluorene (3 mmol) were ground

together to a fine powder. In those cases where the guanidine was a liquid, the same quantities of 9-diazofluorene and copper bronze were ground together and mixed with the guanidine. In each case the mixture was placed in a thin-walled flask which was flushed with oxygen-free nitrogen and plunged into an oil bath at the stated temperature for the period of time stated (see table 6), which was normally 3-6 min. after the cessation of evolution of nitrogen. The flask was then cooled, and workup procedure is illustrated by the typical example given below for N,N'-diphenylguanidine.

The contents of the flask were dissolved in chloroform (25 ml), the copper was filtered off and the solvent was removed *in vacuo*. Ether (5 ml) was added to the residue, resulting in the separation of a pale orange solid which was filtered off, and the filtrate was treated as described below. The pale orange solid was washed well with methanol to give fluorenone ketazine (70 mg, 13%), mpt. 260-6° (lit.[206] 276-7°), identified also by its u.v. spectrum. Crystals separated from the ethereal filtrate after some time, and these were filtered off and were combined with a further precipitate from the methanolic filtrate to give unchanged N,N'-diphenylguanidine (300 mg, 22%). The solvent was removed from the ethereal filtrate *in vacuo* and when the viscous residue was treated with methanol, bifluorenylidene separated (45 mg, 9%), mpt. 158-68° (lit.[195] 187-8°). The bifluorenylidene was washed with further methanol, and when the solvent was removed *in vacuo* from the combined methanolic filtrate and washings, a viscous brown residue was obtained. Trituration with ether-light petrol afforded N-fluorenyl-N-N'-diphenylguanidine (200 mg, 18%), mpt. (from methanol) 139-41°, which was washed with a little ether. (Found: C, 82.9; H, 5.3; N, 11.0. $C_{26}H_{21}N_3$ requires C, 83.1; H, 5.6; N, 11.2%).

Products which had been previously reported in the literature had

correct ultra-violet spectra.

1. With N,N'-diphenylguanidine

See above and table 6.

When the reactants were heated under reflux in ethanol (10 ml/mmol of diazo compound), examination of the solution periodically by intra-red spectroscopy in chloroform solution showed the complete disappearance of the diazo peaks at 2080 and 2060 cm^{-1} after $4\frac{1}{2}$ hr.

N-Fluorenyl-N,N'-diphenylguanidine (ca. 10 mg) and 9-diazofluorene (ca. 10 mg) were dissolved in ether (2-3 ml) and the mixture was kept for 6 weeks. Examination by t.l.c. using chloroform-methanol (5%) as eluant showed the presence of a trace of fluorenone ketazine.

2. With N-methyl-N',N"-diphenylguanidine

See table 6. N-Methyl-N',N"-diphenylguanidine was prepared from diphenylcarbodi-imide and methylamine nitrate after the method of Ferris and Schutz[184], mpt. 105-7° (lit.[208] 106°).

3. With sym-triphenylguanidine

See table 6. N-Fluorenyl-N-phenyl-N',N"-diphenylguanidine was recrystallised from petrol (bpt. 60-80°) (Mol. wt. 451.205. $C_{32}H_{25}N_3$ requires 451.205). sym-Triphenylguanidine was prepared by the method of Ferris and Schutz[184].

4. With guanidine

See table 6. No reaction occurred at room temperature in the presence of copper bronze. Deep blue prisms of an unidentified substance, which were soluble in water, were also isolated from the high temperature reaction.

5. With N,N,N',N'-tetramethylguanidine

See table 6.

(i) At room temperature.

The flask warmed spontaneously to ca. 60° within 5 min., and examination of the solution by i.r. spectroscopy showed no diazo

absorption after 45 min.

(ii) At 0°.

No diazo absorption remained in the i.r. spectrum after 2 hr. Deep purple prisms (80 mg) of an unidentified substance, mpt. 180° (dec.), were also isolated (Found: C, 37.2; H, 7.8; N, 23.5%). When this substance was melted, N,N,N',N'-tetramethylguanidine was evolved (litmus test). The compound decomposed rapidly in methanol solution.

(iii) At -20°.

