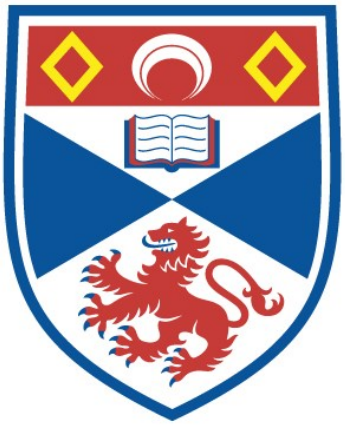
SOME STUDIES IN HYDRIDE TRANSFER

Henry Arthur Sheldon Payne

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1966

SOME STUDIES IN HYDRIDE TRANSFER

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

THE UNIVERSITY OF ST. ANDREWS

by

HENRY ARTHUR SHELDON PAYNE

1966

DECLARATION

I hereby declare that the following thesis is a record of the results of experiments carried out by me, and further that the thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, St. Salvator's College in the University of St. Andrews under the direction of Dr. D.H. Reid.

CERTIFICATE

I certify that Henry A.S. Payne has spent eleven terms at research work under my direction, that he has fulfilled the conditions of Ordinance 61 and of Ordinance 16, so that he is qualified to submit this thesis in application for the degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I first matriculated as a Clyde Henderson Bursar in Queen's College, University of St. Andrews, in October 1956. After two years of study in that College, I continued my studies in the United College of St. Salvator and St. Leonard, St. Andrews, and subsequently graduated with Second Class Honours in June 1960.

I was admitted as a Research Student in the Department of Chemistry, United College, St. Andrews in October 1960 and until October 1963 held a Maintenance Grant awarded by the Department of Scientific and Industrial Research. My research was carried out under the supervision of Dr.D.H. Reid.

ACKNOWLEDGEMENTS

I should like to thank Dr. D.H. Reid for his guidance and encouragement during the course of this work.

I should also like to thank the Technical Staff of the Chemistry Department, St. Andrews for their assistance; the Shell Chemical Company Ltd., for their gift of cycloheptatriene and the Department of Scientific and Industrial Research for a scholarship which made this study possible.

EXPLANATORY NOTE

This thesis is divided into three parts. Part A commences with a brief survey of the hydride-transfer reaction in its widest sense, followed by a discussion of the reagents which may act as hydride donors or acceptors. In conclusion some reactions involving quinones and amines are dealt with.

Part B is a discussion of the result of a series of experiments involving carbonium ions and high potential quinones as hydride acceptors and also of some related experiments.

Part C, complementary to Part B, is devoted to the description of experimental details.

----- SOME STUDIES IN HYDRIDE TRANSFER -----

I N D E X

Introduction

Discussion

Experimental

3. Dehydration-dehydrogenation of Benzo[f]thiachroman-4-ol.

(i) Benzo[f]thiachroman-4-ol.

(ii) 1-Thianaphtho[2,1,b]pyrylium perchlorate.

4. Dehydrogenation of 2-thiachroman-4-one.

(i) 4-Hydroxy-2-thiabenzo[e]pyrylium perchlorate.

5. Dehydration-dehydrogenation of 2-thiachroman-4-ol.

6. Dehydrogenation of 5,6-dihydro-5-methylphenanthridine.

(i) Preparation and reduction of 5-methylphenanthridinium perchlorate.

(ii) Dehydrogenation with triphenylmethyl perchlorate.

7. Dehydrogenation of 5,6-dihydro-5,6-dimethylphenanthridine.

(i) 5,6-Dihydro-5,6-dimethylphenanthridine.

(ii) Dehydrogenation with triphenylmethyl perchlorate.

8. Dehydrogenation of 2,3-dihydro-2,3-dimethylbenzothiazole.

(i) 2,3-Dihydro-2,3-dimethylbenzothiazole.

(ii) Dehydrogenation with triphenylmethyl perchlorate.

C.II Dehydrogenation of hydroaromatic heterocycles using quinones in the presence of acid. ...130

1. Preparation and purification of quinone reagents.

(i) p-Chloranil.

(ii) Tetrachloro-o-benzoquinone. (o-chloranil.)

(iii) 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. (D.D.Q.)

2. Dehydrogenation of thiaxanthene using p-chloranil and perchloric acid.

3. Dehydrogenation of thiaxanthene using D.D.Q. and perchloric acid.

4. Dehydration and dehydrogenation of benzo[f]thiachroman-4-ol using o-chloranil and perchloric acid.

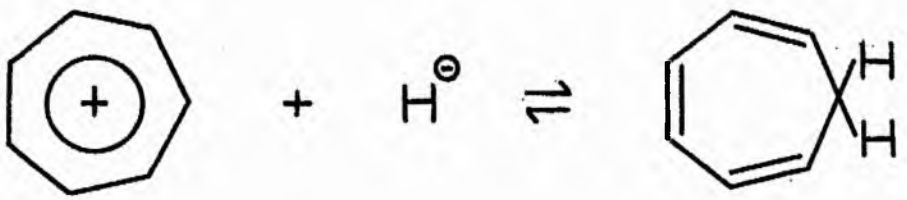
5. Dehydrogenation of 5,6-dihydro-5-methylphenanthridine using p-chloranil and perchloric acid.

----- I N T R O D U C T I O N -----

A.I The Hydride-Transfer Reaction

The term "hydride-transfer" is used to describe the acquisition in a single step of a hydrogen nucleus together with a pair of electrons by one electrophilic centre at the expense of another, either in the same or in another molecule. This process is distinguished from proton-transfer by the absence of isotopic exchange with the labile protons of the medium and by the nature of the polarity at the point of reaction.

The tropylium ion (I) is known to be a hydride acceptor by its ready conversion to cycloheptatriene on addition of a hydride ion.[1]



I

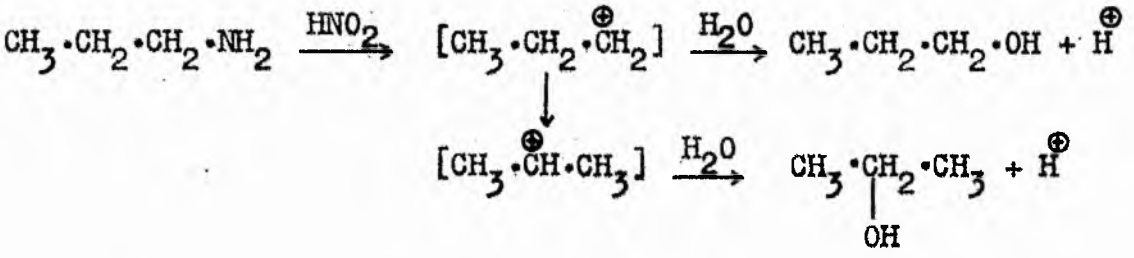
This reaction is reversible and cycloheptatriene may itself act as a hydride donor. Exchange between monodeuterated cycloheptatriene and tropylium ion has been studied in various solvents[1,2] and it was found that after a few hours at room temperature the deuterium was evenly distributed amongst the hydrogens of the cycloheptatriene and those of the tropylium ions.

In addition, it was shown[3] that treatment of tropylium bromide with anhydrous deuterosulphuric acid at room temperature resulted in only 0.3% exchange after 168 hours and in a similar experiment a system of tropylium bromide, deuterium bromide and aluminium bromide kept at room temperature for 94 hours showed only 1% exchange.

Thus hydrogen transfer could not have taken place via proton exchange and no molecular hydrogen was produced as a result of labile protons reacting with independent hydride ions formed during the reaction. The mechanism of the reaction must therefore involve some hydride-transfer step, probably the formation of an activated complex intermediate as the authors suggest.[1] This reaction was the first to display reversible hydride-transfer; it was also one of the first involving deuteride-transfer.

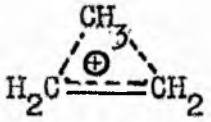
Hydride-transfers are now accepted among the mechanisms of organic chemistry and have been adopted to explain many complex and well-known reactions. The more important of these include the Meerwein -Ponndorf - Verley reaction[4,5] and Oppenauer oxidation, the Cannizzaro reaction[6,7], the Leuckart reaction[8] and the Tishchenko reaction.[9] Hydride-transfer reactions are divided into two groups, those involving intramolecular transfer and those involving intermolecular transfer.

In the case of the former, carbonium ions are generally formed as intermediates which isomerise and give rise to anomalous products. Whitmore[10] suggested this in order to explain the formation of isopropanol and n-propanol from the treatment of n-propylamine with nitrous acid.



Using n-propylamine labelled in the 1-position, Roberts and Halmann[11] suggested that this reaction involved the formation of the non-classical carbonium ion (II). Reutov and Shatkina[12]

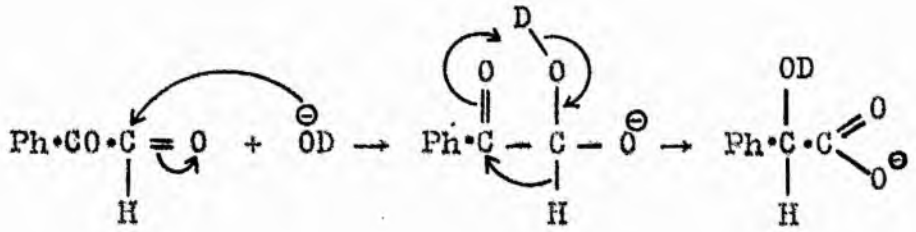
repeated this work, isolating all the products, and showed,



II

by degradation, that the labelled carbon atom was present in either the 1- or 3- position but not in the 2-position. Intramolecular hydride-transfer must therefore have occurred as Whitmore originally proposed.

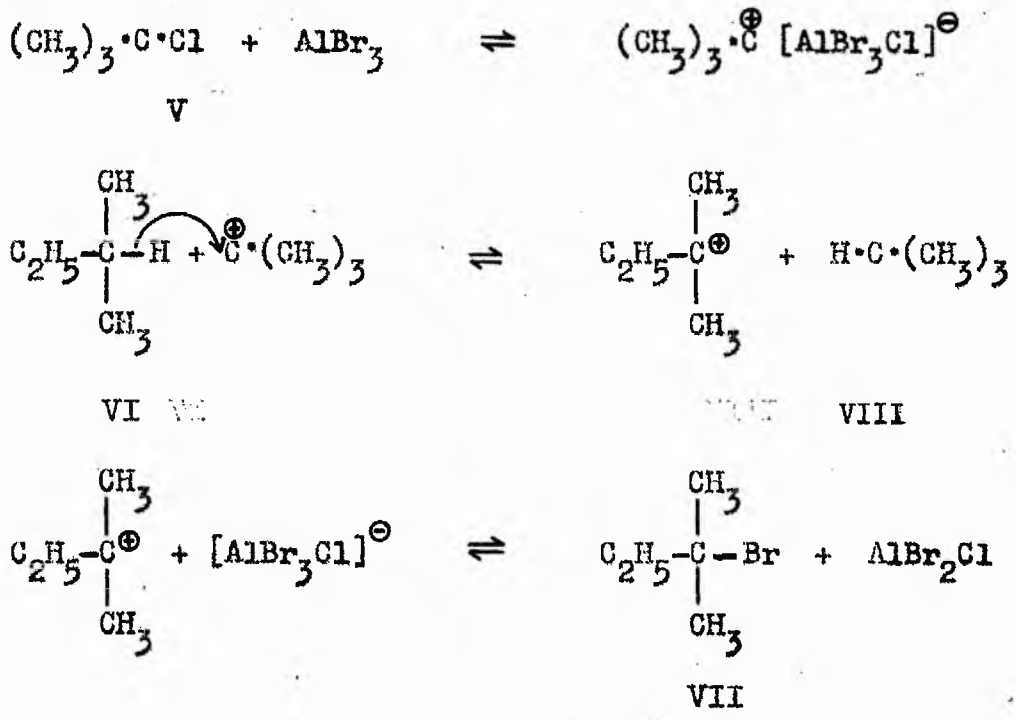
Doering[13] found that when phenylglyoxal (III) was treated with barium deuteroxide the resultant mandelic acid (IV) contained no deuterium attached to a carbon atom. It was shown by Neville[14] that the reaction was first order



III IV

with respect to both the hydroxide ion and the glyoxal and that there was no rearrangement in the carbon skeleton during the transformation. This suggests that the reaction involves hydride-transfer to the carbonyl group by means of an intramolecular path.

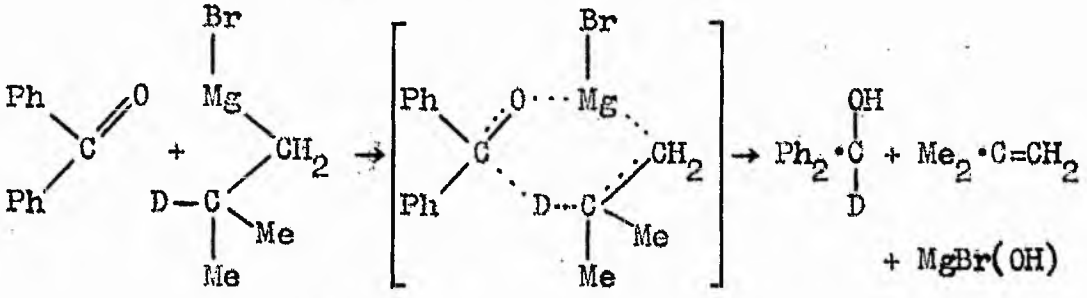
Intermolecular hydride-transfer was first proposed by Bartlett.[15] In the reaction between t-butyl chloride (V) and isopentane (VI) in the presence of aluminium bromide and allowing a very short reaction time (about 10^{-3} sec.), the products were t-amyl bromide (VII) and isobutane (VIII).



The proposed mechanism involved the transfer of a hydride ion from the tertiary position of the isoparaffin via an intermediate carbonium ion. This is essentially an analogue of Whitmore's intramolecular case.

Another example involved the reduction of benzophenone by isobutylmagnesium bromide. Using isobutylmagnesium bromide

deuterated in different positions, Dunn and Warkentin[16] found that only deuterium from the β-position was



X IX

transferred to the benzophenone to give deuterated benzhydrol (IX). This can be explained in terms of hydride donation from the hydrocarbon to the carbonyl compound during transition via the cyclic intermediate (X).

The above examples illustrate the two processes of intra- and intermolecular hydride-transfer. The scope of the latter reaction will now be discussed in terms of hydride donors and acceptors.

A.II Hydride Donors

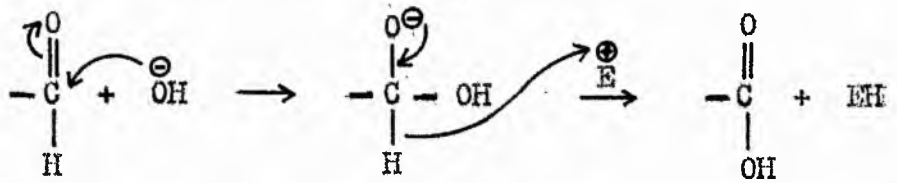
1. Introduction

Hydride donors and acceptors occur in almost every class of organic compounds and show considerable variation in the ease with which the hydride ion is transferred from one to the other. In studying any reaction of this type it is therefore necessary to consider the nature of both donor and acceptor molecules.

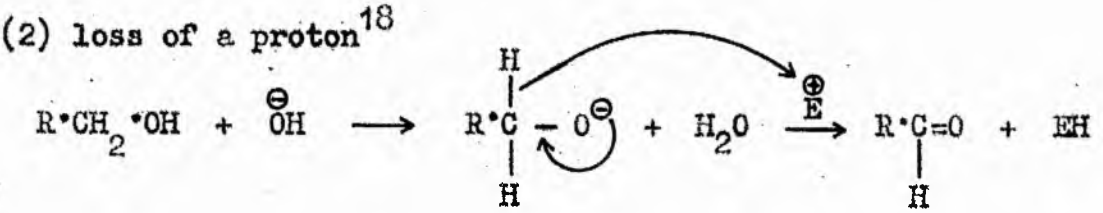
Amongst the properties of the former which may assist the process is an ability to generate a source of electrons adjacent to the carbon holding the hydrogen. This will facilitate the loss of this hydrogen as a hydride ion.

Such a situation may be created by:

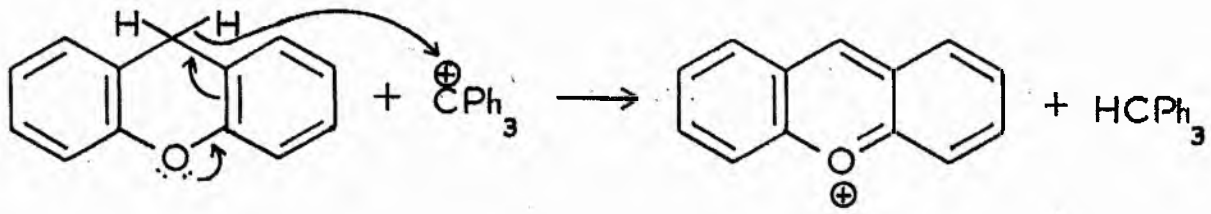
(1) addition of a negative ion[17]



(2) loss of a proton[18]



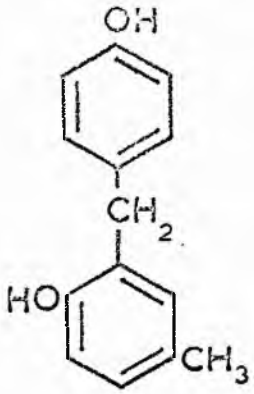
(3) the shift of a lone pair of electrons from an adjacent oxygen, nitrogen or sulphur atom.[19]



The whole operation, including loss of a hydride ion, will involve a polar transition state with the formation of an intermediate carbonium ion, the stability of which will also affect the activity of the hydride donor, i.e. the more stable the resultant ion, the greater the ease of transference. The tropylium, phenalenium and cyclopropenylium ions are good examples of stable carbonium ions which are readily formed by hydride-transfer.[28] In some reactions, however, the existence of carbonium ions can only be deduced from a study of the secondary products.

2. Hydrocarbon Donors

It has already been shown[15] that aliphatic hydrocarbons may act as hydride donors. In a similar



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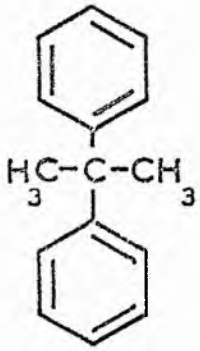

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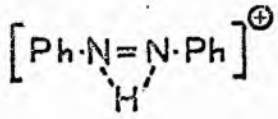

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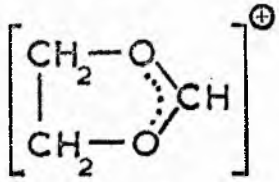

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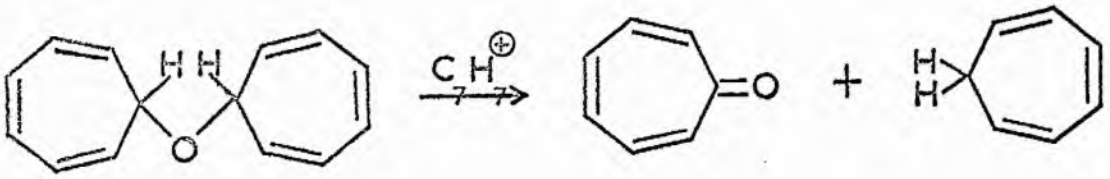
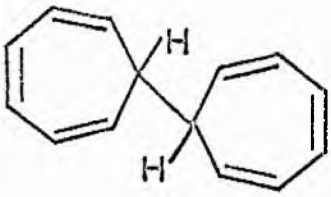


XVI XVII XVIII



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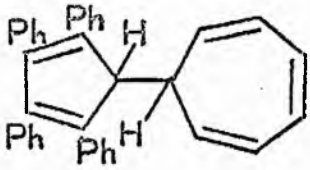

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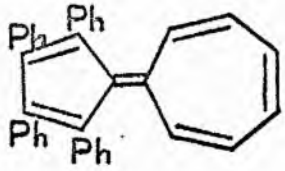

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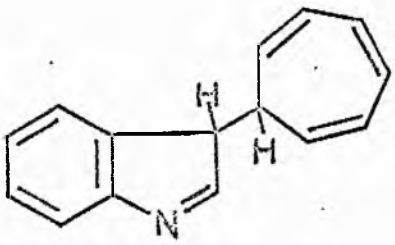

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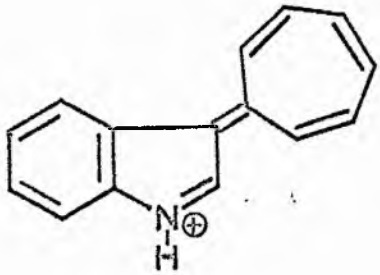
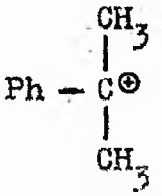


XXIII

series of reactions[20] a variety of donors were used in the alkylation of benzene in the presence of aluminium chloride and a 1,1-dihaloalkane. Such donors included methylcyclohexane, methylcyclopentane, tetralin and decalin.

Synthesis of 2,4'-dihydroxy-5-methyldiphenylmethane (XI) has been accomplished using p-cresol as donor in the presence of a 50 mole % boron trifluoride and t-amyl chloride[21]. It is very probable that the first step involves the formation of benzyl cations by hydride-transfer followed by electrophilic substitution by these cations with other p-cresol molecules giving rise to the product. Schneider[22] reported that 2,2-diphenylpropane (XII) could be produced by the reaction between 2-phenylpropane, benzene and aluminium chloride. This work was extended to a variety of 2,2-diarylpropanes by Serres and Field[23]. They pointed out that hydride-transfer and alkylation by the cumyl carbonium ion (XIII)



XIII

compete with (i) alkylation by the hydride ion acceptors, (ii) isomerisation and (iii) trans-alkylation. The yields

were sufficiently high for the reaction to be of preparative value.

Many hydroaromatic compounds also undergo hydride-transfer. The products are generally fully aromatic and are summarised in Table 1.

Table 1

Dehydrogenation of hydroaromatic hydrocarbons.

Donor	Acceptor	Product	Reference
1,2-dihydrobenzene	Q	benzene	24, 25
1,4-dihydrobenzene	Q	benzene	24, 25
1,2-dihydronaphthalene	Q	naphthalene	24, 25
1,4-dihydronaphthalene	Q	naphthalene	24, 25
9,10-dihydroanthracene	Q,C	anthracene	25, 19
tetralin	Q	naphthalene	26, 27
acenaphthene	Q	acenaphthylene	26, 27
4,5 : 9,10-tetrahydropyrene	C	pyrene	19
2,3-dihydrophenalenone	C	phenalenone	19
phenalene	Q,C	phenalenium perchlorate	19, 28, 29

Q = quinone C = stable carbonium ion.

A number of substituted phenalene derivatives have been dehydrogenated in a similar fashion,[29] the ease of such hydride-transfers being due to the high stability of the resultant

phenalenium ion. The dehydrogenation of substituted dihydroazulenes using quinones may also proceed by a hydride-transfer mechanism.[30,31]

Perhaps the most useful application of dehydrogenation by hydride-transfer has been found in the field of non-benzenoid aromatic chemistry. Once again the ready formation of tropylium (I),[32] substituted tropylium,[32] and substituted cyclopropenylium salts[28] is due to the stability of the resultant ion.

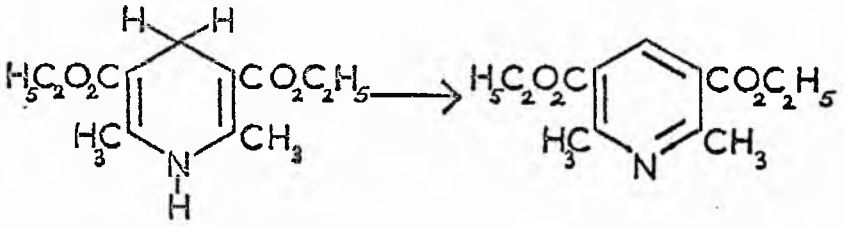
In the formation of the tropylium ion, acceptors include carbonium ions,[32] quinones,[28] protonated azobenzene (XIV)[33] and the 1,3-dioxolenium ion (XV)[34,35]. Cycloheptatriene also yielded up a hydride ion to such Lewis acids as boron trichloride,[36] boron trifluoride,[37] phosphorus pentachloride[1,37] and selenium dioxide[37] and also to sulphuric acid[1,37] and to nitric acid,[37] the tropylium ion being isolated as the perchlorate or chloroplatinate salt. In the presence of phosphoric acid it was found that a similar transfer will take place to benzoic acid esters, benzoyl chloride, benzaldehyde, cyclohexanone, benzyl cyanide, benzyl alcohol and cyclohexanol.[35] This reaction does not occur in acetic

acid and it has been suggested[35] that in phosphoric acid these latter reagents form carbonium, carboxonium or carbammonium ions which act as acceptors.

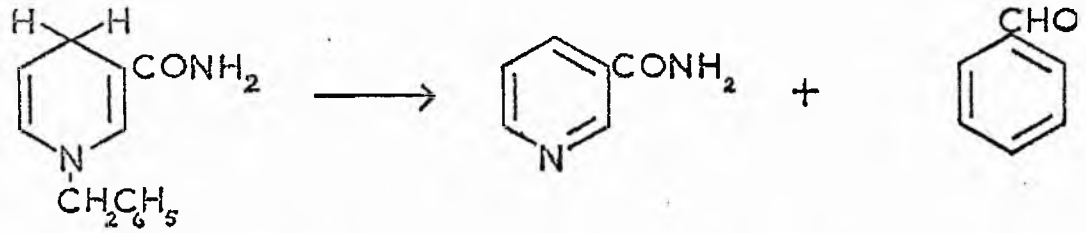
Ditropyl ether (XVI) may act as a hydride donor[38,39,40] and with the tropylium ion as acceptor the products are tropone (XVII) and cycloheptatriene (XVIII). With benzaldehyde as acceptor the sole product is tropone.[35] Using only a catalytic amount of tropylium bromide, ditropyl (XIX) was obtained as a by-product.[41]

Prinzbach[42] has reported the formation of 7,8,9,10-tetraphenylsesquifulvalene (XXI) from the corresponding dihydro-compound (XX) using various haloquinones as the hydride acceptors. An interesting analogue was obtained by treatment of indole with an excess of tropylium perchlorate. The initial product was presumably 3-tropylindole (XXII) which lost a hydride ion to the excess of the tropylium salt yielding an azasesquifulvalene derivative (XXIII) as the perchlorate salt.[43]

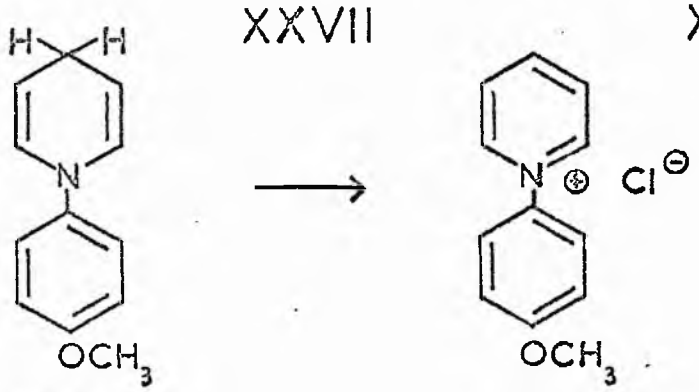
Several examples of hydride transfer from organometallic compounds have also been reported. These will be discussed later.



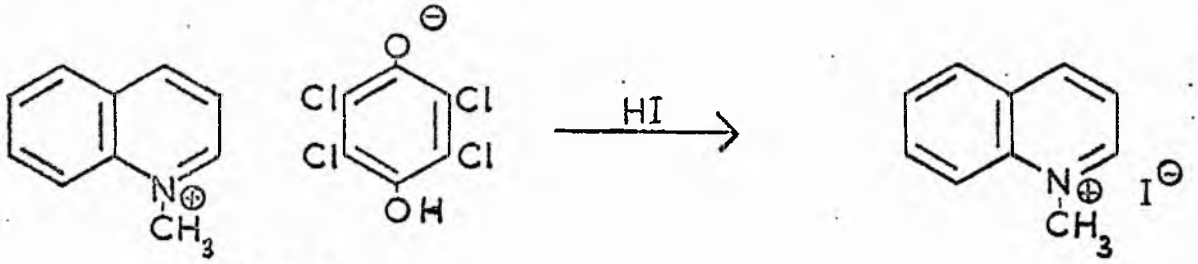
XXIV XXV



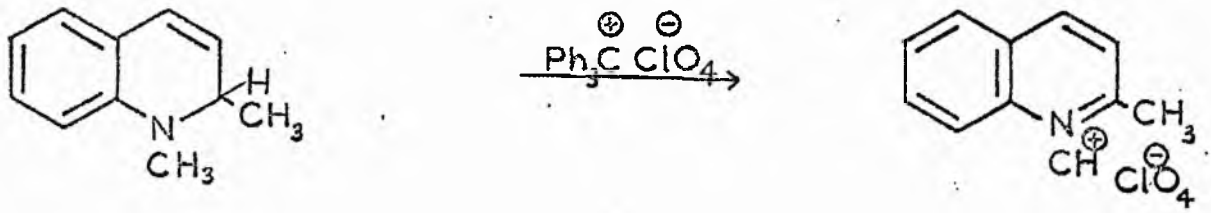
XXVI XXVII XXVIII



XXIX XXX



XXXI XXXII



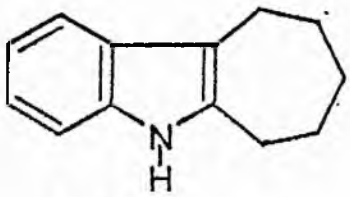
XXXIII XXXIV

3. Heterocyclic Donors

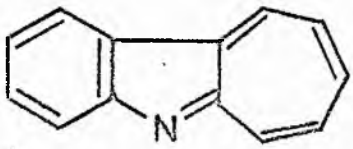
Dehydrogenation of hydroaromatic nitrogen, oxygen and sulphur heterocycles by such reagents as high potential quinones and preformed carbonium ions has been explained in terms of a hydride-transfer mechanism.

Among the hydroaromatic nitrogen heterocycles diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (XXIV) (the Hantzsch ester) has been aromatised to the corresponding pyridine derivative (XXV)[44,45,46]. Using chloranil (XLVII) as hydride acceptor, the reaction is essentially complete after fifteen minutes at room temperature. Similarly[47] 1-benzyl-1,4-dihydronicotinamide (XXVI) gave nicotinamide (XXVII) and benzaldehyde (XXVIII) in a reaction involving hydride-transfer to nitrobenzene.[48] It has also been found that treatment of dihydro-1-p-methoxyphenyl-pyridine (XXIX) with quinone and acid gives the p-methoxy-phenylpyridinium salt (XXX).[49]

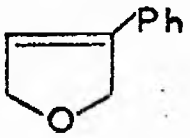
Quinone dehydrogenation of 1,2-dihydroisoquinoline proceeded smoothly to give isoquinoline[44] but under similar conditions 1,2-dihydro-1-methylquinoline gave a product formulated as the monoquinolate salt (XXXI). This on treatment with dilute hydriodic acid gave quinoline



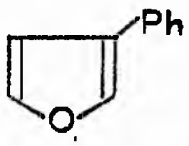
XXXV



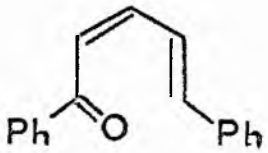
XXXVI



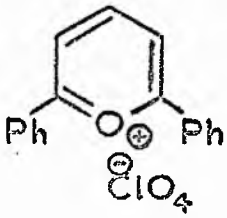
XXXVII



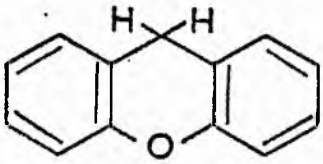
XXXVIII



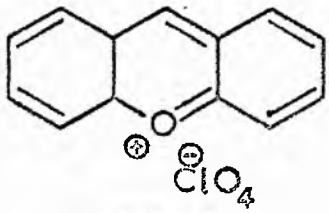
XXXIX



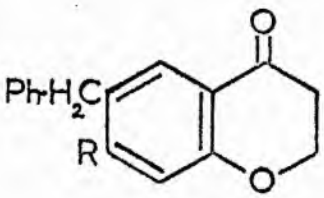
XL



XLI

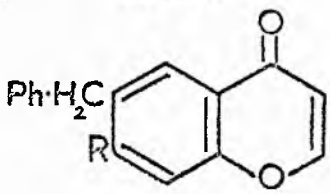


XLII

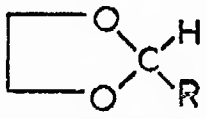


XLIII

R = CH_3O, AcO.

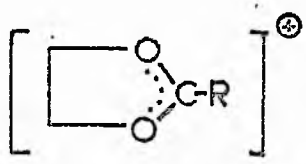


XLIV

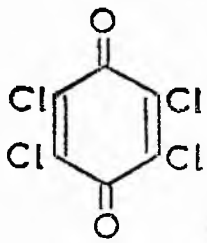


XLV

R = H, CH_3, Ph.



XLVI

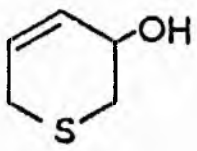


XLVII

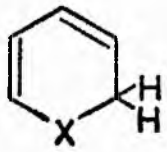
methiodide (XXXII), confirming the original salt structure.[44] A quinone complex was obtained from 1,2-dihydro-1,2-dimethylquinoline (XXXIII). Analysis showed this to contain one molecule of the quinoline and two of the quinone.[44] Using triphenylmethyl perchlorate as the acceptor, complete dehydrogenation of the substrate (XXXIII) was effected to give 1,2-dimethylquinolinium perchlorate (XXXIV).[19]

Other nitrogen-containing heterocycles which have been dehydrogenated by similar means include 1,2-dihydroisoquinoline,[50] 9,10-dihydroacridine,[44,51] 5,6-dihydrophenanthridine[51] and various tetrahydrocarbazoles.[52,53] It should also be mentioned that the benz-azaäzulene (XXXVI) has been obtained by treating the indole (XXXV) with chloranil.[54]

In the field of oxygen heterocycles 3-phenyl-2,5-dihydrofuran (XXXVII) gave the substituted furan (XXXVIII)[55] but the yield (10%) was low, probably due to a competing Diels-Alder reaction with the quinone acting as dienophile. A novel hydride-transfer, ring-closure reaction of 1,5-diphenyl-2,4-pentadienone (XXXIX) yielded 2,6-diphenylpyrylium perchlorate (XL).[56] Triphenylmethyl perchlorate was the hydride acceptor. The same reagent with xanthene (XLI) gave xanthenium perchlorate (XLII),[19] whilst chromanones,

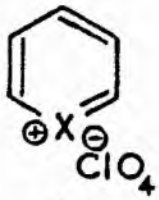


XLVIII

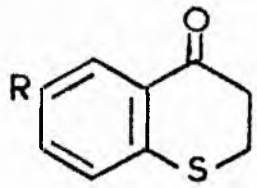


XLIX

X=O,S,Se.

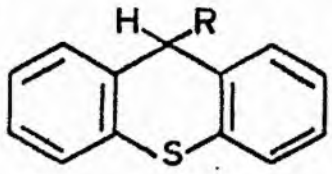


L



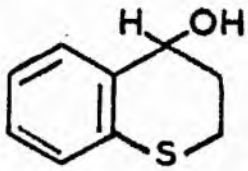
LI

R=H, CH_3.

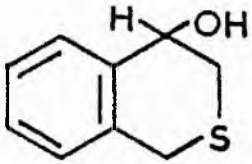


LII

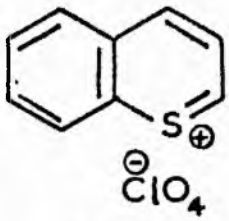
R=H, CH_3, Ph.



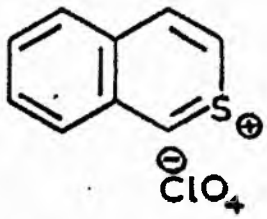
LIIIa



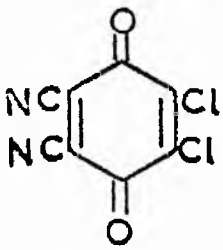
LIIIb



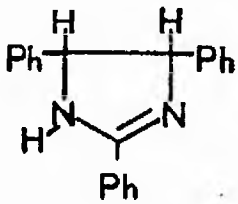
LIVa



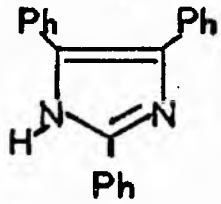
LIVb



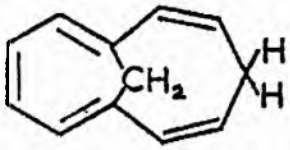
LV



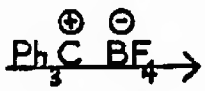
LVI

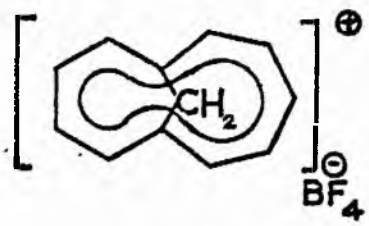


LVII



LXIII





LXIV

e.g. (XLIII), chromanols and flavanones were dehydrogenated to chromones (XLIV),[51,57,58] benzopyrylium salts[51] and flavones[57] respectively. Using triphenylmethyl fluoroborate, 1,3-dioxolane, 2-methyl- and 2-phenyl-1,3-dioxolane (XLV) yielded the corresponding dioxolenium salts[59] (XLVI).

The behaviour of the oxygen heterocycles is paralleled by that of their sulphur counterparts. 3-Phenyl-2,5-dihydrothiophene dehydrogenated smoothly with chloranil as acceptor[60] and thiapyrylium perchlorate (L, X = S) was obtained from 1-thia-3-cyclohexen-5-ol (XLVIII) using triphenylmethyl perchlorate.[61] With the same reagent pyran, thiapyran and selenapyran (XLIX, X = O,S,Se) yielded the corresponding pyrylium salts (L, X = O,S,Se)[62] and similarly, thiachromanone (LI, R = H)[51], 6-methylthiachromanone (LI, R = Me)[57], thiaxanthene (LII, R = H),[51] 9-methyl- and 9-phenylthiaxanthene (LII, R = Me and Ph resp.)[63] gave the thia-aromatic salts. Thiachromanol (LIIIa)[51] and isothiachromanol (LIIIb)[63] behaved likewise, losing water and a hydride ion to give 1- and 2-thianaphthalenium perchlorate (LIV a and b) respectively.

4. Natural Product Donors

Under this heading the dehydrogenation, by hydride-transfer, of such groups of natural products as steroids, carotenes and porphyrins will be dealt with. The use of this mechanism in the explanation of enzymic and other reactions in biological systems falls outwith the scope of the present discussion but may be noted in passing.

