E.S.R STUDIES OF THE DECOMPOSITION OF ACYLARYLNITROSAMINES

Robert Michael Paton

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

1969

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E. S. R. STUDIES OF THE

DECOMPOSITION OF ACYLARYLNITROSAMINES

A Thesis

presented for the degree of

Doctor of Philosophy

in the Faculty of Science of the

University of St. Andrews

by

Robert Michael Paton, B. Sc.

United College of St. Salvator
and St. Leonard, St. Andrews.

September, 1969.
I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor J. I. G. Cadogan and Dr. C. Thomson since the 1st October 1966, the date of my admission as a research student.
I hereby certify that Robert Michael Paton has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research
ABSTRACT

The e. s. r. spectra observed during the decomposition of acylaryl nitrosamines in four series of solvents have been investigated, and the mechanisms of the reactions discussed in terms of the radicals involved.

For aromatic hydrocarbons two signals were detected. The first was that due to the (N-phenylacetamido)phenyl-nitrooxide $\pi$-radical, as reported by Chalfont and Perkins (J. Amer. Chem. Soc., 1967, 89, 3054), while the second was attributed to the phenyldiazotate $\sigma$-radical. The structure of these radicals is discussed in the light of a study of the spectra resulting from variation of the acyl and aryl groups of the nitrosamide and of theoretical calculations using the McLachlan and CNDO methods. The mechanism originally proposed by Rüchardt and Freudenberg (Tetrahedron Letters, 1964, 3623) is preferred to that of Perkins, in view of the failure to detect the chain-carrier radical of the latter scheme in some of the solvents, the intensity of the phenyldiazotate signal remaining constant throughout.

For ethers the two signals observed were assigned to (N-phenylacetamido)phenylnitrooxide and (N-phenylacetamido)-1-alkoxyalkyl nitrooxide resulting from the addition of phenyl and
1-alkoxyalkyl radicals to the nitroso group of the nitrosamide. The mechanism proposed, which is also applicable to the reaction in alcohols, is based on that currently acceptable for the decomposition of diazonium salts in ethers.

Whenever possible assignments have been made for the various other signals detected and the mode of formation of the radicals discussed.
ACKNOWLEDGEMENTS

I should like to express my gratitude to Professor J. I. G. Cadogan for suggesting the topic of research, and to Professor Cadogan and Dr. Colin Thomson for their help and encouragement in all aspects of this work.

My thanks are also due to many members of the teaching, technical and secretarial staffs of the Department of Chemistry and the Computing Laboratory in the University of St. Andrews, for their helpful suggestions and assistance at various times.

I am indebted to the Science Research Council for the award of a Research Studentship for the period during which this investigation was made.
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I THE STUDY OF FREE RADICALS

a) Preamble

The discovery of triphenylmethyl by Comberg in 1900 opened the era of free radical chemistry. Despite several decades of scepticism, based on a rigid adherence to Kekulé's idea of the constant quadrivalency of carbon, other stable radicals were prepared and a number of chemists postulated the existence of transient radical intermediates, both in solution and in the gas phase.

Although, through the years there have been a variety of interpretations of the term "radical", today it can be defined as "an atom or group of atoms which contain one or more unpaired electrons": it thus encompasses not only neutral species such as nitric oxide, the sodium atom and phenyl ($C_6H_5$), but also ions like the naphthalene anion.

The subject has been reviewed in detail by a number of authors, and there follows but a brief summary of the chemistry of free radicals.
3.

b) **Formation**

It was Ingold in 1938 who distinguished between the two possible modes of covalent bond fission as:

Heterolysis - \[ A:B \rightarrow A^- + B^+ \]

Homolysis - \[ A:B \rightarrow A^- + B^- \]

Homolytic fission can be induced by:

(i) The thermolysis of all organic bonds in the gas phase above 800° and of weak bonds in solution.

\[ \text{e.g.} \quad \text{Ph.N:N.CPh}_3 \xrightarrow{70-80^\circ} \text{Ph}^- + \text{N}_2 + \text{CPh}_3 \]

(ii) Photolysis of gases, liquids and solids.

\[ \text{e.g.} \quad \text{Cl}_2 \xrightarrow{hv} 2\text{Cl}^- \]

\[ \text{e.g.} \quad \text{Ph}_2\text{Hg} \xrightarrow{hv} 2\text{Ph}^- + \text{Hg} \]

(iii) Electron transfer.

\[ \text{e.g.} \quad \text{RCO}_2^- \xrightarrow{\text{anode}} \text{RCO}_2^- \]

c) **Reactions**

The reactions of free radicals can be classified thus:

The radical destroying processes of:

(i) Combination. \[ \text{R}^- + \text{R}'^- \rightarrow \text{RR}' \]

\[ \text{e.g.} \quad 2\text{PhCH}_2^- \rightarrow \text{PhCH}_2\text{CH}_2\text{Ph} \]
(ii) Disproportionation. \(2R\text{CH}_2\text{CH}_2 \rightarrow R\text{CH}_2\text{CH}_3 + R\text{CH}:\text{CH}_2\)

and the radical propogating processes of:

(iii) Addition to multiple bonds. \(R^* + X=\text{Y} \rightarrow R-\text{X-Y}^*\)

\[\text{e.g. } \text{Ph}^* + \text{Ph-CH}=\text{CH}_2 \rightarrow \text{Ph-CH-CH}_2-\text{Ph}\]

(iv) Fragmentation. \(R^* \rightarrow R'. + Y\)

\[\text{e.g. } \text{Ph-CO}_2^* \rightarrow \text{Ph}^* + \text{CO}_2\]

(v) Abstraction. \(R^* + R'\text{Y} \rightarrow R\text{Y} + R'.\)

\[\text{e.g. } \text{Ph}^* + \text{CCl}_4 \rightarrow \text{PhCl} + \cdot\text{CCl}_3\]

(vi) Rearrangement. \(R^* \rightarrow R'.\)

\[\text{e.g. } \text{Me-}^0\text{C-CH}_2 \rightarrow \text{MeCOCH}_2^*\]

Radical reactions are often complicated by chain processes.

A reactive radical is generated in an initiation step and products are formed in the chain sequence until termination. A typical example is the chlorination of a hydrocarbon.

Initiation: \(\text{Cl}_2 \rightarrow_{\text{hv}} \text{Cl}^*\)

Propogation: \(\text{Cl}^* + \text{RH} \rightarrow R^* + \text{HCl}\)
\(R^* + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}^*\)

Termination: \(2\text{Cl}^* \rightarrow \text{Cl}_2\)
\(2\text{R}^* \rightarrow \text{R}_2\)
\(\text{Cl}^* + \text{R}^* \rightarrow \text{RCl}\)
Methods of Study and Detection

Stable free radicals such as nitric oxide, galvinoxyl (1) and 2,2-diphenyl-1-picrylhydrazyl (2) can be studied by conventional chemical techniques. The presence of the unpaired electron has well-defined effects, not only on their reactions, but also on the ultraviolet, visible and infrared spectra.

On the other hand, for the majority of reactions involving transient radicals the evidence is circumstantial, resulting from a detailed study of the kinetics and products of the system.