Unreacted 9-diazofluorene was still present after 3½ hr. (i.r. test), but was found to be absent after 2 days (t.l.c. using benzene-petrol (bpt. 60-80°) as eluant).

Reaction of 9-aminofluorene with diphenylcarbodi-imide.

9-Aminofluorene hydrochloride (5.44 g, 25 mmol) was added to a solution of diphenylcarbodi-imide (25 mmol) in dimethylformamide, prepared as described in section 5, and when all of the amine had been dissolved by shaking, the mixture was kept at 50-55° for 16 hr. The solution was poured into water (300 ml) and the milky suspension was made strongly basic (pH >12) with sodium hydroxide solution (40%, ca. 30 ml) and kept overnight. The off-white solid which had crystallised was filtered off, washed with portions of hot methanol and dried to give N-fluorenyl-N',N''-diphenylguanidine (4.2 g, 45%), mpt. 163-5°. One recrystallisation from benzene gave 3.2 g (33%), mpt. 165-6° (Found: C, 82.1; H, 5.5; N, 11.0. $C_{26}H_{21}N_3$ requires C, 83.1; H, 5.6; N, 11.2%).

Table 6. Summary Table of Reactions of 9-Diazofluorene with Guanidines

Reactants			Conditions		Products (%, mpt.)		
Guanidine	Catalyst	Solvent	Temp. (°)	Time (min.)	Fluorenyl-guanidine	Fluorenone Ketazine	Bifluorenylidene
N,N'-diphenyl	None	100% xs guanidine	145-50	20	0	59 (266-9)	0
"	Cu bronze	" " "	140	5	20 (108-20)	13 (260-6)	9 (158-68)
"	"	" " " (repeat)	142	10	29 (118-28)	18.5 (262-6)	22 (110-40)
"	"	400% xs guanidine	150-5	10	0	Trace[1]	0
"	"	Ethanol	78	4½ hr.	0	0	25 (157-62)
N-methyl-N,N'-diphenyl	"	100% xs guanidine	138-40	5	0	9.5 (240-54)	13 (149-60)
sym-triphenyl	"	" " "	140-2	4	2 (118-35)	0	2[2]
Unsubstituted	None	600% xs guanidine	115	(explodes)	-	-	-
"	Cu bronze	" " "	115-22	10	0	24 (264-8)	0
N,N,N',N'-tetramethyl	"	400% " "	60-70	45	0	33 (258-64)	29.5 (165-70)
"	"	" " "	0	2½ hr.	0	58 (209-65)	2
"	"	" " "	-20	24 hr.	0	77 (269-71)	0

[1] Unchanged 9-diazofluorene (25%) was also isolated.

[2] Separation from the fluorenylguanidine was not possible.

§9 MISCELLANEOUS REACTIONS

1 Benzoylation of 2,3,4-Triphenylcyclopentadienyl triphenylphosphorane.

The ylide (110 mg, 0.2 mmol), benzoyl chloride (0.15 ml, 0.9 mmol), freshly washed with dilute sodium bicarbonate solution and dried, and pyridine (0.15 ml) in benzene (25 ml) were heated under reflux for 6 days. The solution was cooled and concentrated in vacuo to ca. 3 ml. 5-Benzoyl-2,3,4-triphenylcyclopentadienyltriphenylphosphorane (85 mg, 65%) separated as a pale yellow solid, mpt. 310-5°. (Found: C, 86.7; H, 5.3. $C_{48}H_{35}OP$ requires C, 87.4; H, 5.3%) ν_{max}^{nujol} (C=O) = 1550 cm^{-1}.

2 Reaction of N,N'-Diphenylthiourea with Methylamine.

To N,N'-Diphenylthiourea (10.3 g, 45 mmol) in ethanol (50 ml) was added an ethanolic solution of methylamine (33% w/v, 10 ml, 75 mmol), and the mixture was heated under reflux for 4½ hr. (Hydrogen sulphide was detected by odour and blackening of lead acetate paper.) The pale brown solution was cooled and solvent was removed in vacuo. Addition of ether (30 ml) to the viscous residue brought down colourless plates which were filtered off and washed with ether to give N-methyl-N'-phenylthiourea, 5.25 g (70%), mpt. 106-7° (lit.[207] 113°). A portion recrystallised from ethanol had mpt. 112-4°. Mpt. undepressed on admixture with an authentic sample (prepared by reaction of phenylisothiocyanate with methylamine).