Quinone dehydrogenation was first applied to the field of steroids by Agnello and Laubach.[64] Steroidal 4-ene-3-ones were converted to the corresponding 4,6-diene-3-ones by treating the substrate with chloranil in t-butanol. This work was later extended to a variety of different steroids using different quinones as acceptors.[65,66] A most efficient selective oxidant was found in 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (LV). It can replace chloranil in dehydrogenations involving steroids with a keto- or hydroxyl- substituent in the C_3 position and has also been used in the dehydrogenation of 3-keto [illegible] or 3-hydroxy steroids which lack a double bond in the C_4 or C_6 position. Depending upon the conditions either 1,2- or 6,7- dehydro-

genation takes place. Thus in the absence of a catalyst or in the presence of a weak proton donor 1,2-dehydrogenation occurs to give the corresponding Δ^1- derivative [67-72]. When anhydrous hydrogen chloride is present, however, 6,7- dehydrogenation occurs. 4,6-Diene-3-ones undergo 1,2-dehydrogenation only[67,69] and those without a double bond at C_4 or C_6 undergo 1,2- and 4,5- dehydrogenation simultaneously.[73-76] Another interesting reaction in this series is the oxidation of 3-ethoxy-3,5-diene steroids to 1,4,6-triene-3-one steroids.[77] Kinetic studies have been made on the oxidation of Δ^4 -3-hydroxy steroids using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and the proposed mechanism involves slow hydride transfer followed by rapid proton loss.[73,78]

Several carotenes have been dehydrogenated by chloranil, e.g. capsanthone is converted into capsanthin,[79,80] and in the field of terpene chemistry abietic acid has been converted into dehydroabietic acid by the same reagent.[81] The conversion of the alkaloid amarine (LVI) to lophine (LVII) using phenanthraquinone has been reported[48] and quinones have found considerable application in the dehydrogenation of porphyrin derivatives. The preparation

of porphins from chlorins has been successfully achieved using high potential quinones[82-85] and similarly, tetracyclohexenotetrazaporphin has yielded phthalocyanine.[86]

5. Alcohol and Aldehyde Donors

Many examples of hydride donation by alcohols and aldehydes occur in the literature. Burton and Cheeseman[87] showed that diphenylcarbinol (LVIII) in the presence of perchloric acid was converted into benzophenone (LX) and diphenylmethane (LXI). Their hydride-transfer mechanism was substantiated by the work of Baddeley and Nield[88] who showed that bisdiphenylmethyl ether (LIX)

$$\left.\begin{array}{l} 2\ Ph_2{\cdot}CH{\cdot}OH \\ \text{LVIII} \\ (Ph_2{\cdot}CH)_2O \\ \text{LIX} \end{array}\right\} \xrightarrow{HClO_4} \left\{\begin{array}{l} Ph_2{\cdot}CH_2 + Ph_2{\cdot}C{=}O \\ \text{LXI} \qquad\quad \text{LX} \end{array}\right.$$

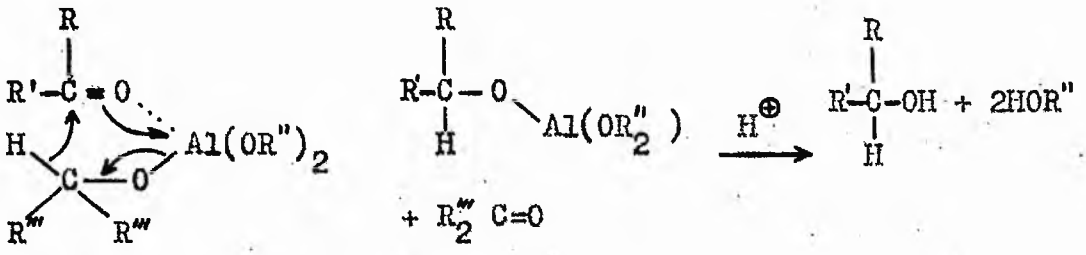
in deuterium perchlorate and benzene gave diphenylmethane (LXI) which contained no deuterium. Benzyl alcohol itself yields a hydride ion to give benzaldehyde.[1,18]

Bartlett and McCollum[89] found that a variety of alcohols would donate a hydride ion when made to react

with triphenylcarbinol in 50% sulphuric acid with the production of triphenylmethane. The kinetics of the reaction involving isopropanol with triphenylcarbinol and with diphenyl-m-tolylcarbinol were studied by Epple et al.,[90,91] who determined the rate constant for the elementary step of hydride-transfer.[91] It was shown[92] that polyphosphoric acid was a better medium for transfer from aliphatic alcohols, esters and ethers, and that the reaction rates were about 10^4 times faster. Isotopic studies[89] using labelled isopropyl alcohol have proved that the hydride ion is transferred from the secondary alcohol to the triphenylmethyl ion which itself is formed by the action of acid on the triphenylcarbinol. Additional reactions which obviously proceed by a similar mechanism include the oxidation of alcohols and ethers by tri(biphenyl)methanol and sulphuric acid[93], and of ethyl alcohol with xanthhydrol and hydrobromic acid[94,95] or methoxytriphenylmethanols and hydrochloric acid.[96]

The Meerwein - Ponndorf - Verley reduction and Oppenauer oxidation reactions involve the equilibrium

between primary and secondary alcohols and their corresponding aldehydes and ketones and are catalysed by aluminium and some other alkoxides. Both are hydride-transfer reactions as has been shown by the fact that the transferred hydrogen does not exchange with labile protons and by tracer work with deuterium[97,98] which has confirmed that the hydride ion comes from the carbinol of the alkoxy group.

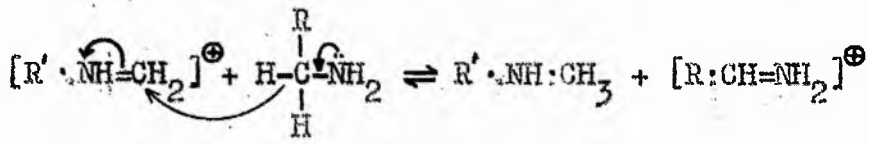


The racemisation of (-) phenylmethyl carbinol and (-) 2-methylbutanol-1 was accomplished by alkoxide ion only in the presence of ketones and probably proceeds by a similar mechanism.[99]

The Cannizzaro reaction has also been explained in terms of hydride-transfer. Transfer of a hydride ion from one aldehyde molecule directly to another occurs without intervention of solvent hydrogens. Reactions carried out in deuterium oxide[100] or potassium deuteroxide[17] resulted in the formation of an alcohol which contained no carbon-deuterium bonds. Whether the mechanism is the same in all cases has

not yet been established, but it seems likely that the transfer step involves some aldehyde-hydroxide adduct and the second molecule of aldehyde. A general mechanism[101] has been proposed to cover both the homogeneous and heterogeneous cases. In the latter it is suggested that the hydride ion has a kinetically independent existence.

The Sommelet reaction may be considered as an ammono analogue of the Cannizzaro reaction.[102] The active intermediate is believed to be the conjugate acid of a Schiff's base (LXII) which abstracts a hydride ion as shown.

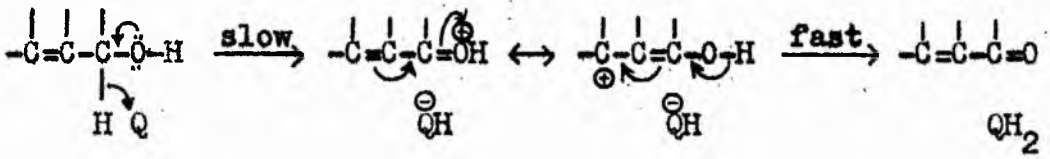


LXII

The allied Leuckart reaction[8] and other reductive alkylations of amines by aldehydes and ketones are similar and their mechanism has been discussed.[102-105] The mechanism of the Tishchenko reaction resembles that of the Cannizzaro reaction[9,106,107] and involves the conversion of an aldehyde into the ester of the corresponding acid and alcohol using an aluminium alkoxide catalyst.

In reactions involving unsaturated alcohols and high

potential quinones the mechanism has been found to be different.[108] Slow abstraction of a hydride ion from



the carbon atom adjacent to the hydroxyl group gave a resonance stabilised oxonium ion and quinol anion. This was followed by rapid proton loss from the hydroxyl group.

Formic acid is also a hydride donor and may be discussed under this heading.

In the reaction of deuterated formic acid with triarylmethyl cations, the resultant triphenylmethane was found to contain 97% deuterium.[109]

A. III Hydride Acceptors

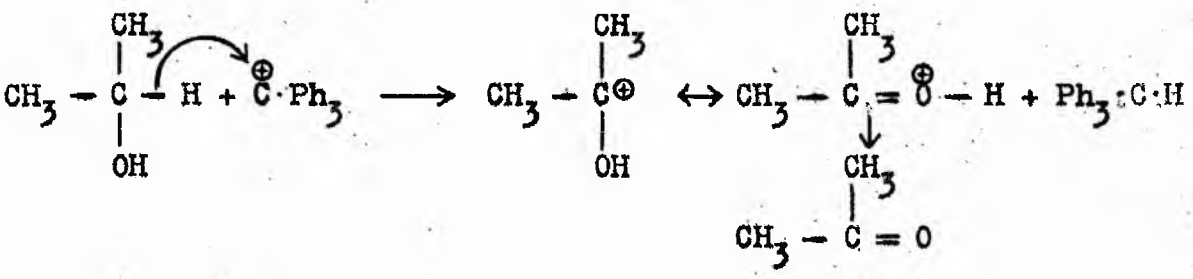
1. Introduction

Hydride acceptors are complementary in character to hydride donors. A carbon atom accepting a hydride ion should have an actual or potentially open sextet of electrons. In the case of carbonium ions capable of an independent existence, the open sextet of electrons is already present but an unsaturated carbon atom can give an open sextet by means of an electron shift. This is particularly important in the presence of acid when protonation of the unsaturated system can provide a suitable site for the acceptance of a hydride ion. In fact, many such transfers are acid catalysed. High potential quinones and preformed carbonium ions are probably the most useful hydride acceptors but others include azobenzene and notably certain Lewis acids.

2. Preformed Carbonium Ions

The stable triphenylmethyl carbonium ion was probably the first to be used in a hydride-transfer reaction.[96] Bartlett and McCollum[89] showed kinetically that the oxidation of isopropyl alcohol in 50% sulphuric acid by triphenylcarbinol

was a second order reaction involving transfer of a hydride ion from the alcohol to the strongly electrophilic cation, followed by loss of a proton from the substrate oxygen. Cryoscopic evidence had already proved the



existence of carbonium ions in such systems.[110,111]

Two factors are important. Other things being equal the electrophilic nature of the reagent largely governs the rate of reaction. In a similar experiment using tri-p-anisylmethyl perchlorate, a more stable carbonium ion, the rate of dehydrogenation was one thousandth that brought about by the triphenylmethyl cation. As has previously been seen, structural features which sufficiently stabilise the resultant carbonium ion to allow its isolation as a salt[32] are also of importance, and for the formation of a neutral product a hydrogen atom capable of ready loss as a proton is essential.

An attempt[92] was made to detect hydride-transfer with simple tertiary alkyl cations in 55% sulphuric acid

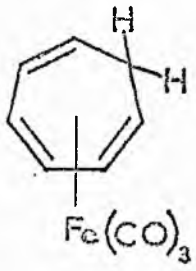
but no reaction took place. Even when the acid concentration was increased to 75% only a trace of product was obtained. The failure of this reaction is believed to be due to the preferential protonation of t-butanol. The abundance of the $(CH_3)_3.C.\overset{\oplus}{O}H_2$ species in 60% sulphuric acid and the failure to remove a hydride ion under those conditions suggests that it does not possess a sufficiently open sextet of electrons.[92] Hydride-transfer, however, will take place with isobutane and concentrated sulphuric acid.[112] Dauben and Harmon have shown that t-butyl halides will react with cycloheptatriene in liquid sulphur dioxide to give low yields of tropylium salts, and tropylium fluoroborate has been obtained by the reaction of t-butyl fluoride and boron trifluoride with cycloheptatriene in pentane. The tetrachloro- and tetrabromoborate have been obtained in a similar manner.[36,113,114]

The preparation of tropylium salts from cycloheptatrienes was the first to utilise the triphenylmethyl carbonium ion as a hydride acceptor[32]. Reaction took place rapidly and quantitatively in solvents which effected the dissociation of the salts, e.g. liquid sulphur dioxide or acetonitrile. Since then several papers have been published

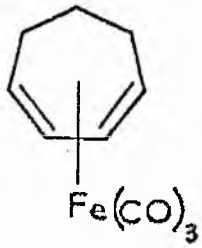
Table 2

Tropylium salts prepared from cycloheptatriene and substituted cycloheptatrienes using the triphenylmethyl carbonium ion

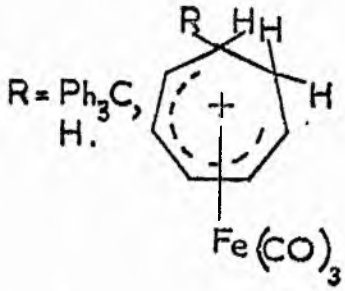
Substituent	Reference
methyl-	32, 115, 119
1,2-dimethyl-	115
phenyl-	116, 117
substituted phenyl-	117
styryl-	119
substituted styryl-	119
methoxy-	32, 115
chloro-	32, 115
bromo-	32
Anion	
perchlorate	32
chloride	32
bromide	32
iodide	32
fluoroborate	32
chloroborate	114
bromoborate	113
iodoborate	118



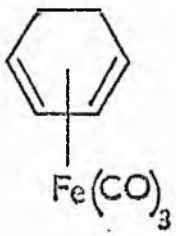
LXV



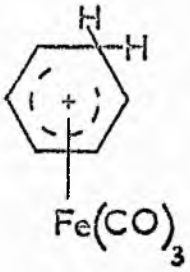
LXVI



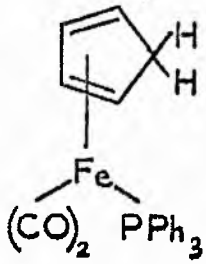
LXVII



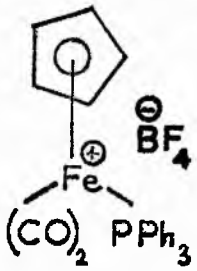
LXVIII



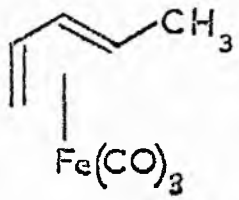
LXIX



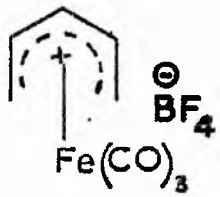
LXX



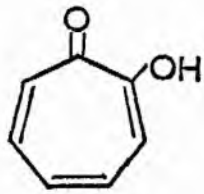
LXXI



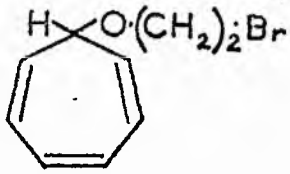
LXXII



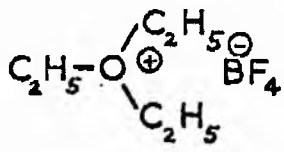
LXXIII



LXXIV



LXXV



LXXVI

in which this method has been utilised for preparing a variety of tropylium and substituted tropylium salts. (see Table 2.)

Triphenylmethyl fluoroborate has also been used in the preparation of the bicyclo [5, 4, 1] dodecapentaenylium cation (LXIV), a delocalised 10π-electron system, from bicyclo [5, 4, 1] dodecapentaene (LXIII).[120]

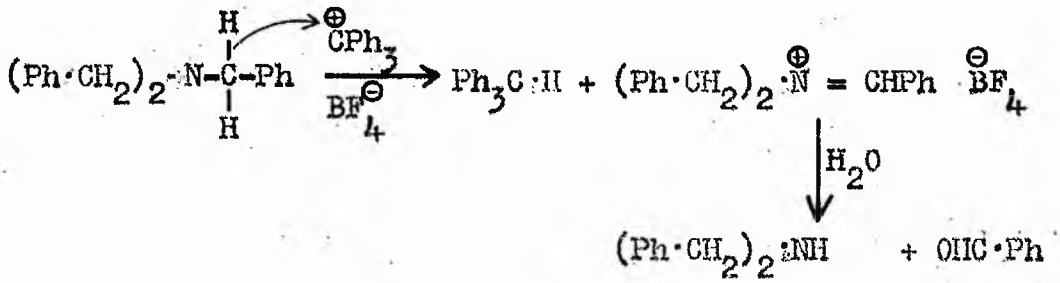
In the field of organometallic chemistry the triphenylmethyl carbonium ion has served as a hydride acceptor in the preparation of various complex cations. Metal carbonyl complexes of the type $(\pi\text{-}C_7H_7^{\oplus})\,M(CO)_3\,X^{\ominus}$ where $X = BF_4^{\ominus}$ or $ClO_4^{\ominus}$ and M = Mo, Cr and W have been prepared[121-124] but an attempt to form a dipositive cycloöctatetraenyl metal carbonyl complex from the triene $(C_8H_{10})Mo(CO)_3$ was unsuccessful.[125] The reaction of triphenylmethyl fluoroborate with cycloheptatriene-iron tricarbonyl complex (LXV) resulted in addition to give the cation (LXVII, R = Ph_3C-) rather than hydride-transfer and no triphenyl-methane was isolated. The cycloheptadiene complex (LXVI) did, however, lose a hydride ion and afforded the cycloheptadienium ion complex (LXVII, R = H)[126]. This

was also true of the cyclohexadiene complex (LXVIII) which in a similar manner yielded the cyclohexadienylium ion complex, (LXIX)[127]. In the case of dicarbonylcyclopentadienetriphenylphosphineiron (LXX) slow loss of a hydride ion to triphenylmethyl fluoroborate resulted in the formation of π-cyclopentadienyldicarbonyltriphenylphosphineiron tetrafluoroborate (LXXI)[128].

Transfer from σ-bonded iron-alkyl complexes has also been achieved, the hydride acceptor attacking the alkyl group. With (π C_5H_5) $Fe(CO)_2R$ (where R = ethyl, n-propyl, iso-propyl), π-ethylenic cations were obtained[129]. In the acyclic system trans-1,3-pentadieneiron tricarbonyl (LXXII), triphenylmethyl carbonium ion failed to react[130], but the cis-isomer gave pentadienyl-iron tricarbonyl fluoroborate (LXXIII).[131]

Dehydrogenation of hydroaromatic heterocycles and carbocycles by carbonium ions has led to the isolation of stable salts of both types as well as of fully aromatic neutral products. All these have already been described individually. (Refs. 19, 29, 34, 51, 57-59, 61-63.)

In the reaction involving hydride-transfer from tribenzylamine[59] a high yield of benzylidenedibenzylammonium fluoroborate and of triphenylmethane was recorded. Hydrolysis



of the salt yielded benzaldehyde and dibenzylamine.

The tropylium ion itself can act as a hydride acceptor. As a result of the strong donor properties of cycloheptatriene, this carbonium ion is a comparatively weak acceptor and cannot, for instance, accept a hydride ion from formic acid. The oven distribution of deuterium between deuterated cycloheptatriene and tropylium perchlorate[1], however, demonstrates the ease with which the transfer takes place between the two and illustrates its reversible nature. In order to use the tropylium ion as a dehydrogenating agent, strong donor properties are required in the substrate. Examples of hydride donors dehydrogenated in this way include triethylstannane, triethylsilane and benzyl alcohol[1]. Using deuterated benzyl alcohol (Ph.CHD.OH) gave rise to deuterated cycloheptatriene and deuterated benzaldehyde. In the reaction with ditropyl ether,[38-41] equimolecular proportions of the ether and tropylium ion afforded 50%

tropone (based on the maximum of two moles of tropone from one of ether), cycloheptatriene being the other product (see above).

A similar reaction occurred when tropylium bromide was dissolved in di-isopropyl ether, cycloheptatriene again being formed. By replacing the ether with aqueous ethylene oxide, β-bromoethanol was obtained in addition and on warming the original mixture to 40° the products were tropolone (LXXIV) and tropyl β-bromoethyl ether (LXXV). It is suggested that the reaction proceeds in two main steps[132], (i) addition of the ethylene oxide to the tropylium ion, (ii) cleavage of a hydride ion by a second tropylium molecule.

One must also mention Meerwein's[59] use of triethyloxonium fluoroborate (LXXVI). This reagent and also the mixture of anhydrous silver fluoroborate and ethyl bromide give rise to a species which is in effect ethyl fluoroborate. One might expect this to be a powerful hydride acceptor and this was shown to be the case by the ready dehydrogenation of 2-phenyl-1,3-dioxolane (XLV, R = Ph). The by-products from the reaction included ethane, diethyl ether and silver bromide.

3. Quinones.

Clar and John[133] were the first to use quinones preparatively as dehydrogenating agents and since then this most powerful group of organic oxidants has found increasing application. Of quinones which have been tried, the most successful have been those with electron-withdrawing substituents[24,26,28]. Such groups affect the redox potential of the quinone and it has been found that increasing potential is paralleled by increasing dehydrogenation efficiency[26,28]. Quinones with electron-donating groups were considerably less reactive. In the case of o-quinones, the reactivity measured relative to the corresponding p-quinone was greater than might be expected from the redox potential. This may be due to hydrogen bonding in the transition state which would give rise to a catecholate type of mono-anion[24].

Despite their great versatility, quinones suffer from several disadvantages. The solubility of the quinone or of its quinol often presents problems of isolation or separation and they are also incapable of dehydrogenating completely saturated carbocycles[27]. Activation in the form of a double bond or benzene ring is required before dehydrogenation will

occur. Side chains are very rarely attacked and this feature is useful in the aromatisation of carbocycles bearing such groups. In the case of unsubstituted quinones, Diels-Alder and nucleophilic addition reactions both interfere and nucleophilic replacement can be a drawback especially with halogenated quinones[134].

Dehydrogenation of hydroaromatic compounds by quinones proceeds by a two-stage ionic mechanism[24,25,28,135,136]. In the initial, rate-determining step, hydrogen is abstracted as a hydride ion. This is followed by immediate loss of a proton from the acidic site in the resultant carbonium ion to the quinol anion.

$$RH_2 + Q \longrightarrow \overset{\oplus}{R}H + \overset{\ominus}{Q}H$$

$$\overset{\oplus}{R}H + \overset{\ominus}{Q}H \longrightarrow R + QH_2$$

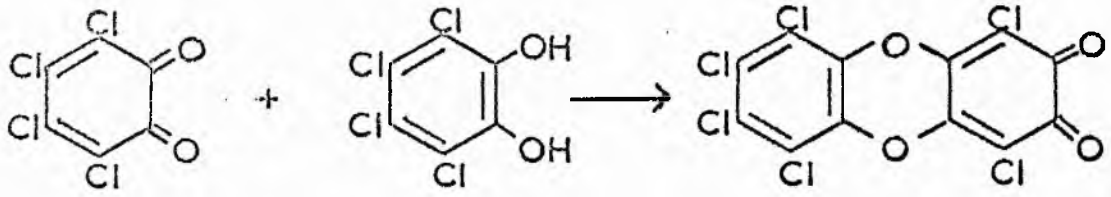
Catalysis by a proton donor has been ascribed to the formation of the quinol cation $\overset{\oplus}{Q}H$ which has a greater affinity for hydride ion than quinone itself.

Another mechanism of quinone dehydrogenation has been proposed by Waters[137]. He suggested that the process was homolytic and involved abstraction of a hydrogen atom by the quinone to give a semiquinone radical.

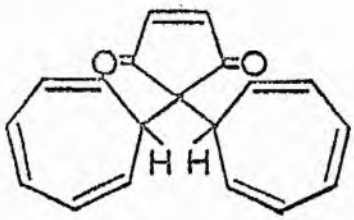
$$Q + H - R \longrightarrow \dot{Q}H + R\cdot$$

This suggestion, based on the observation that quinones inhibit the autoxidation of tetralin, is only one of several possible explanations. Other interpretations do not necessarily involve homolytic hydrogen transfer. Dost and van Nes[27] proposed this radical mechanism for the dehydrogenation of hydroaromatic compounds but their attempts to catalyse the reactions with peroxides or ultra-violet light were unsuccessful. Braude and co-workers[24] also observed a similar lack of acceleration in the presence of radical producing agents.

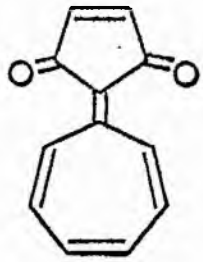
Henbest[49] pointed out that redox potentials for halogenated quinones were only known for the complete two electron process. The fact that quinones of the highest potential (for this process) were in general the most efficient in the dehydrogenation of amines and olefins could not be considered as proof of a hydride-transfer mechanism since the potentials for single electron-transfer were unknown. Some single electron-transfer potentials have since been determined[138] and in the case of halogeno-quinones there appears to be little parallelism between E_o (redox potential measured in alcohol) and E_1 (one electron reduction potential measured polarographically in acetonitrile). Solvent differences are only



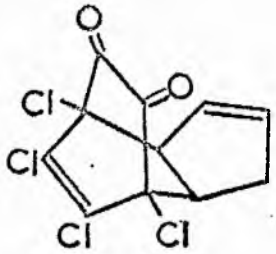
LXXVII LXXVIII LXXIX



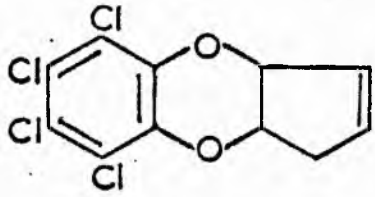
LXXX



LXXXI



LXXXII



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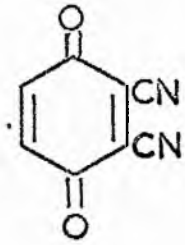
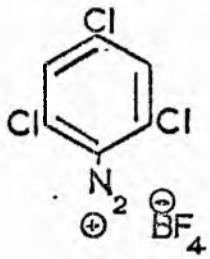
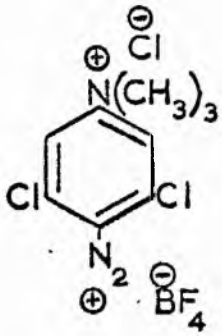


LXXXIV



LXXXV



LXXXVI

believed to be partly responsible for this[139] and more data are required before any firm conclusions can be drawn.

The most recent evidence which supports the single electron-transfer mechanism concerns the oxidation of sterically hindered monohydric phenols and some enolisable ketones[140] using 2,3-dichloro-5,6-dicyano-p-benzoquinone (LV). In the case of the phenols, a number of intermediate phenoxy radicals were formed, several of which were already known to be stable.

Bearing in mind the variety of substrate and of reaction conditions, e.g. large differences in temperature and in solvent polarity, it seems likely that no one mechanism is capable of describing all cases of dehydrogenation by quinones. One thing, however, seems to be agreed. The initial step in the overall reaction sequence appears to involve the formation of a charge-transfer complex between the donor and acceptor molecules.[140,46,48]

A brief discussion of some of the more important quinones will serve to illustrate their versatility and also their major disadvantages.

Tetrachloro-p-benzoquinone (chloranil XLVII) and its ortho isomer (LXXVII) have both been used extensively as

dehydrogenating agents. Of the two, the latter has a higher redox potential (E_o^o = 0.87v. compared with E_o^o = 0.71 v. for XLVII) and it is also the more efficient oxidant.[24,31]

Being readily available p-chloranil was probably the first high potential quinone to be used to any extent in dehydrogenation reactions. Although it is not a particularly strong dienophile, it can undergo Diels-Alder addition reactions[141, 142] and replacement can occur notably in the oxidation of amines[134,49]. The use of chloranil in the oxidation of steroids[64-66, 143,144] and in the aromatisation of hydroaromatic carbocycles[24-26] and heterocycles[44-46] has already been discussed. In addition Henbest[49] has noted the conversion of dihydro-1-p-methoxyphenylpyridine (XXIX) to p-methoxyphenylpyridinium chloride (XXX) by means of the same quinone in the presence of hydrochloric acid and Kitahara has utilised it in the preparation of sesquifulvalene-1,4-quinone (LXXXI) from 4,4'-ditropylcyclopentene-3,5-dione (LXXX)[145].

Tetrachloro-o-benzoquinone (o-chloranil LXXVII) is less readily available and suffers to some extent from its ability to condense with its own quinol (LXXVIII) to give the

condensation product (LXXIX)[48,146]. This normally interferes only with slow reactions. There is also a tendency to form addition products. These are of two types, (i) 1:4 addition giving Diels-Alder type adducts[147], (ii) addition across the quinone function to give benzodioxane derivatives[147,148]. Cyclopentadiene forms both types of adducts see (LXXXII) and (LXXXIII) respectively. In dehydrogenation reactions o-chloranil rapidly converted dihydroisoquinoline to isoquinoline at room temperature[50] and it was found to be more efficient than p-chloranil in the dehydrogenation of dihydroazulenes[31]. It has also been utilised in the preparation of other o-quinones, substituted o-benzoquinones[149,150], amphi-naphthoquinones[151] and phenanthraquinones[152].

3,3',5,5'-Tetrachloro-4,4'-diphenoquinone ($E^{o} = \sim 1.0$ v) has a high potential and will not undergo addition reactions[153]. Its main disadvantages are its insolubility and its tendency to undergo replacement reactions.

The use of 2,3-dicyano-p-benzoquinone (LXXXIV) has been reported in the oxidation of steroids[154] but 2,3-dichloro-5,6-dicyano-p-benzoquinone (LV) (henceforth abbreviated as DDQ) is better known, more efficient, and more widely

used. The latter has a redox potential of 1.0 v.[138] and is one of the most powerful organic oxidising agents available. It was first prepared by Thiele[155] in 1906 but has only come into use in recent years. As previously discussed Peover[138] determined the single electron reduction potentials of several quinones under aprotic conditions for the process shown. Although little parallelism was

$$Q + e \rightleftharpoons Q^{\cdot\ominus}$$

discovered between E_1 and the redox potential E_o for halo- and cyanoquinones, it was found that the value of E_1 for D.D.Q. (0.51 v.) was higher than that for any of the other haloquinones examined. This may account to some extent for the greater ease with which it effects a variety of oxidation reactions. D.D.Q. has been particularly useful in the selective dehydrogenation of steroids[67-76,143,154] (discussed earlier) and in dehydrogenating hydroaromatic compounds[26]. It has also been used in the oxidation of allylic alcohols[78,108,156], enol ethers[77] and benzyl alcohols[157]. As previously mentioned the oxidation of sterically hindered phenols by means of D.D.Q. appears to take place via a single electron-transfer mechanism.[140]

4. Miscellaneous Acceptors

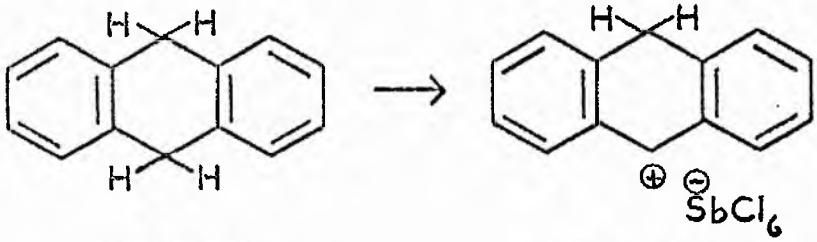
The dehydrogenation of several hydroaromatic heterocycles using nitrobenzene may proceed by a hydride-transfer mechanism.[48] This reagent has been used in the dehydrogenation of the Hantzsch ester (XXIV)[45] and in the oxidation of 1-benzyl-1,4-dihydronicotinamide (XXVI)[47]. Substituted nitrobenzenes have also been used.[47]

Azobenzene[45] and protonated azobenzene[33] (XIV) have both been utilised as acceptors. In the case of the latter, combination with a hydride ion converted it to hydrazobenzene which, in the presence of acid, underwent normal rearrangement to benzidine. This product was often the only proof of reaction. Hydride-transfers with acetone, acetic acid, succinic acid, benzaldehyde and cyclohexanone have been established in this way. With formic acid, carbon dioxide was also identified and in the presence of sulphuric acid, cycloheptatriene gave tropylium bisulphate in good yield. With benzyl alcohol, the characterisation of benzaldehyde provided additional proof for the hydride-transfer mechanism.

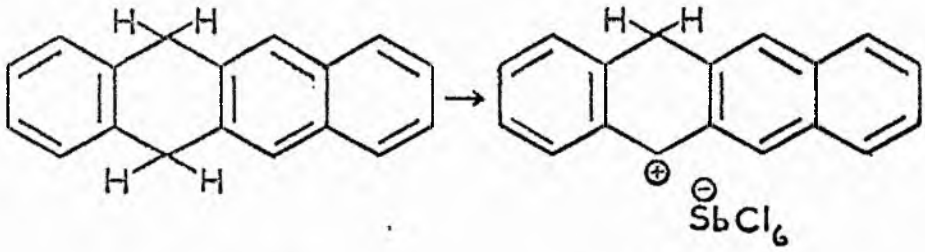
Meerwein[158] has described the use of diazonium salts as dehydrogenating agents. Trimethylamine readily added at the

4-position to 2,4,6-trichlorobenzenediazonium fluoroborate (LXXXV) in acetonitrile to give the double salt (LXXXVI). It was found that this double salt could accept both a hydride ion and a proton from such substrates as 1,4-dihydrobenzene, 1,4-dihydronaphthalene and 1,4-dioxan and yielded, in addition to the dehydrogenated product, nitrogen gas, trichlorobenzene and trimethylammonium fluoroborate. In cases where the loss of a hydride ion yielded a stable salt, e.g. dioxolanes $\longrightarrow$ dioxolenium salts, the by-product was (2,5-dichlorophenyl)-trimethylammonium fluoroborate. Addition of copper powder to this last reaction caused it to follow a free-radical rather than an ionic course.

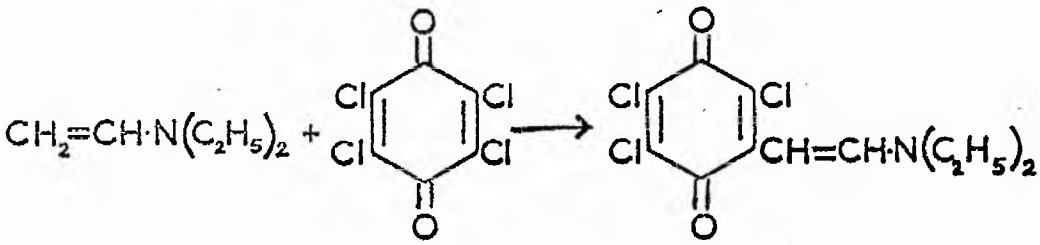
The isolation of tropylium tetrahaloborates from the reaction of t-butyl halides and boron trihalides on cycloheptatriene has been noted[113,114,118]. These salts, however, can be produced simply by the reaction of the boron trihalide on cycloheptatriene. The most probable mechanism[114] involves the acceptance of a hydride ion by the trihalide followed by disproportionation of the anion, so formed, to give the tetrahaloborate anion. This is borne out in the case of boron tribromide by the very high yield



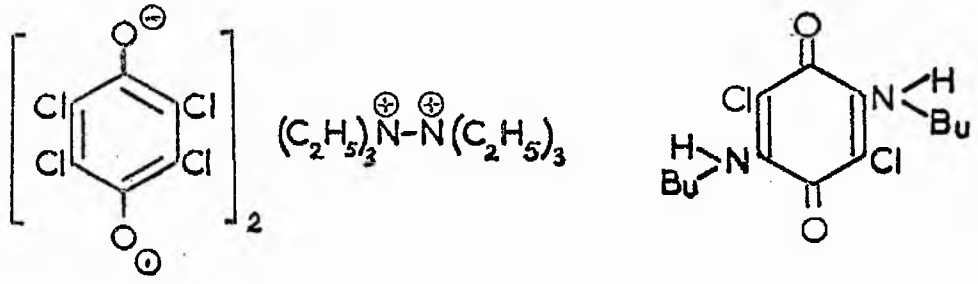
LXXXVII LXXXVIII



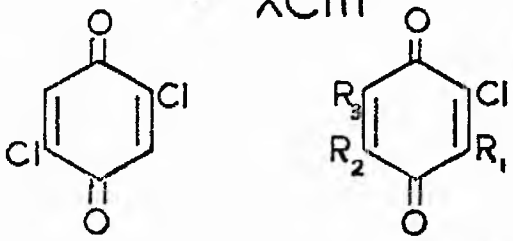
LXXXIX XC



XCI XCII



XCIII XCIV



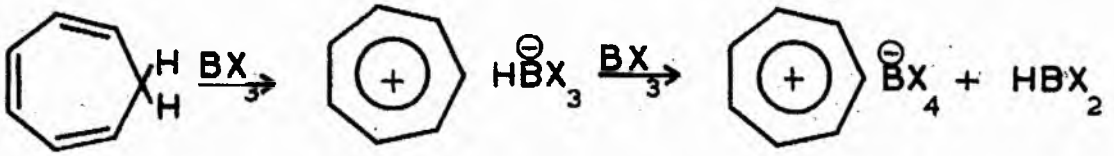
XCV

XCVI $R_1 = R_3 = OCH_3, R_2 = Cl.$

XCVII $R_1 = R_2 = OCH_3, R_3 = Cl.$

XCVIII $R_1 = NHBu, R_2 = OCH_3, R_3 = Cl.$

XCVIX $R_1 = R_3 = NHBu, R_2 = OCH_3.$



X = Cl, Br, I.

of tropylium salt and the presence in the mother liquor of a reduced boron species, the nature of which has not yet been determined.[114] Boron tribromide will also remove a hydride ion from trianisylmethane to give trianisylmethyl tetrabromoborate.[114]

Another Lewis acid which appears to behave as a hydride acceptor is antimony pentachloride[159]. Although there is no direct evidence for it, a hydride-transfer mechanism accounts for the products and seems feasible. In the reaction with cycloheptatriene,

$$RH_2 + SbCl_5 \longrightarrow RH^{\oplus} + HSbCl_5^{\ominus}$$

$$HSbCl_5^{\ominus} + SbCl_5 \longrightarrow SbCl_6^{\ominus} + SbCl_3 + HCl.$$

triphenylmethane, 9,10-dihydroanthracene (LXXXVII) and 9,10-dihydrotetracene (LXXXIX), stable hexachloroantimonate salts were obtained, e.g. (LXXXVIII) and (XC). The production of antimony trichloride and hydrogen chloride in the reaction with 9,10-dihydroanthracene provided

proof that the product was not a product of the sigma or charge-transfer type. (i.e. no antimony-carbon bond.).

Several other reactions are believed to proceed by a hydride-transfer mechanism. Amongst the acceptors are found dichlorocarbene, used in the oxidation of the benzyloxide ion[160], and bromine, hydrogen bromide and hydrogen iodide which, in strong sulphuric acid solution, will oxidise triarylmethanes.[161]

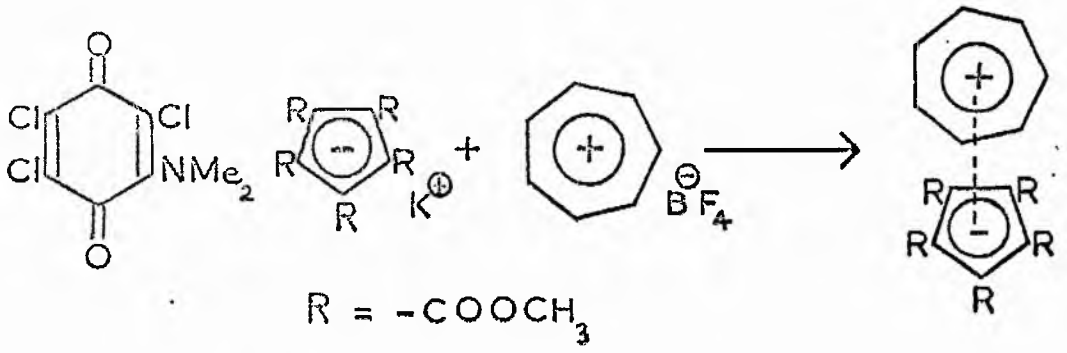
A.IV Reactions and Interactions of Quinones with Amines.

1. Chemical Reactions

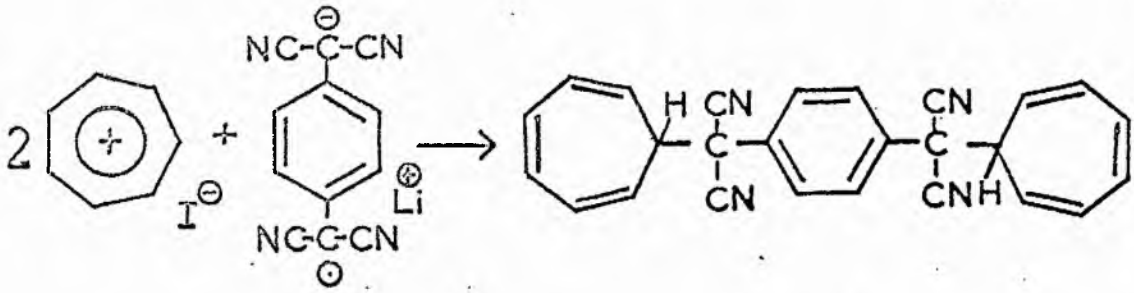
Since 1887[162] quinones, notably haloquinones, have been known to produce intensely coloured solutions[163] with both aliphatic and aromatic amines and solid salt-like complexes have been isolated from these solutions[162,164,165]. Most of these can be decomposed by addition of dilute acid to give a quantitative return of the original components, illustrating the reversible nature of the "reaction". Henbest[49,134] found, however, that triethylamine and other tertiary amines containing a flexible $\geq N\text{-}\overset{|}{C}H.CH\leq$ group dehydrogenate to give an enamine $\geq N.\overset{|}{C}=C\leq$.

Chloranil (XLVII) dehydrogenates triethylamine in benzene to give vinyldiethylamine (XCI)[49]. This in turn behaves as a nucleophile, reacting with a second quinone molecule to give an aminovinylquinone (XCII). The simplest explanation involves transfer of a hydride ion from the amine to the quinone followed by loss of a proton from the resulting conjugate acid of the enamine. The last step is probably rapid and will not affect the rate.

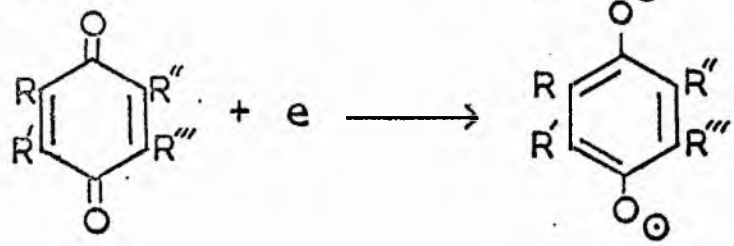
Although the overall reaction is one of hydride transfer, spectral identification of the initially-formed red charge-transfer complex suggested that the first step might involve a single electron transfer which would be in agreement with the general theory of two electron oxidation-reduction processes. This was borne out by Foster's work[165]. Using purified triethylamine as solvent and reactant, a product was isolated which proved to be a charge-transfer semiquinone salt (XCIII). The proposed structure was based on spectral data which showed a marked similarity to that of the sodium salt of chloranil semiquinone. The electron spin resonance (e.s.r.) spectrum showed only one line with no indication of the nitrogen radical and it was suggested that dimerisation of this radical had occurred. Acidification precipitated pure chloranil which precluded the possibility of replacement and in acetone, reaction took place to yield the quinone (XCII) obtained by Henbest. In a similar system, Stamires and Turkevitch[166], studying the triphenylamine-chloranil complex, failed to find resolvable hyperfine structure in the e.s.r. spectrum and concluded that dimerisation of the triphenylamine radical cation had probably occurred.