Although susceptibility measurements have been used to illustrate the paramagnetic nature of free radicals throughout this century, it has been the rapid development of electron spin resonance techniques which has provided, first the physicist and theoretical chemist, and more recently the organic chemist with a sensitive magnetic probe.
6.

e) Electron Spin Resonance of Free Radicals in Solution

Full accounts of the theory and application of e.s.r. spectroscopy appear in a number of books \(^{10, 11, 6d}\) and reviews. \(^{12}\)

A brief outline of the information that can be obtained for organic radicals is given below.

If the electron is considered as a spinning charged particle it has an associated magnetic moment

\[ \hat{\mu} = g \hat{\hbar} \hat{S} = -g \beta \hat{S} \]  

where \( \gamma \) is the magnetogyric ratio, \( \hbar = h/2\pi \) and \( h \) is Planck's constant, \( S \) is the spin vector of the electron, \( g \) is known as the "g-factor" and \( \beta \) is the Bohr magneton.

Since the electron spin is quantised the magnetic moment in a given direction (\( z \)) is

\[ \mu_z = -g\beta M_s \]  

where \( M_s \) is the magnetic spin quantum number equal to \( \pm 1/2 \).

If the electron is placed in a uniform magnetic field in the \( z \) direction the classical interaction energy of the electron with the field \( (H) \) is

\[ E = -\mu \cdot H \]
while the quantum mechanical Hamiltonian is

$$\hat{H} = g\beta \hat{S}_z \cdot \vec{H}$$

(4)

with eigenvalues

$$E = g\beta M_s \vec{H}$$

(5)

Then since $M_s = \pm 1/2$, there are two spin states with energies $E_{1/2} = \frac{1}{2} g\beta H$ and $E_{-1/2} = -\frac{1}{2} g\beta H$.

The energy difference between these states is given by

$$\Delta E = g\beta H$$

(6)

or in frequency units:

$$h\nu = g\beta H$$

(7)

When equation (7) is satisfied an electron in the lower state with magnetic moment parallel to the field may be excited by electromagnetic radiation of frequency $\nu$ to the higher state with moment opposed to the field - and vice versa.

$g$-Values

When the resonance condition is satisfied the "g-value" or "spectroscopic splitting factor" is related to the magnetic field $H$ by equation (7).

For a free electron (possessing only spin angular momentum) the $g$-value is 2.002322, and for electromagnetic radiation at $X$-band frequencies (3cm. wavelength) resonance occurs near 3000 gauss.

However, for paramagnetic molecules there may also be a
contribution to the magnetic moment $\mu$ from orbital angular momentum, which will be observed as a deviation of the $g$-value from that of the free electron, causing resonance to occur at a different value of the field.

As the spin-orbit coupling parameters of most heteroatoms differ from that of carbon, measurements of $g$-values can distinguish between various classes of radicals.

e. g.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylmethyl in toluene</td>
<td>2.002588</td>
</tr>
<tr>
<td>Cumylperoxyl in benzene</td>
<td>2.00155</td>
</tr>
<tr>
<td>N-O$^-$ in water</td>
<td>2.0064</td>
</tr>
<tr>
<td>N-S$^-$ in iodobenzene</td>
<td>2.0171</td>
</tr>
</tbody>
</table>

**Hyperfine Structure**

The interaction of the unpaired electron with nuclei of non-zero spin results in hyperfine structure of the resonance line: for a nucleus of spin $I$ there are $2I+1$ hyperfine lines.

Below are listed some of the nuclei found in organic compounds
with their spins.

<table>
<thead>
<tr>
<th>spin</th>
<th>12C</th>
<th>14C</th>
<th>16O</th>
<th>32S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1H</td>
<td>15N</td>
<td>13C</td>
<td>19F</td>
</tr>
<tr>
<td>1</td>
<td>2H</td>
<td>14N</td>
<td></td>
<td>31P</td>
</tr>
<tr>
<td>3/2</td>
<td>33S</td>
<td>35Cl</td>
<td>37Cl</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>17O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is to the hyperfine coupling constants that the chemist first looks for the identification and theoretical study of free radicals.

**Linewidths and Kinetics**

While the position of the resonance lines is governed by the $g$-value and the splitting constants, their width depends on the relaxation time. Several authors have developed theories relating shape and linewidth to the various spin-spin and spin-lattice contributions to the relaxation, and the subject has recently been reviewed in detail.

The kinetics of such processes as electron transfer and intramolecular motions may also be studied by their inherent linewidth effects.
Long- and Short-lived Radicals

The early e.s.r. studies of radicals in solution dealt mainly with stable species such as cyclopentadienyls, hydrazyls, carbazyls, and nitroxides, most of which may be obtained in a pure crystalline form.

The observation of radicals with half-life time of less than five minutes is less straightforward, but is rewarding as the results may confirm the circumstantial evidence, which has been previously the limit of study.

Several techniques have been employed. In the first radicals are generated in such an environment that their subsequent reactions are slow: for example, the u.v. irradiation of molecules held in rigid glasses.

The second method consists of subjecting the liquid or solution to high intensity radiation so that radicals are formed rapidly, and despite their short life-time are maintained in a measureable concentration.

The third method is to mix flowing solutions of the reactants immediately before they enter the cavity of the spectrometer. In this way the radicals are observed shortly after generation and half-life times of 100 milliseconds can be dealt with. Using this technique Gutch and Waters were
able to observe the spectra of some short-lived nitroxide radicals of the type \( \cdot \text{O-NH-R} \), by oxidation of the corresponding hydroxylamine with ceric ammonium nitrate.

More recently a new probe for homolytic reactions has been developed in which the transient species is scavenged by a nitroso group to form a stable nitroxide. Thus a phenyl radical could be inferred from the observation of the e. s. r. spectrum of \( \text{t-butylphenylnitroxide} \) in the presence of \( \text{2-methyl-2-nitrosopropane} \).

![Chemical Reaction](Ph\(^*\) + N\(_2\text{O}\) \(\rightarrow\) Ph-N-O\(^*\)).

A recent application of this method is the study of radicals involved in the polymerisation of styrene.

A classic example of a free radical reaction is the decomposition of acylarylnitrosamines. The mechanism of the reaction having been the focus of attention and controversy for more than ninety years has recently become the subject of e. s. r. study.
II  ACYLARYLNITROSAMINES

The decomposition of acylarylnitrosamines has been the subject of intensive study since they were first prepared by Fischer in 1876.

Early work centred on establishing that N-nitrosoacetanilide was tautomeric with benzenediazoacetate, and that decomposition in aromatic solvents led to biaryls:

\[
\begin{align*}
\text{Na}^+ \quad \text{O.N:N.P} & + \text{RCOCl} \\
\downarrow \\
\text{Ph.N(NO).COR} & \rightleftharpoons \text{Ph.N:N.COR} \xrightarrow{\text{ArH}} \text{PhAr} + \text{N}_2 + \text{RCO}_2\text{H} \\
\uparrow \\
\text{HO}^- + \text{Cl}^- & \quad \text{Ph}_2\text{N} + \text{RCOCl}
\end{align*}
\]

Grieve and Hey undertook a more thorough examination of the N-nitrosoacetanilide decomposition, and in 1934 published results which appeared to rule out an ionic reaction mechanism. The biaryls formed were invariably substituted in the ortho and para-positions, irrespective of the nature of the substituent groups in the solvent. They suggested that these observations could be explained by a phenyl radical intermediate, which being electrically neutral would not be subject to the polar effects normally associated with ionic substitution: the absence of the dimerisation product biphenyl.
was attributed to the short lifetime of the radical in solution.