§10 SPECTRA

1 Proton Magnetic Resonance Spectra.

Chemical shifts (τ) are given relative to tetramethylsilane as internal standard.

Abbreviations: s = singlet t = triplet dd = double doublet
d = doublet q = quartet br = broad
m = multiplet

2 Ultraviolet and visible spectra.

These were recorded in methanolic solution unless otherwise indicated. (Sh) denotes a shoulder.

Table 7 Spectral data of thiouronium salts not containing the cyclopentadiene ring

R^1	R^2	R^3	R^4	R^5	R^6	P.M.R.[1] τ(multiplicity, relative intensity)	I.R.[2] ν_{max}^{nujol} cm^{-1}	$R^1R^2C(H)-S^+=C(NR^3R^4)(NR^5R^6)$ U.V. λ_{max} nm (log ε)
p-$O_2NC_6H_4$	CO	H	Me	Me	H	H	1.92(m,4);1.83(s,1);6.15(s,2);6.90(s,3); 7.17(s,3)	1655;1520,1350	259(4.08)
"			Me	Me	Me	Me	1.61(m,4);5.14(s,2);6.53(s,12)	1695;1520,1350	260(4.04),376(3.61)
MeO_2C	MeO_2C	"	"	"	"		4.61(s,1);6.20(s,6);6.72(s,12)	1740	253(4.35),312(3.45)
PhCO	PhCO	"	"	"	"		2.5(m,10);2.97(s,1);7.40(s,3);7.45(s,6); 7.51(s,3)[5]	1660	-
$PhSO_2$	$PhSO_2$	H	H	H	H		1.48(br.s,6);2.2(m,10);4.07(s,1)[5]	-	-
"	"		Me	Me	Me	Me	2.25(m,10);6.69(br.s,2);6.85(s,8[3])	1330,1150	227(4.38),260(4.20),270(sh) 277(sh)
EtO_2C	H	"	"	"	"		5.84(q,2);5.97(s,2);7.02(s,6);8.78(t,3)	1735	220(3.84),252(3.58)
Ph	"	CH_2CH_2	H	H			2.57(m,5);5.34(s,2);6.10(s,4);6.53(br.s,2)	-	-
p-$O_2NC_6H_4$	"	"	"	"			1.91(dd,4,J=8Hz);5.48(s,2);6.75(s,12)	1525,1355	
"	"		Me	Me	Me	Me	1.8(dd);6.6(s)[4]	1500,1340	269(3.96)

[1] In D_6-dimethylsulphoxide unless otherwise stated.

[2] Only maxima in the carbonyl, sulphonyl, nitro and nitrile regions are reported

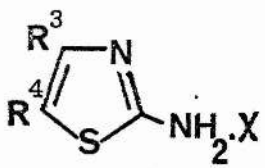
[3] Low integral due to impure sample (see discussion).

[4] In deuteriochloroform (weak solution)

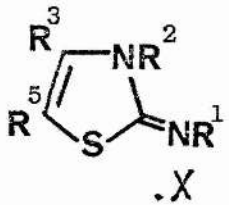
[5] Impurity peaks ignored (see discussion)