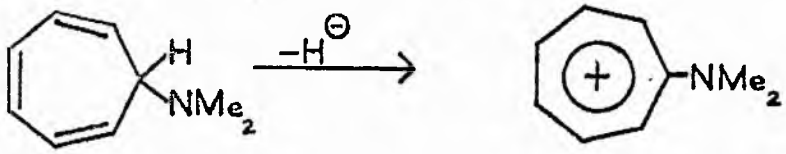
C CI CII



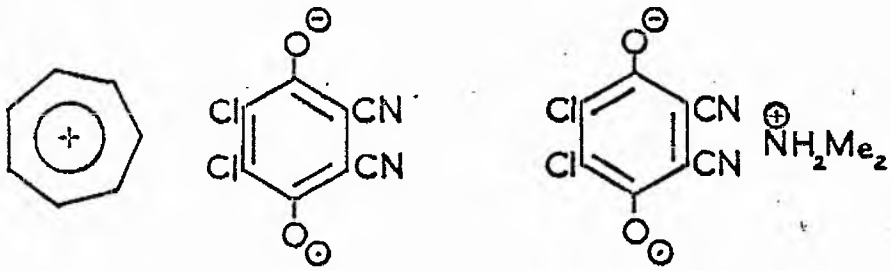
CIII CIV



CV



CVI CVII



CVIII CIX

Reactions of haloquinones with primary and secondary amines have also been studied[167]. In the reaction between n-butylamine and chloranil, 2,5-bis-(N-butylamino)-3,6-dichloroquinone (XCIV) was produced. This product was formed even when a deficiency of amine was used. With 2,5-dichloroquinone (XCV) and 2,5-dichloro-3,6-dimethoxyquinone (XCVI) the same quinone (XCIV) was isolated. Two products were obtained from 2,6-dichloro-3,5-dimethoxyquinone (XCVII) depending upon the amount of amine used. The first derivative 2,6-dichloro-3-N-butylamino-5-methoxyquinone (XCVIII) resulted from replacement of one of the methoxyl groups by an N-butylamino group. Further replacement of the chlorine in the 6-position gave the second derivative 2,5-bis (N-butylamino)-3-chloro-6-methoxyquinone (XCIX).

Several tertiary amines gave somewhat anomalous results with chloranil[49]. Those include trimethylamine, dimethylbenzylamine and tribenzylamine. In benzene solution trimethylamine produced a small amount of 2,3,5-trichloro-6-dimethylaminoquinone (C). The other two amines under similar conditions yielded benzaldehyde. Replacement has also been found to occur in the reactions of other

haloquinones with amines and both di- and tetraminoquinones have been formed from fluoranil in this way[168].

The crystal violet cation was produced in the reaction between chloranil and dimethylaniline[169]. Early observers[170], noted the formation of a charge-transfer complex but re-examination revealed that reaction was occurring[169] and e.s.r. studies have shown semiquinone radicals to be intermediates. Once again several explanations are possible. As in the case of triethylamine and chloranil, no amine radical cation was detected in the e.s.r. spectrum. It is suggested that they are either in too low a concentration or have too short a spin life. No definite mechanism was suggested. Four other tetrahalogenated quinones behave similarly and it was found that reactions involving ortho-quinones proceeded about 100 times faster than those of para-quinones. Dimethylaniline also appears to react with D.D.Q in methylene chloride solution[171].

It is now relevant to discuss briefly the nature and properties of these charge-transfer complexes with special reference to those mentioned above.

2. Charge-transfer Complexes

A charge-transfer or donor-acceptor complex may be formed from two components, one of which is an electron donor (D) and the other an electron acceptor (A). These complexes may often be intensely coloured, the colour generally being associated with the "transfer of electronic charge" from the donor to the acceptor molecule.

By considering the interaction of a non-bonded ground state (D,A) and a polar-bonded excited state (D^+-A^-) Mulliken[172] produced a stabilised ground state having a wave function

$$\psi_0 = \psi(D,A) + \lambda\psi(D^+-A^-)$$

and an excited state

$$\psi_1 = \psi(D^+-A^-) + \mu\psi(D,A)$$

where λ and μ are in most cases small compared to unity.

On the basis of quantum mechanics, the absorption spectrum had to include (in addition to the individual spectra of D and A, somewhat modified by their interaction) a band associated with the transition $\psi_0 \rightarrow \psi_1$ and characteristic of the complex as a whole. Such bands

had already been observed. (See reference 172 and references contained therein.) It is obvious that there must be a considerable range of charge-transfer complexes from the very weak, loosely-bonded type to those formed between strong donors and acceptors and in which the electron is completely transferred in the ground state. These latter one would expect to display free radical behaviour and paramagnetism, detectable by means of e.s.r. techniques. Quinone-amine complexes frequently fall into this category and some examples will serve as illustrations.

Charge-transfer bands in the chloranil-triethylamine and chloranil-dimethylaniline systems have already been noted[49,165,169]. In the former case a salt-like complex could be isolated in which electron-transfer was apparently complete. With dimethylaniline, a weaker donor, the e.s.r. spectrum indicated the presence of the semiquinone radical anion. Charge-transfer spectra of D.D.Q., chloranil and tetracyanoethylene with a variety of N,N-dimethylanilines and N,N,N′,N′-tetramethyl-p-phenylenediamines have been studied in some detail[171]. With methylene dichloride as

solvent, the spectra of chloranil complexes were reasonably constant but those of D.D.Q. tended to vary with time. Chemical reaction was apparently taking place, probably with complete electron transfer[171,173]. Triphenylamine and chloranil also gave a complex with a strong e.s.r. spectrum.[166]

Chloranil forms charge-transfer complexes with a variety of metallocenes.[174] These range from a high melting salt containing two equivalents of nickelocene to a low melting 1:1 cobaltocene derivative. Complexes with ferrocene are also formed but were not isolable as solids.

An examination of the infra-red spectra of many of these quinone complexes shows that they are similar to the superposed spectra of their components, especially when the donor and/or acceptor properties of the components are weak.[175] However, in some quinone-diamine and quinone-diazine complexes, the pattern of the semiquinone ion has been found to replace that of the quinone.[176] This phenomenon has been used to classify molecular complexes into two groups, non-bonding types and dative types. The latter group contains almost all the D.D.Q.

complexes and a number of the chloranil ones. It has already been noted that a very close similarity exists between the spectra of the sodium salt of chloranil semiquinone and those of some of the chloranil-amine charge-transfer complexes[165,177].

Whilst on the subject of charge-transfer it is convenient to mention some compounds containing the tropylium ion which display charge-transfer bands in their ultra-violet-visible spectra. Doering first suggested[178] that the sequence of colours in the solid tropylium halides series indicated charge-transfer from the halide ion to the tropylium ion. The same conclusion was reached by Harmon et al.,[179] who examined the spectra of these tropylium salts in methylene chloride and accounted for the additional bands appearing in the ultra-violet and visible region. The tropylium ion also forms charge-transfer complexes with aromatic hydrocarbons[180] and as an extension to this a salt (CII), formed by the reaction of potassium 1,2,3,4,5-penta-carbomethoxy-cyclopentadienylide (CI) and tropylium fluoroborate in acetone, displayed charge-transfer bands in its ultra-violet-visible spectrum[181].

An attempt[182] to form a charge-transfer complex from tropylium iodide and the lithium salt of tetracyanodiquinomethane (CIII) was unsuccessful. The product was α,α′-ditropyl-α,α,α′,α′-tetracyano-p-xylene (CIV).

3. Semiquinones

From the above discussion, it is clear that the semiquinone species (CV) may be formed by transfer of an electron to a quinone. It therefore represents the oxidation state between quinones and their corresponding quinols.

Semiquinones were first studied in detail by Michaelis and co-workers[183-185] who showed that the reduction of quinones was accompanied by a decrease in measured diamagnetic susceptibility, followed by a rise to the steady final value. He postulated that the mechanism was therefore a two-electron process, taking place via a one-electron intermediate stage. Similarly oxidation of hydroquinone (dianion) to quinone could also be carried out via the intermediate semiquinone.

The decrease in diamagnetic susceptibility was noteworthy. Using strong donors and quinone acceptors it

seemed possible that sufficiently ionic complexes could be obtained in which the ground state would be essentially ionic. These complexes would be expected to contain the semiquinone radical-anion, be paramagnetic and display a strong e.s.r. spectrum. An examination of a number of solid molecular haloquinone-amine complexes by e.s.r. techniques found them to be paramagnetic[186]. The concentration of the paramagnetic species generally increased with the strength of the donor-acceptor tendency and was independent of temperature. Coupling constants for a number of halosemiquinones, produced by other means, have been recorded[187,188] and the use of infra-red and ultra-violet spectra has already been discussed.

A.V Summary of Present Work.

A study has been made of the dehydrogenation of heterocyclic and carbocyclic hydroaromatic compounds by means of (i) preformed carbonium ions (ii) high potential quinones. When carbonium ions are used, or quinones in the presence of acid, the mechanism involves hydride-transfer from the substrate to the dehydrogenating agent[19,51]. Such reactions have preparative value when a stable salt is formed. When quinones are used alone (in the absence of acid) electron-transfer frequently replaces hydride-transfer as the initial step.

A number of hydroaromatic heterocycles and heterocyclic ketones were synthesised and dehydrogenated using triphenylmethyl perchlorate. Reduction of the ketones using lithium aluminium hydride yielded the corresponding alcohols which, by virtue of the equilibrium

$$Ph_3C^{\oplus}\,ClO_4^{\ominus} + CH_3.COOH \rightleftharpoons Ph_3C.OC.OCH_3 + H^{\oplus} + ClO_4^{\ominus}$$

were dehydrated in situ, a reaction rapidly followed by hydride-transfer to give the completely unsaturated salt.

The use of triphenylmethyl perchlorate suffers from two main drawbacks, (i) traces of acid which affect the

dehydrogenation of acid-sensitive compounds are difficult to exclude and (ii) electrophilic substitution of the dehydrogenation product by the triphenylmethyl group can occur.

Although high potential quinones may undergo substitution they are effective dehydrogenating agents and a study was made of their reaction, in the presence of acid, with several of the hydroaromatic heterocycles previously examined. Three quinones proved to be the most useful:- chloranil, tetrachloro-o-benzoquinone (o-chloranil) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (D.D.Q.) and the results were similar to those obtained using carbonium ion.

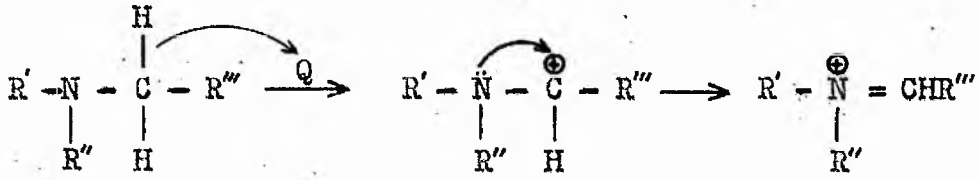
Passing to carbocyclic compounds, cycloheptatrienes were selected as suitable substrates for three reasons, (i) loss of a hydride ion would give a stable cation[32] and hence (ii) provide a new route to tropylium salts and (iii) yield information on the mechanism of dehydrogenation. Several tropylium salts were prepared from cycloheptatriene using a quinone in the presence of the appropriate acid or alkali metal salt. Alkyl- and aryltropylium salts were prepared in a similar manner

but cycloheptatrienyl ethers and thioethers all underwent cleavage to yield the unsubstituted salt. Dimethylaminotropylium perchlorate (CVII) was the only substituted salt obtained (apart from the alkyl and aryl derivatives) and was formed by the reaction of tropylium perchlorate on dimethylaminocycloheptatriene (CVI).

Treatment of substituted cycloheptatrienes with quinones alone (i.e. acid absent) failed to prevent cleavage of the cycloheptatrienyl-substituent bond by a process involving electron-transfer.

From the reaction of cycloheptatriene with D.D.Q. a deeply-coloured solid was obtained. On the basis of analytical and spectral data and from a study of its chemical properties a structure (CVIII) tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone was proposed. This product was obtained from the reaction of D.D.Q. with all the substituted cycloheptatrienes except the alkyl- and aryl- derivatives which gave tropylium semiquinones in which the substituent was retained. Dimethylaminocycloheptatriene behaved anomalously, ring contraction took place yielding benzaldehyde and dimethylammonium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (CIX).

The possible dehydrogenation of tertiary amines using D.D.Q. as hydride acceptor was examined as an alternative to the Hofmann degradation. Removal of a hydride ion from the methylene group of the tertiary amine (CX) would give rise to the immonium salt (CXII), as



CX CXI CXII

depicted via the intermediate (CXI), alkaline cleavage of (CXII) yielding a secondary amine and an aldehyde.

In fact the reaction only takes place to a very limited extent. Deeply-coloured compounds were obtained which from spectral and chemical evidence appear to be complexes of the charge-transfer type formed by partial or complete transfer of an electron from the amine to the quinone.

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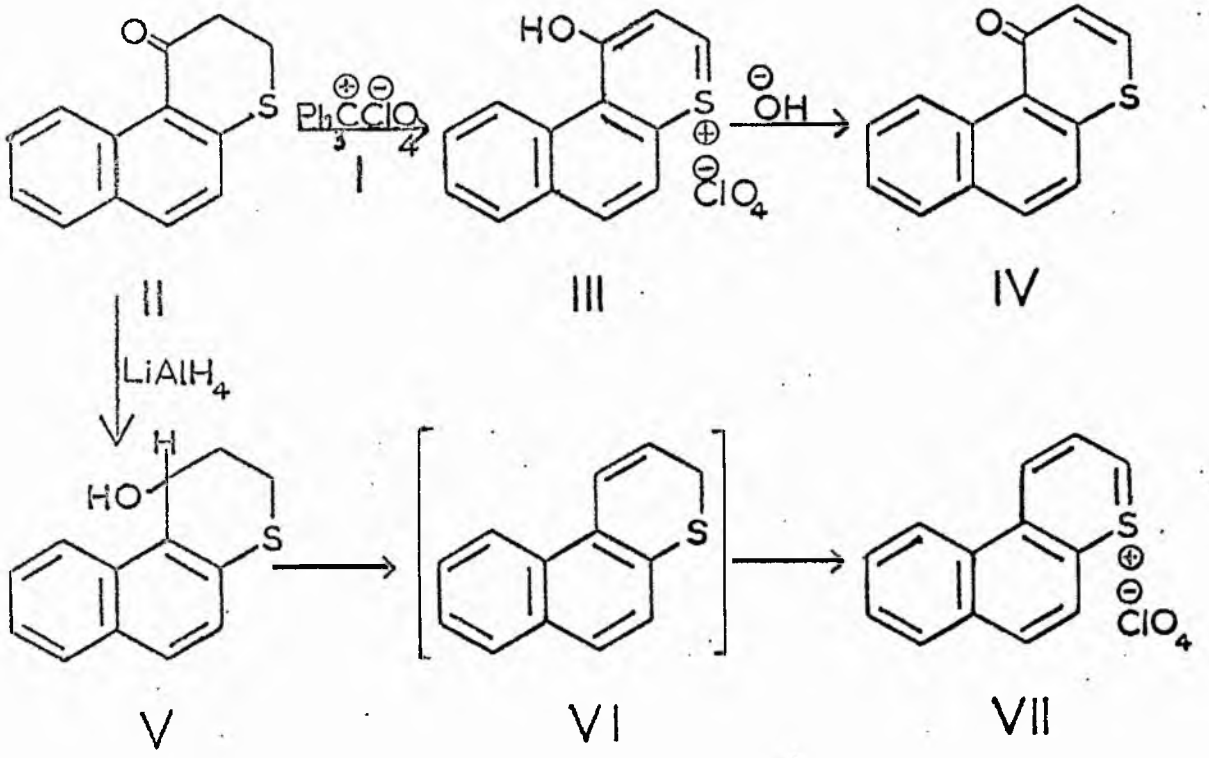
----- D I S C U S S I O N -----

B.I. Dehydrogenation of hydroaromatic heterocycles using Triphenylmethyl Perchlorate

Of the existing methods for the preparation of triphenylmethyl perchlorate[1,2,3], that involving triphenylcarbinol and 70% perchloric acid is the most satisfactory and convenient. The method described in the literature[2,3] was slightly modified in order to eliminate the need to recrystallise the product. Triphenylmethyl perchlorate decomposes on exposure to moist air and also on prolonged exposure to light. The resulting purplish decomposition product has been found to contain 9-phenylfluorene.[3] Although the salt keeps reasonably well in a dark desiccator, fresh material was generally prepared for each new reaction.

A number of dehydrogenations of carbocyclic and heterocyclic hydroaromatic compounds using triphenylmethyl perchlorate (I) or fluoroborate have been described[4-10]. The products were the corresponding fully aromatic structures and included notably the tropylium[6] and phenalenium[4] cations. In order to examine the scope of this method in more detail several hydroaromatic heterocycles were synthesised and their dehydrogenation studied. These included:


O
S
$Ph_3C^{\oplus}\,ClO_4^{\ominus}$
I
HO
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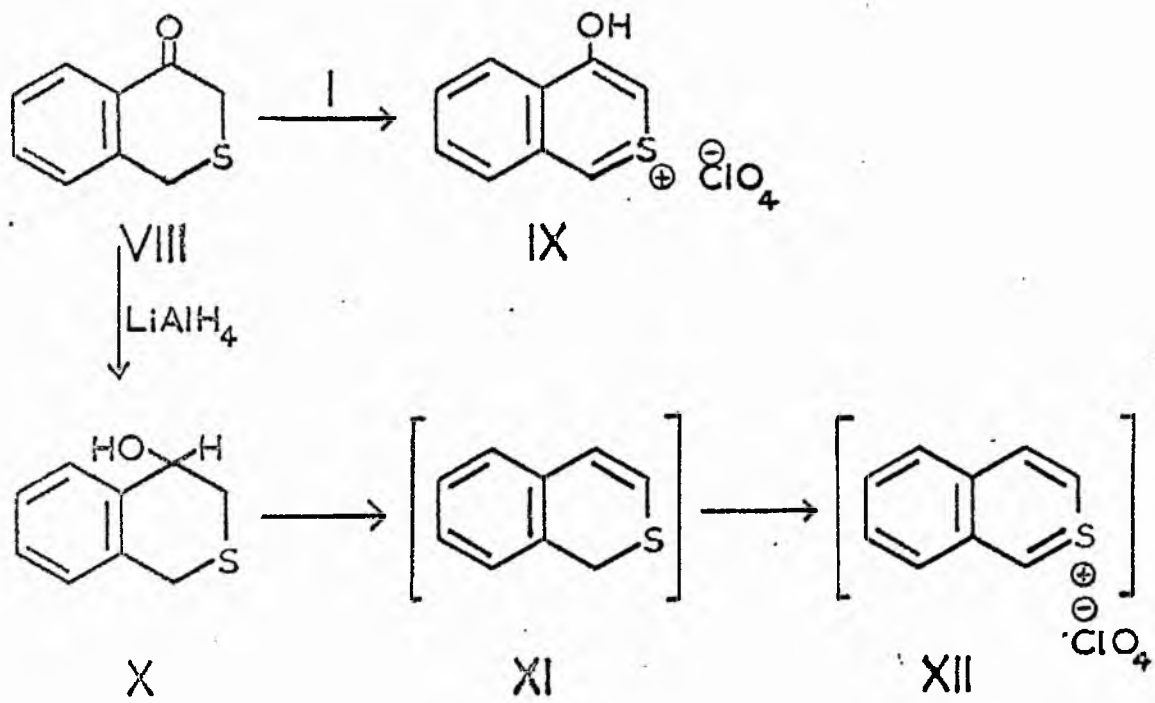
$OH^{\ominus}$
II
III
IV
$LiAlH_4$
H
HO
V
VI
VII


O
S
I
OH
$ClO_4^{\ominus}$
VIII
IX
$LiAlH_4$
HO
H
X
XI
XII

(i) benzo[f]thiachroman-4-one (II)[11].

(ii) 2-thiachroman-4-one (VIII)[12].

(iii) 5,6-dihydro-5-methylphenanthridine (XIII)[13].

(iv) 5,6-dihydro-5,6-dimethylphenanthridine (XV)[14].

(v) 2,3-dihydro-2,3-dimethylbenzothiazole (XVII).

The initial step involved the transfer of a hydrogen atom together with its pair of electrons to the electrophilic carbonium ion giving triphenylmethane and a cation. In cases (i) and (ii) this was followed by spontaneous loss of a proton from the adjacent acidic site to yield the product, in the presence of the resultant perchloric acid, as a salt. In the other cases the product was simply the stable cation formed by the initial loss of a hydride ion. These two types of reaction may be represented by the equation:

$$RH + \overset{\oplus}{R'}\ \overset{\ominus}{ClO_4} \rightleftharpoons R'H + \overset{\oplus}{R}\ \overset{\ominus}{ClO_4}$$

The general method involved treatment of the hydroaromatic substrate with the carbonium ion (I) in acetic acid or acetonitrile, heating where necessary. The choice of solvent, usually acetic acid, was largely governed by the solubility of the product since washing with dry ether sufficed to remove any remaining traces of triphenylmethane. This

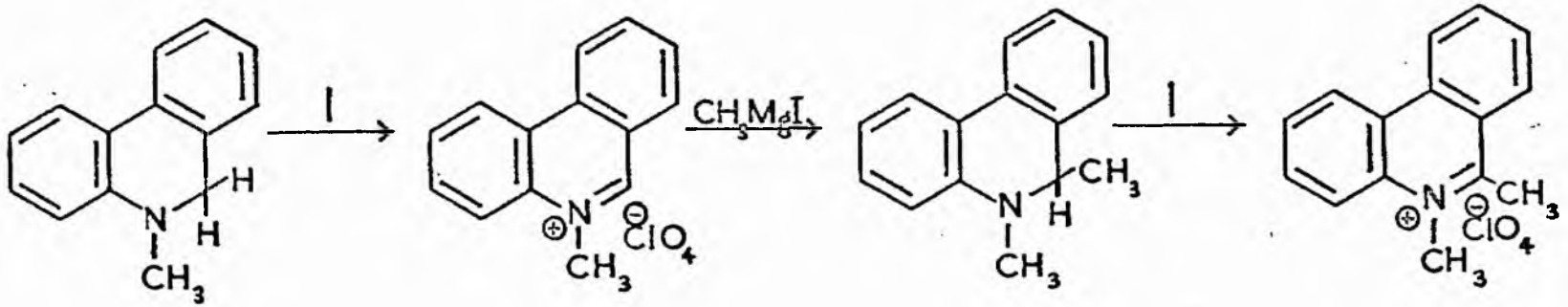
by-product could be isolated by chromatography and served not only as additional proof of the hydride-transfer mechanism but also as a useful check on the reaction-yield.

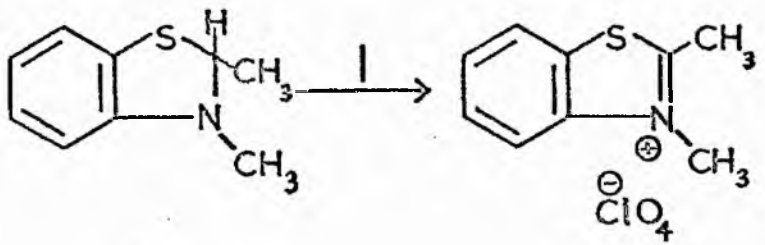
Reduction of the ketones (II) and (VIII) by means of lithium aluminium hydride gave the corresponding alcohols benzo[f]thiachroman-4-ol (V) and 2-thiachroman-4-ol (X). It has been shown[5] that triphenylmethyl perchlorate in acetic acid behaves as a dehydrating as well as dehydrogenating agent, doubtless by virtue of the free perchloric acid produced in the following equilibrium

$$CH_3.COOH + Ph_3\overset{\oplus}{C}\ \overset{\ominus}{Cl}O_4 \rightleftharpoons CH_3CO.OCPh_3 + \overset{\oplus}{H} + \overset{\ominus}{Cl}O_4$$

Thus treatment of the above-mentioned alcohols with the reagent in acetic acid resulted in dehydration to give the dihydro-heterocycle. This product could not be isolated but immediately underwent dehydrogenation to yield the thiapyrylium salt directly.

Benzo[f]thiachroman-4-one (II) reacted smoothly with the reagent (I) to give 4-hydroxy-1-thianaphtho[2,1,b] pyrylium perchlorate (III). The fully unsaturated ketone, benzo[f]thiachroman-4-one (IV), was obtained by treating (III) with concentrated ammonium hydroxide. It has since been reported that this ketone


I
CH3MgI
I
XIII
XIV
XV
XVI


I
XVII
XVIII

(IV) may also be produced by dehydrogenation of benzo[f]thiachroman-4-one (II) using phosphorus pentachloride in benzene.[15] Dehydration-dehydrogenation of the alcohol (V) via the intermediate (VI) gave 1-thianaphtho[2,1,b]pyrylium perchlorate (VII). This salt is also formed in low yield by treating the oily product from the reaction between naphthalene-2-thiol and propargyl aldehyde with perchloric acid.[16]

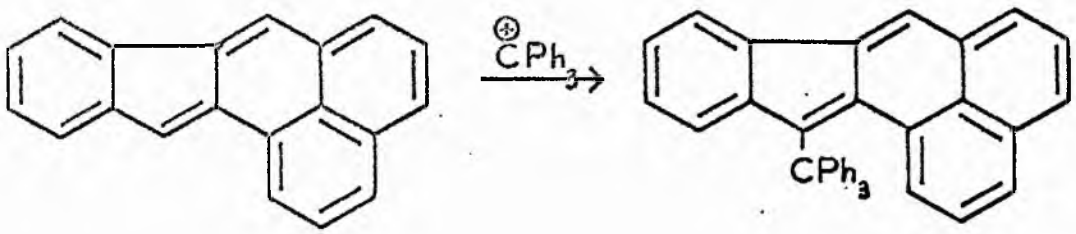
With the sulphur atom in the 2-position there was no apparent difference in the course of the reaction and 2-thiachroman-4-one (VIII) underwent dehydrogenation to give 4-hydroxy-2-thiabenzo[e]pyrylium perchlorate (IX) [cf. 1-thiachroman-4-one[5].]. However, in an attempt to dehydrate-dehydrogenate 2-thiachroman-4-ol (X), the product was a green oil. The reaction mixtures all turned dark green and addition of dry ether merely separated a green oil which resisted all attempts at crystallisation. The isolation of triphenylmethane in good yield from the mother liquors confirmed that hydride-transfer had occurred. 2-Thiabenzo[e]pyrylium perchlorate (XII) has since been obtained as a solid by a similar method using different reaction conditions.[9]

As in the case of dihydro-acridines and unsubstituted dihydrophenanthridines[5], 5,6-dihydro-5-methylphenanthridine (XIII)

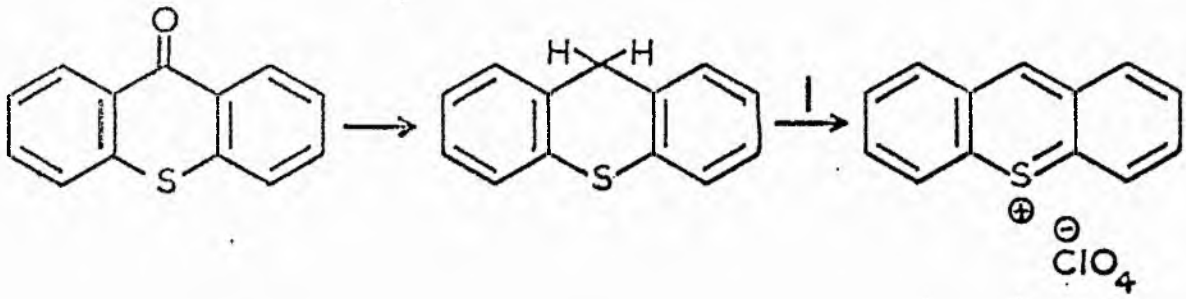
and 5,6-dihydro-5,6-dimethylphenanthridine (XV) underwent dehydrogenation readily to give high yields of 5-methylphenathridinium perchlorate (XIV) and 5,6-dimethylphenanthridinium perchlorate (XVI). The dihydro-substrate (XV) was prepared by the action of methyl magnesium iodide on the 5-methyl derivative (XIV), an adaption of the method of Bradley and Jeffrey[14] for the synthesis of 1,2-dihydro-1,2-dimethylquinoline.

Reduction of 2,3-dimethylbenzothiazolium perchlorate (XVIII) using sodium borohydride gave 2,3-dihydro-2,3-dimethylbenzothiazole (XVII) which underwent dehydrogenation with the reagent (I) in the cold to give an almost quantitative yield of the salt (XVIII).

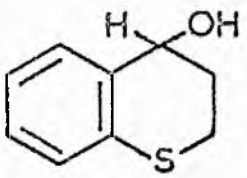
Triphenylmethyl perchlorate is therefore a strong hydride acceptor whose main value lies in the dehydrogenation of substrates which give rise to a cation or neutral product[4] stable under the reaction conditions. In such cases, the reaction occurs smoothly and the products are obtained in good yield. Since traces of acid are almost impossible to exclude, however, difficulties arise in the dehydrogenation of acid-sensitive compounds.



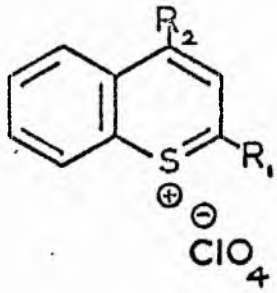
XIX XX



XXI XXII XXIII



XXIV



XXV R_1 = Ph, R_2 = H.
XXVI R_1 = H, R_2 = Ph.
XXVII R_1 = R_2 = Ph.

B.II. Dehydrogenation of hydroaromatic heterocycles using high potential quinones in the presence of acid

Despite its usefulness as a vigorous hydride abstractor, triphenylmethyl perchlorate suffers from a number of disadvantages, (i) the difficulty of excluding traces of acid (already mentioned), (ii) a restriction in the choice of anion and (iii) the occurrence of electrophilic substitution of the dehydrogenation product by the triphenylmethyl group, as in the case of indeno[2,1,a]perinaphthene[4] (XIX). A more selective method of dehydrogenating was sought, in particular one which might be adapted for use in the absence of acid. To this end the potentialities of quinone dehydrogenation were examined.

Dehydrogenation of hydroaromatic compounds by quinones has been rationalised in terms of a two-stage ionic process[17,18,19] in which the initial, rate-determining step involves the abstraction of a hydride ion. This is followed by the swift transfer of a proton from the acidic centre of the resulting carbonium ion to the quinol anion

$$RH_2 + Q \longrightarrow RH^{\oplus} + QH^{\ominus}$$

$$QH^{\ominus} + RH^{\oplus} \longrightarrow R + QH_2$$

Dehydrogenation is catalysed by strong acid and in this case the reactive entity is the conjugate acid of the quinone, i.e.

the quinol cation $\overset{\oplus}{QH}$. This species has a higher affinity for anionic hydrogen than does the quinone itself.

$$Q + HX \xrightarrow{\text{fast}} \overset{\oplus}{QH}.\ \overset{\ominus}{X}$$

$$RH_2 + QH^{\oplus} \xrightarrow{\text{slow}} RH^{\oplus} + QH_2$$

$$RH^{\oplus} + X^{\ominus} \xrightarrow{\text{fast}} R + HX$$

When the resultant carbonium ion $(RH)^{\oplus}$ is sufficiently stable it may be isolated as the cation in the presence of a suitable anion (readily supplied by the acid catalyst), thus providing a useful general method for the preparation of heterocyclic salts.

In all cases the hydroaromatic heterocycle was treated with an equivalent of quinone in acetic acid, the preferred solvent, containing an excess of perchloric acid. The products were separated from the quinol by-product by addition of anhydrous ether or in the case of D.D.Q. by digestion with ethanol or fractional crystallisation. D.D.Q. therefore found only limited application. The easy recovery of the quinol of the other quinones allowed a comparison of the yields of salt and quinol to be made.

o-Chloranil, prepared from tetrachlorocatechol by oxidation with nitric acid[20] using a slightly modified procedure, is

probably the most useful quinone of the three used, both because of its own ready solubility in acetic acid and because of the ready solubility of its quinol in ether. p-Chloranil was also a convenient reagent but in cases where the reaction was incomplete its own insolubility made it an awkward impurity to remove. Its quinol, like that of o-chloranil, was very soluble in ether. D.D.Q., which was used occasionally, was prepared by alternate oxidation (liquid oxides of nitrogen) and hydrochlorination of 2,3-dicyanoquinol[21,22].

The following compounds were dehydrogenated by these quinones:

(i) thiaxanthene (XXII),(Chloranil, D.D.Q.).

(ii) benzo[f]thiachroman-4-ol (V),(Chloranil).

(iii) 5,6-dihydro-5-methylphenanthridine (XIII), (Chloranil).

(iv) 5,6-dihydro-5,6-dimethylphenanthridine (XV),(Chloranil).

(v) 2,3-dihydro-2,3-dimethylbenzothiazole (XVII),(o-Chloranil, p-chloranil).

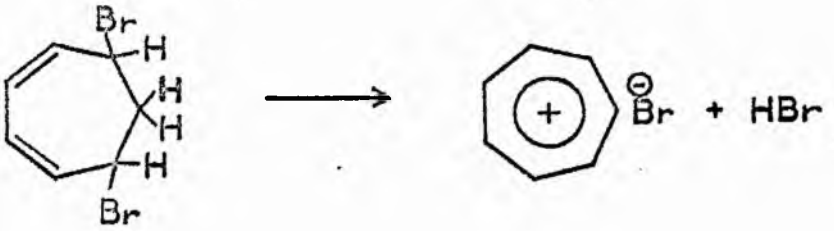
Thiaxanthene (XXII) was prepared from thiaxanthone (XXI) by a modification of the method of Brown and White[23] for the reduction of polarised carbonyl groups. It gave a dark red colour when treated with chloranil but no solid product was

obtained until perchloric acid had been added. Thiaxanthylium perchlorate (XXIII) then crystallised from the solution and was identical with that formed using triphenylmethyl perchlorate.[5] The dark red colour was probably due to the formation of a charge-transfer complex. A similar but more intense red colour was produced when D.D.Q. was added to a solution of thiaxanthene (XXII) in acetonitrile but this time claret-coloured crystals separated. When isolated and treated with perchloric acid these crystals decomposed to give the salt (XXIII) but in lower yield owing to difficulties in purification. Two structures for the intermediate are possible, (i) thiaxanthylium 2,3-dichloro-5,6-dicyano-1,4-quinolate, (ii) a simple solid charge-transfer complex. The former structure is perhaps more likely since 9,10-dihydroacridine afforded a similar product when treated with D.D.Q. in acetic acid.[11] The intermediate was not examined in detail.

The dehydration-dehydrogenation of benzo[f]thiachroman-4-ol (V) occurred as smoothly with o-chloranil and perchloric acid as it had done with triphenylmethyl perchlorate and in equally good yield. Owing to the dark colour of the reagent it was not possible to detect any appreciable colour-change on adding

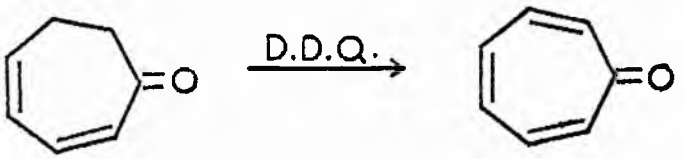
the quinone but no solid was formed until the salt (VII) crystallised out on the addition of acid. 1-Thiachroman-4-ol (XXIV) behaved in a similar manner[11] and Lüttringhaus[24] has also used this dehydrogenation method in the preparation of 2-phenyl-, 4-phenyl- and 2,4-diphenyl-1-thiabenzo[b]pyrylium perchlorates (XXV, XXVI, XXVII).

The dehydrogenation of 5,6-dihydro-5-methylphenanthridine (XIII) and 5,6-dihydro-5,6-dimethylphenanthridine (XV) with chloranil and perchloric acid gave the same salts as were obtained before and in similar yield. This was also the case in the dehydrogenation of 2,3-dihydro-2,3-dimethyl-benzothiazole (XVII) with either o-chloranil or p-chloranil and perchloric acid.



DOERING and KNOX, 1954.

DAUBEN et al. 1957.



VAN TAMELEN, 1956.

B.III. Formation of Tropylium Salts from Cycloheptatrienes using quinones in the presence of acid.

1. Introduction

In 1931, Hückel[25,26] showed theoretically that a seven-membered ring possessing a conjugated system of π electrons and bearing a positive charge could be aromatic and energetically stable.

Twenty-three years passed before this conclusion received experimental confirmation with the formation of tropylium bromide[27a] by the thermal elimination of hydrogen bromide from dibromocycloheptadiene. It is somewhat paradoxical that, forty years before Hückel's prediction, Merling[27b] had apparently prepared tropylium bromide although he himself was unable to identify it as such.

Since 1954 several routes to the tropylium ion have been reported. Of these Dauben's[6] hydride-transfer method involving triphenylmethyl perchlorate is the most useful, yields of 60-90% being recorded. This reaction was later adapted as a general method for the preparation of organic cations[4,5].

High potential quinones in the presence of strong acid have been shown to readily dehydrogenate dihydroheterocycles

to heterocyclic salts by a similar mechanism and thereby present an attractive route to the tropylium, phenalenium and cyclopropenylium systems. The method has proved successful[19] and the resultant carbonium ions have been isolated as the salts of various acids.

2. Dehydrogenation of Cycloheptatriene

There existed in the literature one or two reports of quinone dehydrogenation of seven-membered rings. Using D.D.Q., van Tamelen[28] had succeeded in obtaining tropone from cycloheptadienone in 10% yield. Seto and Ogura[29,30] had found that p-chloranil or p-benzoquinone dibenzene-sulphonamide would not themselves dehydrogenate cyclo-heptatriene but that in the presence of boron trichloride these reagents would given an almost quantitative yield of tropylium salt. The preparative potential of this reaction does not appears to have been realised then but has since been developed as a general method for preparing organic cations.[19]

Tropylium perchlorate, a typical salt, has been prepared from cycloheptatriene using any one of a variety of quinones. It appears that in general the dehydrogenative efficiency of

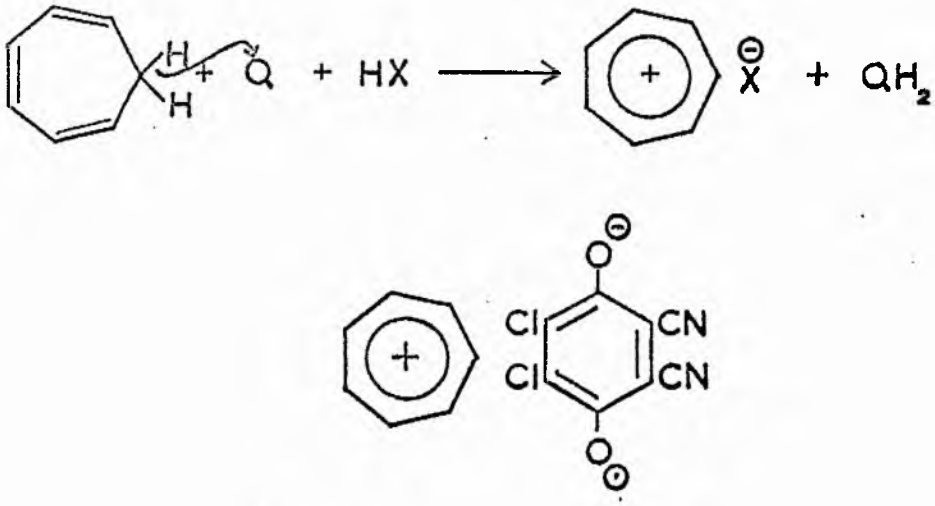
the quinones in this reaction increases with increasing redox potential (see Table 3).