Further examination\(^8, 32\) established that meta-substituted products were also formed, and that similar isomer ratios were obtained from other phenyl radical sources such as benzoyl peroxide and phenylazotriphenylmethane.

Another illustration\(^33\) of the presence of free radicals came from the ability of acylaryl nitrosamine decompositions to initiate polymerisation of such compounds as styrene and acrylonitrile.

Although the necessity of the phenyl radical intermediate was questioned,\(^34\) conclusive evidence, summarised in recent reviews,\(^35\) was presented by Hey and Waters\(^36\) in defence of the now accepted concept of homolytic aromatic substitution.

Butterworth and Hey\(^37\) continued the study of \(N\)-nitrosoacetanilide by measuring the rate of nitrogen evolution in a variety of solvents. With the exception of acetic acid, the kinetics were found to be first order, and the rate constant varied little. In view of this they proposed the following scheme:

\[
\text{Ph. N(NO). Ac} \overset{\text{fast}}{\rightarrow} \text{Ph. N:N. OAc} \overset{\text{slow}}{\rightarrow} \text{Ph}^* + \text{N}_2 + \cdot\text{OAc}
\]

Some years later Huisgen and Horeld\(^38\) showed that the rate of coupling with \(\beta\)-naphthol was very similar to the rate
of nitrogen evolution as measured by Hey. They concluded that the rate determining step must be the diazoacetate formation thus:

\[
\text{Ph.} \text{N(NO). Ac} \xrightarrow{\text{slow}} \text{Ph.} \text{N:N. OAc} \xrightarrow{\text{fast}} \text{Ph}^+ + \text{N}_2 + \cdot \text{OAc}
\]

\[
\text{coupling with } \beta\text{-naphthol}
\]

De Tar \cite{DeTar} examined the possibility of heterolytic fission of the diazoacetate by studying the decomposition in methanol plus additives. For pure methanol and methanol plus sodium acetate he found formaldehyde, benzene and traces of biphenyl as reported previously, \cite{previous} but for methanol plus sulphuric acid anisole resulted, suggesting carbonium ion formation. He modified Huisgen's scheme to account for his observations:

\[
\text{Ph.} \text{N(NO). Ac} \xrightarrow{\text{slow}} \text{Ph.} \text{N:N. OAc} \xrightarrow{\text{fast}} \text{Ph}^+ + \text{N}_2 + \cdot \text{OAc}
\]

\[
\text{very fast}
\]

\[
\text{Ph}^+ + \text{N}_2 \xrightarrow{\text{slow}} \text{PhN}_2^+ + \cdot \text{OAc}
\]

The decomposition of fluorine substituted acylaryl nitrosamines, studied by Suschitzky \cite{Suschitzky} and co-workers, also indicated the necessity of including heterolysis in the mechanism even for non-polar solvents. They observed substitution of ortho and para-fluorine by acetoxy, thus indicating acetate ions in solution.
The mechanism of the nitrogen to oxygen migration of the acyl group was examined independently by Hey and Huisgen, both of whom considered two possibilities:

(A) \[
\begin{align*}
\text{Ar-N-C}_R^O & \xrightarrow{\text{slow}} \text{Ar-N}^+ \rightarrow \text{COR} \xrightarrow{\text{fast}} \text{Ar-N}^\prime \\
N=O & \quad N=O & \quad N-O-COR
\end{align*}
\]

(B) \[
\begin{align*}
\text{Ar-N-C}_R^O & \rightarrow \text{Ar-N}^\prime \rightarrow \text{Ar-N-C}_R^O \\
N=O & \quad N=O & \quad N-O
\end{align*}
\]

(B) was chosen in preference to (A) as a result of a series of tests:

(i) **Electronic effects**: the rate altered little, no matter what the electronic nature of m- and p- substituents in the aryl ring.

(ii) **Steric effects**: bulky ortho-groups in the aryl ring decreased the rate by hindering formation of the cyclic intermediate in (B): on the other hand bulky acyl groups assisted its formation.

(iii) **Salt and solvent effects**: for decompositions in ethanol, ethanol plus water and ethanol plus lithium chloride no variation in the rate was found.

(iv) **Intermolecular deacylation**: the introduction of a strong nucleophile such as piperidine resulted in an increase in rate, suggesting intramolecular rearrangement to the cyclic
intermediate was being replaced by easier intermolecular deacylation.

(v) **Configuration of the diazoester:** mechanism (B) demands that the diazoester be trans. This was confirmed by Huisgen's experiments on the rearrangement of N-Nitrosolactams to diazoesters, and by the formation of indazole from the decomposition of o-methyl-N-nitrosoacetanilide in chloroform.

A number of features of the system still remained a puzzle.

First, although Waters had shown qualitatively the formation of carbon dioxide, the amounts as measured by De Tar and Huisgen were quite incompatible with the existence of free acetoxy radicals in solution, which were known to decompose readily to carbon dioxide and methyl.

Secondly, by analogy with the decomposition of dibenzoyl peroxide in benzene, the arylcyclohexadienyl radical resulting from addition of phenyl to the aromatic substrate might be expected to dimerise and disproportionate. Yet Eliel, Eberhardt and Simamura's careful examination of the products of N-nitrosoacetanilide/benzene and phenylazotriphenylmethane/benzene decompositions failed to find any quaterphenyls or dihydrobiaryls.
In order to explain these discrepancies a "diffusion controlled" mechanism was proposed, whereby acetoxy and arylcyclohexadienyl radicals were generated in a solvent "cage"; rapid abstraction of hydrogen by the acetoxy radical would result in acetic acid and biaryl as observed.

On the other hand Denney, Gershman and Appelbaum found that in the presence of a radical interceptor such as styrene or acrylonitrile the yield of nitrogen remained constant, while that of biaryl decreased. This was followed by Elieel and Saha's report of the scavenging of 90-100\% of the phenyl radicals formed in the decomposition of $\text{N}$-nitrosoacetanilide in benzene containing iodine in low concentration. Thus a "free" phenyl radical was indicated and a cage mechanism ruled out.

The absence of dimerisation and disproportionation products for phenylazotriphenylmethane was shown by several groups of workers to be due to the high stationary state concentration of stable triphenylmethyl radicals concomitantly formed in the decomposition.

Rühardt and Freudenberg then proposed a scheme for $\text{N}$-nitrosoacetanilide in benzene, which also contained a stable
SCHEME 1

Rüchardt 1964

Ph. N(NO). Ac $\rightarrow$ Ph. N:N. OAc $\leftrightarrow$ PhN$_2^+$ + OAc

Initiation: Ph. N(NO). Ac + OAc $\rightarrow$ Ph. N:N. O$^-$ + Ac$_2$O

Chain Process:

\[
\begin{align*}
\text{PhN}_2^+ & \quad \text{Ph. N:N. O}^- & \quad \text{AcOH} \\
\downarrow & \quad \quad & \quad \quad \quad \uparrow & \quad \text{AcO}^-
\end{align*}
\]

Ph. N:N. O. N:N. Ph

Ph. N:N. OH

Ph$_2$$^*$ N$_2$ O. N:N. Ph

(3)

PhH $\rightarrow$ PhPh
free radical capable of abstracting hydrogen and thus cleanly oxidising phenylcyclohexadienyl to biphenyl. Another satisfactory feature of their mechanism (Scheme 1) was the formation of acetic acid, in a chain process, from acetate ions and not from the unstable acetoxy radical.