Table 8. Spectra of thiazole derivatives

Compound						P.M.R.[1]	I.R.[2]	
Type	R^1	R^2	R^3	R^4	R^5	X	τ(multiplicity, relative intensity)	ν^{nujol}_{max}	U.V. λ_{max} nm (log ε)
A	-	-	p-$O_2NC_6H_4$	H	-	HBr	1.90(m,4);2.45(s,1);3.25(br.s,7)	1510,1345	218(4.09),237(4.08),262(4.04),350(3.94)
A	-	-	"	H	-	-	1.95(m,4);2.69(s,1);2.89(s,2)	1500,1325	216(4.14),239(4.10),266(4.09),362(4.02)
D	Ph	Ph	"	OH	H	HBr	1.91(m,4);2.56(m,10);5.4(br.s,4); 5.99(dd,2,J=13Hz)	1510,1345	263(4.34)
C	-	-	-	-	MeO_2C	-	4.85(br.s,2);6.29(s,3)	1640	219(4.33),249(3.94),309(3.20)
B	Me	Me	Me	-	HO_2C	HBr	3.3(v.br.s.);6.27(s,3);6.76(s,3); 6.89(s,3)	1765,1750	217(3.98),253(3.31),260(3.30),311(3.49).
B	"	"	H_2N	-	NC	"	2.08(br.s,1);6.49(s,3);7.03(s,3)	2210	252(sh,ca.3.79),292(4.24)
B	CH_2CH_2		"	-	"	"	0.23(br.s,1);1.9(br.s,2);6.08(m,4)	2205	-



A



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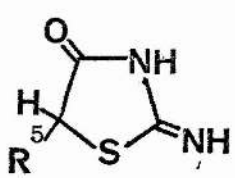

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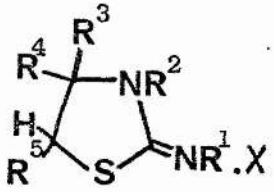


D

[1] In D_6-dimethylsulphoxide

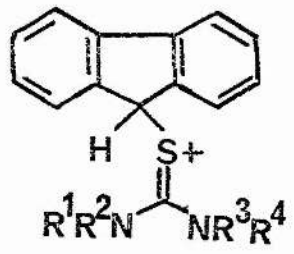
[2] See note 2, table 7

Table 9 Spectral data of thiouronium salts containing the cyclopentadiene ring

Compound Type	R^1	R^3	R^2	R^4	P.M.R. τ(multiplicity, relative intensity)	U.V. λ_{max} nm (log ε)	Mass Spectrum m/e (relative intensity)
A	H	H	H	H	[3]0.30(br.s,5);2.44(m,8)	258(4.12),270(4.15),282(sh)	[5]240(4)210(4)196(10)180(20) 166(100)165(∞) 76(140)
"	Me	Me	"	"	[1]1.88(br.s,2);2.55(m,8);4.00(s,1); 7.04(br.d,6)	230(sh),256(4.09),270(4.10), 282(sh)	[5]268(3)196(4)194(3)180(4) 166(100)165(∞) 104(85)
"	CH_2CH_2		"	"	[2]2.36(m,8);3.55(s,1);5.92(s,4)	-	[5]266(80)234(62)196(25)166(100) 165(∞) 102(115)
"	Ph	Ph	"	"	[1]2.65(m,18);4.27(br.s,1)	257(sh),269(4.39),282(sh), 305(sh)	[5]-240(4)238(4)225(10)224(6) 195(30)180(7)166(100)165(∞)
"	Me	Me	Me	Me	[1]2.45(m,8);4.51(s,1);6.58(s,12)	234(4.35),267(4.34),284(sh)	[5]-240(8)238(8)209(3)181(10) 180(4)166(100)165(∞)132(150)
B	H	H	H	H	[2]0.92(s,2);2.82(m,15);5.93(s,1); 6.58(s,1)	235(4.48);341(4.53),410(sh)	-
"	Me	Me	"	"	[2]2.80(m,16);5.92(s,1);6.61(s,2); 7.05(m,6) [1]1.24(s,2);2.90(m,16);6.05(s,1); 6.56(s,2); 6.91(m,6)	235(sh),347(4.32),410(sh)	[6]396(1)364(1)326(200)294(100) ..276(20)..215(120) 104(550)
"	CH_2CH_2		"	"	[2]2.80(m,16);5.89(s,2);6.13(s,4)	232(sh),344(4.37)	[6]394(0.2)362(3)327(19)..294 (100)..215(70) 102(600)
"	Me	Me	Me	Me	[1]2.83(m,15);6.14(s,2);6.81(s,12)	245(4.32),262(sh),340(3.92)	[6]-392(12)..348(5).334(4)330 (30).328(80)294(100)132(∞)
C	Me	Me	H	H	[1]2,82(m,20);3.89(s,1);7.2(m,6)	[4]247,335	[7]-400(205)370(240)321(94)289 (95)276(34)..215(100)104(750)
D	H	H	H	H	[2]0.77(br.s,8);3.82(s,1);3.87(s,1); 4.92(m,2); 6.54(s,2)	-	[8]-162(22)140(100)128(30)..97 (250) 76(∞)
"	CH_2CH_2		"	"	[2]3.72(s,2);4.95(d,2,J=8Hz);6.08(s,8); 6.60(s,2)	222(4.25)	[8]-231(25)..166(100)-158(cluster) 128(37)..102(∞)97(125)

For footnotes and structural types A-D see following page.