Table 3

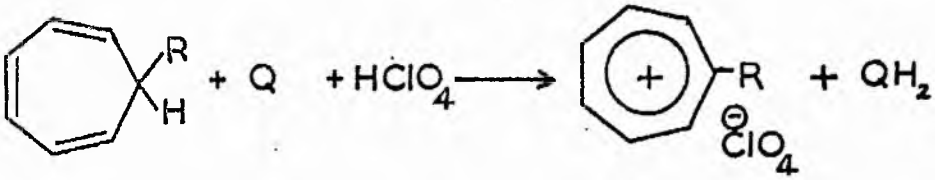
Effect of quinone redox potential on the yield of tropylium perchlorate

Quinone (Solvent)	E^{o}(v)	Yield (pure material)
D.D.Q. (CH_2Cl_2)	~ 1.0	90%
D.D.Q. ($CH_3.CO_2H$)	~ 1.0	95%
o-Chloranil ($CH_3.CO_2H$)	0.87	95%
p-Chloranil ($CH_3.CO_2H$)	0.71	70%
p-benzoquinone ($CH_3.CO_2H$)	0.70	30%
D.D.Q.(with $NaClO_4$ in $CH_3.CO_2H$)	~ 1.0	75%

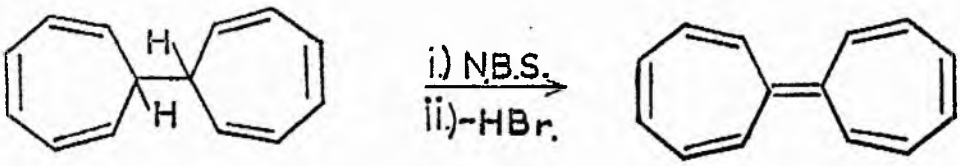
As in the dehydrogenation of dihydroheterocycles, o-chloranil was again the most convenient reagent and in reactions involving D.D.Q. the removal of 2,3-dichloro-5,6-dicyano-1,4-quinol presented minor difficulties as before. With p-chloranil some decomposition occurred and this was even more marked with p-benzoquinone where the product required considerable purification. In the last reaction with D.D.Q., replacement of perchloric acid by sodium perchlorate resulted



XXVIII



R = Me, Ph.



XXIX XXX

in a lowering of the yield. This may reflect higher efficiency in dehydrogenations involving the protonated quinone although some losses did occur during the separation from the sodium quinolate.

Tropylium picrate, prepared in methylene chloride, was obtained in two different, coloured forms both of which had the same melting-point. These two forms were produced by different rates of crystallisation and were interconvertible. The yield (51%) was not improved by replacing the methylene chloride with acetic acid or by using a larger excess of picric acid.

With o-chloranil and oxalic acid dihydrate as dehydrogenating agent, tropylium tetroxalate was obtained in good yield.

In the absence of acid, D.D.Q. and cycloheptatriene react to form a dark-coloured product (discussed later under section B.IV.1.). This product, formulated as tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (XXVIII), yielded tropylium salts on treatment with acid or alkali metal salts. Lithium bromide and the above tropylium semiquinone (XXVIII) gave a small quantity of tropylium bromide. Factors contributing to the low yield were the difficulty in isolation

(it separated as an oil) and the hygroscopic nature of the salt which caused it to decompose slowly in the atmosphere.

Addition of boiling acetic acid to a mixture of the tropylium semiquinone (XXVIII) and sodium iodide yielded a stable crystalline solid whose composition corresponded to $C_7H_7I_2$. Treatment of the compound with acetone gave scarlet crystals of tropylium iodide and subsequent addition of ether to the acetone mother liquor afforded the garnet-coloured tri-iodide. This information suggests that the compound would be better formulated as $C_{14}H_{14}I_4$, a lattice complex containing both the iodide and tri-iodide ions.

The product formed from the tropylium semiquinone (XXVIII) and p-toluene-sulphonic acid had a comparatively low melting-point and was unstable in moist air being slowly converted to a brownish oil. These properties suggest that it is probably more covalent than ionic in character.

3. Dehydrogenation of Alkyl- and Arylcycloheptatrienes.

Only a few substituted tropylium salts are known and in fact no really satisfactory method has yet been devised for their preparation. A number of unsubstituted and alkyl-substituted salts have been prepared from the corresponding

cycloheptatriene using the triphenylmethyl carbonium ion[6] but in the reaction with methoxycycloheptatriene, methoxyl transfer occurred and tropylium bromide was produced.[6] Other known substituted tropylium salts include the carboxytropylium salts[31] and halotropylium salts.[6] With the successful preparation of unsubstituted tropylium salts using quinones and acid, it was hoped that substituted salts might be obtained from 7-substituted cycloheptatrienes in a similar manner. Such a reaction might also provide more information about the mechanism of the process and, by means of a suitable derivative, afford a new route to tropone.

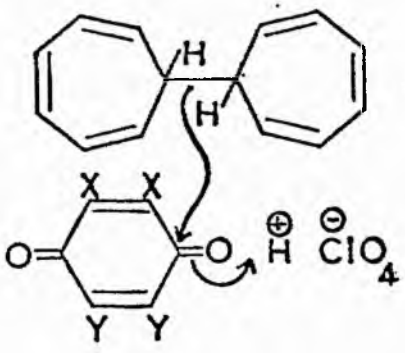
When treated with o-chloranil and perchloric acid, 7-methylcycloheptatriene yielded methyltropylium perchlorate. The product, initially an oily solid, required considerable purification and consequently the yield was low. Even the purified salt decomposed slowly in atmospheric moisture.

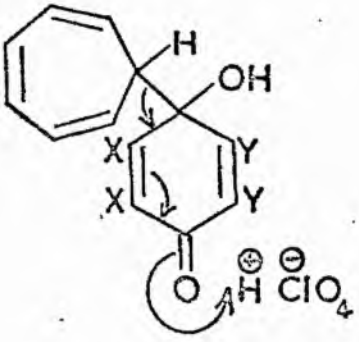
7-Phenylcycloheptatriene gave a more satisfactory yield of perchlorate when treated with the same reagent and the product displayed a greater stability. The presence of two aromatic rings contributes largely to this stability and the molecule may be compared to biphenyl of which it is the π-electron analogue[32]. p-Phenylene-bis (tropylium)

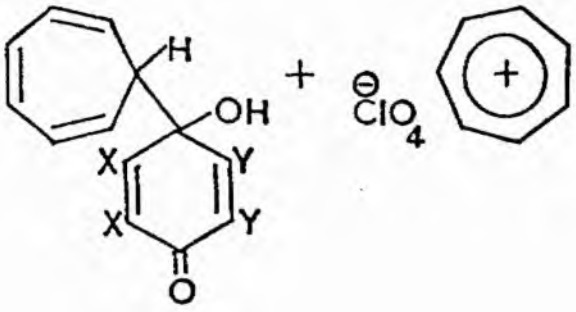
perchlorate displays a similar stability[33]. Phenyltropylium picrate was obtained in the same manner as the perchlorate but in preparing the tri-iodide, o-chloranil and sodium iodide were used, adapting an earlier procedure which involved D.D.Q. This time no solid intermediate was isolated.

(i) Ditropyl

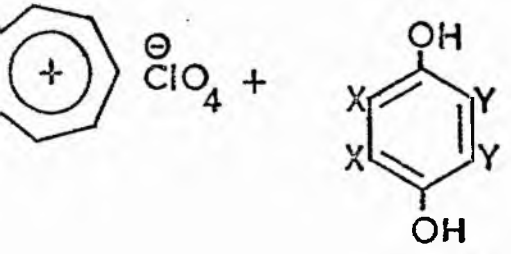
By brominating and dehydrobrominating ditropyl (XXIX), Doering and Mayer[34] succeeded in preparing the relatively stable heptafulvalene (XXX). This compound might be expected as a product from the reaction between ditropyl and a quinone in the presence of perchloric acid, formed by removal of a hydride ion followed by loss of a proton. This did not, however, happen. Instead tropylium perchlorate was produced and it was apparent from the yield that both tropyl groups contributed to its formation. Two electrons must therefore be lost from the molecule and it is most likely that the carbon-carbon bond between the two groups is attacked. Geske[35], who studied the electro-oxidation of ditropyl in acetonitrile also noted the formation of two molecules of tropylium ion by the loss of two electrons. A tentative mechanism is proposed.


H
H
X
X
O
O
Y
Y
⊕ H
⊖ ClO4


H
OH
X
X
Y
Y
O
⊕ H
⊖ ClO4



XXXI



When solutions containing the reactants and excess perchloric acid were mixed, dark red or brown colours developed and then faded before the products had begun to precipitate. These colours are frequently indicative of charge-transfer species which, in this case, may be formed before cleavage of the carbon-carbon bond yields the tropylium cation and an intermediate (XXXI). This latter will in turn decompose to quinol and the second molecule of tropylium perchlorate.

Table 4

Yields of tropylium perchlorate from ditropyl

Quinone	Yield	Yield of quinol
D.D.Q.	51%	-
p-chloranil	72% (crude)	93%
o-chloranil	50%	-
p-benzoquinone	84%	-

Table 4 shows several noteworthy features: (1) the yield of quinol and of product using p-chloranil is high, (2) the yield using o-chloranil is comparatively low. These facts suggest that some steric requirement may be necessary for this reaction. This is supported to some extent by molecular models which display the predicted[36]

boat-shape of the seven-membered rings and the proposed[37] axial orientation of the methylene hydrogens.

(ii) 7-(Triphenylmethyl)cycloheptatriene

The tropylium and triphenylmethyl cations are both sufficiently stable to be isolated as their salts. An interesting case therefore arises when the tropyl and triphenylmethyl groups are combined to form 7-(triphenylmethyl)-cycloheptatriene (XXXII) and this molecule is treated with quinone and perchloric acid.

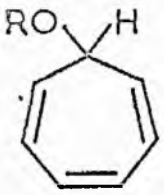
The synthesis of this cycloheptatriene derivative (XXXII) was similar to that of 7-phenylcycloheptatriene. Triphenylmethyl lithium, obtained from the reaction

$$C_3H_7^{\ominus}\ Li^{\oplus} + H.C.Ph_3 \longrightarrow C_3H_8 + Li^{\oplus}\ CPh_3^{\ominus}$$

$$Li^{\oplus}\ CPh_3^{\ominus} + C_7H_7^{\oplus}ClO_4^{\ominus} \longrightarrow LiClO_4 + Ph_3C - C_7H_7$$

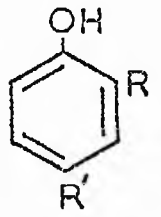
XXXII

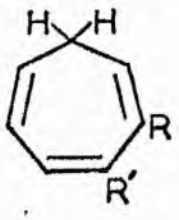
of triphenylmethane with n-propyl lithium,[38] crystallised out as dark red spars and to it was added a slight excess of tropylium perchlorate. The reaction was initially exothermic and its completion was marked by the spectacular disappearance of the red colour. The products were separated on a column of activated alumina and a colourless, brittle solid was isolated



XXXIII R = Me.
XXXIV R = Et.
XXXV R = C_7H_7.

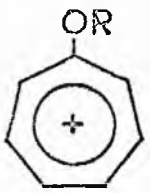
XXXVI R = CH_3CO-.
XXXVII R = Ph.
XLI R = p(OH)·C_6H_4-.



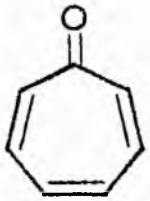


XXXVIII R = C_7H_7, R′ = H.
XXXIX R = R′ = C_7H_7.

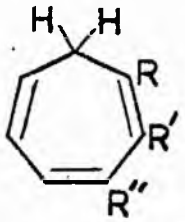
XL a R = p(OH)·C_6H_4-, R′ = H.
b R = H, R′ = p(OH)·C_6H_4-.



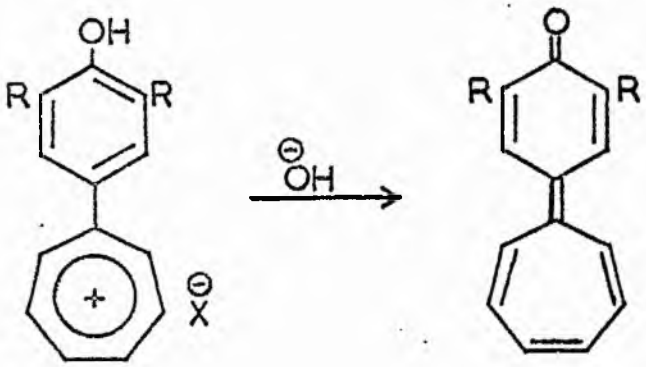
XLII R = Me.
XLIII R = Et.



XLIV



XLV a R = OMe, R′ = R″ = H.
b R′ = OMe, R = R″ = H.
c R″ = OMe, R = R′ = H.



XLVI R = H, X = $\overset{\ominus}{ClO_4}$, PICRATE.
XLVII R = H.
XLVIII R = Me, X = $\overset{\ominus}{Cl}$, $\overset{\ominus}{BF_4}$.
XLIX R = Me.

whose composition corresponded to $C_{26}H_{22}$, the same as that for 7-(triphenylmethyl)cycloheptatriene (XXXII). The melting point of this material, however, is not in agreement with that obtained by Dauben[39] who prepared this compound from triphenylmethane and the tropylium anion. The product was insoluble in most of the common solvents and was generally unreactive. It gave a yellow colour with perchloric acid alone or in the presence of D.D.Q. and the substrate was recovered. It can only be suggested that failure to react is due to steric hindrance but further confirmation of the structure of the material is now required.

4. Reaction of 7-Tropyl ethers with D.D.Q and Perchloric Acid.

Tropyl ethers are readily prepared by treating tropylium perchlorate with the appropriate alcohol in the presence of aqueous sodium bicarbonate[40,41]. Both 7-methoxy- (XXXIII) and 7-ethoxycycloheptatriene (XXXIV) were obtained in this way whilst addition of tropylium perchlorate to the base alone yielded ditropyl ether (XXXV).[27] An attempt to prepare 7-acetoxycycloheptatriene using aqueous sodium acetate also yielded ditropyl ether (XXXV). The structures of these ethers were established by treating them with cold

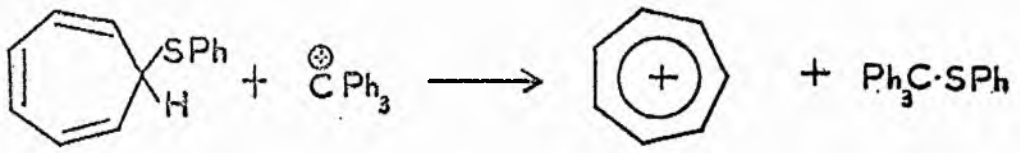
60% perchloric acid in acetic acid. A high yield of tropylium perchlorate in each case was accepted as proof of substitution in the 7- position. In addition treatment of 7-methoxycycloheptatriene (XXXIII) with picric acid afforded tropylium picrate.

The behaviour of sodium phenate with tropylium perchlorate was anomalous. At least part of the initial product, isolated by evaporation of the solvent under reduced pressure, was the 7-phenoxy-derivative (XXXVII), since tropylium perchlorate was formed on treating the crude product with cold perchloric acid. After distillation, however, the purified material did not react with acid indicating that the phenoxy group no longer occupied the 7-position. Nozoe[42] reported four products from this reaction, o-tropyl phenol (XXXVIII), 2- or 3-(p-hydroxy)-cycloheptatriene (XL a or b), 2,4-ditropyl phenol (XXXIX) and a derivative later shown, on spectral grounds[43], to be 7-(p-hydroxyphenyl)cycloheptatriene (XLI). At first the reaction was thought to be a Claisen rearrangement[44] but when the major product was found to be the para-derivative (XL a or b) rather than the ortho compound (XXXVIII) it was considered to be more electrophilic in

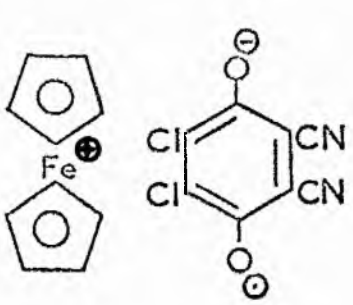
character[42]. Jutz and Voithenleitner[43] obtained 7-(p-hydroxyphenyl)cycloheptatriene (XLI) as the sole product of the reaction between 7-methoxycycloheptatriene and phenol.

As in the case of cycloheptatriene, dark-coloured intermediates were formed when D.D.Q. was added to solutions of methoxy-(XXXIII), ethoxy-(XXXIV) and tropyloxycycloheptatriene (XXXV). With perchloric acid each of these intermediates yielded tropylium perchlorate and treatment of the methoxy-derivative (XXXIII) with picric acid afforded tropylium picrate. In no case was a substituted tropylium salt isolated. These intermediates were later examined in detail and found to be identical with that from cycloheptatriene (see Section B.IV.3).

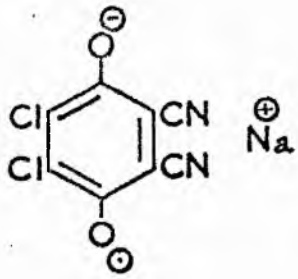
The methoxytropylium cation (XLII) has since been prepared[45,46] by thermal isomerisation of 7-methoxycycloheptatriene (XXXIII) to 1-, 2- or 3- methoxycycloheptatriene (XLV a, b and c), the last-mentioned being the major product, and dehydrogenating with triphenylmethyl perchlorate[45] or phosphorus pentachloride[46]. The ethoxytropylium ion (XLIII), prepared in a similar manner using phosphorus pentachloride, gave tropone (XLIV) when warmed with dilute aqueous sodium bicarbonate solution.[46]



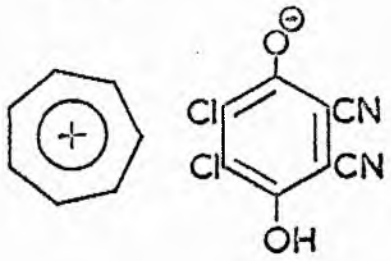
L LI



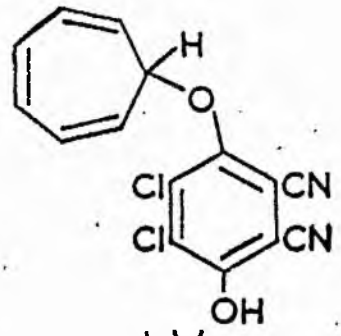
LII



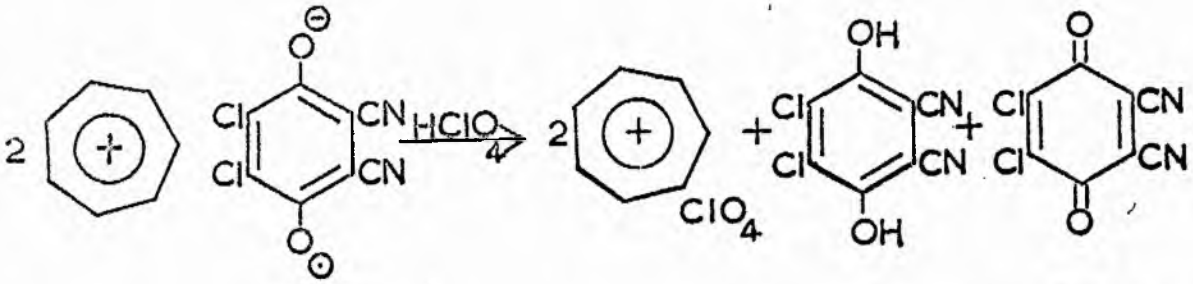
LIII



LIV



LV



LVI LVIa

When solutions of (p-hydroxyphenyl)cycloheptatriene (XL) and D.D.Q. were mixed, a dark brown intermediate was formed (see section B.IV.3) which with perchloric or picric acid yielded the (p-hydroxyphenyl)tropylium salt (XLVI). This salt has also been prepared by dehydrogenation of 7- (p-hydroxyphenyl)cycloheptatriene (XLI) with triphenylmethyl perchlorate[43]. The perchlorate dissolves in water to give a yellow solution which, when treated dropwise with dilute sodium hydroxide, slowly turns magenta and on addition of excess base becomes colourless. The coloured product is the ketone[43] (XLVII). The reaction was reversible and addition of dilute acid restored first the magenta then the yellow colour. A similar reaction was investigated by ter Borg[47] who prepared the (4-hydroxy-3,5-dimethylphenyl)-tropylium cation (XLVIII) from 2,6-dimethylphenol and ditropyl ether or tropylium fluoroborate. He also obtained a magenta - coloured ketone (XLIX) but was unable to isolate it in the pure state.

5. Reaction of 7-Phenylthiocycloheptatriene and 7-Cyano-cycloheptatriene with D.D.Q. and perchloric acid.

7-Phenylthiocycloheptatriene (L) was readily prepared

by the reaction of sodium thiophenate with tropylium perchlorate. The position of the phenylthio-group was confirmed by obtaining a good yield of tropylium perchlorate on addition of cold perchloric acid to the purified product (L). In this case there was also a strong smell of phenyl mercaptan. Degani and Fochi[48] have since published a similar method for the preparation of tropyl thioethers using tropyl chloride, the sodium mercaptide and sodium methoxide. They have also shown that the behaviour of tropyl thioethers with triphenylmethyl perchlorate is similar to that of methoxycycloheptatriene[6]. Cleavage of the sulphur-tropyl bond occurs to give tropylium perchlorate and the trityl thioether (LI).

As with the O-ethers, a black intermediate formed in the reaction of 7-phenylthiocycloheptatriene (L) with D.D.Q. (see section B.IV.3). This intermediate likewise yielded tropylium perchlorate on addition of perchloric acid.

7-Cyanocycloheptatriene, prepared by the method of Doering and Knox[49] using tropylium perchlorate, was singularly unreactive. It gave no product with perchloric acid alone and the structure was confirmed by means of an n.m.r. spectrum where the methylene proton appeared as a triplet. No solid product was obtained when treated with

D.D.Q. alone or in the presence of perchloric acid. This unreactivity most likely results from the electron-withdrawing nature of the nitrile-group.

B.IV. Reactions of Cycloheptatriene and its derivatives with quinones in the absence of acid.

1. Reaction of Cycloheptatriene with D.D.Q.

Whilst studying the dehydrogenation of cycloheptatriene by means of D.D.Q. and acid, it was found that in reactions where the acid was omitted initially a dark crystalline intermediate formed. This intermediate when later treated with acid or with alkali metal salts yielded tropylium salts (see section B.III.2). Similar intermediates were also formed by substituted cycloheptatrienes. In addition to their intrinsic interest, it was obvious that knowledge of these structures could provide useful information concerning the mechanism of D.D.Q. dehydrogenations and therefore more detailed studies were undertaken.

A stable, black, crystalline solid, red in solution, was obtained from the reaction of cycloheptatriene with D.D.Q. in acetonitrile or methylene dichloride. The yield was higher in the latter solvent but a cleaner product was obtained using the former. Elemental analysis was consistent with the composition $C_{15}H_7Cl_2N_2O_2$ or $C_7H_7;C_6Cl_2(CN)_2O_2$ which suggested that the product was formed from one molecule of each of the reactants. It was evident from the infra-red

spectrum that this intermediate was not a simple charge-transfer complex of the non-bonding type[50,53] since the spectrum contained very few peaks in common with the spectra of cycloheptatriene or D.D.Q. whilst it was also noted that peaks characteristic of the tropylium ion and semiquinone radical-anion[74] were present. (see Spectra 1-5).

The ultra-violet spectrum (see Plate 1) displayed two bands 221 mμ ($\log \epsilon$ = 4.65) and 270 mμ ($\log \epsilon$ = 3.97) which compare well with similar bands in the tropylium spectrum[6] [217 mμ ($\log \epsilon$ = 4.61) and 275 mμ ($\log \epsilon$ = 3.62)]. The second band was later found to be common to all the D.D.Q. intermediates. The other ultra-violet bands and those in the visible region (see Plate 2.) were also found in the spectrum of a derivative formed from ferrocene and D.D.Q. It was readily obtained by mixing boiling acetonitrile solutions of the reactants and was isolated as black needles, similar to, but more stable than its cycloheptatriene counterpart and showing little appreciable change in melting-point after several months. Elemental analysis was satisfactory for $C_{18}H_{10}Cl_2FeN_2O_2$ or $C_{10}H_{10}Fe;C_6Cl_2(CN)_2O_2$ and suggested some interaction between one molecule of each of the reactants.

On spectral grounds it was evident that one entity, derived from the quinone, was common to both of these products. In this case the only plausible explanation involved the donation of an electron from the ferrocene to the quinone. This would result in the formation of both the cation and the anion-radical, to give ferricenium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LII). It has been shown[52] that ferrocene will form charge-transfer complexes with various acceptors including p-chloranil. None of these could be isolated but similar products of nickelocene and cobaltocene were obtained as stable solids, some of which displayed e.s.r. signals. In the ferricenium semiquinone (LII) the transfer of the electron is apparently complete and it may therefore be considered as an end-member of the above charge-transfer series.

Electron spin resonance measurements were carried out on the cycloheptatriene - D.D.Q. intermediate and the spectrum displayed five equally-spaced lines (see Plate 3.). This spectrum is consistent with a semiquinone structure in which the unpaired electron interacts with two equivalent nitrogen atoms. There was no evidence in this spectrum of the tropyl radical.

Additional proof for the presence of the D.D.Q. radical-anion came from the preparation of sodium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LIII)[54]. Here the spectrum can only be that of the anion-radical. In table 5 the absorption bands of the sodium salt and the cycloheptatriene intermediate are compared.

Table 5

Comparison of the U.V. and Visible absorption spectra of tropylium and sodium 2,3-dichloro-5,6-dicyano-1,4-benzosemiquinone

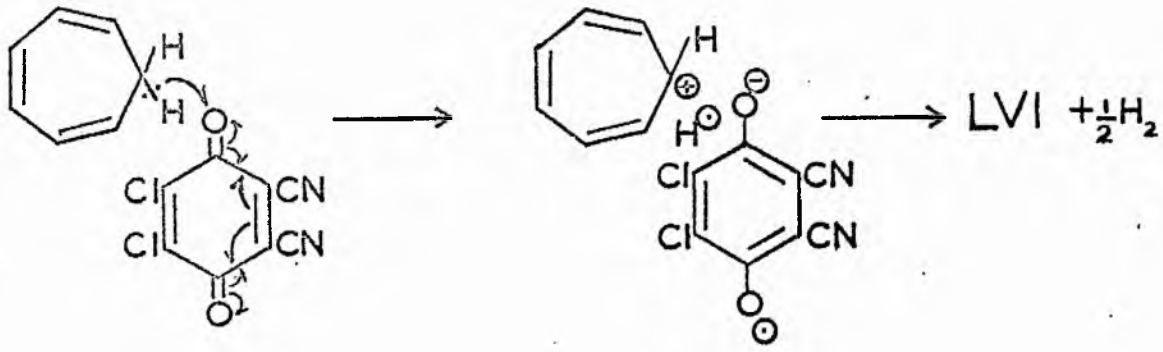
Tropylium mμ (log ε)	Sodium mμ (log ε)
221 (4.65)	-
246 (4.22)	246 (4.24)
255 (4.17)	256 (4.15) shoulder
270 (3.97)	267 (3.74)
346 (3.89)	346 (3.88)
455 (3.74)	455 (3.76)
546 (3.72)	546 (3.78)
585 (3.76)	585 (3.82)

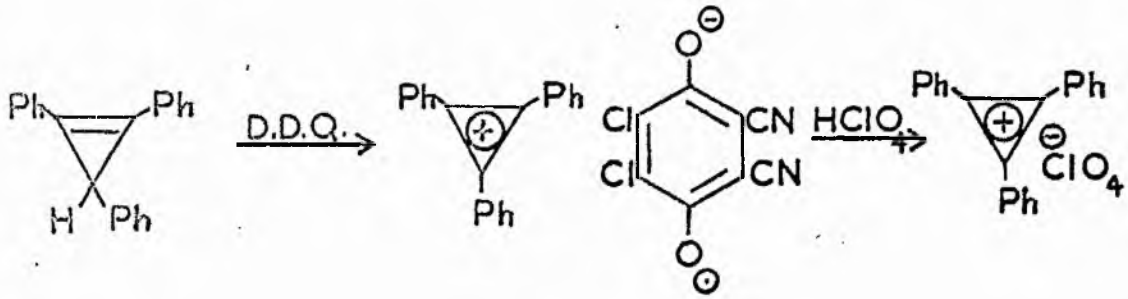
A number of ancillary reactions were carried out, (1) to investigate the catalytic effect (if any) of the

presence of light or oxygen and (2) to examine the possibility of simple salt or covalent structures (e.g. LIV, LV) for the cycloheptatriene intermediate.

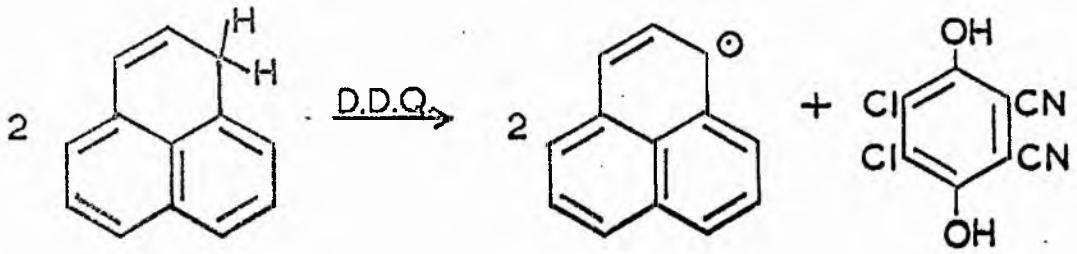
Using a modified Schlenk apparatus (see Plate 4), solutions of D.D.Q. and cycloheptatriene were mixed in a stream of nitrogen in complete darkness. The black product found on the sintered plate was proof that neither light nor oxygen are essential for this reaction. There was little reduction in yield.

An attempt to obtain the mono-potassium salt of 2,3-dichloro-5,6-dicyanoquinol was unsuccessful and instead the di-potassium salt was treated with tropylium perchlorate in aqueous ethanol (no reaction occurred in absolute ethanol as a result of the insolubility of the potassium salt.) The orange colour of the potassium salt rapidly disappeared, a fine white precipitate of potassium perchlorate formed and addition of ether yielded the quinol. In dry acetonitrile a red colour, produced initially, faded rapidly on boiling and the same products were obtained. On no occasion was the characteristic dark crimson colour of the radical-anion seen. This seems reasonable since it is unlikely that either a simple salt or covalent structure would be as intensely coloured. Such structures were therefore rejected.

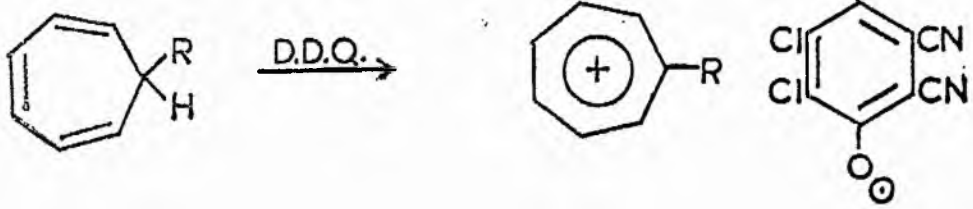




LVII LVIII



LIX



LX R = Me.
LXI R = Ph.

LXII R = Me.
LXIII R = Ph.

The chemical properties were also in agreement with a structure containing the tropylium ion and the D.D.Q. radical-anion. The presence of the former might be deduced from the high yield of tropylium salts obtained on addition of acid and the quinol by-product effectively ruled out the possibility of a simple charge-transfer complex. The stoichiometry of this reaction also requires the formation of a molecule of quinone (see LVI and LVIa equation) and, although it was not isolated, the yellow colour of the mother liquor would seem to indicate its presence.

On the basis of all the physical and chemical evidence only one structure (LVI) satisfies all the requirements.

One major problem remains, that of accounting for the hydrogen lost during the formation of the tropylium ion. Its fate is open to speculation and several possibilities exist. The transfer of an electron from cycloheptatriene to the quinone followed by spontaneous loss of a hydrogen atom could give both the tropylium and semiquinone species. The hydrogen atoms might dimerise or attack the solvent, reagents or products.

Further information concerning the course of the reaction was gained from the reactions of substituted

cycloheptatrienes (especially thate of the 7-phenylthio-derivative, see section B.IV.3).

Before passing on to discuss these derivatives it is relevant to consider the reaction of D.D.Q. with two other carbocycles, triphenylcyclopropene (LVII) and phenalene (LIX). Triphenylcyclopropene and D.D.Q. gave a purple crystalline product[19] which was shown spectrally to contain D.D.Q. as the radical-anion and which yielded triphenyl-cyclopropenylium salts (LVIII) on addition of acid. This behaviour is entirely analogous with that of cycloheptatriene, the only difference being in the size of the aromatic system involved. A somewhat different result was obtained with phenalene[19] which, when treated with D.D.Q. in either polar or non-polar solvents, gave the phenalenyl radical and quinol.

The preparation of this radical demonstrates the ability of D.D.Q. to dehydrogenate both by hydrogen atom transfer and by overall hydride transfer, the course of the reaction depending on the substrate.

2. Reaction of 7-Alkyl- and 7-Arylcycloheptatrienes with D.D.Q.

It has been shown that 7-methyl- (LX) and 7-phenylcycloheptatriene (LXI) react with quinones in the presence of perchloric acid to give the corresponding substituted tropylium perchlorate and that under the same conditions ditropyl (XXIX) yields tropylium perchlorate. In the absence of acid all three formed semiquinone salts of varying stability with D.D.Q., the derivative from 7-phenylcycloheptatriene (LXI) being the most stable and that from ditropyl (XXIX) the least.

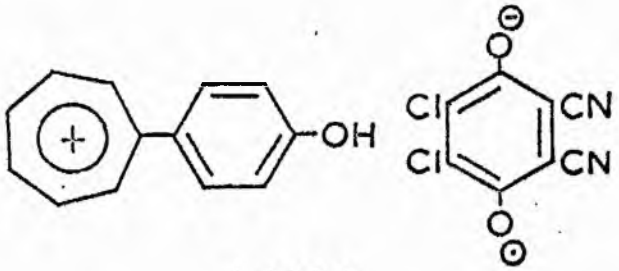
Methylcycloheptatriene and D.D.Q. in acetonitrile reacted to produce a dark crimson solution from which bronze needles separated. If allowed to stand in solution the product, methyltropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXII), decomposed rapidly and it could only be isolated in low yield by allowing the shortest possible reaction time. Decomposition also occurred in methylene chloride and the product was contaminated with quinol. Once isolated, however, this semiquinone (LXII) could be kept fairly well. Two by-products were obtained from the mother liquors, the quinol and a small quantity of yellow oil.

The latter failed to form a derivative with acidified 2,4-dinitrophenylhydrazine and showed a carbonyl absorption band at 5.85μ. Tropone (XLIV) absorbs[55] at 5.86μ and may comprise at least part of this material.

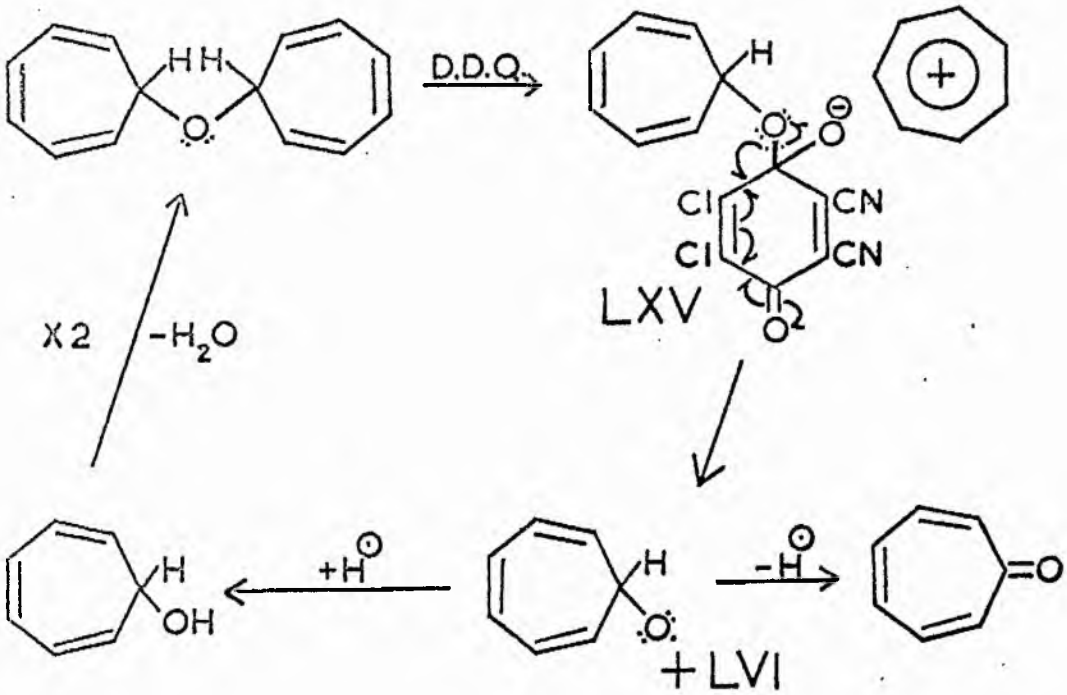
There are several possible explanations for the low yields and for the instability of the product. From a molecular model it may be seen that the hydrogen at the 7- position would, in the preferred conformation, occupy the axial position and that the hydrogens of the methyl group would thereby be more readily accessible for attack. However, it is not unreasonable to suppose the methyltropylium semiquinone (LXII) is the main product and that it undergoes further reaction in solution possibly with another molecule of quinone.

Unlike its methyl counterpart, phenyltropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXIII) is stable. This stability is not entirely unexpected since the product contains the completely aromatic phenyltropylium cation. Quinone attack must be limited to the axial hydrogen in the 7-position which is again lost, thereby resurrecting the problem of its fate.

The ready decomposition of the product from ditropyl and D.D.Q. may result from an inherent instability of the

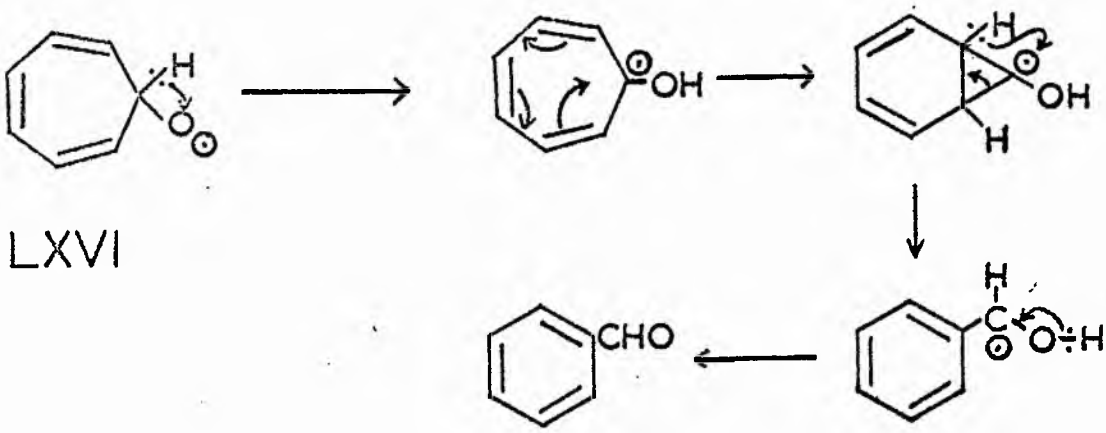


LXIV



LXVII

LXVI



LXVI

tropyl-tropylium system, if it is formed, or from reaction with a second molecule of quinone. During the formation of the methyltropylium (LXII) and phenyl-tropylium (LXIII) semiquinone derivatives, overall loss of the axial hydrogen atom in the 7- position took place. Ditropyl contains two such hydrogen atoms and both are liable to attack. The cleavage of the central carbon-carbon bond which occurs in the presence of acid might be expected in this case to give rise to the tropylium semiquinone (LVI). This was not observed.

3. Reactions of 7-Tropyl ethers and thioethers with D.D.Q.

Tropyl ethers and thioethers reacted with D.D.Q. in a somewhat different way to those substrates in which the substituent was linked to the tropyl ring by a carbon-carbon bond.

The unsuccessful attempt to prepare 7-phenoxy-cycloheptatriene had yielded one of these latter derivatives, i.e. a p-tropylated phenol (see section B.III.4.). When treated with D.D.Q. this phenol behaved as a phenyl-cycloheptatriene and afforded (p-hydroxyphenyl)tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXIV). The

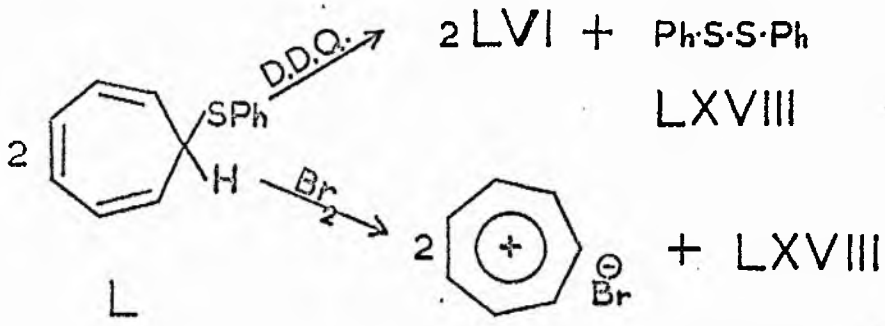
structure was confirmed by analysis and ultra-violet and visible spectra which were typical of the semiquinone salts. Here again the overall loss was a hydrogen atom, the substituent being retained.