The essentials of this mechanism were common to the one Rüchardt and Merz had earlier proposed for the closely related Gomberg arylation with diazonium salts and alkali:

\[
\begin{align*}
\text{PhN}_2^+ + \text{OH}^- & \rightarrow [\text{PhN}:\text{N}.\text{OH}]^{-}\text{OH} \rightarrow \text{PhN}:\text{N}.\text{O}^- + \text{H}_2\text{O} \\
\text{PhN}:\text{N}.\text{O}^- + \text{PhN}_2^+ & \rightarrow \text{PhN}:\text{N}.\text{O}.\text{N}:\text{N}.\text{Ph} \\
\text{PhN}:\text{N}.\text{O}.\text{N}:\text{N}.\text{Ph} & \rightarrow \text{Ph}^* + \text{N}_2^0 + \text{PhN}:\text{N}.\text{O}^0
\end{align*}
\]

(3)

\[
\begin{align*}
\text{Ph}^* + \text{PhH} & \rightarrow [\text{PhC}_6\text{H}_5\text{H}]^* \\
[\text{PhC}_6\text{H}_5\text{H}]^* + \text{PhN}:\text{N}.\text{O}^0 & \rightarrow \text{PhPh} + \text{PhN}:\text{N}.\text{OH} \\
\text{PhN}:\text{N}.\text{OH} + \text{OH}^- & \rightarrow \text{PhN}:\text{N}.\text{O}^- + \text{H}_2\text{O}
\end{align*}
\]

The intermediacy of the diaryldiazoanhydride, as a highly explosive yellow solid, in diazonium hydroxide systems had long since been suggested by Bamberger and later by Gomberg, but it was not until 1960 that Kauffmann, Friestad and Henkler determined its structure with any certainty.

Suschitzky agreed that the diazoanhydride was a likely
TABLE 1

Hyperfine coupling constants ($a_i$), experimental and calculated spin density distributions ($\rho$) for the phenyldiazotate radical (3).

![Diagram](Image)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$a_i$ in gauss</th>
<th>$\rho$ (exp.)$^*$</th>
<th>$\rho$ (calc.)$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.5442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>+1.67</td>
<td>-0.0244</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>+11.61</td>
<td>0.2179</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0264</td>
<td></td>
<td>0.0264</td>
</tr>
<tr>
<td>5, 9</td>
<td>-2.60</td>
<td>0.1095</td>
<td>0.0944</td>
</tr>
<tr>
<td>6, 8</td>
<td>0.89</td>
<td>-0.0375</td>
<td>-0.0407</td>
</tr>
<tr>
<td>7</td>
<td>-2.73</td>
<td>0.1152</td>
<td>0.1286</td>
</tr>
</tbody>
</table>

$^*$ Calculated assuming $Q = -23.7$ gauss

$^{**}$ McLachlan calculations using: $\lambda = 1.1$, $h_N = 0.5$, $h_o = 1.0$, $k_{NN} = 1.5$
intermediate source of phenyl radicals for $N$-nitrosoacetanilide as well, but questioned its mode of formation: an alternative was heterolysis of the nitrosamide to diazotate anion and subsequent combination with diazonium ions.

\[
\text{Ph. N(NO). Ac} \quad \text{Ph. N:N. OAc}
\]

\[
\text{[Ph. N:N. O}^{-} \quad \text{[PhN}_2^{+} \quad \text{OAc]}
\]

\[
\text{[Ph. N:N. O}^{-} \quad \text{[AcO}^{-} \quad \text{Ac]}
\]

Rüchardt supported his mechanism with the observation of a long-lived e. s. r. signal when the decomposition took place in the cavity of an e. s. r. spectrometer. He claimed that the assignment of the signal to the diazotate $\pi$-radical (3) in his scheme was supported by McLachlan molecular orbital calculations. The splitting constants, experimental and calculated spin density distributions are reproduced in Table 1.

For the protons attached to carbon atoms 5 to 9 the hyperfine splitting constant $a_H$ is related to the $\pi$-electron spin density $\rho$ on the adjacent carbon by the McConnell equation:

\[a_H = Q \rho\]

where $Q$ is the constant of proportionality and has a value of
about -23.7 gauss for this type of radical. Thus experimental spin densities can be compared with those found from M.O. calculations.

However, for the nitrogen nuclei no such simple relationship holds, there being possible contributions to the coupling constant from spin density on neighbouring atoms and on the nitrogen itself.

The more detailed paper which followed reported the use of isotopic labelling to analyse the signal further. For the p-deutero radical it was shown that the $a_{\text{p-H}}$ values were not equivalent, thus suggesting an angled structure for the system. By synthesising N-nitrosoacetanilide from $^{15}$N ammonia and benzoyl chloride the nitrogen atoms were effectively labelled:

$$\text{PhCOCl} + ^{15}\text{NH}_3 \rightarrow ^{15}\text{NH}_2\text{Cl} + \text{PhCO}^{15}\text{NH}_2 \xrightarrow{\text{NaOCl}} \text{Ph}^{15}\text{NHCOCH}_3$$

Contrary to the predictions of the McLachlan calculations, these results assigned the major splitting ($a_N = 11.61$ gauss) to the nitrogen No. 2, adjacent to the oxygen and not to nitrogen No. 3.
The offered explanation for this reversal was large contributions from the spin density on neighbouring atoms.

This apparently satisfactory explanation for the decomposition and the e. s. r. signal was brought into question by the observation by Perkins et al. of essentially the same signal on mixing benzene solutions of nitrosobenzene and N-bromoacetanilide.

C-Nitroso compounds were known to scavenge phenyl radicals to give nitroxides, and here, they claimed, a similar process would result in radical (4). It could likewise be formed from nitrosobenzene and the acetamido radical derived from the homolysis of the N-Br bond in N-bromoacetanilide.

\[
\begin{align*}
\text{Ph}^- & \quad \text{N}=\text{O} & \quad \text{Ph}^a^-\text{N}-\text{O}^- & \quad \text{Ph}^b^-\text{N}-\text{Ac} \\
\rightarrow & & \leftarrow \\
\text{Ph}-\text{N}-\text{Ac} & \quad \text{Ph}^a^-\text{N}-\text{Ac} & \quad \text{Ph}^-\text{N}-\text{Ac}
\end{align*}
\]

(4)

In this way the nitrogen adjacent to the oxygen would have the large splitting as suggested by Rüchardt's data. Very low spin density on ring Ph\textsubscript{b} would account for the failure to observe splittings from its protons.

Perkins modified Rüchardt's mechanism to feature the
SCHEME 2

Perkins 1967

Ph. N(NO). Ac \rightarrow \text{Ph. N:N. OAc}

Initiation: Ph. N:N. OAc \rightarrow \text{Ph.} + N_2 + \cdot\text{OAc}

Chain Process:

\[
\begin{align*}
\text{Ph. N:N. OAc} & \quad \text{Ph-N-OH} \\
\text{Ph-N-Ac} & \quad \text{Ph-N-Ac} \\
\text{Ph-N-Ac} & \quad \text{Ph-N-Ac} \\
\text{AcOH} + N_2 + \text{Ph} & \quad \text{PhH}
\end{align*}
\]
(N-phenylacetamido)phenylnitrooxide (4) and not the phenyl-diazotate (3) in the chain process. His mechanism is shown in Scheme 2.