Table 9 (contd.)



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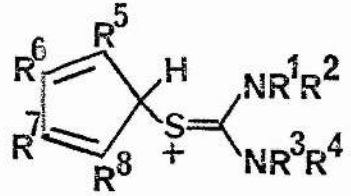


B $R^5=R^6=R^7=Ph$, $R^8=H$

C $R^5=R^6=R^7=R^8=Ph$

D

Solvents:

[1]Deuteriochloroform

[2]D_6-Dimethylsulphoxide

[3]D_5-pyridine

[4]Diethyl ether

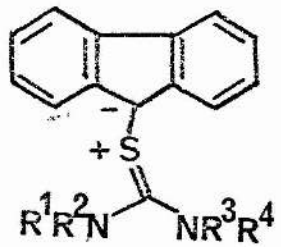
[5]Based on m/e 166 (fluorene, $C_{13}H_{10}$) as 100%

[6]Based on m/e 294 (triphenylcyclopentadiene $C_{23}H_{18}$) as 100%

[7]Based on m/e 215 (diphenylcyclopentadienyl, $C_{17}H_{11}$) as 100%

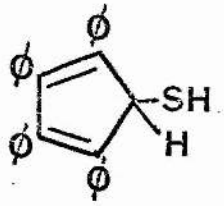
[8]Based on peak at m/e value for corresponding ylide as 100%

Table 10 Structural types



A

B



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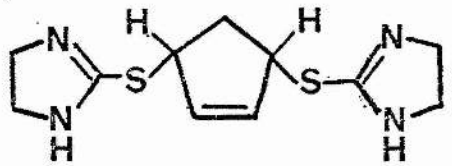


D

Table 10. Spectral data of cyclopentadienylidene diaminomethylenesulphuranes or other basification products of thiouronium salts

Compound					P.M.R.	U.V.	Mass spectrum
[6]Type	R^1	R^3	R^2	R^4	τ (multiplicity, relative intensity)	λ_{max} (log ε)	m/e (relative intensity)
A	H	H	H	H	[2]2.21(m,4),2.62(m,4);3.59(br.s,4)	258(4.06),270(4.11),283(sh) 296(sh),306(3.17)	240(5)198(63)197(18)..166(100) 165(∞) 76(16)
"	Me	Me	"	"	[1]2.5(m,8);4.60(br.s,1);6.15(br.s,1) 7.10(br.s,6)	258(4.16),269(4.15),283(sh) 296(sh),306(3.23)	268(4)198(17)..166(100)165(∞) .... 104(23)
"	CH_2	CH_2	"	"	[1]2.29(m,4);2.67(m,4);3.97(s,1) 5.65(br.s,1);6.29(s,4)	254(4.12),270(4.12),283(sh) 296(sh),306(3.15)	266(70)234(68)198(40).196(700) ...166(100)165(∞) 102(500)
"	Ph	Ph	"	"	[1]2.8(m)	248(sh),258(4.42),273(4.39), 304(sh),312(sh)	-
"	Ph	Me	"	"	[1]2.68(m,13);4.62(br.s,1);5.68(br.s,1) 7.31(s,3)	226(4.38),259(4.22),269(4.21), 283(sh),306(sh)	-
"	Me	Me	Me	Me	-	[3]244,257(sh),281(sh), 392	-
B	H	H	H	H	[1]2.88(m,15);6.3(br.s,1)	-	[5]-368(18)...326(110),309(30),294(105)... 215(100) 76(1000)
"	Me	Me	"	"	[1]2.84(m,15);3.35(br.s,2);5.00(br.s,1) 7.26(m,6)	-	[5]-394(120)..324(180),310(160),308(250)... 215(100),203(250) 104(900)
"	CH_2	CH_2	"	"	[1]2.86(m,18);6.37(s,2);6.40(s,2)	-	[5]-360(8),312(25),310(28),294(150),215(100 ...170(400) 102(∞)
"	Me	Me	Me	Me	[1]2.93(m,16);7.16(m,12)	-	[5]-422(250),392(170)...364(55),348(70), 344(75),323(115)...289(80)...215(100) 132(500)
C	CH_2	CH_2	"	"	[1]2.89(m,20);6.85(s,1)	[3]248,275(sh),347	
D	"	"	"	"	-	[4] -	166(∞)...102(∞)