In contrast, the product from the reaction of 7-methoxy-(XXXIII), 7-ethoxy-(XXXIV), 7-tropyloxy-(XXXV) and 7-phenylthiocycloheptatriene (L) with D.D.Q. was the same in each case namely tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LVI). The spectra (I.R., U.V. visible.) of all the derivatives were identical with that of the tropylium derivative but the melting-point of each of the methoxy-, ethoxy- and tropyloxy- derivatives was lower by ten degrees, as were mixed melting-points with the tropylium derivative. It was noted that the rate at which the melting-point block was heated had a considerable effect on the melting-point. This factor may partly explain the discrepancy.

The formation of tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LVI) from these various cycloheptatriene derivatives involves overall transfer of an electron from the cycloheptatriene to the quinone accompanied by the loss from the ring of the substituent. The fate of the latter was of interest.

By-products could not be detected in the reactions of methoxy-(XXXIII) and ethoxycycloheptatriene (XXXIV) with D.D.Q. and the yields of the tropylium semiquinone (LVI) were of the same order as those obtained from cycloheptatriene. Ditropyl ether (XXXV) afforded a higher yield of product in acetonitrile but in methylene chloride a 96% yield (based on D.D.Q.) was recorded. This suggested the possibility that both tropyl residues were being utilised and the experiment was repeated using half the quantity of ditropyl ether (XXXV). A 63% yield (based on D.D.Q.) substantiated the hypothesis. In addition a brownish oil was isolated from the mother liquors by steam-distillation. It failed to give a convincing D.N.P. derivative but from its characteristic smell of bitter almonds and from the carbonyl absorption band at 5.9μ(s) (benzaldehyde 5.91μ) must have contained some proportion of benzaldehyde. The latter is a common decomposition product of the tropyl ring[56] and was again encountered as such in later experiments.

A reaction scheme can be devised to account for the products. The first step involves the formation of the tropylium ion and an intermediate (LXV) which rapidly breaks down to give the tropylium semiquinone (LVI) and a tropyloxy



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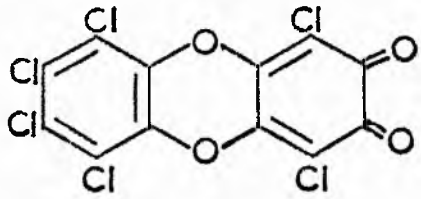
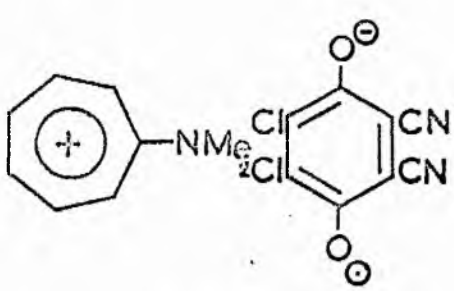
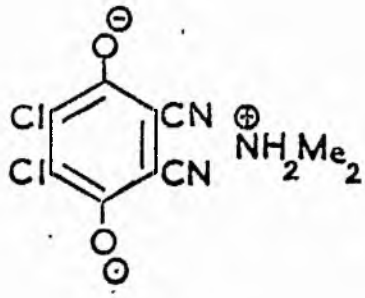


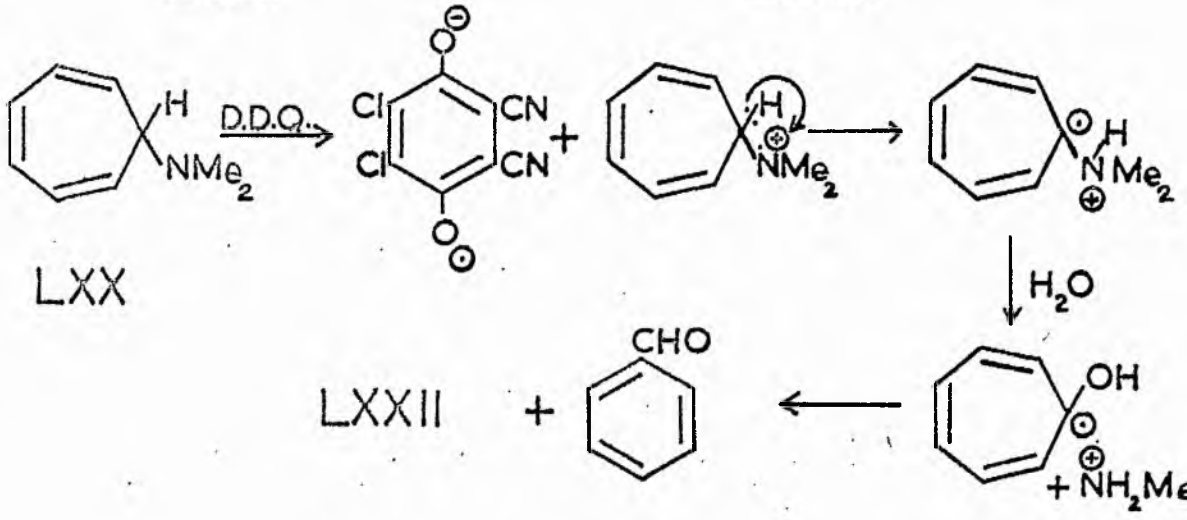
LXIX



LXXI



LXXII



LXX

LXXIII

radical (LXVI). The latter may react in one or more of the following possible ways. It may (1) dimerise, (2) abstract a hydrogen atom from the solvent or substrate, (3) break down to form benzaldehyde or (4) lose a hydrogen atom to form tropone. The extent to which any of these reactions takes place will depend upon the life-time of the radical. As there is no evidence to suggest that it would be particularly long-lived, dimerisation would appear to be unlikely. Although benzaldehyde was the only other product isolated, tropone might also be formed during the reaction. Abstraction of a hydrogen atom by the radical would give hydroxycycloheptatriene (LXVII) which is known[34a,49] to dehydrate to give ditropyl ether. The remainder of the semiquinone could be produced by the reaction of the re-formed ditropyl ether or hydroxycycloheptatriene with D.D.Q.

The mechanism of all these reactions was considerably clarified by the reaction of phenylthiocycloheptatriene (L) with D.D.Q. In addition to the tropylium semiquinone (LVI), a second product was isolated from the mother liquors. This proved to be diphenyl disulphide (LXVIII) formed by dimerisation of two phenylthio-radicals which are produced

during the course of the reaction or by the decomposition of unreacted phenylthiocycloheptatriene (L) during the work-up. Phenylthio-radicals, which are comparatively stable, have been formed photolytically from diphenyl disulphide and the unpaired electron appears to be localised mainly on the sulphur atom.[57] There is no possibility of ring-contraction and the radical must therefore dimerise or abstract a hydrogen atom to give thiophenol. To determine how much diphenyl disulphide came from unreacted phenylthiocycloheptatriene (L), parallel experiments were carried out in which samples of (L) with and without D.D.Q. were worked up separately under identical conditions. The yield of disulphide from the reaction with D.D.Q. was almost double that from the blank run. A large part of the disulphide therefore comes from the dimerisation of phenylthio-radicals formed by electrophilic attack on the substrate (L). Degani and Fochi have reported[58] that tropyl thioethers treated with bromine yielded tropylium bromide and the disulphide.

It is now convenient to discuss a general mechanism for the reaction of ethers and thioethers with D.D.Q. Here the overall loss is not of a hydrogen atom but of the

substituent as a radical. From models, it may be seen that groups bearing two lone pairs of electrons on oxygen or on sulphur appear to be more vulnerable to the electrophilic attack of the quinone. Cleavage of the tropyl-oxygen (-sulphur) bond therefore takes place probably with the immediate formation of the tropylium cation and of an intermediate of the type (LXV) which would facilitate the transfer of an electron to D.D.Q. thus affording the required semiquinone (LVI) together with a radical. If the radical is stable, dimerisation may occur, if reactive, it will probably abstract a hydrogen atom to form an alcohol (e.g. methanol) or break down as previously described.

The reaction of methoxycycloheptatriene with other quinones was also studied. With chloranil in acetonitrile a greenish-brown solution was obtained on heating but only chloranil was isolated from the mixture. A dark red colour developed with o-chloranil but on heating this faded to orange-red and orange crystals were isolated. This material proved to be a known self-condensation product (LXIX) of o-chloranil.[20]

4. Reactions of 7-Dimethylaminocycloheptatriene with quinones

(i) With D.D.Q.

The reaction of 7-dimethylaminocycloheptatriene (LXX) with D.D.Q. was examined and found to be fairly similar to the D.D.Q. reactions previously investigated. A tertiary amine was selected in order to eliminate possible attack on hydrogen directly attached to nitrogen and to present the minimum number of different centres for reaction. Dimethylaminocycloheptatriene was prepared from tropylium perchlorate using Doering's method.[49]

The ultra-violet spectrum of the amine (LXX) in acetonitrile displayed an absorption maximum at 248 mμ (log ϵ = 3.59) and a minimum at 220 mμ (log ϵ = 3.26). These bands lie in the same region but at slightly lower wavelengths than those known to be characteristic of cycloheptatriene derivatives substituted at position 7. The extinction coefficients are also of the same order (see Table 6). It will be noted that when the phenyl substituent in phenylcycloheptatriene is moved from position 7 to position 3 there is a considerable bathochromic shift. An even greater shift was recorded for a material which consisted mainly of 1-phenylcycloheptatriene[36b] (see table 6.).

Table 6

Ultra-violet Absorption Spectra of Cycloheptatriene Derivatives

	Solvent	λ_{max} mμ(log ε)	λ_{min} mμ(log ε)	Ref.
Tropylacetic acid	-	258 (3.56)	225 (2.94)	49b
Tropylacetonitrile	-	258 (3.57)	226 (3.10)	49b
Ditropyl	iso-octane	255 (3.85)	227 (2.82)	49a
7-cyanocyclo-heptatriene	ethanol	255 (3.57)	218 (2.09)	49a
7-methoxycyclo-heptatriene	pentane	256 (3.54)	-	41
7-phenylcyclo-heptatriene	iso-octane	258 (3.53)	-	36b
3-phenylcyclo-heptatriene (92%)	"	283 (3.94)	231 (4.15)	36b
1-phenylcyclo-heptatriene (63%)†	"	295 (3.90)	234 (4.18)	36b

† remainder mainly 3-phenylcycloheptatriene.

It therefore seems reasonable to assume that the dimethylamino- group is present in the 7- position.

The reaction with D.D.Q. could follow several possible courses:

(1) the loss of a hydride ion from position 7 could give dimethylaminotropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXXI).

(2) the loss of the dimethylamino group could give the unsubstituted tropylium semiquinone (LVI). (cf. phenylthiocycloheptatriene)

(3) formation of a simple charge-transfer complex could occur (cf. ref.59 dimethylaniline with quinones)

(4) attack on the readily available lone pair of electrons on the nitrogen might occur followed by break down of the seven-membered ring.

In appearance, this reaction was similar to the other reactions of D.D.Q. with tropyl derivatives. A crimson colour developed immediately and after a short period dark brown crystals were deposited. The ultra-violet-visible absorption spectrum of this material contained all the bands characteristic of the semiquinone species but lacked notably the band at 221 mμ associated with the tropylium ion. Analysis indicated that the product contained considerably less carbon than that required for dimethylaminotropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXXI) and the cation appeared to be the dimethylammonium ion. This was

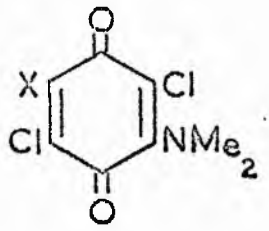
confirmed by the isolation of dimethylammonium picrate and perchlorate from the product when treated with picric or perchloric acid respectively. Benzaldehyde was isolated from the mother liquors by steam distillation and estimated as the 2,4-dinitrophenylhydrazone derivative. This explained the disappearance of the tropyl residue and accounted for 41% of the degraded seven-membered ring.

In an attempt to estimate the semiquinone present, an acetonitrile solution of the salt, dimethylammonium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXXII), was treated under standard conditions with an excess of solid sodium iodide and warmed to boiling. When cold, the liberated iodine was estimated with thiosulphate solution but only widely varying results were obtained. It was later found that sodium 2,3-dichloro-5,6-dicyano-1,4-semiquinone could be prepared from the reaction between sodium iodide and D.D.Q.

Further proof of the correctness of the structure (LXXII) was derived from the absorption spectrum of a solution containing equivalent quantities of the dimethylammonium derivative and tropylium perchlorate. If the proposed structure were correct then any absorption of this solution

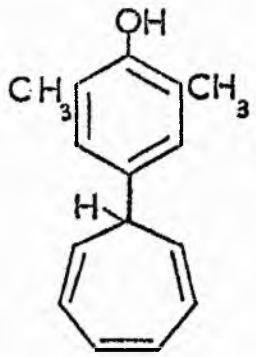
in the ultra-violet and visible regions would be due to tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone. Equivalent volumes of standard solutions of the dimethylammonium derivative and tropylium perchlorate were mixed and diluted to a suitable known concentration. The spectrum of this solution was identical with that from the tropylium semiquinone derivative (LVI) thus providing additional evidence for the dimethylammonium semiquinone structure.

A problem of this reaction is to account for the formation of the dimethylammonium ion from the dimethylamino-group. It is unlikely that the first step involves any cleavage of the tropyl-amine bond since this would probably result in the formation of the tropylium semiquinone (LVI). It is also unlikely that the dimethylaminotropylium ion is formed first by overall loss of a hydride ion since this ion was later produced by a different method (see section B.V) and was found to be stable under the conditions of this reaction. Therefore the first step probably involves one-electron transfer from the lone electron-pair on the nitrogen atom to the quinone. This was supported by later work on the reaction between D.D.Q. and tertiary amines (see section B.VI).

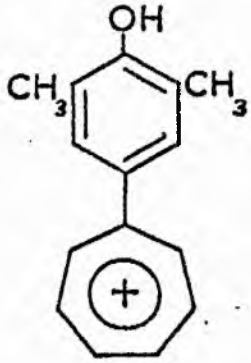


LXXIV X = NMe_2.

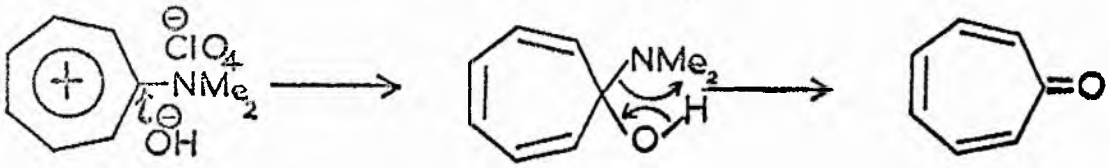
LXXV X = Cl.



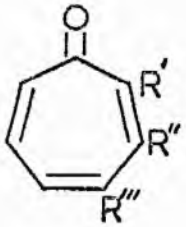
LXXVI



LXXVII



LXXVIII

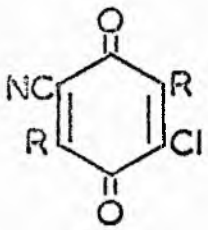


LXXIX

a. R′ = NMe_2, R″ = R‴ = H.

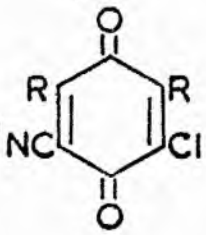
b. R″ = NMe_2, R′ = R‴ = H.

c. R‴ = NMe_2, R′ = R″ = H.

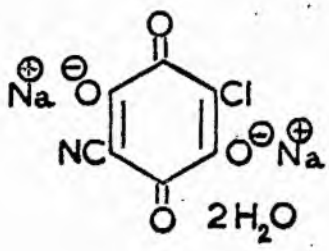


LXXXIV

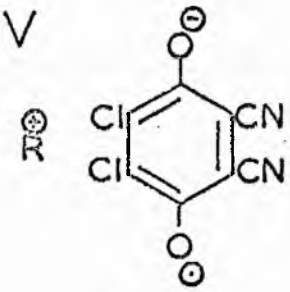
R = -NH·CH_2·Ph



LXXXV



LXXXVIII



LXXXVI a $R^{\oplus}$ = $PhCH_2\overset{\oplus}{N}Me_2$.

b $R^{\oplus}$ = $PhCH=\overset{\oplus}{N}Me_2$.

LXXXIX a $R^{\oplus}$ = $CH=\overset{\oplus}{N}Me_2$.

b $R^{\oplus}$ = $CH_3\cdot\overset{\oplus}{N}Me_2$.

Transfer of hydrogen from position 7 to the nitrogen followed by addition of water across the carbon-nitrogen bond would result in the formation of the dimethylammonium cation and the hydroxycycloheptatriene radical (LXXIII), the latter decomposing to benzaldehyde as shown in the case of ditropyl ether.

(ii) With Chloranil

The reaction of 7-dimethylaminocycloheptatriene (LXX) with chloranil in acetonitrile was also studied. It was found to be fairly complex and only low yields of a variety of products were isolated.

The first product 2,5-bis(N-dimethylamino)-3,6-dichloroquinone (LXXIV), was filtered from the reaction mixture. It was probably formed by nucleophilic displacement of two of the quinone chlorine atoms. The mother liquors were divided into two parts and benzaldehyde obtained by steam-distillation of one part (estimated as before as the D.N.P. derivative). The yield was low (11%) and a considerable tarry residue remained in the distillation flask.

The other portion of the mother liquors was allowed to stand for three days during which time colourless crystals,

soluble in ethanol, dilute acid and dilute alkali but only sparingly in ether, were deposited. These were too deliquescent to allow analysis to be carried out. The amphoteric properties suggest that the product(s) may be a dimethylamino quinol. The only other product to be characterised was tetrachloroquinol, obtained by alkali extraction of the second portion of the mother liquors.

The acetonitrile mother liquors afforded some reddish-brown oil which was analysed by thin-layer chromatography. One of the several spots which separated was identified as the brown quinone (LXXIV) previously obtained and another, which was purple in colour, may be 2-dimethylamino-3,5,6-trichloro-1,4-benzoquinone (LXXV).[61]

It is relevant to discuss here the reactions between o-and p-chloranil and aqueous dimethylamine in acetonitrile. With p-chloranil the solution turned dark purple and brown needles of the quinone (LXXIV) separated. After evaporating the solvent and chromatographing the residue on a column of activated alumina the purple quinone (LXXV)[61] was also obtained (see above).

In the reaction between o-chloranil and dimethylamine the solution turned dark red and black needles were deposited.

Two dimethylamino groups had again displaced two chlorine atoms and the main product was a bis-(dimethylamino)-dichloro-o-benzoquinone. The disposition of the groups was not, however, determined.

B.V. Tropylium Perchlorate as a hydride abstractor

A number of reactions have already been described (see section A.III.2.) in which the tropylium ion accepts a hydride ion[62-66]. As the former is a comparatively weak acceptor this reaction can only take place when the substrate yielding the hydride ion is a particularly good donor. Many of the donors were themselves tropyl derivatives and they included deuterocycloheptatriene[66], ditropyl ether[62-65] and 2,6-dimethyl-4-(7-tropyl)phenol (LXXVI)[47], the main product from (LXXVI) being the tropylium salt (LXXVII). This method therefore appeared to provide a route to substituted tropylium salts and the reactions of several cycloheptatriene derivatives with tropylium perchlorate were studied. Success, however, was limited and dimethylaminotropylium perchlorate (LXXVIII) was the only new salt obtained, produced by the reaction of tropylium perchlorate on dimethylaminocycloheptatriene (LXX) in acetonitrile.

Methoxy-, phenylthio- and cyanocycloheptatriene, treated in a similar way, gave orange solutions of varying intensity but no new product was formed and in each case tropylium perchlorate was recovered almost quantitatively.

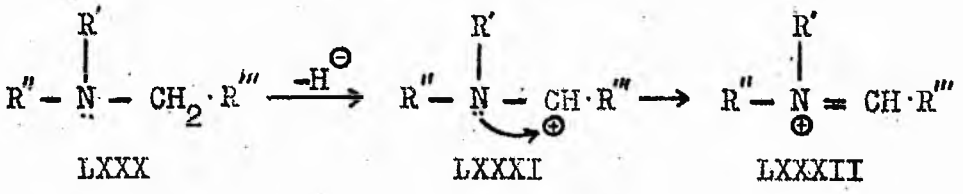
The colours may result from some decomposition of the substrates owing to the presence of traces of perchloric acid in the perchlorate.

It was hoped that treatment of dimethylaminotropylium perchlorate (LXXVIII) with base would yield tropone as the only product. The initial step was visualised as an attack by the hydroxide ion at the carbon bearing the substituent, this being followed by transfer of the hydroxyl hydrogen to nitrogen and loss of the dimethylamino group as dimethylamine. Several products, however, were formed in approximately equal amounts. The dropwise addition of dilute alkali to an ethanolic solution of the perchlorate (LXXVIII) produced an intense yellow colour which gradually turned to dark red as more alkali was added. Chromatography of the mixture on a column of activated alumina yielded three yellow and four red components. Three of these may be the isomeric dimethylaminotropones (LXXIX a, b and c) formed by hydroxyl attack at all the possible ring positions but their small quantity precluded further examination. The same result was obtained using milder bases.

B.VI. Reaction of D.D.Q. with tertiary amines.

1. Reaction of D.D.Q. with dimethylbenzylamine.

The possible dehydrogenation of tertiary amines using D.D.Q. as a hydride acceptor was examined as an alternative to the Hofmann degradation. Removal of a hydride ion from the methylene group of the tertiary amine (LXXX) would give rise to an immonium salt (LXXXII) as depicted via the intermediate (LXXXI). This in turn would undergo alkaline cleavage to give a secondary amine and an aldehyde.



LXXX LXXXI LXXXII

An alternative to this would be the formation of a charge-transfer type of complex similar to those formed by some tertiary amines and chloranil[67].

N,N-Dimethylbenzylamine (LXXXIII) was chosen as a suitable substrate for several reasons, 1) its behaviour would provide an interesting comparison with that of the isomeric dimethylaminocycloheptatriene, 2) it presented a limited number of different centres for attack, 3) the products from hydride transfer and alkaline cleavage would be easily isolated and characterised.

Before carrying out the reaction with N,N-dimethylbenzylamine, benzylamine itself was treated with D.D.Q. in acetonitrile. The product, tangerine-coloured needles, displayed a quinone carbonyl and a nitrile band in its infra-red spectrum. The analytical data indicated that one chlorine group and one nitrile group had been replaced by N-benzylamino groups which allows two possible structures (LXXXIV) and (LXXXV). Buu-Hoï[68] showed that in the reaction of primary and secondary amines with chloranil replacement took place at both 2- and 5- positions. The preferred structure is therefore 2,5-bis (N-benzylamino)-3-chloro-6-cyano-1, 4-benzoquinone (LXXXIV).

Henbest[61], studying the reaction of tertiary amines with chloranil, found that prolonged refluxing of the latter with dimethylbenzylamine (LXXXIII) in benzene gave benzaldehyde (26%), a large part of the quinone being recovered. Benzaldehyde was also obtained in the reaction of dimethylbenzylamine with D.D.Q. in acetonitrile but in much lower yield (7%). This reaction was exothermic, the solution turning chocolate brown then dark red before depositing a black crystalline solid. The benzaldehyde was isolated and estimated as in previous experiments. The ultra-violet and visible spectra of the product were very similar to those of the semiquinone

derivatives of D.D.Q. and on the basis of spectral and analytical evidence two structures could be put forward (LXXXVI a and b).

The formation of LXXXVIb by loss of a hydride ion from the α-carbon atom would be analogous to the production of benzylidene-dibenzylimmonium fluoroborate (LXXXVII) by the reaction of triphenylmethyl fluoroborate on tribenzylamine[10a]

$$Ph\ CH = \overset{\oplus}{N}(CH_2\ Ph)_2\ \overset{\ominus}{BF_4}$$

LXXXVII

(see section A.III.2.). A product with such a structure, however, might be expected to show an absorption band in the ultra-violet region characteristic of the conjugated immonium group and also to react with alkali to give dimethylamine and benzaldehyde. Several reactions were carried out under various alkaline conditions and attempts were made to isolate any amine and aldehyde liberated. Dimethylammonium picrate was obtained in low yield by bubbling the volatile products from the reaction of alkali on the black product into an ethanolic solution of picric acid. A dark red water-soluble crystalline solid remained in the reaction flask. Insoluble in most organic solvents, its composition C_7ClNO_4, $Na2H_2O$

suggested 2-chloro-5-cyano-3,6-dihydroxy-1,4-benzoquinone disodium salt dihydrate (LXXXVIII) as a probable structure. The location of the two hydroxyl groups was not confirmed but the case is analogous to that of chloranil which reacts with alkali to yield 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone[69].

Steam distillation of the alkaline solution of the semiquinone from dimethylbenzylamine gave yields of 7-8% of benzaldehyde. These yields were unaffected by the introduction of various reducing agents, e.g. sodium bisulphite, dithionite or sulphide to eliminate possible oxidation by the semiquinone radical anion.

Chemical and spectral evidence therefore suggest that dimethylbenzylamine 2,3-dichloro-5,6-dicyano-1,4-benzosemiquinone (LXXXVIa) formed by partial or complete transfer of an electron from the amine to the quinone, is the most likely structure for this product. This was confirmed by a study of the reaction between D.D.Q. and trimethylamine.

2. Reaction of D.D.Q. with trimethylamine.

By virtue of the equivalence of all the trimethylamine hydrogens the number of possible products from the reaction with D.D.Q. is reduced to a minimum. Removal of any hydride ion from the amine would yield the dimethylimmonium ion which would

cleave on treatment with alkali to give formaldehyde and dimethylamine. If, however, the process involves partial or complete electron transfer as described for dimethylbenzylamine then we should obtain trimethylamine 2,3-dichloro-5,6-dicyano-1,4-semiquinone (LXXXIXb).

The product, black crystals, with an ultra-violet-visible absorption spectrum almost identical to that of the semiquinone from dimethylbenzylamine LXXXVIa, was added to a hot ethanolic solution of picric acid and trimethylammonium picrate crystallised from the cold solution. In order to confirm the structure of this picrate, dilute alkali was added and the liberated amine passed into fresh picric acid. The precipitated product was identical to the starting material. This evidence confirms the trimethylamine structure (LXXXIXb) at the same time eliminating the possibility of a dimethylimmonium salt (LXXXIXa).

Horner and Spietschka[70] have studied the reaction between o-chloranil and trimethylamine and it provides an interesting comparison.

The product, a brown precipitate, was obtained from a dark red solution and was found to contain a 1:1 proportion of the original reactants. When treated with alkali it afforded

trimethylamine and with steam gave formaldehyde and a precipitate, the filtrate from which afforded dimethylamine and trimethylamine hydrochlorides. No conclusion was drawn as to the final structure of the brown material but it is probably similar to that of its D.D.Q. counterpart.

These derivatives of D.D.Q. with tertiary amines which involve total or partial electron transfer might be expected to display an e.s.r. signal as did tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone. In fact the trimethylamine semiquinone did give a signal (see Plate 5) which consisted of only a single line. There appears to be no satisfactory explanation of this spectrum since other e.s.r. spectra attributable to the trimethylamine cation-radical contain 30 lines in three groups of ten lines[71] and also the spectrum of the D.D.Q. semiquinone ion obtained previously contained five lines.

Triethylamine has been found to behave in an exactly similar way to trimethylamine forming triethylamine 2,3-dichloro-5,6-dicyano-1,4-semiquinone.[72]

B.VII. The Spectra of the 2,3-dichloro-5,6-dicyano-1,4-benzosemiquinones

The ultra-violet and visible spectra of these semiquinone derivatives all show the same general pattern (see plates 1 and 2), the absorption in the visible region being almost entirely due to the semiquinone radical-anion. A number of minor differences may be noted in the ultraviolet region, (1) band I (221 mμ) is only associated with the tropylium derivatives, (2) band II is absent from the (p-hydroxyphenyl)tropylium derivative (LXIV) which also shows strong absorption at 432 mμ due to the ion (LXIV).[43]

Table 7

Spectra of Semiquinone Derivatives

Ultraviolet (mμ (log ε))

Cation	I	II	III	IV
1. tropylium	221 (4.65)	246 (4.22)	255 (4.17)	270 (3.97)
2. tropylium[a]	221	246	254	270
3. tropylium[b]	221	246	255	268
4. tropylium[c]	223	245	255	270
5. tropylium[d]	222 (4.52)	248 (4.12)	255	265 (3.98)
6.(p(OH)phenyl)tropylium	229 (4.53)	-	255	267 (4.12)
7. dimethylammonium	-	249 (4.20)	257	268 (4.16)
8. dimethylbenzylamine	-	246 (4.19)	255	268 (3.66)
9. trimethylamine	-	246 (4.19)	254	268 (3.68)
10. sodium	-	246 (4.24)	256*(4.15)	267 (3.74)
11. ferricenium	-	248 (4.43)	-	270*

* shoulder. For explanation of superscripts see over

Table 7 (contd.)

Visible (mμ (log ∈))

Cation	I	II	III	IV
1. tropylium	346 (3.89)	453 (3.74)	545 (3.72)	581 (3.76)
2. tropylium[a]	346	456	544	585
3. tropylium[b]	346	452	545	583
4. tropylium[c]	347 (3.85)	456 (3.68)	546 (3.66)	585 (3.70)
5. tropylium[d]	346 (3.89)	454 (3.43)	542 (3.30)	581 (3.45)
6.(p(OH)phenyl)tropylium	345 (3.96)	432 (4.26)	542 (3.71)	580 (3.70)
7. dimethylammonium	347 (3.77)	454 (3.63)	542 (3.62)	581 (3.65)
8. dimethylbenzylamine	346 (3.89)	453 (3.78)	542 (3.77)	585 (3.79)
9. trimethylamine	347 (3.88)	458 (3.77)	545 (3.75)	585 (3.79)
10. sodium	346 (3.88)	455 (3.76)	546 (3.78)	585 (3.82)
11. ferricenium	346 (3.84)	457 (3.69)	546 (3.68)	585 (3.72)

[a] ex methoxycycloheptatriene, [b] ex ditropyl ether,

[c] ex phenylthiocycloheptatriene, [d] from equivalent quantities of the dimethylammonium semiquinone (7.) and tropylium perchlorate.

and (3) band III (256 mμ) is absent from the ferrocene derivative which absorbs strongly at 248 mμ. In this last case the absorption is affected by the absorption of the ferricenium ion at 253 mμ (log ∈ = 4.12)[73].

In the infra-red spectra there are considerable differences between the spectrum of the product and the superimposed spectra of the components (see Spectra 1-5). This is due to the formation of

the semiquinone species[50]. Matsunaga, studying similar derivatives, noted a difference in the wavelength of the carbonyl absorption band from 6.0μ in the quinone to 6.4μ in the semiquinone and also that the absorption band of the nitrile group (4.5μ) is very much stronger in the semiquinone than in the quinone. He concluded that the electron was completely transferred and that these "complexes" were of the dative type.[74]

The infra-red spectra of all the semiquinone derivatives examined during the course of this work were found to contain similar features.

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----- EXPERIMENTAL SECTION -----

Notes

Infra-red spectral measurements were carried out on a Grubb-Parsons G.S.2A Double Beam instrument and also on a Perkin Elmer Infracord Model 137. Ultraviolet and visible spectra were measured on "Unicam" SP 700 and SP 600 instruments and unless otherwise stated the solvent was acetonitrile.

Micro-analyses were conducted by Drs. Weiler and Strauss, Oxford.

Melting-points were determined on a Kofler-type heating stage and are corrected; boiling-points are uncorrected.

Unless where otherwise stated "Analar" grade glacial acetic acid and perchloric acid (72% $^{w}/_{w}$) were used. Acetonitrile, commercial grade, was purified by distillation from phosphorus pentoxide followed by redistillation through a Claisen-Vigreux column.

Activated alumina used for column chromatography was Spence Grade H (100-200 mesh) and thin layer chromatography plates were made by Stahl's method (E.Stahl, Chemiker Zeitung, 1958, 82, 323) using equipment supplied by C. Desaga. G. m.b. H.Heidelberg.

The terms light petroleum and petroleum ether refer to those solvents commonly designated as petroleum ether (b.p. 40-60°) and petroleum ether (b.p. 60-80°). Standard hexane consists of approximately 70% n-hexane, the remainder being isomeric methylpentanes.

C.I. Dehydrogenation of hydroaromatic heterocycles using the Triphenylmethyl carbonium ion

1. Preparation of Triphenylmethyl Perchlorate.

Triphenylmethyl perchlorate was obtained by a method similar to that of Hofmann and Kirmreuther[3] by the addition of an acetic acid solution of perchloric acid to a solution of triphenyl carbinol[1,2] in an acetic acid, acetic anhydride mixture. The product, orange-brown prisms with a violet reflex, was stored in a desiccator away from light. Yields of up to 90% were recorded.

2. Dehydrogenation of Benzo[f]thiachroman-4-one.

Benzo[f]thiachroman-4-one was prepared by the method of Krollpfeifer and Schultze[4] from β-[naphthalene-2-thio]propionic acid using concentrated sulphuric acid. The product was recrystallised from petroleum ether as pale yellow needles (m.p. 68-69°; lit.[4] 68-69°).

(i) 4-Hydroxy-1-thianaphtho[2,1,b]pyrylium perchlorate.

Triphenylmethyl perchlorate (1.715 g.; 5 m.mole) was added to a solution of benzo[f]thiachroman-4-one (1.12 g.; 5 m.mole) in acetic acid (35 ml.); the mixture brought to the

boil and heated under reflux for twenty minutes. The colour, initially dark red, decreased in intensity on boiling and finally became reddish-orange. On cooling, orange crystals of the crude perchlorate salt separated and were collected. After washing with a little anhydrous ether the product was recrystallised from a mixture (5:1) of glacial acetic acid and acetonitrile containing one drop of perchloric acid. Pure 4-hydroxy-1-thianaphtho-[2,1,b]pyrylium perchlorate (1.38 g.; 88%) was obtained as orange plates (m.p. 230-232° dec.). Further recrystallisation, with charcoal, affected neither the colour nor the melting-point of the material, a sample of which was dried for 8 hours at 80°/0.5 mm. prior to analysis.

Analysis.

S.A. 1235	Found	C	49.97	H	3.41	S	9.42%
$C_{13}H_9ClO_5S$	requires	C	49.91	H	2.90	S	10.25%

The acetic acid mother liquors containing triphenylmethane, uncrystallised perchlorate and any unreacted ketone were poured into water (200 ml.), neutralised with concentrated ammonia and extracted with benzene (2 x 150 ml.). The benzene extracts were washed with water, dried (Na_2SO_4), filtered and extracted with concentrated

sulphuric acid (4 x 75 ml.). The sulphuric acid extracts were poured slowly into water (1½ l.), extracted with ether (3 x 500 ml.) and the ethereal extracts washed thoroughly with water, dried and evaporated. The product, unreacted benzo[f]thiachroman-4-one (114 mg.), crystallised from petroleum ether as yellow prisms (m.p. 69-70°).

The benzene solution was washed with water, saturated sodium bicarbonate solution and water and dried (K_2CO_3). Evaporation of the solvent and recrystallisation of the product from light petroleum gave triphenylmethane (960 mg.; 79%) as colourless prisms (m.p. 92-93°; lit.[5] 92.5-93°). Triphenylmethane was also isolated by chromatography on a column of activated alumina eluting with petroleum ether.

(ii) Benzo[f]thiachrom-4-one.

An ether suspension of 4-hydroxy-1-thianaphtho[2,1,b] pyrylium perchlorate (624 mg.; 2 m.mole.) was shaken up with two volumes (each 30 ml.) of a mixture (1:1) of concentrated ammonia (Sp.Gr.= 0.88) and water. The ether layer was separated, washed thoroughly with water and dried (Na_2SO_4). Evaporation of the solvent and recrystallisation from light petroleum (25 ml.) yielded benzo[f]thiachrom-4-one (377 mg.; 89%) as pale cream-coloured prisms (m.p. 116-117° ; lit.[49]

116-117.5°). A sample was dried for 8 hours at 80°/0.5 mm. prior to analysis.

Analysis

S.A. 1239	Found	C	73.55	H 4.05%
$C_{13}H_8OS$	requires	C	73.56	H 3.80%

3. Dehydration-dehydrogenation of Benzo[f]thiachroman-4-ol.

(i) Benzo[f]thiachroman-4-ol.

A solution of benzo[f]thiachroman-4-one (2.14 g.; 10 m.mole) in anhydrous ether (100 ml.) was added dropwise over a period of thirty minutes to a stirred suspension of lithium aluminium hydride (200 mg.; 2.5 m.mole + 100% excess.) in anhydrous ether (50 ml.). When the addition was complete the mixture was boiled under reflux for half an hour then allowed to cool. The cold contents of the flask were poured onto a mixture of crushed ice (150 g.) and 2N sulphuric acid (50 ml.) and the ether layer separated. The water layer was re-extracted with several volumes of fresh ether and the combined ether extracts washed with water, 5% sodium bicarbonate solution and water and dried (Na_2SO_4). Evaporation of the solvent and recrystallisation of the oily product from a mixture (2:1) of benzene and light petroleum gave benzo[f]-

thiachroman-4-ol (1.88 g.; 87%) as small colourless prisms (m.p. 127-128°). An analytical sample was dried for 8 hours at 80°/0.5 mm before analysis.

Analysis

S.A. 1240	Found	C	71.95	H	5.47%
$C_{13}H_{12}OS$	requires	C	72.19	H	5.59%

(ii) 1-Thianaphtho[2,1,b]pyrylium perchlorate.

Experiment 1.

Triphenylmethyl perchlorate (860 mg.; 2.3 m.mole) was added to a solution of benzo[f]thiachroman-4-ol (504 mg.; 2.3 m.mole) in acetic acid (17 ml.) containing one drop of perchloric acid. The solution, initially colourless, rapidly became dark red. After boiling under reflux for twenty minutes and cooling thoroughly, fine khaki platelets were deposited. Recrystallisation from acetic acid, with charcoal, and one drop of perchloric acid, yielded 1-thianaphtho[2,1,b]pyrylium perchlorate (560 mg.; 85%) as dark yellow platelets (m.p. 210-214°), λ_{max} 433 mμ ($\log \epsilon = 3.82$); lit.[6] λ_{max} 428 mμ ($\log \epsilon = 3.84$).

Experiment 2

The experiment was repeated reducing the boiling period to five minutes and in the absence of perchloric acid.

Yellow needles (m.p. 210-212°; lit.[6] 208-210°.) were obtained from an orange solution. Recrystallisation, as before, gave yellow platelets (670 mg.; 95%) with the same melting-point. Before analysis a sample was dried for 8 hours at 80°/0.5 mm.

Analysis

S.A. 1241	Found	C 51.81	H 2.94	S 11.43	Cl 12.50%
$C_{13}H_9ClO_4S$	requires	C 52.61	H 3.06	S 10.80	Cl 11.95%

4. Dehydrogenation of 2-thiachroman-4-one.

S-Benzylthioacetic acid[7] was prepared from monochloroacetic acid and toluene-ω-thiol. Cyclisation was effected using phosphorus pentoxide[8] to give 2-thiachroman-4-one as colourless plates (m.p. 55-57° ; lit.[8] 59-60°) from light petroleum.

(i) 4-Hydroxy-2-thiabenzo[e]pyrylium perchlorate.

Triphenylmethyl perchlorate (686 mg.; 2 m.mole) and 2-thiachroman-4-one (328 mg.; 2 m.mole) in acetic acid (10 ml.) were warmed gently to boiling and boiled for two minutes. The solution gradually became dark reddish-brown then slowly turned green and, on cooling, green plates (399 mg.; 75%) separated. 4-Hydroxy-2-thiabenzo[e]pyrylium perchlorate was recrystallised (with charcoal) from acetic acid as pale green plates which, on a block preheated to 165°, melted slowly over a range, resolidified

and melted sharply 176.5 - 177.5° (dec.). After drying for 3 hours at 50°/0.5 mm. a specimen was analysed.

Analysis

S.A. 1505 Found C 40.61 H 2.91 S 11.45%

$C_9H_7O_5SCl$ requires C 41.15 H 2.69 S 13.50%

I.R. (nujol) μ. 2.91 (broad) -OH, 9.1-9.3 (broad)-perchlorate anion.

5. Dehydration-dehydrogenation of 2-thiachroman-4-ol.

2-Thiachroman-4-ol was prepared by reduction of 2-thiachroman-4-one with lithium aluminium hydride.[9] The crude product was sublimed under vacuo to give a colourless solid which recrystallised from petroleum ether (b.p. 80-100°) as colourless plates of the required alcohol (m.p. 51.5 - 52.5° ; lit.[9] 50°.).

Triphenylmethyl perchlorate (343 mg.; 1 m.mole) and 2-thiachroman-4-ol (166 mg.; 1 m.mole) in acetic acid (10 ml.) were boiled for two minutes. The colour changed rapidly from dark red to dark green but on cooling no solid separated. Addition of anhydrous ether precipitated a dark green oil which failed to crystallise. Attempts to obtain a solid product by crystallisation of the oil from various solvents, with or without charcoal, were unsuccessful.