A third route to (4) was provided by Forrester\textsuperscript{62} in 1968, when he oxidised N-acetylhydrazobenzene with t-butylhydroperoxide: this, he claimed, clearly supported Perkin's view that (4) was the radical in the arylation process.

Although these schemes explained many of the experimental observations, they could not account for the anomalous behaviour of o-t-butyl-N-nitrosoacetanilide reported by Hey, Cadogan and Williams\textsuperscript{63} in 1954. The participation of an aryne was indicated\textsuperscript{64} by a 46\% yield of o- and m-t-butylphenyl acetates and by the formation of the aryne adduct 1-t-butyltriptycene when anthracene was present.

Two routes to the aryne have been suggested.

Firstly,\textsuperscript{63} via the cis-configuration forced on the diazoacetate by the size of the ortho-substituent thus:
Secondly, by the rapid expulsion of nitrogen from the ortho-substituted diazonium ion to yield a carbonium ion:

\[
\begin{align*}
\text{Bu}^+ \text{N}_2^+ & \xrightarrow{-\text{N}_2} \text{Bu}^+ \text{N}^+ \xrightarrow{-\text{OAc}} \text{O-acetate} \\
\text{Bu}^+ \text{N}^+ & \xrightarrow{-\text{H}^+} \xrightarrow{\text{HOAc}} \text{o- and m-acetates}
\end{align*}
\]

The question of aryne participation was again raised when Brydon and Cadogan discovered that unsubstituted \(\text{N-nitrosoacetanilide}\) formed the benzyne "adduct" 1, 2, 3, 4-tetraphenylnaphthalene in the presence of 2, 3, 4, 5-tetraphenylcyclopentadienone; however no adducts were formed with furan and anthracene - normally accepted traps. This anomaly was the subject of much study, and it was suggested that while the \(\text{o-t-butyl-N-nitrosoacetanilide}\) decomposition proceeded via a true aryne, that of \(\text{N-nitrosoacetanilide}\) did not, the adduct being formed from the dipolar conjugate base of the aryldiazonium cation. The mechanism outlined in Scheme 3 allows for normal radical reaction and adduct formation in the presence of the trap.
Another anomaly arose from the observation by several workers that the decomposition of N-nitrosoacetanilide in carbon tetrachloride resulted in acetic acid and benzenediazonium chloride as major products, and that though chlorobenzene was also formed, there was no sign of the trichloromethyl solvent residue.

Scheme 3 above accounted for the formation of acetic acid, but it could not explain the benzenediazonium chloride. Nor has there been a satisfactory explanation of the abstraction products of radicals produced by acylarylnitrosamines and other aryl sources. For example, when N-nitrosoacetanilide is used both chlorine and bromine are abstracted from bromotrichloromethane, but other aryl sources show almost negligible chlorine abstraction. Also radicals from N-nitrosoacetanilide...
abstract both chlorine and hydrogen from chloroform, while
those from dibenzoyl peroxide take only hydrogen.\textsuperscript{44, 51a, 70-72}

So while either the Rüchardt (Scheme 1) or the Perkins
(Scheme 2) mechanisms can account for many of the experimental
observations, there remains a number of problems which
still require solution.
III NITROXIDE RADICALS

Much of the controversy surrounding the Rüchardt - Perkins schemes for the decomposition of N-nitrosoacetanilide centres on the nature of the nitroxide radicals involved: thus a brief discussion of nitroxides, their chemistry, inherent stability and e. s. r. spectra seems appropriate.

a) History

In 1845 Frewy reported the first nitroxide - the inorganic compound potassium nitrosodisulphonate (5). This was followed more than fifty years later by the first isolation of an organic radical porphyreoxide (6), although Pilory and Schwerin, assigned it structure (7).

\[
\begin{align*}
\text{(5)} & \quad \text{\begin{tikzpicture}[baseline=-0.5ex]
\node at (0,0) {\text{KSO}_3};
\node at (1.5,0) {\text{N—O—N}^—};&
\node at (1.5,1) {\text{KSO}_3} & \\
\end{tikzpicture}} \\
\text{(6)} & \quad \text{\begin{tikzpicture}[baseline=-0.5ex]
\node at (0,0) {\text{H—N—N—H}^—};
\node at (1.5,0) {\text{N—O—N}^—};
\node at (1.5,1) {\text{H—N—N—H}^—}; & \\
\end{tikzpicture}} \\
\text{(7)} & \quad \text{\begin{tikzpicture}[baseline=-0.5ex]
\node at (0,0) {\text{H—N—N—H}^—};
\node at (1.5,0) {\text{N = O}}; & \\
\end{tikzpicture}}
\end{align*}
\]

Over the years since then there have been a wide range of other examples varying considerably in stability: thus the aliphatic nitroxides (8) and (9) are short-lived and can only be detected by e. s. r. spectroscopy using flow or
irradiation techniques, while the dianisylnitrooxide (10) of Meyer, 3 the arylalkylnitrooxide (11) of Kenyon 79 and di-t-alkyl-nitrooxides e.g. (12) 80 are stable and can be isolated as crystalline solids.

\[ \text{PhCH}_2^+ \text{MeO}^- \text{C}_6\text{H}_4^+ \text{N}=\text{O}^- \]

\[ \text{PhCH}_2 \text{MeO}^- \text{C}_6\text{H}_4^+ \text{N}=\text{O}^- \]

\[ \text{Bu}^+ \text{O}^- \text{Bu}^- \]

The chemistry and e.s.r. spectra of this class of compounds have been the subject of reviews by Buchachenko, 11a Rozantsev 31 and Forrester, Hay and Thomson. 6d

b) Structure

Nitroxides can be regarded as derivatives of the stable inorganic radical nitric oxide. There have been several representations of the N-O bond, to which the stability of these compounds is attributed.

Firstly, as a resonance hybrid:

\[ \begin{align*}
\cdot \text{N}=\text{O}^- & \quad \leftrightarrow \quad \cdot \text{N}=\text{O}^+ \\
\text{R} \cdot \text{N}=\text{O}^- & \quad \leftrightarrow \quad \text{R} \cdot \text{N}=\text{O}^+ \\
\text{R} \cdot \text{N}=\text{O}^- & \quad \leftrightarrow \quad \text{R} \cdot \text{N}=\text{O}^+ \\
\end{align*} \]
Secondly, as a $\sigma$-bond and a three electron bond:

$$\text{R - N - O - R}$$

Thirdly, by Linnett's double quartet hypothesis, in which he considers that six electrons of one spin are arranged as in (A) and the remaining five as in (B). In this way each atom has an octet of electrons, interaction is at a minimum and there are five bonding electrons.

The observation that neither nitric oxide nor any organic nitroxides show any tendency to dimerise is also explained, as the number of bonding electrons would not increase, while interelectronic repulsion would.