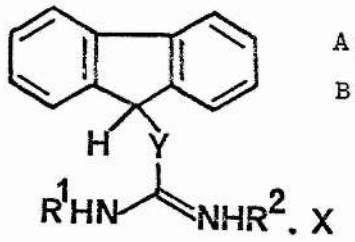
Solvents: [1]Deuteriochloroform
[2]D_6-Dimethylsulphoxide

Notes: [3]Spectrum of basified solution in situ
[4]No λ_{max} >220 nm
[5]See note 7, table 9
[6]See preceding page

Table 11 Spectral data of fluorenylguanidine and fluorenylselenourea derivatives

Compound					P.M.R.	U.V.	Mass Spectrum
					τ (multiplicity, relative intensity)	λ_{max} nm (log ε)	m/e (relative intensity)
Type	R^1	R^2	R^3	X			
A	H	H	H	HNO_3	[2]2.67(d,1);2.36(m,8);4.01(d,1); 6.6(br.s,4)	232,271,294,305	[4]-181(48),180(100),165(10),152(13)
A	CH_2	CH_2	H	Picrate	[2]1.44(s,2);2.46(m,8);4.26(s,1); 6.25(s,4)	225(4,50);233(4,5); 256(4,25);262(4.76)	[4]-195(19),194(36),181(39),180(100), 166(18),165(72)
A	"	"	"	-	[1]2.44(m,8) 4.45(br.s,3); 6.84(s,4)	257;272(sh);287(sh),295, 305(sh)	[4]249(100),248(38),180(74),179(48) 166(22),165(57),85(16),84(22).
A	Ph	H	Ph	-	[1]2.75 (m,18);3.65(br.s,1); 4.2(br.s,1);5.6(br.s,1)	231(4.42),263(4.33), 296(3.61),308(3.43)	[5]375(20),255(45),253(35),210(35), 180(90),166(100),165(∞),139(65),119(37
A	Ph	Ph	H	-	[1]2.70(m,18);3.53(s,1); 5.6(br.s,1)	229(4.45),263(4.41), 295(sh),306(3.60)	[5]375(125),281(57),195(86),194(67), 180(125),166(100),165(∞)
A	Ph	Ph	Ph	-	-	240,265,278(sh),292(sh), 304	[5]451(17),419(24),355(33),354(30),287(230 255(67),195(300),194(∞),166(100),165(∞
B	Ph	Ph	-	-	[1]2.72(m,18);4.3(br.s,1);4.83(d,1)	227(4.56),275(sh),310(sn)	[5]410(2),330(7),276(1)[6],244(2)[6],195(40), 194(400),183(27),180(13),166(100), 165(400)
B	"	"	-	Picrate	-	240,258(sh),274(sh), 310(sh)	

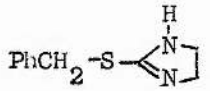
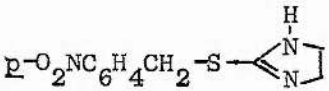
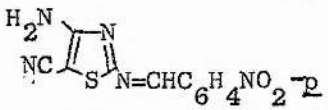
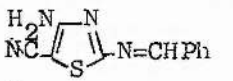
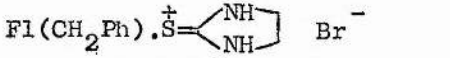
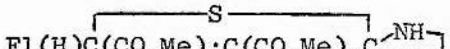
Solvents: [1]Deuteriochloroform
[2]D_6-Dimethylsulphoxide
[3]Tetrahydrofuran



A: Y=NR^3
B: Y=Se

Notes: [4]Based on base peak as 100%.
[5]Based on fluorene ($C_{13}H_{10}$=166) as 100%.
[6]Cluster.