Other attempts to obtain a solid product included (a) mixing hot acetic acid solutions of the reactants and allowing to cool and (b) adding a hot solution of triphenylmethyl perchlorate to a cold solution of the alcohol. The isolation of triphenylmethane provided the only proof of reaction.

The mother liquors were poured into water and extracted with ether. After working up, the resultant oil was chromatographed on a column of activated alumina using light petroleum. Evaporation of the first fraction (500 ml.) to small bulk allowed the triphenylmethane (186 mg.; 75%) to crystallise as colourless spars. (m.p. and mixed m.p. 90-91°).

The isolation of 2-thiabenzo[e]pyrylium perchlorate by a method involving triphenylmethyl perchlorate has since been reported.[10]

6. Dehydrogenation of 5,6-dihydro-5-methylphenanthridine.

(i) Preparation and reduction of 5-methylphenanthridinium perchlorate.

5-Methylphenanthridinium sulphate[11] (3.22 g.) was dissolved in acetic acid (20 ml.) and treated with perchloric acid (1.2 ml.). The solution was boiled for fifteen seconds and on cooling colourless crystals precipitated. Recrystallisation

from acetic acid gave 5-methylphenanthridinium perchlorate (2.92 g.; 92%) as needles (m.p. 192 - 194° ; block preheated to 180°.). A sample was dried for 8 hours at 80°/0.5 mm. prior to analysis.

Analysis

S.A. 1316	Found	N	4.46%
$C_{14}H_{12}ClNO_4$	requires	N	4.77%

5,6-Dihydro-5-methylphenanthridine was obtained as colourless needles (m.p. 47-48°; lit.[12] 48°) in 85% yield by the reduction of 5-methylphenanthridinium perchlorate using lithium aluminium hydride.[12]

(ii) Dehydrogenation with triphenylmethyl perchlorate.

Triphenylmethyl perchlorate (699 mg.; 2 m.mole.) was added to a solution of 5,6-dihydro-5-methylphenanthridine (390 mg.; 2 m.mole) in acetic acid (10 ml.). In the cold, the initial brown colour faded quite rapidly to yellow. The mixture was boiled for about thirty seconds and on cooling the perchlorate salt separated. Anhydrous ether (30 ml.) was added and the product filtered off. Recrystallisation from acetic acid gave 5-methylphenanthridinium perchlorate (553 mg.; 94%) as needle aggregates (m.p. 192-194°; block preheated to 180°.).

7. Dehydrogenation of 5,6-dihydro-5,6-dimethylphenanthridine

(i) 5,6-Dihydro-5,6-dimethylphenanthridine.

Methyl iodide (3.15 g.; 1.4 ml.) was added in ½ ml. portions to pure magnesium turnings (620 mg.) in dry ether (50 ml.). After the initial effervescence had died down, the mixture was gently heated on a water bath (about 40°) until the reaction was complete. The flask was cooled to room temperature, the stirrer started and solid 5-methylphenanthridinium perchlorate (2.5 g.) added slowly. There was a vigorous effervescence and the solution turned pale yellow. When all the perchlorate had been added, stirring was continued for a further ten minutes and the flask warmed on a water bath (about 40°) - an oily layer separated. Water was added dropwise, the mixture effervesced and a solid precipitated. After the addition of a few more mls. of water and 20% hydrochloric acid (30 ml.) stirring was continued, allowing all the solid to dissolve. Ammonium chloride (2 g.) was added and the solution made slightly alkaline by the addition of dilute ammonia. The ether layer was separated and the aqueous layer extracted with fresh ether (3 x 100 ml.). The combined extracts were washed with water, dried (K_2CO_3) and evaporated to leave a green solid

(2.29 g.). Recrystallisation from ethanol, with charcoal, gave colourless, hexagonal prisms (m.p. 63.5-64.5°) of 5,6-dihydro-5,6-dimethylphenanthridine. The best yield (65%) was obtained when the crude product was sublimed (110°/0.5 mm.) before recrystallising.

A sample was dried for 4 hours at 40°/0.5 mm. prior to analysis.

Analysis

S.A. 1326	Found	C 85.76	H 7.09	N 7.04%
$C_{15}H_{15}N$	requires	C 86.08	H 7.22	N 6.69%

(ii) Dehydrogenation with triphenylmethyl perchlorate.

Triphenylmethyl perchlorate (686 mg.; 2 m.mole) was added to a solution of 5,6-dihydro-5,6-dimethylphenanthridine (418 mg.; 2m.mole) in acetic acid (15 ml.). The mixture was boiled for about one minute and became orange-brown, orange, then almost colourless. Yellow needles crystallised from the cold solution and were filtered off after adding anhydrous ether (45 ml.). Recrystallisation from a mixture (1:1) of acetic acid and acetonitrile gave 5,6-dimethylphenanthridinium perchlorate (544 mg.; 89%) as cream-coloured needles (m.p.302° (dec) ; block preheated to 295°). A sample dried for 8 hours at 90°/0.5 mm. was analysed.

Analysis

S.A. 1325	Found	N	4.94%
$C_{15}H_{14}ClNO_4$	requires	N	4.55%

8. Dehydrogenation of 2,3-dihydro-2,3-dimethylbenzothiazole.

(i) 2,3-Dihydro-2,3-dimethylbenzothiazole.

A solution-suspension of 2,3-dimethylbenzothiazolium perchlorate (5.27.; 20 m.mole) in hot methanol (80 ml.) was treated with sodium borohydride (800 mg.). When all the solid had disappeared the mixture was poured into water and extracted with ether. The extracts were washed with water, dried (Na_2SO_4) and evaporated to leave 2,3-dihydro-2,3-dimethylbenzothiazole (3.27 g.) which was purified by distillation under reduced pressure (b.p. 105°/0.1 mm.; lit.[50] 120-121°/10 mm.). The yield was quantitative.

(ii) Dehydrogenation with triphenylmethyl perchlorate

A solution of 2,3-dihydro-2,3-dimethylbenzothiazole (329 mg.; 2 m.mole.) in acetic acid (2 ml.) was added to a solution-suspension of triphenylmethyl perchlorate (692 mg.; 2 m.mole.) in acetic acid (8 ml.) at room temperature. The reaction was slightly exothermic and the colour changed rapidly from orange-brown to pale yellow. The mixture was warmed on a

water bath (about 45°) for a few minutes and on cooling an oil separated which solidified on standing. Recrystallisation from ethanol gave 2,3-dimethylbenzothiazolium perchlorate (503 mg.; 95%) as fine colourless needles (m.p. 122-124°; lit.[14] 124-125°).

C.II. Dehydrogenation of hydroaromatic heterocycles using quinones in the presence of acid

1. Preparation and purification of quinone reagents.

(i) p-Chloranil

Commercial chloranil was purified by recrystallisation (twice) from benzene (with charcoal), filtering the hot solution through several layers of filter paper.

(ii) Tetrachloro-o-benzoquinone. (o-chloranil.)

Tetrachloro-o-benzoquinone was prepared by a modification of Jackman's method.[15] Tetrachlorocatechol, obtained in 76% yield by chlorination of catechol[16], was oxidised with nitric acid using a 9% excess. The crude product was recrystallised from carbon tetrachloride to give dark red prisms (m.p. 129-130°; lit.[16c] 131-132°) in a 42% yield.

(iii) 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (D.D.Q.)

2,3-Dicyanoquinol was prepared from p-benzoquinone and potassium cyanide by the method of Creighton and Jackman[17] (see also reference 18). The product was obtained as tan plates from hot water (average yield about 50%). Oxidation with oxides of nitrogen and hydrochlorination were carried out using Brook's[19,17] method. Crude D.D.Q. was dissolved in benzene, washed with water to remove traces of the oxides of

nitrogen and dried (Na_2SO_4). The solvent bulk was reduced and olefin-free petroleum ether was added. The quinone crystallised as ruby-red crystals containing benzene of crystallisation. By air drying at about 30° the benzene of crystallisation was lost to leave a fine yellow powder. The average yield was 71% and melting-point 201-203° (lit.[17] 201-203°).

2. Dehydrogenation of thiaxanthene using p-chloranil and perchloric acid.

Thiaxanthone was prepared from thiosalicylic acid and benzene[20] and recrystallised from acetic acid as yellow needles (m.p. 209°; lit.[20] 209°).

An attempt to reduce thiaxanthone to thiaxanthene using lithium aluminium hydride alone[21] was unsuccessful and the ketone was recovered. The method of Brown and White[22] for the reduction of aromatic carbonyl groups was used with modifications.

The reagent consisted of a suspension of anhydrous aluminium chloride (4.63 g.; 35 m.mole) and lithium aluminium hydride (668 mg.; 17.5 m.mole) in anhydrous ether (50 ml.). To this thiaxanthone (1 g.; about 5 m.mole) in anhydrous ether (40 ml.) was added with stirring over a period of five minutes

and the mixture boiled under reflux for thirty minutes. When cold, excess hydride was destroyed by careful addition of ethyl formate and the contents of the flask hydrolysed by pouring onto a mixture of ice (100 g.) and 10% sulphuric acid (100 ml.). The ether layer was removed and the aqueous layer extracted with fresh ether. The combined extracts were washed with water, sodium bicarbonate solution and water and dried (Na_2SO_4). Evaporation of the ether left an oil which solidified on standing and was crystallised from a chloroform-ethanol mixture (1:5) to give thiaxanthene (720 mg.; 78%) as colourless prisms (m.p. 128.5-130°; lit.[47] 128°).

Chloranil (985 mg.; 4 m.mole) was added to a solution of thiaxanthene (789 mg.; 4 m.mole) in acetic acid (40 ml.). The mixture was heated to boiling, became dark red and when cooled fine needles separated. Perchloric acid (0.44 ml.; 4 m.mole + 25% excess) was added and the mixture again boiled. Cooling produced scarlet rosettes of thiaxanthenium perchlorate in addition to fine colourless needles of tetrachloroquinol. Anhydrous ether (60 ml) was added and the salt (642 mg.; 54%) collected and recrystallised from acetic acid as scarlet needles (m.p. 216-218° (dec.); lit.[23] 217-219° (dec.).).

Evaporation of the ether allowed the quinol to reprecipitate. Recrystallisation from acetic acid gave the pure quinol (1.085 g.; 87%) as colourless needles (m.p. 230-231°; lit.[25] 230-231°).

3. Dehydrogenation of thiaxanthene using D.D.Q. and perchloric acid.

Thiaxanthene (200 mg.; 1 m.mole) was dissolved in acetonitrile (5 ml.) and whilst the solution was still warm (about 30°) an acetonitrile (3 ml.) solution of D.D.Q. (227 mg.; 1 m.mole) was added. The solution turned dark red and on cooling, fine, wine-coloured needles (185 mg.) separated. Attempts to recrystallise this material were unsuccessful and on the melting-point block it sublimed with decomposition above 200°.

A solution-suspension (105 mg.) of this product in acetic acid (2 ml.) was treated with perchloric acid (0.5 ml.) and boiled for one minute. When cold, thiaxanthenium perchlorate and some 2,3-dichloro-5,6-dicyanoquinol crystallised. The former was isolated by fractional crystallisation as scarlet prisms (40 mg.; 54%, based on 1:1 composition of the intermediate) m.p. 215-218° (dec.), block preheated to 205°.

A similar experiment in acetic acid, in which the intermediate was not isolated, gave the same percentage yield.

4. Dehydration and dehydrogenation of Benzo[f]thiachroman-4-ol using o-chloranil and perchloric acid.

Solutions of benzo[f]thiachroman-4-ol (224 mg.; 1 m.mole) and o-chloranil (246 mg.; 1 m.mole) in acetic acid (4 ml.each) were mixed and boiled for fifteen seconds. The colour changed from crimson to claret but nothing crystallised out on cooling. Perchloric acid (0.17 ml.; 1 m.mole + 100% excess) was added and the solution warmed to boiling when it rapidly turned orange. After boiling for about half a minute then cooling, anhydrous ether (16 ml.) was added and a dark yellow, crystalline solid separated. Recrystallisation from acetic acid, with charcoal, gave 1-thianaphtho[2,1,b]pyrylium perchlorate (281 mg.; 95%) as dark yellow plates (m.p. 210-212°; block preheated to 198°). A mixed melting-point with previously-prepared material (see section C.I.3) showed no depression.

5. Dehydrogenation of 5,6-dihydro-5-methylphenanthridine using p-chloranil and perchloric acid.

Chloranil (484 mg.; 2 m.mole) dissolved in acetic acid

(6 ml.) was added to a solution of 5,6-dihydro-5-methylphenanthridine (387 mg.; 2 m.mole) also in acetic acid (4 ml.). On warming, the solution turned dark brown then gradually dark orange. The mixture was cooled and perchloric acid (0.34 ml.; 2 m.mole + 100% excess) added. Pale yellow needles of the salt formed immediately. After boiling for one minute, cooling thoroughly and adding anhydrous ether (30 ml.), the product was collected and recrystallised from acetic acid. 5-Methylphenanthridinium perchlorate (550 mg.; 91%) was obtained as colourless needles. (m.p. 192-195°; block preheated to 180°). A mixed melting-point with authentic material showed no depression.

6. Dehydrogenation of 5,6-dihydro-5,6-dimethylphenanthridine using p-chloranil and perchloric acid.

Chloranil (490 mg.; 2 m.mole) was dissolved in a mixture of perchloric acid (0.35 ml.; 2 m.mole + 100% excess) and acetic acid (20 ml.) and the solution warmed to boiling. Whilst the solution was still hot (about 85°), 5,6-dihydro-5,6-dimethylphenanthridine (420 mg.; 2 m.mole) in acetic acid (5 ml.) was added slowly and the mixture boiled for one minute. When cold, anhydrous ether (50 ml.) was added and the pale

yellow needles of the perchlorate (414 mg.; 69%) filtered off. Evaporation of the solvents to small bulk and addition of more ether yielded a further 100 mg. of product (overall yield 514 mg.; 83%). Pure 5,6-dimethylphenathridinium perchlorate was obtained as cream needles from a mixture (1:1) of acetonitrile and acetic acid. A mixed melting-point with an authentic specimen showed no depression.

7. Dehydrogenation of 2,3-dihydro-2,3-dimethylbenzothiazole using p-chloranil and perchloric acid.

2,3-Dihydro-2,3-dimethylbenzothiazole (324 mg.; 2 m.mole), dissolved in acetic acid (3 ml.), was added to a mixture of chloranil (488 mg.; 2 m.mole) and perchloric acid (0.35 ml.; 2 m.mole + 100% excess) in acetic acid (6 ml.). The solution became dark green and on warming gradually turned brown, then pink then finally colourless. As the solution cooled, an oil separated which solidified on standing. It was dissolved in the minimum volume of hot ethanol, filtered rapidly through a sintered glass funnel and allowed to cool. 2,3-Dimethylbenzothiazolium perchlorate (460 mg.; 87%) crystallised as colourless needles (m.p. 122-124°) from the cold solution.

8. Dehydrogenation of 2,3-dihydro-2,3-dimethylbenzothiazole using o-chloranil and perchloric acid.

The procedure was similar to that described above, 2,3-dihydro-2,3-dimethylbenzothiazole (171 mg.; 1 m.mole) in acetic acid (1.5 ml.) being added to a mixture of o-chloranil (253 mg.; 1 m.mole) and perchloric acid (0.17 ml.; 1 m.mole + 100% excess) in acetic acid (4 ml.) in the cold. The dark red colour faded slowly at that temperature, more rapidly on warming, until the solution was almost colourless. The salt (220 mg.; 84%) was isolated and purified as described above.

C.III Formation of Tropylium salts from Cycloheptatrienes using quinones in the presence of acid.

1. Reaction of Cycloheptatriene with D.D.Q. and perchloric acid.[24]

Experiment 1.

Cycloheptatriene (1 ml.; 4 m.mole + 100% excess) in methylene chloride (40 ml.) was added to a boiling methylene chloride solution (40 ml.) of D.D.Q. (908 mg.; 4 m.mole) and perchloric acid (0.67 ml.; 4 m.mole + 100% excess). The initial yellow colour faded rapidly and a white precipitate separated immediately from the almost colourless solution. After filtration, the product was washed (methylene chloride, ether), extracted with boiling ethanol (10 ml.) containing perchloric acid (0.25 ml.) and cooled. Colourless tropylium perchlorate (685 mg.; 90%) was collected and recrystallised from an acetic acid - acetonitrile mixture as dendritic plates (533 mg.; 70%) m.p. 285° (decomposition and effervescence); (lit.[28] m.p. above 300°.).

Experiment 2.

D.D.Q. (908 mg.; 4 m.mole) was dissolved in warm acetic acid (20 ml.), cooled to room temperature and perchloric acid (0.67 ml.; 4 m.mole + 100% excess) in acetic acid (20 ml.)

added. This mixture was treated with cycloheptatriene (0.75 ml.; 4 m.mole + 100% excess) in acetic acid (5 ml.). The colour became orange-brown then faded rapidly until almost colourless and an off-white solid precipitated. Anhydrous ether (50 ml.) was added and after the mixture had stood for five minutes the product was filtered off and extracted with boiling ethanol (15 ml.). Colourless, quinol-free tropylium perchlorate (720 mg.; 95%) was obtained from the cold solution and was recrystallised from acetic acid (60 ml.) as fern-like aggregates with melting-point behaviour as previously described.

2. Reaction of Cycloheptatriene with o-chloranil and perchloric acid.[24]

Cycloheptatriene (0.75 ml.; 4 m.mole + 50% excess) in acetic acid (5 ml.) was added to o-chloranil (984 mg.; 4 m.mole) and perchloric acid (0.67 ml.; 4 m.mole + 100% excess) in acetic acid (20 ml.) at room temperature. The deep red colour faded rapidly and the perchlorate salt crystallised. Anhydrous ether (50 ml.) was added before filtration. The precipitate, colourless crystals (737 mg.; 97%), was washed with ether and required no further purification.

3. Reaction of Cycloheptatriene with p-chloranil and perchloric acid.

Cycloheptatriene (0.6 ml.; 4 m.mole + 20% excess) was added to a boiling solution of chloranil (984 mg.; 4 m.mole.) and perchloric acid (0.67 ml.; 100% excess) in acetic acid (30 ml.) and the resulting brown solution boiled for two minutes. When cold, anhydrous ether (60 ml.) was added to dissolve the precipitated quinol. The tropylium perchlorate was collected and washed with ether before recrystallising from acetic acid (with charcoal) to give feather-like plates (530 mg.; 70%) with melting-point behaviour as previously described.

The mother liquors were diluted with ether (300 ml.) and washed with water and sodium hydroxide solution. The alkaline extracts were washed with ether, acidified with concentrated hydrochloric acid and the precipitated quinol taken up in ether. The combined extracts were washed thoroughly with water, dried (Na_2SO_4) and evaporated under reduced pressure on a water bath. Tetrachloroquinol (1.02 g.; 82%) was obtained as a crystalline mass.

4. Reaction of Cycloheptatriene with p-benzoquinone and perchloric acid.[24]

Cycloheptatriene (1.5 ml.; 10 m.mole + 20% excess) in acetic acid (10 ml.) was added to a boiling solution of p-benzoquinone (1.08 g.; 10 m.mole) in acetic acid (20 ml.), the solution heated to boiling and perchloric acid (1.35 ml.; 10 m.mole + 60% excess) in acetic acid (10 ml.) added. The solution became dark brown and was boiled for four minutes. Anhydrous ether (40 ml.) was added to the cold solution and the resultant brown precipitate filtered off, washed with ether and recrystallised from acetic acid (with charcoal). The product, orange crystals (736 mg.), was again crystallised from acetic acid (with charcoal) to give pure tropylium perchlorate (574 mg.; 30%).

5. Reaction of Cycloheptatriene with D.D.Q. and sodium perchlorate.

A solution of cycloheptatriene (0.5 ml.; 3 m.mole + 50% excess) and sodium perchlorate (735 mg.; 6 m.mole) in acetic acid (15 ml.) was treated with a solution of D.D.Q. (681 mg.; 3 m.mole.) in acetic acid (15 ml.) - both solutions at the boiling point. An initial blood-red colour

faded to pale brown and a colourless solid rapidly crystallised. This solid was filtered off from the cold solution (910 mg.) and extracted with ethanol (50 ml.) containing perchloric acid (1 ml.). The undissolved solid was added to a colourless solid which had crystallised slowly from the cold solution and the total (430 mg.; 75%) recrystallised as dendritic colourless crystals of tropylium perchlorate from an acetic acid/acetonitrile mixture (6:1).

6. Reaction of Cycloheptatriene with D.D.Q. and picric acid.[24]

Cycloheptatriene (1 ml.; 4 m.mole + 100% excess) in methylene chloride (10 ml.) was added to a boiling solution of picric acid (1.008 g.; 4 m.mole + 10% excess) and D.D.Q. (908 mg.; 4 m.mole) in methylene chloride (40 ml.). A yellow solid precipitated at once and was filtered from the cold solution to be recrystallised from the minimum volume of dry ethanol. Rapid cooling gave yellow needles (m.p. 120-125° (dec.); lit.[26] 115°). Slow cooling gave orange needles with the same melting-point. Rapid cooling of a solution of the orange crystals gave the yellow needles. Neither a greater excess of picric acid nor the use of acetic acid as solvent improved the yield of tropylium picrate (645 mg.; 51%). A sample was dried for 5 mihutes at 80°/A.P. before being analysed.

Analysis

S.A. 1272	Found	C 49.29	H 3.14	N 14.25%
$C_{13}H_9N_3O_7$	requires	C 48.93	H 2.84	N 13.16%
S.A. 1273	Found	C 49.63	H 3.09	N 13.70%

7. Reaction of Cycloheptatriene with D.D.Q. and lithium bromide.

When cycloheptatriene and D.D.Q. are allowed to react in acetonitrile or methylene chloride a black crystalline solid separates. This black intermediate, later shown to be tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (see section C.VI.1.) was used in the preparation of several tropylium salts.

A mixture of the black intermediate (957 mg.; 3 m.mole) and lithium bromide (652 mg.; 75 m.mole.) in acetic acid (25 ml.) was raised to the boiling point to give a reddish-brown solution. When cold, a precipitate of brownish-coloured quinol (494 mg.; 64%) was filtered off and the filtrate was treated with anhydrous ether (175 ml.). A yellow-brown oil separated and partly solidified. The mother liquor was carefully decanted and the oil washed by swirling with 2-3 small volumes of ether. The oil was finally dissolved in ethanol (5 ml.) with warming and the addition of dry ether (50 ml.) precipitated crude tropylium bromide as a yellow powder. Sublimation at 150°/0.1 mm. gave pure tropylium

bromide (62 mg.; 12%) as pale yellow prisms (m.p. 198-204°. (dec.); block preheated to 195°; lit.[26,27] 203°.). In the atmosphere the salt decomposed slowly to a brown oil.

8. Reaction of Cycloheptatriene with D.D.Q. and sodium iodide.

Boiling acetic acid (45 ml.) was added to a mixture of the black intermediate (957 mg.; 3 m.mole) (see section 7 above) and sodium iodide (1.125 g.; 7.5 m.mole). The solution immediately became dark brown and was boiled for about one minute. The hot solution was filtered through a sintered-glass funnel and allowed to cool. Whilst still warm, dark brown needles crystallised from the solution. This product (820 mg.; 79% on "di-iodide") was recrystallised twice from absolute ethanol and melted 128.5 - 129.5°, block preheated to 125°. A sample was dried for 5 minutes at 100°/A.P. before analysis.

Analysis

S.A. 1297	Found	C 24.82	H 2.01	I 72.1%
$C_{14}H_{14}I_4$	requires	C 24.37	H 2.05	I 73.57%

This material was found to be better represented as a lattice complex of tropylium iodide and tropylium tri-iodide into which components it could be separated.

The "di-iodide" (945 mg.) was shaken with acetone (15 ml.) for two mihutes at room temperature. The dark brown crystals

were replaced by scarlet prisms and the mother liquors became dark brown. The product (160 mg.; 54%) was the mono-iodide (m.p. 131-133°; block preheated to 125°). Dauben[28] reports a melting point of 127° and Dewar[26] one of 117°. A sample was dried for 5 minutes at 100°/A.P. before analysis.

Analysis

S.A. 1299	Found	C 38.24	H 3.29%	
C_7H_7I	requires	C 38.55	H 3.24%	

Addition of anhydrous ether (150 ml.) to the mother liquors gave crimson needles of the tri-iodide (327 mg.; 58%) which was recrystallised from boiling ethanol as garnet needles (m.p. 132-133°; block preheated to 125°). Before analysis a sample was dried for 5 minutes at 100°/A.P.

Analysis

S.A. 1298	Found	C 18.82	H 1.76	I 78.8%
$C_7H_7I_3$	requires	C 17.82	H 1.50	I 80.71%

9. Reaction of Cycloheptatriene with D.D.Q. and p-toluene-sulphonic acid.

The black intermediate (1.595 mg.; 5 m.mole) (see section 7 above), p-toluene-sulphonic acid (1.032 g.; 5 m.mole

+ 20% excess) and acetic acid (30 ml.) were heated to boiling then cooled rapidly under cold running water. Addition of dry ether (2 ml.) completed the precipitation of the quinol which was collected, washed (acetic acid, ether) and dried as an off-white solid (598 mg.; 53%). The mother liquor was diluted with ether to 200 ml. and an orange oil separated. After two hours at room temperature, this oil solidified. The supernatant liquid was carefully decanted and warm ethanol (10 ml.) added to dissolve the solid. Dry ether (40 ml.) was added and the product crystallised as tan plates (722 mg.; 55%). This process was repeated as a method of purification. The final product tropylium p-toluenesulphonate, lustrous tan plates (m.p. 125-130°.; block preheated to 115°), was unstable in atmospheric moisture, being converted slowly to a brown liquid. Drying before analysis was for 5 minutes at 100°/A.P.

Analysis

S.A. 1301	Found	C 61.62	H 5.48	S 11.20%
$C_{14}H_{14}O_3S$	requires	C 64.12	H 5.34	S 12.23%

10. Reaction of Cycloheptatriene with o-chloranil and oxalic acid.[24]

Cycloheptatriene (0.75 ml.; 4 m.mole + 50% excess)

in acetic acid (5 ml.) was added to a warm solution of o-chloranil (984 mg.; 4 m.mole) and oxalic acid dihydrate (756 mg.; 4 m.mole + 50% excess) in acetic acid (15 ml.), the mixture heated to 100°, then cooled. Colourless needles were deposited and after 15 minutes anhydrous ether (20 ml.) was added and the solution filtered.

The product was washed with ether (50 ml.) and dried to give crude tropylium tetroxalate (675 mg.; 83%). Recrystallisation successively from acetic acid and acetonitrile gave colourless needles which darkened at 130° and melted 140-145° with effervescence and decomposition. After drying for 10 minutes at 100°/A.P. asample was analysed.

Analysis

S.A. 1329	Found	C 48.14	H 4.06%
$C_{11}H_{10}O_8$	requires	C 48.77	H 4.00%

C.IV. Reactions of Alkyl- and Arylcycloheptatrienes with quinones and acid.

1. Reaction of 7-Methylcycloheptatriene with o-chloranil and perchloric acid.

7-Methylcycloheptatriene was prepared from 7-ethoxy-cycloheptatriene and methyl magnesium iodide.[29] The product was a colourless oil (b.p. 30°/11 mm., refractive index n_D = 1.5030; lit.[29] 50°/42 mm.; 1.5032).

A mixture of o-chloranil (984 mg.; 4 m.mole.) and perchloric acid (0.65 ml.; 4 m.mole + 100% excess) dissolved in acetonitrile (4 ml.) was added at room temperature to a solution of methylcycloheptatriene (424 mg.; 4 m.mole) in acetonitrile (4 ml.). The colour, initially red, darkened then gradually turned orange and finally golden-yellow. Addition of anhydrous ether precipitated a yellow oil which solidified on standing. The crude perchlorate (744 mg.) was filtered off and recrystallised several times (with charcoal) from a mixture of acetonitrile and ethyl acetate (1:6) to give colourless plates (m.p. 109-111°; block preheated to 104°; lit.[29] 111-112°), of methyltropylium perchlorate (140 mg.; 17%).

2. Reaction of 7-Phenylcycloheptatriene with o-chloranil and perchloric acid.

7-Phenylcycloheptatriene[32] was prepared from phenyl magnesium bromide and tropylium perchlorate. The product, a colourless mobile liquid (b.p. 134-136°/12 mm.; lit.[33] 57-59°/ 0.05 mm.) was obtained in 88% yield.

A solution of 7-phenylcycloheptatriene (700 mg.; 4 m.mole + 4% excess) in acetic acid (5 ml.) was added to a warm solution of o-chloranil (984 mg.; 4 m.mole.) and perchloric acid (0.67 ml.; 4 m.mole + 100% excess) in acetic acid (20 ml.). The solution was heated at 100° for one minute, cooled and anhydrous ether (25 ml.) added. Phenyltropylium perchlorate (849 mg.; 80%) crystallised as light yellow plates which were washed (ether), dried and recrystallised from acetonitrile to give bright yellow tablets (m.p. 181-185° (dec.)). An analytical specimen was dried for 15 minutes at 100°/A.P. before analysis.

Analysis

S.A. 1331.	Found	C 59.15	H 4.36	Cl 15.15%
$C_{13}H_{11}ClO_4$	requires	C 58.57	H 4.16	Cl 13.29%

3. Reaction of 7-Phenylcycloheptatriene with o-chloranil and sodium iodide.

7-Phenylcycloheptatriene (700 mg.; 4 m.mole + 4% excess) was added to a solution of o-chloranil (984 mg.; 4 m.mole) in acetic acid (20 ml.). The solution was heated to 100°, maintained at that temperature for half a minute then cooled to about 40°. Powdered sodium iodide (630 mg.; 4 m.mole + 5% excess) was then added, the mixture swirled until the sodium iodide had dissolved and cooled under cold running water. Dark brown needles crystallised along with the sodium salt of the quinol. The product was filtered off, washed (acetic acid) and shaken with water (25 ml.). After collecting and washing (ether) it was dried under vacuum (P_2O_5). The orange-red solid (442 mg.; 20%) was recrystallised twice from an ether/acetone mixture (2:1) as flat orange-red needles of phenyltropylium tri-iodide (m.p. 107-108.5°). A sample was dried for 5 minutes at 80°/A.P. before analysis.

Analysis

S.A. 1334	Found	C 28.84	H 2.14	I 69.00%
$C_{13}H_{11}I_3$	requires	C 28.50	H 2.02	I 69.49%

4. Reaction of 7-Phenylcycloheptatriene with o-chloranil and picric acid.

o-Chloranil (984 mg.; 4 m.mole) and picric acid (962 mg.; 4 m.mole + 4% excess) dissolved in acetic acid (15 ml.)were treated at room temperature with a solution of phenylcycloheptatriene (700 mg.; 4 m.mole + 4% excess) in acetic acid (10 ml.). The mixture, from which the product had partly crystallised, was warmed to about 60°, cooled and anhydrous ether (50 ml.) added. The picrate, orange-yellow needles (1.56 g.; 99%), was recrystallised from acetonitrile as golden-yellow needles (m.p. 115-116.5°(dec.)). A sample was dried for 5 minutes at 110°/A.P. before being analysed.

Analysis

S.A. 1335	Found	C 57.39	H 3.44	N 10.29%
$C_{19}H_{13}N_3O_7$	requires	C 57.72	H 3.31	N 10.63%

5. Reaction of Ditropyl with p-chloranil and perchloric acid.

Ditropyl[30] (728 mg.; 4 m.mole) was dissolved in acetic acid (10 ml.) and added to a boiling solution of chloranil (984 mg.; 4 m.mole) and perchloric acid (2 ml.; excess) in acetic acid (50 ml.). The mixture became orange,

slowly turning brown, and was boiled for one minute before cooling thoroughly. Dry ether (120 ml.) was added to the solution from which quinol and tropylium perchlorate had crystallised. After 5 minutes the product was collected and washed (ether). The crude perchlorate (1.1g.; 72%) was recrystallised from acetic acid, with charcoal, as colourless fern-like aggregates.

The quinol was recovered (93% yield) by alkali extraction.

6. Reaction of Ditropyl with o-chloranil and perchloric acid.

A boiling solution of o-chloranil (984 mg.; 4 m.mole.) and perchloric acid (2 ml.; excess) in acetic acid (25 ml.) was treated with a solution of ditropyl (728 mg.; 4 m.mole) in acetic acid (5 ml.) and the solution boiled for one minute. The solution turned brown and a grey crystalline solid (937 mg.; 62%) separated. Recrystallisation, with charcoal, from acetic acid gave pure tropylium perchlorate (757 mg.; 50% based on 2 moles of tropylium salt from one of ditropyl.).

7. Reaction of Ditropyl with D.D.Q. and perchloric acid.

Ditropyl (728 mg.; 4 m.mole) in acetic acid (10 ml.) was added to a boiling solution of D.D.Q. (908 mg.; 4 m.mole)

and perchloric acid (1 ml.; 12.5 m.moles) in acetic acid (15 ml). The mixture became red then brown and was boiled for one minute before cooling thoroughly. Addition of anhydrous ether (75 ml.) completed precipitation and the grey product was filtered off, washed with ethanol (20 ml.), ether and dried. Recrystallisation from acetic acid, with charcoal, gave colourless tropylium perchlorate (776 mg.; 51% on the same basis as 6 above).

8. Reaction of Ditropyl with p-benzoquinone and perchloric acid.

Perchloric acid (2 ml.; 25 m.moles) in acetic acid (5 ml.) was added, near the boiling point, to a solution of ditropyl (728 mg.; 4 m.mole) and p-benzoquinone (432 mg.; 4 m.mole) in acetic acid (25 ml.). The transitory red colour became brown almost immediately and after boiling for one minute and cooling rapidly, anhydrous ether (60 ml.) was added. The residual salt, a buff solid (1.388 g.; 91%), was collected, washed (ether) and recrystallised from acetic acid, with charcoal, to give tropylium perchlorate (1.276 g.; 84%).

9. Attempted preparation and dehydrogenation of 7-(Triphenylmethyl)cycloheptatriene.

(i) Triphenylmethyl lithium.[34]

Pure triphenylmethane (25.4 g.) was added portionwise over a period of about one hour to a stirred solution of n-propyl lithium[31] in anhydrous ether, whilst dry, oxygen-free nitrogen was swept through the system. The addition was accompanied by a vigorous effervescence and the temperature was controlled by immersing the reaction flask in a bath of ice-cold water. Stirring was continued overnight. Several colour changes took place during the first three hours, the solution turning from bluish-grey to green, then yellow, orange and finally to red which gradually became more intense. After stopping the stirrer, the solution was allowed to stand at room temperature for a further 24 hours (total reaction time 41 hours), during this period dark red, spar-shaped crystals settled out. Tomboulian[35] has also prepared triphenylmethyl lithium from triphenylmethyl chloride and lithium metal.

(ii) Reaction of Triphenylmethyl lithium with Tropylium perchlorate.

Tropylium perchlorate (34.6 g.) was added through a stream of dry, oxygen-free nitrogen to the rapidly stirred

solution-suspension of triphenylmethyl lithium prepared above. The addition took place over a period of about half an hour, during the first 15 minutes of which the temperature was maintained at -10° by immersing the reaction flask in an acetone/"dry-ice" bath. The reaction was initially exothermic but after approximately half the perchlorate had been added the rate of reaction became much slower and the cooling bath was removed. It was found that sufficient tropylium perchlorate had to be added to react with the total estimated amount of organometallic material present, showing that little decomposition had occurred. As the reaction neared completion, the colour changed from red through blue to olive green and finally the mixture became colourless as a thick white precipitate began to settle out. A small excess of tropylium perchlorate (1 g.) was added and the mixture stirred for a further two hours at room temperature.

The precipitate (mainly lithium perchlorate) was filtered off, washed with several portions of ether and the washings combined with the filtrate. The latter was then poured into 0.5N hydrochloric acid (100 ml.), shaken up and the organic layer removed. The aqueous phase was extracted

with fresh ether (100 ml.) and with benzene (75 ml.) and the ether and benzene extracts worked up separately in the same manner. After washing in turn with water, saturated sodium bicarbonate solution, water and drying (Na_2SO_4), the solvents were evaporated. The benzene extract yielded a colourless solid (8 g.) whilst the ether solution gave a pleasant-smelling yellow oil (37.1 g.) from which a colourless solid (13.28 g.) slowly crystallised on standing.

(iii) Analysis of the mixture and separation of the products.

The two solid fractions and the oil were analysed by thin-layer chromatography on silica gel plates using hexane as eluent and iodine vapour as developing agent. The oil contained three major and three minor components whilst both the solids consisted mainly of two major products. By running the unknowns with standard mixtures, unreacted triphenylmethane was tentatively identified as one of the major components. This was later confirmed.

A sample of the brown oil (2 g.) from the ether extracts was chromatographed on a column of activated alumina (25 cm. x 3.1 cm.) eluting with light petroleum, benzene and mixtures of these solvents. Fractions (200 ml.) were collected, evaporated and analysed by thin-layer chromatography. The

following products were isolated:

(a) colourless, refractive liquid (840 mg.; 42% of sample).

(b) waxy, colourless solid (m.p. 92°) (408 mg.; 20%).

(c) brittle, colourless solid (m.p. 157-158°)(203 mg.; 10%).

(d) viscous, yellow oil (166 mg.; 8.3%).

Other fractions containing mixtures of the above components accounted for the rest of the material. Product (b) was shown to be triphenylmethane (m.p. and mixed m.p.). Product (a), although not examined in detail is probably n-propylcycloheptatriene. Product (c) was later found to give a reasonable analysis for triphenyl-methylcycloheptatriene.

A sample (2 g.) of the solid product was chromatographed as described above. The products were similar and were as follows:

(a) colourless, refractive oil. (197 mg.; 9.8%).

(b) colourless, waxy solid. (m.p.92°)(444 mg.; 22%).

(c) brittle, colourless solid. (m.p. 156-158°)(904 mg.; 45%).

On a larger scale (10 g.) using a larger column of alumina (30 cm. x 5.7 cm.) the proportions were

(a) 730 mg.; 7.3%., (b) 2.6 g.; 26%., (c) 4.31 g.; 43%.

A sample of (c) was recrystallised from acetone to give small cream needles (m.p. 157-158°; block preheated to 150°) and drying for 2 hours at 35°/0.5 mm. was carried out

before analysis.

Analysis

S.A. 1532	Found	C 93.23	H 6.71%
$C_{26}H_{22}$	requires	C 93.37	H 6.63%

I.R. spectrum (carbon disulphide) (μ).

3.28 (s), 3.33 (s), 8.26 (m), 8.35 (m), 9.26 (m), 9.69 (s), 10.00 (w), 11.43 (s).

Dauben[36] reports the preparation of triphenylmethylcycloheptatriene from the tropenide anion and triphenylmethane but only gives a melting-point (260°).

(iv) Attempted reactions

Triphenylmethylcycloheptatriene was found to be soluble in benzene or carbon disulphide, sparingly soluble in acetone or methylene chloride and only slightly soluble in alcohol, acetonitrile or acetic acid.

When mixed with D.D.Q. and perchloric acid in acetonitrile or methylene chloride no reaction took place and the substrate was recovered quantitatively. When treated with perchloric acid alone in acetonitrile or acetone, a yellow colour developed but the substrate was recovered.

[1,1,1,2-Tetraphenylethane[51] has a melting-point of 144° and the same molecular proportions.]

C.V. Reactions of Tropyl Ethers and Thioethers.

1. Reaction of 7-Methoxycycloheptatriene with picric and with perchloric acids.

7-Methoxycycloheptatriene[37] (b.p. 50°/10 mm.; lit.[37] 54°/13 mm.) was prepared from sodium methoxide and tropylium perchlorate.

Perchloric acid (0.16 ml.; 2 m.mole) was added to a solution of methoxycycloheptatriene (122 mg.; 1 m.mole) in acetic acid (6 ml.) and warmed to 100° on a water bath. A cream-coloured solid (183 mg.; 96%) precipitated. The product, recrystallised from acetic acid, was tropylium perchlorate (m.p. 305°(dec.) with effervescence at 270°).

Solutions of picric acid (229 mg.; 1 m.mole) and methoxycycloheptatriene (122 mg.; 1 m.mole) in ethanol (6 ml. each) were mixed and the mixture heated on a warm water bath (about 60°). Yellow needles precipitated from a dark yellow solution. Pure tropylium picrate (204 mg.; 64%) was obtained from ethanol as needles (m.p. 121-124° (dec.); block preheated to 115°; lit.[26] 115°.). No depression was observed when melted with an authentic specimen.