Further evidence for five bonding electrons in the N-O fragment comes from the low dipole moment, and from the bond lengths and infrared spectra, which are intermediate between those of $N_2$ and $O_2$ and of $N=O$ and $N\equiv O$. 
Thus nitroxides differ from other long-lived radicals in that their stability is not derived from conjugation or steric factors but is an inherent property of the N-O group.

c) **Stability**

Although dimerisation at the nitrogen or oxygen atoms is almost unknown, reaction can occur by fragmentation, disproportionation or attack at other parts of the radical. Thus delocalisation of the unpaired electron through an aromatic ring can give rise to a less stable nitroxide. As an illustration, diphenylnitroxide is stable in dilute solution, but on concentration decomposes to diphenylamine and quinonimine-N-oxide.

\[
\text{Ph}_2\text{N-O} \rightarrow \text{Ph}_2\text{N-O}^+ \rightarrow \text{Ph}_2\text{N-O}^+ \rightarrow \text{Ph}_2\text{N-O}^+ \rightarrow \text{Ph}_2\text{N-O}^+ \\
\text{Ph}_2\text{NH} \rightarrow \text{Ph}_2\text{N-O}^+ \rightarrow \text{Ph}_2\text{N-O}^+ \\
\]

Only when the active para-position is blocked, or the unpaired electron localised in the N-O group by bulky ortho-substituents preventing coplanarity, is the nitroxide stable.
e. g. 4, 4′-dimethyl- \textsuperscript{84} (13) and 2, 2′, 6, 6′-tetramethoxydiphenyl-

Likewise for alkyl nitroxides the presence of an α-hydrogen atom allows ready disproportionation to nitrone and hydroxyl-

On the other hand, the nitroxide is stable when nitrone formation is prevented by the alkyl group being tertiary or, in the particular case of the radical (15) derived from nor-

\textsuperscript{87} pseudopelletrierine, \textsuperscript{88} by Brendt's \textsuperscript{88} rule prohibiting the introduction of a double bond at a bridgehead of a bicyclic system.
d) E.S.R. Spectra

The stability of nitroxides has made them an ideal subject for e.s.r. examination: as might be expected from the localisation of the electron in the N-O group, their spectra are characterised by large nitrogen hyperfine coupling constants, the magnitude of which depends on the extent of delocalisation. Typical examples are shown in Table 2.

**TABLE 2**

Hyperfine Coupling Constants for Nitroxides RR'NO.

<table>
<thead>
<tr>
<th>type</th>
<th>R</th>
<th>R'</th>
<th>solvent</th>
<th>$a_N$ in gauss</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkoxyalkyl</td>
<td>Bu'O</td>
<td>PhCMe$_2$</td>
<td>cumene</td>
<td>28.0</td>
<td>89</td>
</tr>
<tr>
<td>dialkyl</td>
<td>Bu$^t$</td>
<td>Bu$^t$</td>
<td>benzene</td>
<td>15.36</td>
<td>90</td>
</tr>
<tr>
<td>alkylaryl</td>
<td>Bu$^t$</td>
<td>Ph</td>
<td>ethylene glycol</td>
<td>13.4</td>
<td>91</td>
</tr>
<tr>
<td>diaryl</td>
<td>Ph</td>
<td>Ph</td>
<td>xylene</td>
<td>9.66</td>
<td>92</td>
</tr>
<tr>
<td>alkylacyl</td>
<td>Bu$^t$</td>
<td>COMe</td>
<td>benzene</td>
<td>8.0</td>
<td>93</td>
</tr>
<tr>
<td>arylacyl</td>
<td>Ph</td>
<td>COMe</td>
<td>benzene</td>
<td>7.3</td>
<td>93</td>
</tr>
<tr>
<td>diacyl</td>
<td></td>
<td></td>
<td>methylene chloride</td>
<td>4.2</td>
<td>94</td>
</tr>
</tbody>
</table>
e) **Iminoxy Radicals**

All the nitroxides so far mentioned have been of the type where the unpaired electron is in a molecular orbital of \( \tau \)-symmetry. For the iminoxy radicals obtained by the oxidation of oximes \(^{95-97}\) the orbital is best represented thus:

![Diagram of iminoxy radical]

The unpaired electron is in an orbital, derived from a nitrogen \( sp^2 \)-orbital and an oxygen \( p \)-orbital, which lies in the nodal plane of the \( C-N \ \tau \)-bond. This orbital is orthogonal to the molecular \( \tau \)-system, so that the radicals are described as \( \sigma \)-radicals. \(^{98,99}\) This type of orbital has a larger \( s:p \) ratio \(^{12a,100}\) and so, as the hyperfine coupling constant depends on the spin density at the nucleus, iminoxy radicals are characterised by large \( a_N \) values in the region of 30 gauss.

Unlike many \( \tau \)-nitroxides iminoxy radicals are unstable even in dilute solution and interest has been restricted mainly to their e.s.r. spectra.
In Table 3 are listed a few of the iminoxy radicals which have been observed with their hyperfine coupling constants in gauss.

**TABLE 3**

Splitting Constants for Iminoxy Radicals

<table>
<thead>
<tr>
<th>iminoxy radical derived from:</th>
<th>$a_N$</th>
<th>$a_H$ of aldehyde</th>
<th>other $a_H$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn-Benzaldoxime</td>
<td>29.2</td>
<td>26.9</td>
<td></td>
<td>96a</td>
</tr>
<tr>
<td>anti-Benzaldoxime</td>
<td>29.4</td>
<td>6.2</td>
<td>ortho-H, 1.4</td>
<td>96a</td>
</tr>
<tr>
<td>syn-Acetaldoxime</td>
<td>31.9</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>anti-Acetaldoxime</td>
<td>33.7</td>
<td>5.2</td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>Benzophenone oxime</td>
<td>31.4</td>
<td></td>
<td>two ortho-H from one ring, 1.4</td>
<td>96a</td>
</tr>
<tr>
<td>Fluorenone oxime</td>
<td>30.85</td>
<td>2.7, 1.0</td>
<td></td>
<td>96a</td>
</tr>
</tbody>
</table>

The restricted delocalisation of the unpaired electron is illustrated by the small change in the nitrogen hyperfine coupling constant when the attached group is varied from aryl to alkyl.

Notable features of these radicals are the "through space" and long-range couplings they often exhibit. The former is clearly illustrated for the radical (16)$^{101}$ derived from fluorenone.
oxime: splittings of 2.7 and 1.0 gauss are observed for $H_1$ and $H_2$ respectively. The marked stereochemical discrimination between the aldehyde protons of syn- and anti-benzaldoximes is similar to that observed for the well substantiated $\sigma$-radical vinyl (17)\textsuperscript{102} for which the $a_H$ values are 68 and 34 gauss for $H_1$ and $H_2$ respectively.

Another system which illustrates the difference between $\sigma$- and $\pi$-radicals is the radical ions of nitrosobenzene. Lemaire, Rassat et al.\textsuperscript{103} observed the e.s.r. spectrum of the nitrosobenzene cation, generated electrochemically, and compared it with that obtained for the anion.\textsuperscript{104} From the results, reproduced in Table 4, they concluded that the anion was a normal $\pi$-radical, exhibiting the usual coupling to all the aromatic ring protons, while the cation was a $\sigma$-radical, for which the largest proton splitting was due to long-range coupling with a meta-hydrogen. The notable difference between anion and cation was related to the electronic structure of the
TABLE 4

g-factors and splitting constants for nitrosobenzene radical-ions

<table>
<thead>
<tr>
<th></th>
<th>a_N gauss</th>
<th>a_H gauss</th>
<th>g-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>7.97</td>
<td>H_{ortho} = 3.84 or 4.14 and 2.97</td>
<td>2.0060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H_{meta} = 0.96 and 1.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H_{para} = 4.14 or 3.84</td>
<td></td>
</tr>
<tr>
<td>Cation</td>
<td>37.0</td>
<td>1 H_{meta} = 3.8</td>
<td>2.0007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 or 3 H = 1.3</td>
<td></td>
</tr>
</tbody>
</table>

Nitroso compound. For the parent nitrosyl H-N=O molecule the highest occupied orbital is of σ-symmetry, whereas that of the lowest unoccupied is Π⁻. Removal of an electron to form the cation thus leaves the unpaired electron in a σ⁻-orbital, while addition of an electron will produce a Π⁻ anion radical.