Table 12 Spectral data of miscellaneous compounds

Formula	P.M.R. τ(multiplicity, relative intensity)	I.R. ν_{max}^{nujol} cm^{-1}	U.V. λ_{max} nm (log ε)
p-$O_2NC_6H_4COCH_2S.C(:NMe).NHMe$	[2]1.94(m,4);2.26(br.s,1);6.31(s,2) 6.93(s,3);7.29(s,3)	1655;1520,1350	263(4.06)
p-$O_2NC_6H_4COCH_2S.C(:O).NMe_2$	[2]1.70(m,4);5.50(s,2);7.05(s,6)	1690,1645;1525, 1350	-
$(PhCO)_2CH.S.C(:O).NMe_2$	[2]2.48(m,10);4.56(s,1);6.45(s,3); 6.49(s,3)	1685,1665	251(4.15),335(3.55)
	[1]2.71(m,5);5.60(s,1);5.70(s,2); 6.37(s,4)	-	-
	[3]2.10(m,4);5.66(s,2)6.39(s,4)	1500,1340	270(4.01)
	[2]0.89(s,1);1.76(dd,4,J=8Hz)	2230;1520,1350	228(4.14),288(4,39),394(3.93)
	[2]0.92(s,1);1.71(m,5);6.62(br.s,2)	2205	218(3.84),227(3.83),273(4.29),356(3.81)
[5]Fl(H).NH.CO.NHMe	[2]2.49(m,8);4.16(s,2):6.32(s,2)	1630	-
	[2]2.42(m,8):6.00(s,4);6.16(d,2,J=4Hz)	-	256,278(sh),303(sh),336
	[1]2.50(m,8);6.15(m,10)	1725	-

Solvents: [1]Deuteriochloroform
[2]D_6-Dimethylsulphoxide
[3]D_4-Methanol

[4]See note 2, table 7

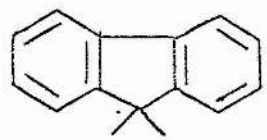
[5]Fl = 

Table 12 (contd.) Spectral data of miscellaneous compounds

Compound	P.M.R. τ (multiplicity, relative intensity)	I.R. ν_{max}^{nujol} cm^{-1}	U.V. λ_{max} (log ε)
253	[6]2.78(m,19);5.79(s,4)	1515,1345	-
255	[6]2.82(m,19);6.82(s,3);6.87(s,3)	-	[7]394(4.06)
256	[6]2.70(m) [1]2.85(m)	1520,1350	[7]289(4.49);376(4.15);520(2.91)
259	[1]2.9(m)	-	-
317	-	1550	[7]291(4.01);455(3.05)
210	[1]2.9(m,20);7.83(s,1)	-	-
199	-	-	[7]325(sh);350(sh)
$(PhSO_2)_2\bar{C}-\overset{+}{S}=C(NMe_2)_2$	[1]2.70(m,10);6.80(s,12)	1285,1125	244(4.15),259(sh),328(sh)

[6]Trifluoroacetic acid

[7]Chloroform.

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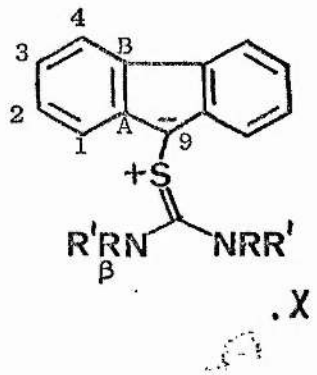
APPENDIX

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA.

1. ^{13}C.M.R. SPECTRA OF FLUORENYLIDENEDIAMINOMETHYLENESULPHURANES.