2. Reaction of 7-Methoxycycloheptatriene with D.D.Q. and perchloric or picric acid.

Solutions of 7-methoxycycloheptatriene (244 mg.; 2 m.mole) and D.D.Q. (454 mg.; 2 m.mole) in acetonitrile (4 ml. each) were mixed. The reaction was exothermic and a black crystalline solid precipitated. This was later examined in detail and shown to be tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (see section C.VIII.1). The black intermediate was collected and part of it (348 mg.) dissolved in acetic acid (6 ml.) and treated with perchloric acid (0.2 ml.; 2.5 m.mole). A cream precipitate formed at once and the mixture was heated for two minutes at 100°. The product was collected, washed (ether) and recrystallised from acetic acid to give fern-shaped aggregates of tropylium perchlorate (175 mg.; 85% based on semiquinone derivative).

The black intermediate (1.396 g.) and picric acid (962 mg.; 4.2 m.mole) in ethanol (30 ml.) were boiled for two minutes. The solution became brownish-red and on cooling, orange needles of tropylium picrate (535 mg.; 38%) were deposited. The purification was as described above.

3. Reaction of 7-Ethoxycycloheptatriene with D.D.Q. and perchloric acid.

7-Ethoxycycloheptatriene[29] (b.p. 62°/10 mm.; lit.[29] 62°/8 mm.) was prepared from tropylium perchlorate and sodium bicarbonate in aqueous ethanol.

The behaviour of 7-ethoxycycloheptatriene was analogous to that of methoxycycloheptatriene. With perchloric acid it gave tropylium perchlorate (95% yield) and with D.D.Q. in acetonitrile it gave a black intermediate from which tropylium perchlorate (91% yield) was obtained on addition of perchloric acid.

4. Reaction of Ditropyl ether with D.D.Q. and perchloric acid.

Ditropyl ether[27] (b.p. 100-110°/0.5 mm.; lit.[27] 100-110/0.5 mm.) was prepared by the reaction of aqueous sodium bicarbonate on tropylium perchlorate.

Solutions of D.D.Q. and ditropyl ether in acetonitrile were mixed at room temperature. The reaction was exothermic and the solution became dark crimson. Black spar-shaped crystals were precipitated. This was later shown to be tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (see section C.VIII.5). A sample (199 mg.) of this black product

dissolved in acetic acid (5 ml.) was treated with excess perchloric acid (0.2 ml.). After warming for a few minutes, the white precipitate, which had been formed immediately, was collected and recrystallised from acetic acid to give fern-like crystals of tropylium perchlorate (93.6 mg.; 79% based on semiquinone derivative).

5. Attempted preparation of 7-Acetoxycycloheptatriene.

Sodium acetate trihydrate (3.74 g.; 27.5 m.mole.) in water (15 ml.) was added to a suspension of tropylium perchlorate (4.8 g.; 25 m.mole) in water (15 ml.). The mixture was shaken and allowed to stand with occasional shaking for one hour when it was extracted with ether (3 x 50 ml.). The combined extracts were washed (water) and dried (K_2CO_3) and the solvent evaporated to leave a yellow oil (1.9 g.). This oil was distilled under reduced pressure (b.p. 120°/1.0 mm.) through a Claisen-Vigreux column to yield a colourless refractive oil (n_D = 1.5733) which proved to be ditropyl ether.[27] (n_D = 1.5735, b.p. 100-110°/0.5 mm.).

6. Attempted preparation of 7-Phenoxycycloheptatriene.[38,39]

Sodium phenate, made by dissolving excess phenol in sodium hydroxide, was purified by washing with ether and drying under vacuo.

A suspension of tropylium perchlorate (4.8 g.; 25 m.mole) in methanol (25 ml.) was treated with sodium phenate (2.89 g.; 25 m.mole). There was an immediate exothermic reaction and the solution turned yellow. After standing at room temperature for two hours with occasional shaking, the mixture was poured into water (50 ml.), extracted with ether (3 x 50 ml.) and the combined extracts washed thoroughly with water and dried (K_2CO_3). The ether was evaporated to leave an orange-red oil (3.8 g.) which gave some tropylium perchlorate on addition of perchloric acid. After distillation through a Claisen-Vigreux column (b.p. 112-120°/0.5 mm.) no tropylium perchlorate was formed on addition of acid. The distillate, a yellow viscous oil (1.2 g.; 26%), crystallised slowly from the melt as a mass of fine needles (m.p. 70-78°). From this data it seemed probable that most of the product was a p-tropylphenol.

lit.[39] o-tropylphenol m.p. 77-78°. b.p. 110-130°/ 3 mm.

p-tropylphenol m.p. 77-78°. b.p. 130-170/3 mm.

Infra-red data. (μ).

Found	3.14(s), 3.31(s),	12.10(s)* ,	13.05(s),	14.22(s),	14.73(s)
o-tropylphenol[39]	2.82 ,	13.32 ,	13.55 ,	14.1	
p-tropylphenol[39]	3.09 ,	12.14* ,	13.05 ,	14.20 ,	14.71

*two adjacent hydrogens on a benzene ring.

7. Reaction of p-Tropylphenol with D.D.Q. and perchloric acid or picric acid.

Solutions of D.D.Q. and p-tropylphenol in acetonitrile were mixed. A brown precipitate formed immediately and after warming (about 40°) for five minutes and cooling thoroughly this product was collected and washed (ether). Later examination showed it to be (p-hydroxyphenyl)tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (see section C.VIII.6).

A sample of this brown product (205 mg.) was partly dissolved in warm acetonitrile (6 ml.) and treated with perchloric acid (0.1 ml.; 1.2 m.mole.). The brown colour rapidly turned to yellow as the solid dissolved and pale yellow frond-like crystals were deposited. After warming gently (50°) and cooling, the product (50 mg.; 35%) was filtered and recrystallised from acetic acid (with charcoal). A sample of p-hydroxyphenyltropylium perchlorate (m.p. 193-196° (dec); block preheated to 160°; lit.[52] 201-202°) was dried at 75°/0.5 mm. for two and a half hours before analysis.

Analysis

S.A. 1442 Found C 54.84 H 3.37%

$C_{13}H_{11}ClO_5$ requires C 55.23 H 3.92%.

The low melting-point may reflect the presence of some of the ortho derivative. With acetic acid as solvent the yield of salt was 74%.

A hot solution of picric acid (115 mg.; 0.5 m.mole) in ethanol (4 ml.) was added to a hot solution/suspension of the brown product (207 mg.; 0.5 m.mole; see above) in ethanol (4 ml.) and the mixture boiled for 15 seconds. The brown colour vanished at once and on cooling elongated plates (70 mg.; 35%) separated. A sample of (p-hydroxyphenyl)tropylium picrate (m.p. 141-143°; block preheated to 135°) was dried for two hours at 55°/0.5 mm. before analysis.

Analysis.

S.A. 1465 Found N 9.47%

$C_{19}H_{13}N_3O_8$ requires N 10.22%.

A sample of (p-hydroxyphenyl)tropylium perchlorate (10 mg.) in water (2 ml.) was treated dropwise with aqueous 0.1N sodium hydroxide solution. The colour, initially yellow, turned dark red and finally became colourless.

8. Preparation of 7-Phenylthiocycloheptatriene.

Tropylium perchlorate (9.53 g.; 50 m.mole) and sodium thiophenate (6.6 g.; 50 m.mole) in methanol (50 ml.) were allowed to stand at room temperature for two hours with occasional shaking. The solids gradually dissolved and a yellow colour developed. The mixture was poured into water (500 ml.), extracted with ether (2 x 300 ml.) and the combined extracts washed (water) and dried (K_2CO_3). Evaporation of the ether yielded a yellow oil which was distilled (b.p. 102-106°/0.5 mm.; lit.[40] 104°/0.002 mm.) through a short Claisen-Vigreux column to give a pale yellow oil (8.04 g.; 80%).

A sample prepared by distillation in a closed system was analysed.

Analysis.

S.A. 1398	Found	C 77.82	H 5.75	S 16.22%.
$C_{13}H_{12}S$	requires	C 77.95	H 6.04	S 16.01%.

Degani and Fochi[40] have since reported a preparation of phenylthiocycloheptatriene from tropyl chloride.

Phenylthiocycloheptatriene (200 mg.; 1 m.mole) dissolved in acetic acid (6 ml.) was treated with perchloric acid (0.1 ml.; 1.2 m.mole). A white precipitate and yellow oil formed immediately. The product was filtered off and

recrystallised from acetic acid to give tropylium perchlorate with melting-point behaviour as previously described. (Yield 174 mg.; 91%).

9. Reaction of 7-Phenylthiocycloheptatriene with D.D.Q. and perchloric acid.

As in the case of the O-ethers, a black intermediate (tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone) was formed from 7-phenylthiocycloheptatriene and D.D.Q. in acetonitrile (see section C.VIII.7). A sample of this intermediate (186 mg.) with perchloric acid (0.16 ml.; 2 m.mole) in acetic acid (4 ml.) gave tropylium perchlorate (104 mg.; 89% based on the semiquinone derivative).

10. Preparation and reactions of 7-Cyanocycloheptatriene

7-Cyanocycloheptatriene[30] (b.p. 91-92°/10 mm.) was prepared from tropylium perchlorate and potassium cyanide. The product, a colourless refractive liquid (n_D = 1.520; lit.[30] n_D = 1.533) was purified by fractionation through a Claisen-Vigreux column and the presence of the nitrile in position 7 was confirmed by means of an n.m.r. spectrum which displayed a triplet in the aliphatic region.

When treated with perchloric acid in acetonitrile or acetic acid, cyanocycloheptatriene gave no solid derivative. The same was true when it was treated with D.D.Q. and perchloric acid in either of the above-mentioned solvents. D.D.Q. alone produced a slight red coloration whilst addition of anhydrous ether to any of these mixtures failed to precipitate any product.

C.VI. Reactions of Cycloheptatriene with quinones in the absence of acid.

1. Reaction of Cycloheptatriene with D.D.Q.

Solutions of freshly distilled cycloheptatriene (1 ml.; 4 m.mole + 100% excess) and D.D.Q. (908 mg.; 4 m.mole) in acetonitrile (10 ml. each) were mixed at room temperature. The reaction was slightly exothermic and dark crimson spar-shaped crystals were immediately formed in a dark crimson solution. After allowing the mixture to stand for 5 minutes, it was chilled under cold running water and the crystals (690 mg.; 54%) filtered off. Recrystallisation in low yield from acetonitrile gave tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone, very dark crimson spars, black in appearance (m.p. 179-180° (dec.); block preheated to 175°). The melting-point varied over a few degrees depending upon the rate of heating or upon the temperature to which the block was preheated. The highest value is recorded.

The reaction was found to give a higher yield (91%) when carried out in methylene chloride. A sample was dried for 5 minutes at 110°/A.P. before being analysed.

Analysis.

S.A. 1269 Found C 56.59 H 2.05 Cl 22.95 N 8.88%

$C_{15}H_7Cl_2N_2O_2$ requires C 56.63 H 2.22 Cl 22.28 N 8.81%

Visible and u.v. spectrum (mμ): 346(3.85),456(3.69),546(3.67),585(3.70);
221(4.65),246(4.22),255(4.17),270(3.97).

I.R. spectrum. see Spectrum No.1.

2. Reaction of Cycloheptatriene with D.D.Q. in the absence of light or oxygen.

For this reaction a modification of Schlenk's apparatus was used (see Plate 4). D.D.Q. (908 mg.; 4 m.mole) in acetonitrile (10 ml.) was placed in bulb A and freshly distilled cycloheptatriene (1 ml.; about 8 m.mole) in acetonitrile (10 ml.) in the second bulb B. The solvent had been previously purified by distilling from phosphorus pentoxide (twice) followed by fractionation through a Claisen-Vigreux column. With the reactants in the vessel, dry, oxygen-free nitrogen was flushed through the apparatus for half an hour and a tap-funnel C, with a built-in sintered-glass plate D, attached to the outlet joint of bulb B. The light was extinguished.

With the stop-cock of the tap-funnel open and with nitrogen still passing through the system, the two solutions

were mixed by rotating the apparatus in a clockwise direction. That the reaction was taking place could be determined by feeling the rapid rise in temperature of bulb B. Still holding the tap-funnel in place the apparatus was again rotated until the product in bulb B was blown through the exit tube E into the funnel. The product was collected on the sintered-glass plate and the filtrate in a flask. The colour, form (dark crimson spars) and melting-point were identical with those of a sample previously prepared in the atmosphere and in daylight. The yield, including material washed out of the apparatus, was 700 mg. (55%).

3. Reaction of Tropylium Perchlorate with the dipotassium salt of 2,3-dichloro-5,6-dicyanoquinol.

(i) Preparation of dipotassium 2,3-dichloro-5,6-dicyanoquinolate

A solution-suspension of D.D.Q. (2.27 g.; 10 m.mole) in ethanol (10 ml.) was treated with a cold, saturated, aqueous solution of sulphur dioxide (30 ml.). The reaction was exothermic and the colour was immediately discharged to leave an off-white solid. The mixture was brought to the boil and allowed to cool when fluffy colourless needles of quinol crystallised. The product (2.07 g.; 88%)

recrystallised from ethanol as colourless spars (melts slowly with sublimation above 250°; lit.[48] blackens 265°).

2,3-Dichloro-5,6-dicyanoquinol (456 mg.; 2 m.mole) in ethanol (4 ml.) was treated dropwise with 3.4N aqueous potassium hydroxide solution (2.35 ml.; 8 m.mole) in ethanol (6 ml.). The solution immediately turned dark yellow and on standing, the product precipitated as long yellow plates. The mixture was heated for five minutes (about 60°), cooled and acetone (15 ml.) added. The salt, golden plates (519 mg.; 78%), was filtered off and washed (acetone). Purification was effected by dissolving the salt in the minimum volume of hot water and precipitating with acetone. The pure material darkened but failed to melt below 300°. A sample was dried for 4 hours at 58°/0.5 mm. before analysis.

Analysis

S.A. 1620	Found	C 30.67	H 0.62%
$C_8Cl_2N_2O_2K_2;H_2O$	requires	C 29.73	H 0.62%

(ii) Reaction with Tropylium Perchlorate

Experiment 1.

Dipotassium 2,3-dichloro-5,6-dicyanoquinol (308 mg.;

about 1 m.mole) was dissolved in 85% aqueous ethanol (12 ml.) and tropylium perchlorate (387 mg.; 2 m.mole) added slowly with stirring. The yellow colour of the salt began to fade immediately and a fine precipitate of potassium perchlorate started to separate. The mixture was boiled and cooled before filtering the solution to remove the slightly soluble potassium perchlorate.

Evaporation of the solvent under reduced pressure left a buff, tacky solid which was recrystallised, with charcoal, from ethanol to give colourless needles (melted slowly with sublimation above 270°) of quinol (105 mg.; 41%).

A mixture of quinol salt and tropylium perchlorate in anhydrous ethanol failed to react even when heated.

Experiment 2.

The experiment was repeated on twice the scale using 70% aqueous acetonitrile (14 ml.) as solvent. The colour, initially dark yellow turned red slowly then faded on standing. Potassium perchlorate (306 mg.) was completely precipitated by the addition of ether (150 ml.). After filtering, the solution was washed (water), dried (Na_2SO_4) and evaporated to give buff needles of crude quinol.

Recrystallisation from a large volume of acetonitrile yielded prisms which exhibited the melting-point behaviour described above.

A sample was dried for 2 hours at 50°/A.P. before analysis.

Analysis.

S.A. 1622	Found	C 43.41	H 0.74	N 12.29%
$C_8H_2Cl_2N_2O_2$	requires	C 41.95	H 0.88	N 12.23%

4. Reaction of Ferrocene with D.D.Q.

A solution of D.D.Q. (908 mg.; 4 m.mole) in acetonitrile (15 ml.) at the boiling-point was added to a solution of ferrocene (744 mg.; 4 m.mole) in acetonitrile (15 ml.) also at the boiling-point and the resultant solution boiled then cooled to room temperature. The product, which crystallised partly from the boiling solution, was filtered off and washed (small volume acetonitrile). Ferricenium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (1.59 g.; 96%) was recrystallised, without change in form, as black needles (m.p. 180-184°(dec.)) from acetonitrile. The material was found to be stable with no appreciable change in melting-point after 6 months. A sample was dried for 15 minutes 110°/A.P. prior to analysis.

Analysis.

S.A. 1330 Found C 52.77 H 2.41 Cl 15.45 N 6.37%

$C_{18}H_{10}Cl_2FeN_2O_2$ requires C 52.34 H 2.44 Cl 17.16 N 6.78%.

Visible and U.V. spectra (mμ).: 346 (3.84), 457 (3.69), 546 (3.68), 585 (3.72) ; 248 (4.43), 270 (shoulder.).

C.VII. Reaction of Alkyl- and Arylcycloheptatrienes with D.D.Q.

1. Reaction of 7-Methylcycloheptatriene with D.D.Q.

7-Methylcycloheptatriene (212 mg.; 2 m.mole) in acetonitrile (2 ml.) was added to a solution of D.D.Q. (454 mg.; 2 m.mole) also in acetonitrile (2 ml.), both at room temperature. The colour immediately became dark crimson and the solution was filtered within 10 seconds of mixing to give bronze needles (33 mg.; 5%) of methyltropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone. The addition of anhydrous ether precipitated only quinol and some oily material. Within half a minute of mixing the mother liquors had turned to an orange-brown and quinol had begun to separate.

The crystals failed to melt but decomposed slowly on the heating block. They also decomposed rapidly in all the common solvents and in atmospheric moisture. Without further purification, a sample was dried for one hour at 16°/0.5 mm. before analysis.

Analysis.

S.A. 1487 Found C 55.99 H 3.00%

$C_{16}H_9Cl_2N_2O_2$ requires C 57.85 H 2.73%.

I.R. spectrum (nujol) (μ).: 5.90(m),6.29(w),6.41(m),7.49(m),8.33(s) 9.29(s),10.15(w),11.20(m),12.79(w),13.90(m).

A similar reaction in methylene chloride (9 ml.) gave a higher yield (151 mg.; 23%) but the product was contaminated with quinol and could not be purified.

The mother liquors from the first reaction were poured into water and steam-distilled. The distillate was extracted with ether and the extracts washed (water), dried (Na_2SO_4) and evaporated. A pungent yellow oil (48.mg.) remained which failed to give a derivative with acidified 2,4-dinitrophenylhydrazine but whose I.R. spectrum displayed a band at 5.85 μ (cf. tropone 5.86 μ.).

2. Reaction of 7-Phenylcycloheptatriene with D.D.Q.

Filtered solutions of D.D.Q. (908 mg.; 4 m.mole) in acetonitrile (20 ml.) and 7-phenylcycloheptatriene (700 mg.; 4 m.mole + 4% excess) in acetonitrile (20 ml.) were mixed at room temperature. The solution became dark red immediately and phenyltropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone crystallised almost at once as brown plates. After being allowed to stand for 10 minutes at room temperature, the crystals (1.24 g.; 79%) were filtered off, washed (acetonitrile) and dried. A sample was recrystallised from a large volume of acetonitrile as brown needles (m.p. 180-181° ; block preheated to 175°) and dried for 10

minutes at 110°/A.P. before being analysed.

Analysis.

S.A. 1332	Found	C 64.34	H 2.76	Cl 18.30	N 6.88%
$C_{21}H_{11}Cl_2N_2O_2$	requires	C 63.96	H 2.81	Cl 17.99	N 7.11%.

3. Reaction of Ditropyl with D.D.Q.

A solution of ditropyl (364 mg.; 2 m.mole) in methylene chloride (10 ml.) was filtered into a filtered solution of D.D.Q. (454 mg.; 2 m.mole) in methylene chloride (20 ml.) at room temperature. A dark chocolate brown solid (336 mg.; 41%) separated. This solid became a light brown powder after drying under vacuum. It did not melt but decomposed slowly on the heating block, crystals of quinol subliming from it above 200°. The material was too unstable for analysis decomposing rapidly in the atmosphere.

C.VIII. Reaction of Tropyl ethers and thioethers with quinones.

1. Reaction of 7-Methoxycycloheptatriene with D.D.Q.

A solution of 7-methoxycycloheptatriene (488 mg.; 4 m.mole) in acetonitrile (5 ml.) was added to a boiling solution of D.D.Q. (908 mg.; 4 m.mole) in acetonitrile (10 ml.). The solution at once became dark red and a dark-coloured crystalline solid was deposited. After heating the mixture and cooling it rapidly, the product was filtered off. Recrystallisation from acetonitrile gave dark crimson spars, black in appearance (m.p. 169.5-170°(dec); block preheated to 165°), of tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (720 mg.; 57%). At room temperature the reaction was exothermic and gave a higher yield (860 mg.; 68%).

Before being analysed a sample was dried for two hours at 55°/0.5 mm.

Analysis.

S.A. 1473 Found C 56.42 H 2.50 N 8.24%

methoxytropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone $C_{16}H_9Cl_2N_2O_2$ requires C 55.19 H 2.61 N 8.05%

tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone $C_{15}H_7Cl_2N_2O_2$ requires C 56.63 H 2.22 N 8.81%

I.R. spectrum (Nujol) (μ): 6.48(w), 6.58(w), 7.88(m), 8.17(s), 8.41(s), 9.56(s), 10.11(m), 11.34(m), 12.88(s).

Visible and U.V. spectra (mμ): 346, 456, 544, 585; 221, 246, 254, 269.

2. Reaction of 7-Methoxycycloheptatriene with o-chloranil.

Solutions of methoxycycloheptatriene (488 mg.; 4 m.mole) in acetonitrile (5 ml.) and o-chloranil (984 mg; 4 m.mole) in acetonitrile (10 ml.) were mixed. The solution became dark red but on boiling the colour faded to orange-red and on cooling, orange plates (357 mg.) crystallised. Recrystallisation from acetonitrile gave the same crystal form (darkening with decomposition below 160° but does not melt below 320°). No solid product was obtained on treatment with acid. The product proved to be a known self-condensation product of o-chloranil.

A sample was analysed after drying for 10 minutes at 110°/A.P.

Analysis.

S.A. 1356.	Found	C 37.08	H 0.72	Cl 46.4%
$C_{12}Cl_6O_4$	requires	C 34.25	H 0.00	Cl 50.54%
$C_{12}Cl_6O_4$; CH_3CN	requires	C 36.4	H 0.65	Cl 45.9%

3. Reaction of 7-Methoxycycloheptatriene with p-chloranil.

Chloranil (246 mg.; 1 m.mole) dissolved in hot acetonitrile (8 ml.) was added to a solution of methoxycycloheptatriene (120 mg.; 1 m.mole) in acetonitrile (4 ml.). The solution turned greenish-brown and after boiling and cooling thoroughly, yellow plates (196 mg.) separated. This proved to be chloranil (m.p. and mixed m.p., colour and form.). The yield indicated an 80% recovery.

4. Reaction of 7-Ethoxycycloheptatriene with D.D.Q.

This reaction was exactly similar to that of methoxycycloheptatriene with D.D.Q. at room temperature. The reactants (4 m.mole samples) in acetonitrile (10 ml. each) were mixed and allowed to stand. The product tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (540 mg.; 42%) was collected and recrystallised from acetonitrile as micro-needles (m.p. and I.R. spectrum identical with an authentic specimen.).

5. Reaction of Ditropyl ether with D.D.Q.

Experiment 1 (in actonitrile).

A solution of D.D.Q. (717 mg.; 3.2 m.mole) in acetonitrile (5 ml.) was added to a solution of ditropyl

ether (622 mg.; about 3.2 m.mole) in acetonitrile (5 ml.). The reaction was exothermic and the solution turned dark crimson. Dark crimson spars of tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (729 mg.; 73%) crystallised out and were recrystallised from acetonitrile to give dark crimson spars (m.p. 166.5-168.5°(dec.)). The I.R. spectrum was identical with that of an authentic specimen.

Before analysis a sample was dried for 2½ hours at 48°/0.5 mm.

Analysis.

S.A. 1454 Found C 56.49 H 2.43 N 8.37%

Tropyloxytropylium semiquinone $C_{22}H_{13}Cl_2N_2O_3$

requires C 62.28 H 3.09 N 6.6%

Tropylium semiquinone $C_{15}H_7Cl_2N_2O_2$

requires C 56.63 H 2.22 N 8.81%

Experiment 2. (in methylene chloride. one equivalent of D.D.Q.)

Solutions of D.D.Q. (458 mg; 2 m.mole) and ditropyl ether (380 mg.; 2 m.mole) in methylene chloride (20 ml. and 5 ml. respectively) were mixed. The dark red colour developed and after five minutes black crystals began to precipitate. The mixture was allowed to stand for a further 15 minutes when the product was collected and washed (ether). The crude

product (610 mg.; 96% based on D.D.Q.) was recrystallised from acetonitrile and was identical with the product in the above reaction.

Experiment 3 (in methylene chloride, two equivalents of D.D.Q.)

The above experiment was repeated using half the quantity of ditropyl ether (1 m.mole). The product was carefully washed with methylene chloride and ether before drying and the yield (398 mg.) was 63% based on D.D.Q.

Evaporation of the solvent gave a brown oil which was steam-distilled. The distillate (1.5 l.) was extracted with ether (2 x 250 ml.), the extracts dried (K_2CO_3) and the solvent evaporated to leave a brownish-yellow oil (128 mg.) which was divided into two parts. The first part was treated with an acidified, saturated solution of 2,4-dinitrophenylhydrazine in ethanol. The fine brown precipitate which formed was collected, dried and found to melt slowly above 60°. From the characteristic smell of bitter almonds and from the I.R. spectrum of the second part (carbonyl absorption band 5.90 μ (s); benzaldehyde 5.91 μ) it was deduced that part of the material consisted of benzaldehyde.

6. Reaction of p-Tropylphenol with D.D.Q.

Solutions of D.D.Q. (227 mg.; 1 m.mole) and p-tropylphenol

(184 mg.; 1 m.mole) in acetonitrile (2 ml. and 3 ml. respectively) were mixed. A brown precipitate separated immediately from a crimson solution and after gentle warming (40°) and allowing the mixture to stand for five minutes, the product was filtered off and washed (ether). Recrystallisation from a large volume of acetonitrile gave (p-hydroxyphenyl)-tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (430 mg.; 56%) as dark brown prisms (m.p. 158.5 - 159.5° (dec.); block preheated to 150°).

A sample was dried for 1½ hours at 50°/0.5 mm. prior to analysis.

Analysis.

S.A. 1439	Found	C 60.07	H 3.24	N 6.64%
S.A. 1464	Found	C 60.50	H 2.70	N - %
$C_{21}H_{11}Cl_2N_2O_3$	requires	C 61.45	H 2.70	N 6.83%

I.R. spectrum (Nujol) (μ): 6.57(m), 8.20(m), 8.41(s), 9.58(m), 10.1(m), 11.36(m), 12.83(m), 14.17(m).

Visible and U.V. spectra (mμ) : 345(3.97), 432(4.26), 5.42(3.71), 580(3.70); 229(4.53), 255(4.27), 267(4.12).

7. Reaction of 7-Phenylthiocycloheptatriene with D.D.Q.

A solution of 7-phenylthiocycloheptatriene (800 mg.; 4 m.mole) in acetonitrile (10 ml.) was added to one of D.D.Q.

(908 mg.; 4 m.mole) in acetonitrile (10 ml.) at room temperature. The reaction was exothermic and the colour became an intensely dark crimson. Almost at once tiny dark crimson spars crystallised out. After five minutes the crystals (764 mg.; 60%) were collected, washed (ether) and recrystallised without change in form from acetonitrile. The pure product, tropylium 2,3-dichloro-5,6-dicyano-1,4-semiquinone (m.p. 179-180° (dec.); block preheated to 175°), was identical (I.R. spectrum and m.p.) with the product from cycloheptatriene and a mixed melting-point showed no depression.

A sample was dried for one hour at 60°/0.5 mm. before being analysed.

Analysis

S.A. 1405 Found C 56.31 H 2.30 Cl - N - S - %

S.A. 1406 Found C 56.96 H 2.43 Cl - N - S - %

S.A. 1431 Found C - H - Cl 22.6 N 8.96 S 0.32%

Phenylthiotropylium semiquinone $C_{21}H_{11}Cl_2N_2O_2S$

requires C 59.16 H 2.61 Cl 16.63 N 6.57 S 7.52%

Tropylium semiquinone $C_{15}H_7Cl_2N_2O_2$

requires C 56.63 H 2.22 Cl 22.3 N 8.81 S 0.00%

Visible and U.V. spectra (mμ): 346(3.86),456(3.68),546(3.67),585(3.71);
221(4.65),246(4.22),255(4.17),270(3.97).

The mother liquors of the above reaction were poured into water (100 ml.), filtered and extracted with ether. The combined extracts were washed in turn with 0.5N hydrochloric acid, water, 0.5N sodium hydroxide solution, water, acid and water and dried (K_2CO_3). Evaporation of the solvent yielded a colourless solid which was recrystallised from ethanol as small prisms (m.p. 59.5-61°; lit.[42] 60°) of diphenyl disulphide. This product gave a characteristic red colour with concentrated sulphuric acid which turned blue on warming.

In order to determine if diphenyl disulphide might be produced by the reaction of phenylthiocycloheptatriene (unreacted) and water during the work-up, phenylthiocycloheptatriene (200 mg.) in acetonitrile (4.5 ml.) was poured into water (50 ml.) and worked up as described above. After isolating and recrystallising from ethanol, the product was characterised as diphenyl disulphide (40 mg.; m.p. 60-61°).

Two exactly similar experiments were now carried out and pure diphenyl disulphide isolated from each. From the mother liquors of the reaction between phenylthiocycloheptatriene (800 mg.; 4 m.mole) and D.D.Q. (908 mg.; 4 m.mole) the yield of

disulphide was 268 mg. (62%). Diphenyl disulphide resulting from simple hydrolysis of phenylthiocyclo-heptatriene (800 mg.; 4 m.mole) amounted to 148 mg. (34%).

C.IX. 7-Dimethylaminocycloheptatriene.

1. Reaction of 7-Dimethylaminocycloheptatriene with D.D.Q.

Dimethylaminocycloheptatriene[30], a colourless oil (b.p. 25-27°/0.1mm.; lit.[30] 55-65°/1 mm.) was prepared from aqueous dimethylamine and tropylium perchlorate.

Dimethylaminocycloheptatriene (540 mg.; 4 m.mole) in acetonitrile (6 ml.) was added to a solution of D.D.Q. (908 mg.; 4 m.mole.) in acetonitrile (8 ml.). The reaction was exothermic, the solution turned dark red and a dark brown precipitate separated. When cold, the solid (1.04 g.; 95% based on dimethylammonium semiquinone) was collected, washed (ether) and recrystallised from acetonitrile as brown prisms (m.p. 159-160° (dec.); block preheated to 155°). A strong smell of benzaldehyde was noted in the mother liquors. Using methylene chloride as solvent the yield of dimethylammonium 2,3-dichloro-5,6-dicyano-1,4-semiquinone was quantitative.

Samples were dried for 2 hours at 40°/0.1 mm. before analysis.

Analysis.

S.A. 1481	Found	C 44.45	H 3.02	N 15.10%
S.A. 1491	Found	C 43.52	H 2.80	N 10.95%

Dimethylaminotropylium 2,3-dichloro-5,6-dicyanosemiquinone

$C_{17}H_{12}Cl_2N_3O_2$

requires C 56.52 H 3.35 N 11.63%

Dimethylammonium 2,3-dichloro-5,6-dicyanosemiquinone $C_{10}H_8Cl_2N_3O_2$

requires C 43.98 H 2.95 N 15.39%

I.R. spectrum (Nujol)(μ): 6.52(m), 7.89(m), 8.07(m), 8.27(m) 8.45-8.58 (broad), 9.37(m), 9.52(m), 9.89 (m), 10.11(m), 11.32-11.48 (broad), 12.71(m), 13.32(m), 13.51(m), 14.31(m).

Visible and U.V. spectra (mμ): 346(3.87), 444(3.63), 542(3.62), 581(3.66); 245(4.21), 257(4.23), 275(4.16).

(i) Examination of mother liquors.

The mother liquors of the above reaction were diluted with ether (500 ml.) and filtered to remove the last traces of the semiquinone. The bulk of the solvent was removed by evaporation (through a Claisen-Vigreux column) and the residue steam-distilled until no smell remained. A pale yellow oil separated from the distillate. This oil was taken up in ether, the ether solution dried (Na_2SO_4) and evaporated to leave crude benzaldehyde (259 mg.). Treatment of the benzaldehyde with a saturated solution of 2,4-dinitrophenylhydrazine in acidified ethanol gave the hydrazone derivative (470 mg.). This corresponds to a 41% yield of benzaldehyde.

Recrystallisation from acetic acid gave yellow needles of the derivative (m.p. 237-239° alone or mixed with an authentic specimen).

(ii) Reaction of dimethylammonium 2,3-dichloro-5,6-dicyano-1,4-semiquinone with picric acid.

A solution-suspension of the dimethylammonium semiquinone (271 mg.; 1 m.mole) in ethanol (4 ml.) was treated with a hot solution of picric acid (270 mg.; 1.2 m.mole) in ethanol (4 ml.) and the mixture boiled for one minute. The colour, initially red, turned brown as the solid dissolved and finally became yellow. Dimethylammonium picrate (180 mg.; 66%) crystallised from the cold solution. Recrystallisation from ethanol gave yellow spars (m.p. 156-159°; block preheated to 152°). A mixed melting-point with an authentic specimen showed no depression.

(iii) Attempted estimation of the radical with iodide ion.

Attempts to estimate the amount of radical-anion present by addition of iodide ion and volumetric estimation of the iodine liberated failed to give consistent results.

One millimole samples of the dimethylammonium semiquinone salt in acetonitrile (20 ml.) were treated separately with an excess of solid sodium iodide (500 mg.) and the solutions boiled for one minute. The dark brown solutions were cooled

under cold running water and the presence of free iodine was confirmed by testing with starch-iodide paper. Titration against standard sodium thiosulphate solution, however, gave widely varying results.

(iv) Spectrum from mixture of the dimethylammonium semiquinone derivative and tropylium perchlorate.

Standard solutions of the dimethylammonium semiquinone salt and tropylium perchlorate were made up in acetonitrile. A third solution was made up by mixing a sample (10 ml.) of the dimethylammonium semiquinone salt solution with an exactly molecular equivalent of the tropylium perchlorate solution and diluting to 50 ml. The U.V. and visible spectra of this solution were exactly superimposable on the spectrum of the tropylium semiquinone derivative formed from cycloheptatriene and D.D.Q.

U.V. and visible spectra (mμ): 222(4.52), 248(4.12), 255(4.10), 265(3.98); 346(3.89), 454(3.43), 542(3.30), 581(3.45).

2. Reaction of 7-Dimethylaminocycloheptatriene with p-chloranil.

Chloranil (1.47 g.; 6 m.mole) was added to a solution of dimethylaminocycloheptatriene (1.62 g.; 12 m.mole) in acetonitrile (20 ml.). The reaction was exothermic, the solution turned brown, red then magenta and brown needles

were precipitated. There was a strong smell of benzaldehyde. The mixture was boiled, cooled under the cold tap and dry ether (15 ml.) added. The product, 2,5-bis(dimethylamino)-3,6-dichloro-1,4-benzoquinone (165 mg.; 13%) was collected, washed (ether) and recrystallised from acetonitrile to give brown needles (m.p. 165-170°(dec.); block preheated to 160°; lit.[43] reports no m.p. but the visible spectra are the same (see section C.XI.1)). The mother liquors were divided in two.

Steam-distillation of the first portion yielded benzaldehyde which was taken up in ether (500 ml.). The ether extracts were dried (Na_2SO_4) and evaporated and the residual oil dissolved in ethanol and treated with an excess of a saturated ethanolic solution of 2,4-dinitrophenylhydrazine containing one drop of concentrated hydrochloric acid. The D.N.P. derivative (96 mg.; 11%) was obtained as orange needles (m.p. 235-236°; alone or mixed with an authentic specimen) from acetic acid. A considerable amount of tar remained after steam-distillation.

The second portion was allowed to stand for three days during which time colourless prisms were deposited. These were filtered off with difficulty because of their hygroscopic nature. After drying over phosphorus pentoxide for two days, a sample of these crystals melted 160-164°. The crystals

(280 mg.) were soluble in ethanol, dilute acid and dilute alkali but only slightly soluble in ether. Attempts to purify this material for analysis were unsuccessful.

The filtrate was extracted with 2N sodium hydroxide solution, the extracts washed with ether, neutralised with dilute hydrochloric acid and re-extracted with ether. After work-up a buff-coloured hygroscopic solid (520 mg.) remained. This solid melted over a wide range, attempts to recrystallise or sublime it were unsatisfactory. The solid was extracted with 2N hydrochloric acid (5 ml.) and the brown residue recrystallised, with charcoal, from acetic acid to give buff needles of tetrachloroquinol (m.p. 225-230°; lit.[25] 230-231°). The acid extracts were neutralised and extracted with ether. After work-up a small amount of unidentified brown oil remained.

The original acetonitrile-ether solution was washed (water) to remove traces of alkali, dried (Na_2SO_4) and evaporated. The reddish-brown oil which remained was chromatographed on thin-layer plates using benzene and chloroform. There were five coloured products including the brown quinone previously identified. The small quantity of oil precluded any further examination.

C.X. Tropylium Perchlorate as a Hydride Abstractor.

1. Reaction of 7-Dimethylaminocycloheptatriene with Tropylium Perchlorate.

Solid tropylium perchlorate (1.91 g.; 10 m.mole) was added to a solution of dimethylaminocycloheptatriene (1.35 g.; 10 m.mole) in acetonitrile (25 ml.) and boiled under reflux for 15 minutes on a steam bath. The perchlorate dissolved rapidly and the solution became dark yellow; there was a noticeable smell of cycloheptatriene. When cold, anhydrous ether (50 ml.) was added and a crop of yellow needles (1.09 g.) was precipitated. This material was collected and more ether (100 ml.) added to give a second crop (400 mg.) of a less pure product. Dimethylaminotropylium perchlorate (1.49 g.; 65%) was purified by dissolving in the minimum volume of acetonitrile and precipitating with anhydrous ether to give yellow needles (m.p. 137-139°; block preheated to 133°).

An analytical sample was dried for 5 minutes at 80°/A.P.

Analysis.

S.A. 1553	Found	C 46.60	H 5.17	N 5.98 %
$C_9H_{12}ClNO_4$	requires	C 46.26	H 5.18	N 5.99 %

A suspension of dimethylaminotropylium perchlorate (351 mg.; 1.5 m.mole) in ethanol (5 ml.) was treated dropwise with cold N sodium hydroxide solution (1.5 ml.). The solution rapidly turned from yellow to dark red and the mixture was poured into water (40 ml.) and extracted with ether (3 x 50 ml.). The extracts were washed with water, dried (Na_2SO_4) and evaporated. The residual red oil was chromatographed on a column of activated alumina (1.7 cm. x 18 cm.) using a 1:1 mixture of methylene chloride and ether. Three yellow and four red fractions were obtained as oils (yields ranging 3 mg. - 8 mg.) none of which was characterised. Weaker bases produced a similar result.

2. Attempted reaction between 7-Methoxycycloheptatriene and Tropylium Perchlorate.

Solid tropylium perchlorate (378 mg.; 2 m.mole) was added to a solution of freshly distilled methoxycycloheptatriene (268 mg.; 2 m.mole) in acetonitrile (6 ml.). The mixture was brought to the boil and the colour changed from yellow to brownish-orange. When cold, dry ether (25 ml.) was added a buff precipitate settled out. The product

(370 mg.) was collected, washed (ether) and recrystallised from acetonitrile as fern-like plates of tropylium perchlorate (m.p. 300° with effervescence at 270°; block preheated to 250°).

Similar results were obtained with phenylthiocycloheptatriene and cyanocycloheptatriene as substrates. In each case over 90% of the tropylium perchlorate was recovered.

C. XI. Reactions of Quinones with amines.

1. Reaction of p-chloranil with aqueous Dimethylamine.

Chloranil (1.23 g.; 5 m.mole) in acetonitrile (10 ml.) was treated with 25% $^{w}/_{w}$ aqueous dimethylamine (4 ml.). The solution became dark purple and brown needles were deposited. After boiling for one minute and cooling under the cold tap, the product (1.26 g.) was collected and recrystallised, without change in form, from acetonitrile to give brown needles (m.p. 165-170° (dec.); block preheated to 160°). This quinone, 2,5-bis(dimethylamino)-3,6-dichloro-1,4-benzoquinone, was also produced in the reaction between dimethylaminocycloheptatriene and chloranil. A mixed melting-point showed no depression and their I.R. spectra were identical (carbonyl absorption 6.04 μ). Their U.V. and visible spectra contained the same maxima ($\lambda_{max.}$ 238 mμ, 415 mμ). Henbest[43] reported this compound but gave only spectral data.

The filtrate was evaporated, more solvent being added to assist in removing water as an azeotrope, and the residue chromatographed on a column of activated alumina (3 cm. x 15 cm.) eluting with a benzene - 5% ether mixture. The product, 2-N-dimethylamino-3,5,6-trichloro-1,4-benzoquinone,

consisted of purple needles (m.p. 117-119°; block preheated to 115°), visible absorption $\lambda_{max.}$ 545 mμ, $\lambda_{min.}$ 411 mμ. (lit.[44] m.p. 120-122°; $\lambda_{max.}$ 545 mμ.).