The striking contrast between the a_N values for the two ions, resulting from differing delocalisation, distinguishes the e.s.r. spectra of typical Π-nitroxides from those of σ-iminoxy radicals.
IV PROGRAMME OF RESEARCH

At the outset of the investigation, reported subsequently in this thesis, it was intended to reinvestigate the decomposition of acylarylnitrosamines in various solvents in an attempt to finally resolve the conflicting opinions on the mechanism of the reaction or reactions.
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V REACTIONS OF ACYLARYLNITROSAMINES

a) Decomposition of \( \text{N-Nitrosoacetanilide} \) in Benzene  

b) Decomposition of \( \text{N-Nitrosoacetanilide} \) in Mesitylene  

VI E.S.R. STUDY OF THE DECOMPOSITION OF ACYLARYLNITROSAMINES

a) General Technique  

b) Determination of Splitting Constants and \( g \)-Values  

c) Purification of Solvents  

d) \( \text{N-Nitrosoacetanilide} \)
   (i) In Aromatic Hydrocarbons  
   (ii) In Alcohols  
   (iii) In Ethers  
   (iv) In Halogenated Solvents  
   (v) In Other Solvents
e) **p-t-Butyl-N-nitrosoacetanilide**

(i) In Aromatic Hydrocarbons 75
(ii) In Alcohols 76
(iii) In Diethyl Ether 77
(iv) In Halogenated Solvents 79
(v) In Pyridine 80

f) **p-Methoxy-N-nitrosoacetanilide**

(i) In Benzene 80
(ii) In Pyridine 81
(iii) In Cumene 81

 g) **p-Nitro-N-nitrosoacetanilide**

(i) In Benzene 82
(ii) In Pyridine 82
(iii) In Cumene 82

h) **p-Methyl-N-nitrosoacetanilide**

(i) In Benzene 84
(ii) In Pyridine 84
(iii) In Cumene 85

i) **p-Carbethoxy-N-nitrosoacetanilide**

(i) In Benzene 85
(ii) In Pyridine 85
(iii) In Cumene 86
<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Solvent</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>j)</td>
<td>N-Nitrosoformanilide</td>
<td>(i) In Benzene</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Pyridine</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii) In Cumene</td>
<td>88</td>
</tr>
<tr>
<td>k)</td>
<td>p-t-Butyl-N-nitrosoformanilide</td>
<td>(i) In Pyridine</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Cumene</td>
<td>90</td>
</tr>
<tr>
<td>l)</td>
<td>N-Nitrosoformanilide-1-d</td>
<td>(i) In Benzene</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Pyridine</td>
<td>91</td>
</tr>
<tr>
<td>m)</td>
<td>N-Nitrosopropionanilide</td>
<td>(i) In Benzene</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Pyridine</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii) In Cumene</td>
<td>93</td>
</tr>
<tr>
<td>n)</td>
<td>N-Nitrosoisobutyranilide</td>
<td>(i) In Benzene</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Pyridine</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii) In Cumene</td>
<td>95</td>
</tr>
<tr>
<td>o)</td>
<td>N-Nitrosobenzanilide</td>
<td>(i) In Benzene and Cumene</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) In Pyridine</td>
<td>96</td>
</tr>
<tr>
<td>p)</td>
<td>4-Chloro-N-nitrosobenzanilide</td>
<td>In Pyridine</td>
<td>97</td>
</tr>
<tr>
<td>q)</td>
<td>p-t-Butyl-N-nitrosobenzanilide</td>
<td>In Pyridine</td>
<td>97</td>
</tr>
</tbody>
</table>
r) The Use of Degassed Solvents  

s) Summary of E. S. R. Signals Observed during the Decomposition of Acyclarylnitrosamines

VII E. S. R. STUDY OF RELATED SYSTEMS

a) Decomposition of Phenylazotriphenylmethane

b) Reaction of Aniline and Pentyl Nitrite

c) Isolation and Study of Solids Precipitated during the Decomposition of Ayclaryl-nitrosamines

(i) The Solid from N-Nitrosobenzanilide in Carbon Tetrachloride

(ii) The Solid from N-Nitrosobenzanilide in Mesitylene

(iii) The Solid from N-Nitrosoacetanilide in Carbon Tetrachloride

(iv) The Solid from N-Nitrosoacetanilide in Cumene

d) Decomposition of Benzenediazonium Acetate
Abbreviations

In addition to those abbreviations in common use, the following appear in this thesis:

- m/e: mass/charge ratio
- N: normality
- m/100m: moles of product per 100 moles of starting material
- mod.: peak to peak modulation amplitude
- PNO: phenyl nitroxide
- DPNO: diphenyl nitroxide
- PAPN: (N-phenylacetamido)phenyl nitroxide
I INSTRUMENTATION

Electron Spin Resonance Spectroscopy

E.s.r. spectra were obtained using a Decca Radar Limited X3 spectrometer, with a Newport Instruments 11-inch magnet system.

Simple detection with 100kc. /sec magnetic field modulation was used throughout. The manufacturer's specifications state a klystron frequency of 9270.4 Mc. /sec. (microwave X-band) and magnetic field homogeneity of 20 milligauss.

Spectra were recorded at room temperature, unless otherwise stated, and then the temperature was controlled by means of a Decca Radar Limited variable temperature cavity insert.

Gas-Liquid Chromatography

Qualitative and quantitative investigations were carried out on a Varian Aerograph 1520 B chromatograph with flame ionisation detector, and using the following 2 m. x 2.2 mm. i. d. packed columns:

10% Polyethylene glycol adipate (PEGA) on 100-120 mesh celite
2% Neopentylglycol succinate (NPGS) on 100-120 mesh celite.
Infrared Spectroscopy

Spectra were recorded on Perkin-Elmer Models 137, 237 and 257 spectrophotometers. Liquids were examined as thin films and solids as nujol mulls.

Mass Spectrometry

Mass spectra were obtained using an Associated Electrical Industries MS902 mass spectrometer.

Proton Magnetic Resonance Spectroscopy

A Perkin-Elmer Model R-10 nuclear magnetic resonance spectrometer, operating at 60 Mc. /sec. and probe temperature of 35.5° was used.
II PREPARATION OF ACYLARYLAMINES

a) Propionanilide and Isobutyranilide

Propionanilide. - Propionic anhydride (21 ml.) was gradually added to aniline (20.5 g., 0.221 mole) and zinc dust (0.3 g.) in glacial acetic acid (20 ml.). The mixture was boiled under reflux for 30 min. and poured into 500 ml. iced water. The resulting white solid was collected, washed with water, dried, and recrystallised from benzene to give propionanilide (17.3 g., 0.116 mole, 52%), m. p. 104-5° (lit. 105 105-106°).