I R=R^1=H

II R=Me, R^1=H

III RR=$(CH_2)_2$ R^1=H

IV R=Ph R^1=H

V R=Me, R^1=H, X=$HClO_4$

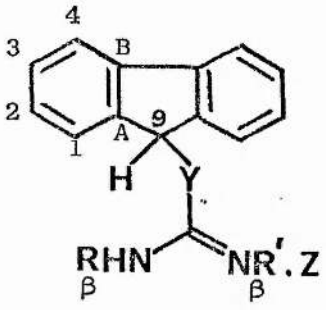
Assignment	IV p.p.m.(P.H.)[1]	I p.p.m.(P.H.)[1]	II p.p.m.(P.H.)[1]	III p.p.m.(P.H.)[1]	V p.p.m.(P.H.)[2]
α	-[3]	159.85 (4)	151.79 (6)	163.96 (8)	167.48 (71)
A	143.74 (6)	143.39 (6)	144.33 (32)	144.30 (8)	140.81 (115)
B	140.26 (6)	140.51 (7)	140.23 (26)	140.36 (9)	140.38 (83)
o	128.75 (120)	-	-	-	-
1-4	128.49 (68)	128.69 (41)	128.31 (119)	128.28 (100)	129.79 (189)
1-4	127.84 (55)	127.97 (30)	127.64 (107)	127.56 (87)	128.44 (208)
1-4	125.23 (73)	125.33 (32)	125.13 (112)	125.72 (107)	125.28 (204)
p	123.29 (38)	-	-	-	-
m	121.06 (33)	-	-	-	-
1-4	120.11 (67)	120.28 (31)	120.01 (113)	119.82 (120)	120.70 (187)
β	-	-	-	50.69 (23)	-
9	48.66 (27)	49.15 (16)	48.35 (41)	48.27 (46)	49.45 (97)
β	-	-	33.86 (5) 33.79 (5) 33.69 (5) 33.58 (5) 33.50 (5)	-	31.65 (46) 30.92 (42)

Solvents [1]Chloroform
[2]Dimethylsulphoxide

Notes [3]Peak missing.

*Chemical shifts are given in p.p.m. downfield from tetramethylsilane as internal reference.
All spectra were noise decoupled. P.H. denotes peak height.

2. ^{13}C.M.R. SPECTRA OF N-FLUORENYL-N',N''-DISUBSTITUTED GUANIDINES AND Se-FLUORENYL-N,N'-DIPHENYLISOSELENOUREA



VI	Y=NPh,	R=H, R^1=Ph
VII	Y=NH,	R=R^1=Ph
VIII	Y=NH,	R,R^1=CH_2CH_2
IX	Y=Se,	R=R^1=Ph
X	Y=NH,	R,R^1=CH_2CH_2, Z=HI

	VI		VII		VIII		IX		X	
Assign-ment	p.p.m.(P.H.)[3]		p.p.m.(P.H.)[4]		p.p.m.(P.H.)[3]		p.p.m.(P.H.)[3]		p.p.m.(P.H.)[4]	
α	151.1	(5)	148.69	(10)	-	[2]	-	[2]	159.86	(29)
A	140.67	(28)	145.49	(19)	140.31	(25)	144.50	(8)	142.42	(57)
B	139.18	(12)	139.78	(16)	134.75	(35)	140.17	(9)	139.63	(51)
m	129.21	(88)	128.49	(45)	-		128.69	(64)	-	
	128.56	(90)	128.16	(24)	129.12	(50)	128.40	(37)	129.15	(45)
1-4	127.85	(86)	127.43	(24)	127.19	(36)	128.06	(40)	127.85	(45)
	126.96	(111)	125.00	(21)	126.17	(21)	125.71	(35)	125.08	(42)
o	125.81	(80)	-	[2]	124.35	(39)[1]	123.23	(22)	-	
p	121.79	(44)	120.64	(35)	120.35	(50)[1]	120.34	(40)	-	
1-4	119.65	(82)	119.92	(23)	119.19	(31)	119.96	(8)	120.42	(39)
9	61.41	(22)	79.14	(3)	42.82	(24)	43.91	(11)	57.68	(17)
β	-		-		42.67	(15)	-		42.72	(36)
	-		-		42.81	(21)	-			

Notes: [1]Possibly due to impurities

[2]Peak missing

Solvents: [3]Chloroform

[4]Dimethylsulphoxide