2. Reaction of o-chloranil with aqueous dimethylamine.

o-Chloranil (1.23 g.; 5 m.mole) in acetonitrile (10 ml.) was treated with 25% w/w aqueous dimethylamine (4 ml.). The reaction was exothermic, the solution turned dark red and fine black needles of the bis(dimethylamino)-derivative (920 mg.; 73%) crystallised out. Recrystallisation from acetonitrile gave crystals of the same form (m.p. 176-179° (decomposition to white solid); block preheated to 170°).

An analytical sample was dried for 5 minutes at 120°/A.P.

Analysis.

S.A. 1578 Found N 10.48%

dichloro-bis(dimethylamino)quinone $C_{10}H_{12}Cl_2N_2O_2$

requires N 10.65%

3. Reaction of Benzylamine with D.D.Q.

Solutions of D.D.Q. (1.13 g.; 5 m.mole.) and benzylamine (1.07 g.; 10 m.mole) in acetonitrile (5 ml.each) were mixed. The reaction was slightly exothermic, the solution

turned dark orange and a precipitate of fine orange needles separated. The mixture was boiled for 30 seconds, filtered hot through a sintered-glass funnel and allowed to cool. Cream plates of benzylamine hydrochloride (m.p. 246-248° alone or with an authentic specimen) remained in the funnel. The orange product was collected, washed (water) to remove the last traces of the hydrochloride and recrystallised from acetonitrile as tangerine-coloured needles (m.p. 211-217°; block preheated to 207°) of 2,5-bis(N-benzylamino)-3-chloro-6-cyano-1,4-benzoquinone (1.15 g.; 90%).

A sample was dried for 4 hours at 50°/0.5 mm. before analysis.

Analysis.

S.A. 1577	Found	C 65.92	H 4.45	N 9.78%
$C_{21}H_{16}ClN_3O_2$	requires	C 66.75	H 4.27	N 11.12%

4. Reaction of N,N-dimethylbenzylamine with D.D.Q.

N,N-Dimethylbenzylamine[45], a colourless refractive oil (b.p. 59-60°/10 mm.; lit.[45] 183-184°/765 mm.), was prepared from dimethylamine and benzyl chloride.

Dimethylbenzylamine (270 mg.; 2 m.mole) in acetonitrile (5 ml.) was added all at once to a solution of D.D.Q. (454 mg.; 2 m.mole) in acetonitrile (3 ml.). The reaction was exothermic

and the solution immediately turned chocolate brown. The mixture was heated for 30 seconds at 100° and the colour changed rapidly to dark crimson. On cooling, a black, crystalline mass was deposited. The product, dimethylbenzylamine 2,3-dichloro-5,6-dicyano-1,4-semiquinone (230 mg.; 32%) was recrystallised from acetonitrile as black, truncated tetrahedra (m.p. 129.5 - 131°; block preheated to 125°). On the 10 m.mole scale with less solvent a 55% yield was recorded.

An analytical sample was dried for 2 hours at R.T./0.5 mm. before analysis.

Analysis

S.A. 1584	Found	C	55.70	H	4.11	N	11.88 %
S.A. 1593	Found	C	55.76	H	4.08	N	- %
$C_{17}H_{13}Cl_2N_3O_2$	requires	C	56.37	H	3.62	N	11.60 %

I.R. spectrum (Nujol) (μ): 4.56(-CN), 6.38(m), 6.48(m), 6.60(m), 8.21(m), 8.42(s), 9.53(m), 10.75(m), 11.31(m), 12.79(m), 13.30(m), 13.50(m), 14.37(m).

Visible and U.V. spectra (mμ): 346(3.89), 453(3.78) 542(3.77), 585(3.80); 246(4.19), 255(4.10) 268(3.66).

In order to estimate the benzaldehyde (detected by smell)

present, the mother liquors were poured in 2N aqueous sodium hydroxide (20 ml.) and steam-distilled. The oil from the distillate yielded benzaldehyde 2,4-dinitrophenylhydrazone from which the yield of benzaldehyde (74 mg.; 7%) was determined.

(i) Reaction of N,N-dimethylbenzylamine 2,3-dichloro-5,6-dicyanosemiquinone with alkali.

The dimethylbenzylamine semiquinone (722 mg.; about 2 m.mole) in acetonitrile (5 ml.) was treated with 0.8 N sodium hydroxide solution (20 ml.) and a stream of nitrogen passed through the alkaline mixture. The gases evolved were passed into a solution of picric acid in ethanol (10 ml.) and the mixture was warmed periodically. After 18 hours N sodium hydroxide solution (8 ml.) was added and bubbling, with occasional warming, continued for a further 3 hours. A small amount of solid which precipitated from the picric acid solution was recrystallised to give dimethylammonium picrate (m.p.145-152° ; lit.[46] 158-159°).

In the reaction-flask a precipitate of dark red needles formed on cooling. The product was collected and washed (ether) and found to be insoluble in alcohols, acetonitrile and ether. It dissolved in water or acetic acid to give dark

red solutions and a sample was prepared for analysis by dissolving in the minimum volume of hot water and precipitating with boiling ethanol. The form was unchanged, fine, scarlet needles which failed to melt below 300° and a sample was dried for 3 hours at 50°/0.5 mm. prior to analysis. The product was found to be 2-chloro-5-cyano-3,6-dihydroxy-1,4-benzoquinone disodium salt dihydrate.

Analysis.

S.A. 1592 Found C 32.25 H 1.31 N 5.40 Cl 13.90%

$C_7ClNO_4Na_2,2H_2O$ requires C 32.77 H 1.57 N 5.46 Cl 13.82%.

I.R. (Nujol)(μ) : 2.81, 2.9-3.1(H_2O, broad), 4.54 (-CN), 6.17(m), 6.22(m), 7.12(m), 11.67(m).

Several attempts were made to estimate the benzaldehyde produced by the alkaline hydrolysis of the semiquinone derivative (described above) isolating the aldehyde as the 2,4-dinitrophenylhydrazone after steam-distillation. In order to prevent oxidation by the semiquinone anion-radical various reducing agents (sodium bisulphite, dithionite or sulphide) were added in excess. These reagents had little effect on the yields which were all of the order of 7-8%.

5. Reaction of Trimethylamine with D.D.Q.

A solution of 3.5M trimethylamine in acetonitrile (7 ml.) was added all at once to D.D.Q. (908 mg.; 4 m.mole) dissolved

in acetonitrile (15 ml.). The reaction was mildly exothermic; the solution turned dark red and black short needles were deposited. The product (480 mg.; 42%), black needles with a green reflex, was filtered from the cold solution and recrystallised from acetonitrile to give trimethylamine 2,3-dichloro-5,6-dicyano-1,4-semiquinone (m.p. 155-158°(dec.); block preheated to 140°). Using methylene chloride as solvent the yield was 79%.

When a 3.5M trimethylamine solution (10 ml.) was run in slowly to D.D.Q. (3.63 g.; 16 m.mole) in acetonitrile (30 ml.), the product formed immediately. After cooling under cold running water, methylene chloride (40 ml.) was added and the product (3.74 g.; 82%) collected. A sample for analysis was dried at 80°/A.P. for 5 minutes.

Analysis

S.A. 1609 Found C 46.43 H 3.17 Cl 25.9 N 15.20%

$C_{11}H_9Cl_2N_3O_2$ requires C 46.16 H 3.17 Cl 24.78 N 14.69%

Visible and U.V. spectra (mμ): 347(3.89), 458(3.78), 545(3.75), 585(3.79);
246(4.19), 254(4.16), 268(3.68).

(1) Trimethylamine Picrate.

The semiquinone (1.14 g.; 4 m.mole) prepared above was

added to a boiling mixture of picric acid (1.10g.; 4.8 m.mole) in ethanol (32 ml.) and the mixture boiled for about 3 minutes. The resulting red solution was allowed to cool to room temperature and stand for a further hour before being filtered. The product was collected and washed with a small volume of ethanol then ether, to remove a red impurity, leaving yellow needles. Two recrystallisations from ethanol gave yellow plates (m.p. 200-215° ; sublimation above 150°) of trimethylamine picrate.

Analysis.

S.A. 1614 Found C 37.79 H 4.33 N 15.51 %

$C_9H_{10}N_4O_7$ requires C 37.77 H 3.52 N 19.57 %.

To confirm the structure aqueous 2 N potassium hydroxide (3 ml.; 6 m.mole) was added to a suspension of the picrate (286 mg.; 1 m.mole) in ethanol (12 ml.). Nitrogen was passed through to carry over the amine produced into a saturated solution of picric acid (10 ml. containing about 2 m.mole). The mixture was slowly warmed to boiling and the resultant gases passed over in a vapour of ethanol. When cooled, yellow needles of the picrate crystallised and dry ether (10 ml.) was added. The product, trimethylamine picrate (155 mg.; 54%) melted 200-215° (sublimation above 150°; lit.[46] 216°) after recrystallisation from ethanol.

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LITERATURE ABBREVIATIONS

Acad.rep.populare Romîne, Studii cercetări Chim. - Academie Republicii poplare Romîne Studii si cercetări di Chimie.

Acta Chem.Scand. - Acta Chemica Scandinavica.

Am. Chem.J. - American Chemical Journal

Anal.Chem. - Analytical Chemistry.

Angew.Chem. - Angewandte Chemie.

Ann. - Annalen der Chemie (Liebeg's).

Ber. - Chemische Berichte (Berichte der deutschen chemischen Gesellschaft.)

Boll.Sci.Fac.Chim.Ind. Bologna - Bolletino Scientifico della Facolta di Chimica Industriale di Bologna.

Brit. Pat. - British Patent.

Bull. Chem.Soc. Jap. - Bulletin of the Chemical Society of Japan.

Bull.Soc.Chim.France - Bulletin de la Société Chimique de France.

C.A. - Chemical Abstracts.

Can. J. Chem. - Canadian Journal of Chemistry.

Chem. & Ind. - Chemistry and Industry.

Chem. Rev. - Chemical Reviews.

Comptes rendus - Comptes rendus Hebdomadaires des Séances de l'Academie des Sciences.

Dokl.Akad.Nauk S.S.S.R. - Doklady Akademii Nauk S.S.S.R. (Proceedings of the Academy of Sciences of the U.S.S.R.)

Gazz.Chim.Ital. - Gazzetta Chimica Italiana.

Helv.Chim.Acta - Helvetica Chimica Acta.

Izv.Akad.Nauk S.S.S.R. Otdel.Khim.Nauk - Izvestiya Akademii Nauk S.S.S.R. Otdelenie khimicheskikh Nauk Moscow (Bulletin of the Academy of Sciences of the U.S.S.R.)

J.A.C.S. - Journal of the American Chemical Society.

J.C.S. - Journal of the Chemical Society.

J.Chem.Phys. - Journal of Chemical Physics.

J.Chim.Phys. - Journal de Chimie Physique.

J.Org.Chem. - Journal of Organic Chemistry.

J. Phys.Chem. - Journal of Physical Chemistry.

Nature - Nature.

Naturwissenschaften - Naturwissenschaften.

Nippon Kagaku Zasshi - Journal of the Chemical Society of Japan.

Proc.Chem.Soc. - Proceedings of the Chemical Society.

Rec.Trav.Chim. - Recueil des Travaux chimiques des Pays-Bas et de la Belgique.

Russian Chem.Rev. - Russian Chemical Reviews.

Spectrochim.Acta. - Spectrochimica Acta.

Tet. - Tetrahedron

Tet.Let. - Tetrahedron Letters.

Trans. Farad. Soc. - Transactions of the Faraday Society.

Uspekhi Khim. - Uspekhi Khimii (Russian Chemical Reviews).

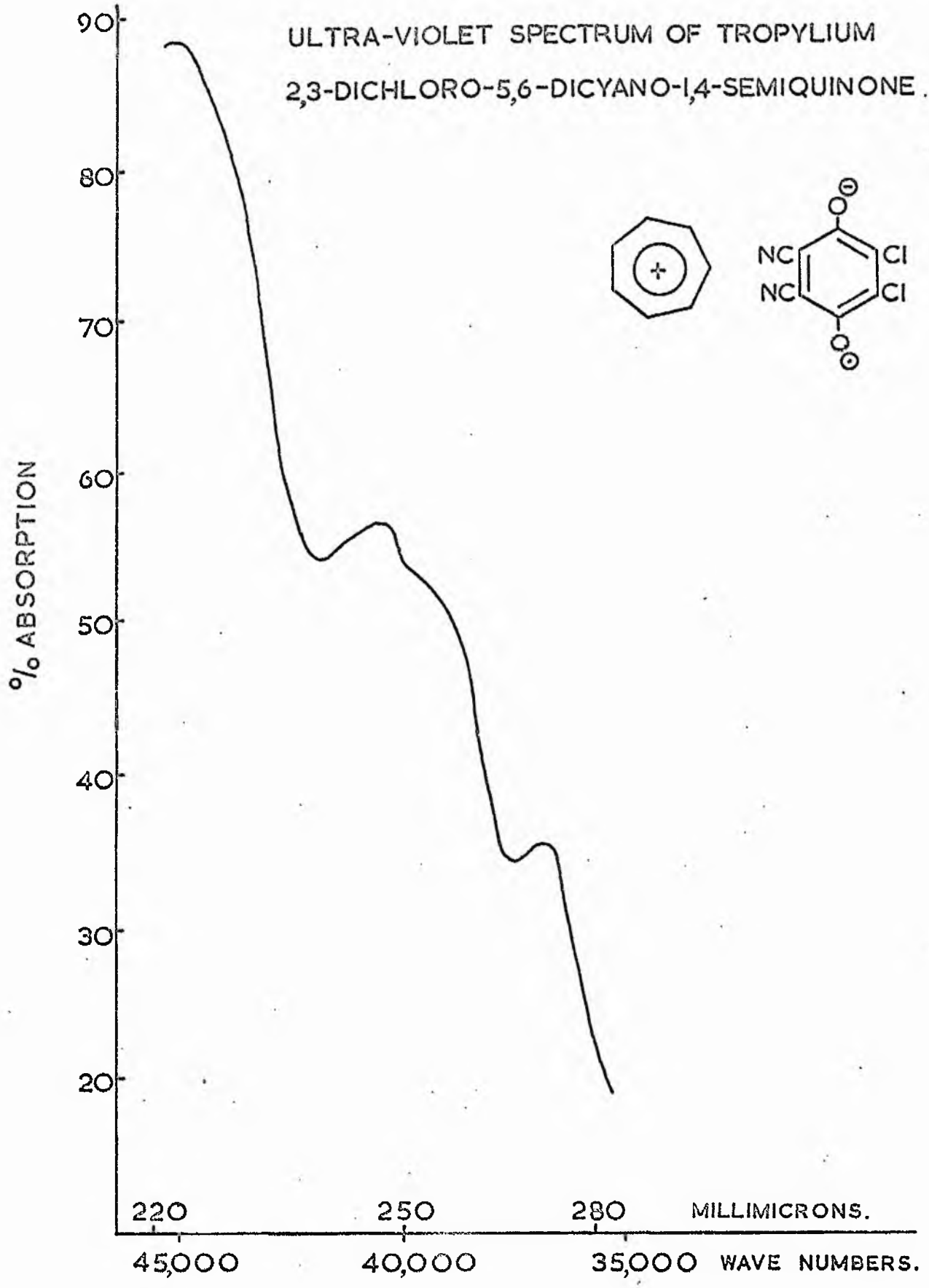
Z. Electrochem. - Zeitschrift für Electrochemie.

Zhur. Obshchei Khim. - Zhurnal Obshchei Khimii. (Journal of General Chemistry U.S.S.R.)

Z. Naturforsch. Zeitschrift für Naturforschung.

Z. Phys.Chem. - Zeitschrift für Physikalische Chemie.

----- P L A T E S -----


ULTRA-VIOLET SPECTRUM OF TROPYLIUM
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NC
NC
Cl
Cl
% ABSORPTION
90
80
70
60
50
40
30
20
220
250
280
MILLIMICRONS.
45,000
40,000
35,000
WAVE NUMBERS.

PLATE I

VISIBLE SPECTRUM OF TROPYLIUM
2,3-DICHLORO-5,6-DICYANO-1,4-SEMIQUINONE.

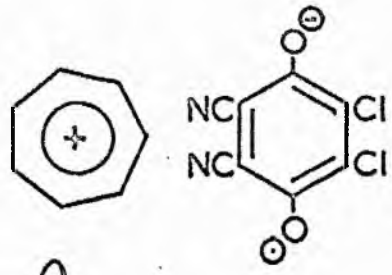
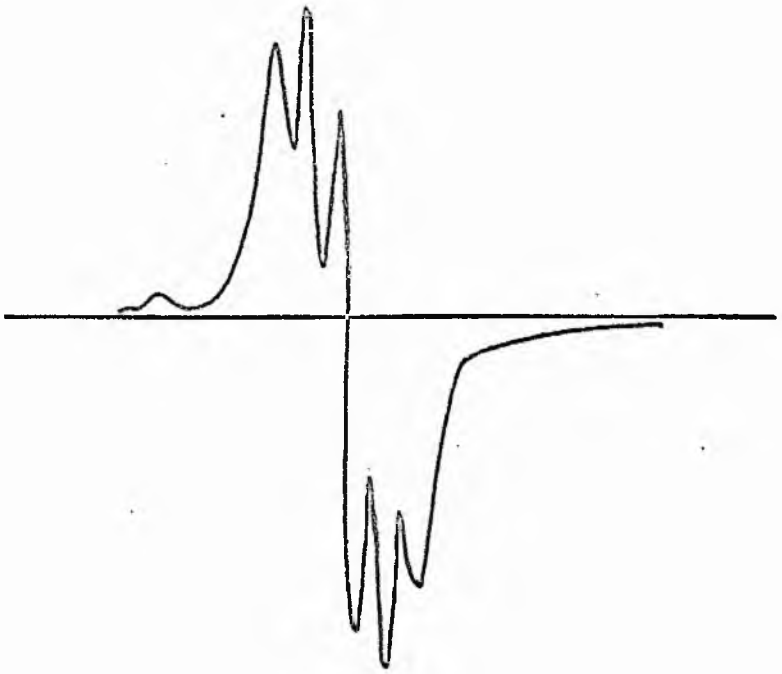
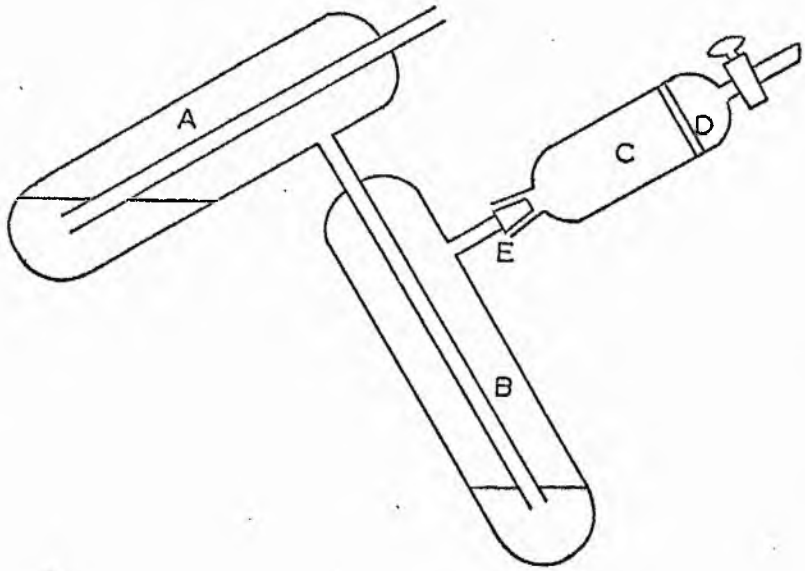


PLATE 2.



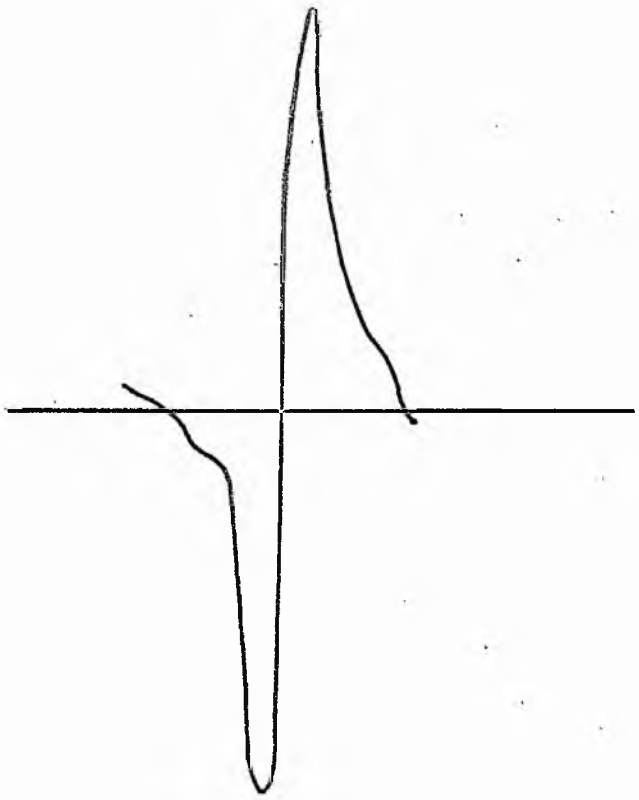
ELECTRON SPIN RESONANCE SPECTRUM OF
TROPYLIUM 2,3-DICHLORO-5,6-DICYANO-1,4-SEMIQUINONE.

PLATE 3.



MODIFIED SCHLENCK APPARATUS

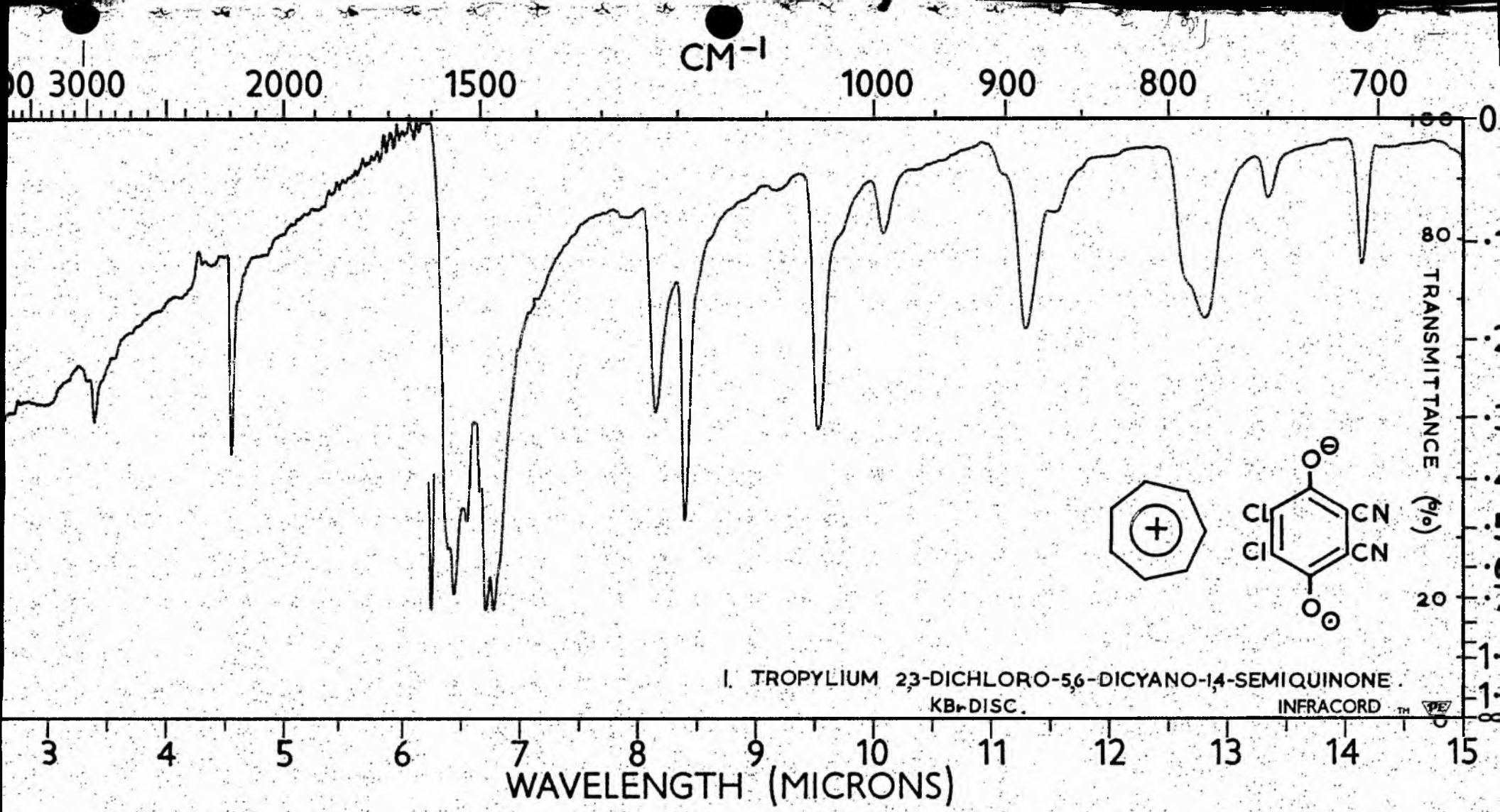
PLATE 4.



ELECTRON SPIN RESONANCE SPECTRUM OF
TRIMETHYLAMINE 2,3-DICHLORO-5,6-DICYANO-1,4-SEMIQUINONE.

PLATE 5.

----- S P E C T R A -----



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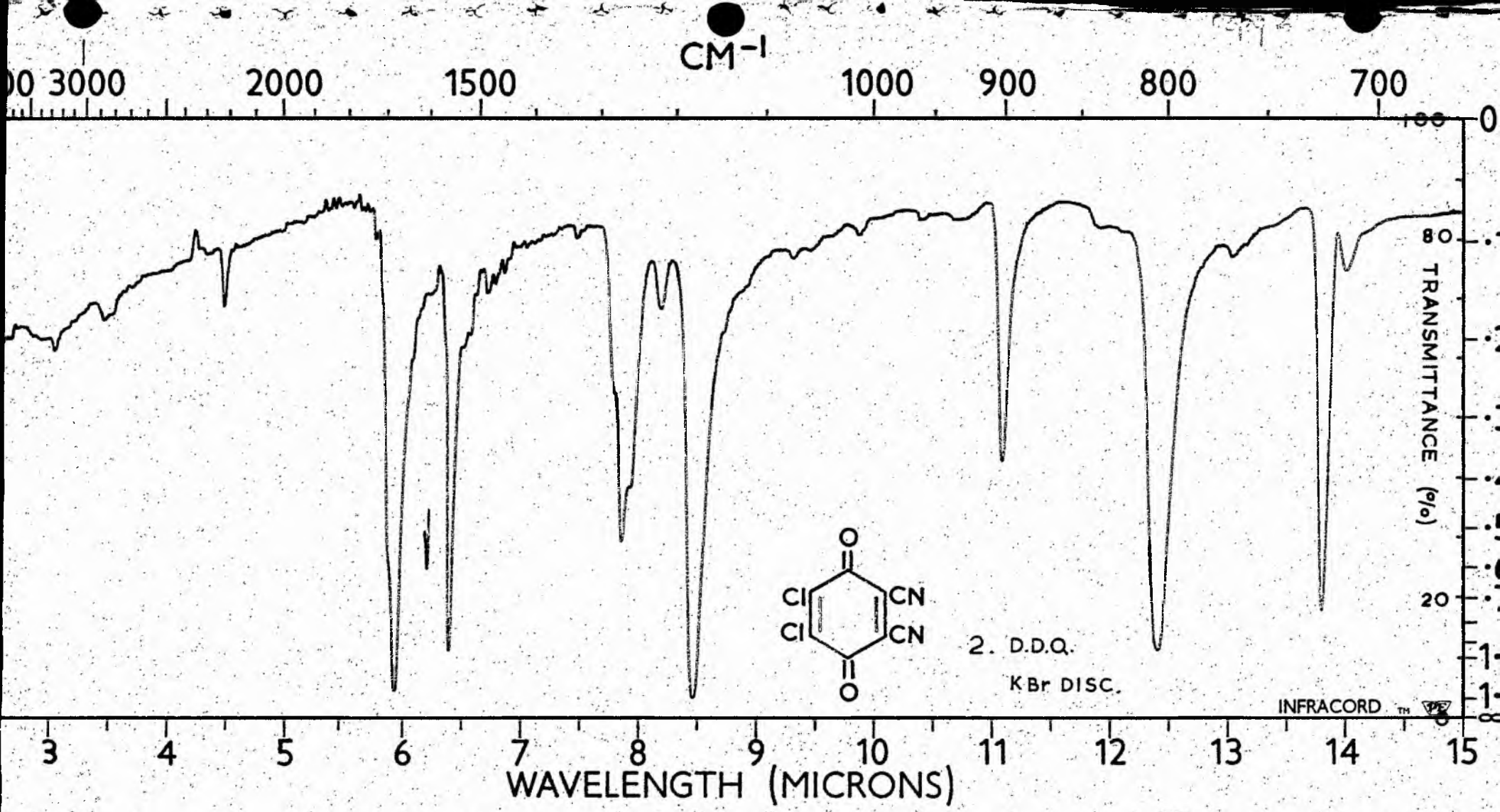
	THICKNESS	OPERATOR	

SAMPLE



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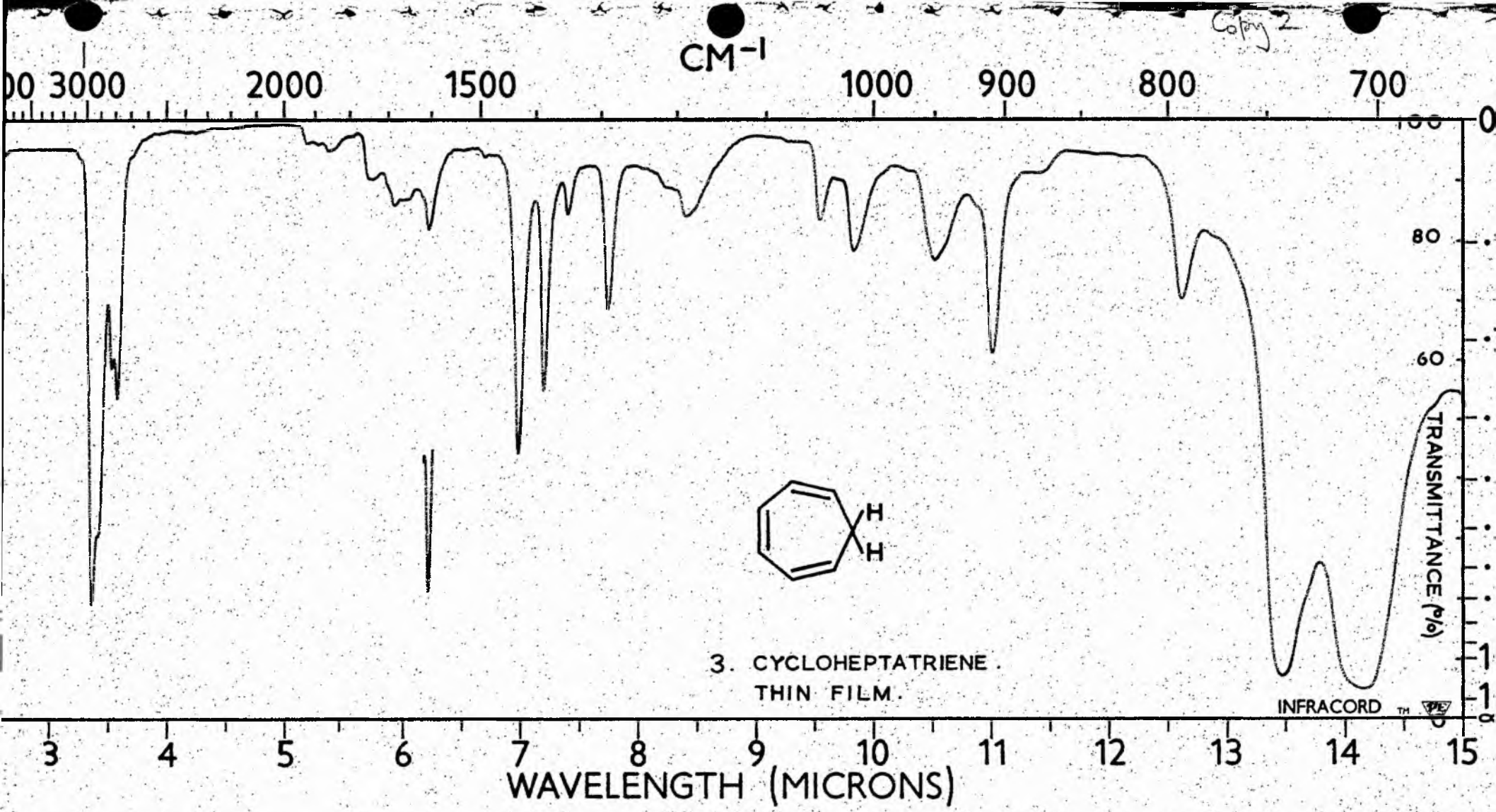
SAMPLE

Copy 2



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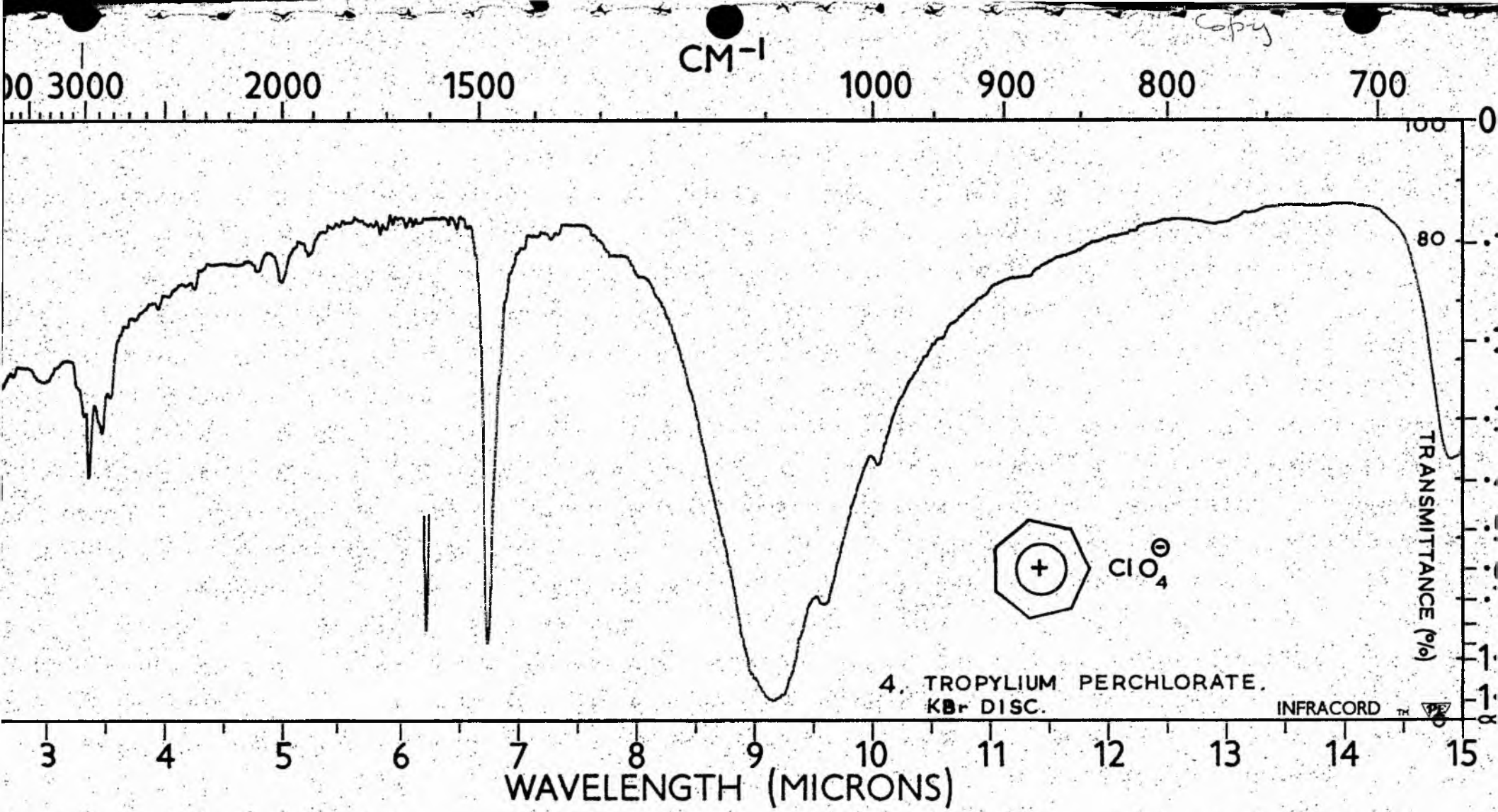

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
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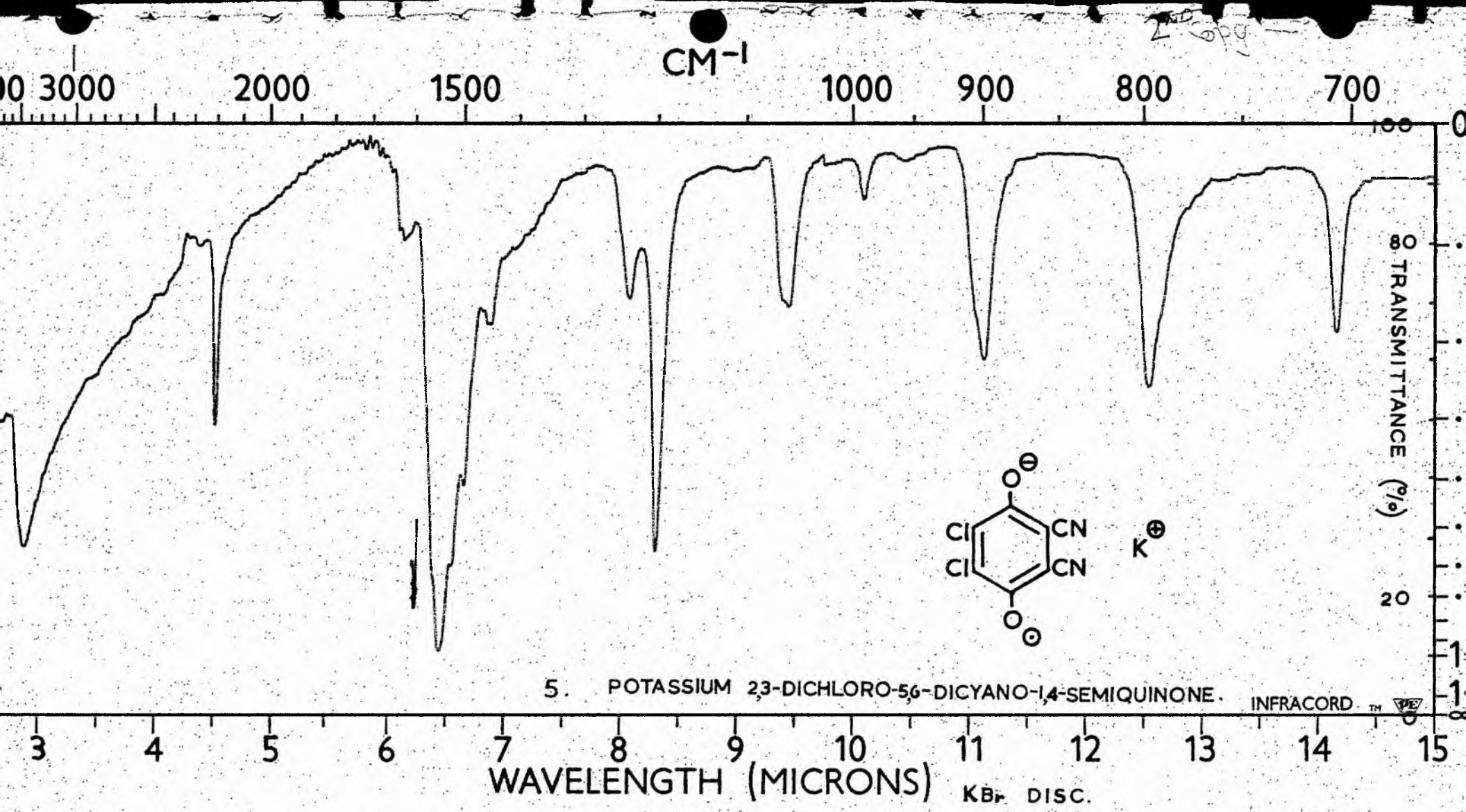
SAMPLE



5. POTASSIUM 2,3-DICHLORO-5,6-DICYANO-1,4-SEMIQUINONE. INFRACORD ™

SPECTRUM NO.____

SAMPLE____

ORIGIN____

PURITY____

PHASE____

LEGEND____

1.____

2.____

DATE____

REMARKS____

SAMPLE____