Isobutyranilide was prepared in a similar manner from isobutyric anhydride and aniline in 35% yield, m. p. 106-107° (lit. 105 104-5°).

b) Formanilide and Formanilide-1-d

Formanilide. - A mixture of formic acid (0.99 g., 0.215 mole) and aniline (2.00 g., 0.215 mole) was boiled under reflux for 3 hr. The pale brown solid formed on cooling was recrystallised from xylene-petroleum to give formanilide (1.76 g., 0.146 mole, 68%), m. p. 46.5-47° (lit. 106 45-47°).

N. m. r. (CDCl₃): τ 1.20 (broad, NH), 1.64 (formyl H), 2.35-3.00 (complex, 5H, Ph).

I. r. (Nujol): 3280-3140 (complex, NH) and 1670 cm.⁻¹ (C=O).
Formanilide-1-d was prepared similarly from aniline and dideuteroformic acid (Merck, d- 99% minimum) in 46% yield, m. p. 47-49°. The n. m. r. spectrum showed no absorption at r 1.64. The infrared spectrum showed absorption at 2200 cm. -1 and 2160 cm. -1 not present for formanilide, due to C-D (formyl) stretching modes.

Mass spectrum: comparison of m/e 122:121 indicated 97. 5% deuteration.

c) p-t-Butylacylanilides

p-t-Butylaniline was prepared following the procedure of Harger. 67 Hydrochloric acid (sp. gr. 1.16, 4.8 g.) was added slowly to a mechanically stirred mixture of iron powder (44.8 g.), p-t-butylnitrobenzene (35.8 g., 0.200 mole), ethanol (80 g.) and water (80 g.), and the mixture boiled under reflux for 14 hr. After cooling and neutralisation with 10% sodium hydroxide solution, solids were removed by filtration and washed with methanol. The washings were combined with the filtrate and most of the alcohol removed by distillation. Water (25 ml.) and ether (75 ml.) were added and the layers separated. The aqueous layer and the original solid residue were washed with ether (100 ml.). The ether extracts were combined and dried over potassium hydroxide pellets. Evaporation of solvent left p-t-butylaniline
as a brown liquid (27 ml.), which was used without further purification.

**p-t-Butylacetanilide** was prepared, by the method described (part a) for the propionylation of aniline, from the crude p-t-butylanilinium in 88% yield (based on p-t-butylnitrobenzene), m. p. and mixed m. p. 173° (lit., 63°, 174°).

**p-t-Butylformanilide** was prepared by the method described (part b) for the formylation of aniline from the crude p-t-butylnilin in 60% yield (based on p-t-butylnitrobenzene), m. p. 59° (lit., 107°, 59°).

**p-t-Butylbenzanilide** was prepared from the crude p-t-butylnilin by the Schotten-Baumann method as described by Vogel. 108 p-t-Butylanilinium (9 ml.) was mixed with 10% sodium hydroxide solution (80 ml.) and benzyol chloride (13 ml.) and shaken in a stoppered flask for 25 min. The alkaline solution was diluted with water and filtered. The resulting white solid was dried and recrystallised from ethanol-petroleum to give p-t-butylenzanilide (8.8 g., 0.035 mole, 52% based on p-t-butylnitrobenzene), m. p. 146-147° (lit., 109°, 143-144°).

d) **Other Acylarylamines**

Acetanilide, p-carbethoxyacetanilide, p-nitroacetanilide, p-methylacetanilide and 2, 2, 2-trifluoroacetanilide were used without further purification.
III PREPARATION OF ACYLARYL NITROSAMINES

a) **Method A - for Soluble Acylarylamines**

*N*-Nitrosoacetanilide was prepared by the method of France, Heilbron and Hey.\(^{110}\) A solution of acetanilide (5.0 g., 0.037 mole) in a mixture of glacial acetic acid (35 ml.) and acetic anhydride (15 ml.) containing fused potassium acetate (5.0 g.) and phosphorus pentoxide (0.5 g.) was stirred at 5-10° under anhydrous conditions. Nitrosyl chloride (3.0 g., 0.046 mole) as a 25% solution in acetic anhydride was added over 15 min. and stirring continued for a further 15 min. The yellow reaction mixture was poured into iced water (500 ml.) and the precipitated yellow solid was collected and washed with iced water. The product was dried between filter paper and over phosphorus pentoxide at 0.05 mm., to give *N*-nitrosoacetanilide (4.1 g., 0.025 mole, 68%), m. p. 50-51° (decomp.); lit.,\(^{42}\) 50.5-51° (decomp.).

I. r. (Nujol): 1740 cm.\(^{-1}\) (C=O); no absorption at 3265 cm.\(^{-1}\) (NH in amide).

b) **Method B - for Sparingly Soluble Acylarylamines**

*N*-Nitrosobenzanilide was prepared by the method of Miles and Suschitzky.\(^{40b}\) A solution of benzanilide (2.50 g., 0.0127 mole) in a mixture of glacial acetic acid (30 ml.), acetic anhydride (12 ml.)
and anhydrous pyridine (3 ml.) was stirred at 5-10°. Nitrosyl chloride (1.05 g., 0.016 mole) as a 25% solution in acetic anhydride was added over 15 min., and stirring continued for a further 30 min. The yellow reaction mixture was poured into iced water, and the precipitated yellow solid was collected and washed with iced water. The product was dried between filter paper and over phosphorus pentoxide at 0.05 mm., to give N-nitrosobenzenilide (2.79 g., 0.0124 mole, 98%), m.p. 64° (lit., 40b 76°).

I.r. (Nujol): 1715 cm. -1 (C=O); no absorption at 3340 cm. -1 (N-H in amide).

c) Method C - for the Preparation of Acylarylnitrosamines in the Absence of Acid

N-Nitrosoformanilide-1-d - A solution of formanilide-1-d (0.05 g., 0.0041 mole) in a mixture of anhydrous ether (9 ml.) and anhydrous pyridine (0.37 g., 0.0041 mole) was stirred at 0°. Nitrosyl chloride (0.30 g., 0.0046 mole) as a 25% solution in ether was added over 10 min., and stirring continued for a further hour. The white precipitate of pyridine hydrochloride was removed by filtration through cold apparatus and the filtrate distilled at room temperature and 20 mm. pressure to remove ether. Unreacted pyridine was evaporated off at 0.05 mm. to
leave a yellow-brown solid of partially decomposed N-nitrosoformanilide-1-d (0.36 g., 0.0026 mole, 62%), m. p. 44-47° (decomp.).

The infrared spectrum indicated incomplete nitrosation of the amide and partial decomposition of the nitrosamide to a diazonium salt: \(3280-3160 \text{ cm}^{-1}\) (complex, weak, NH); \(2290 \text{ cm}^{-1}\) (medium, \(-\text{N}^=\text{N}\)); \(2200 \text{ cm}^{-1}\) (broad, medium, C-D formyl); \(1735 \text{ cm}^{-1}\) (strong, C=O of nitrosamide); \(1670 \text{ cm}^{-1}\) (medium C=O of unnitrosated amide).

The nitrosamide decomposed rapidly at room temperature and was stored under card ice.

N-Nitrosoformanilide was prepared by method C to check the validity of the technique. The product was a brown solid of partially decomposed N-nitrosoformanilide, m. p. 39-41°.

The infrared spectrum indicated incomplete nitrosation and partial decomposition: \(3280-3160 \text{ cm}^{-1}\) (complex, weak, NH); \(2290 \text{ cm}^{-1}\) (medium, \(-\text{N}^=\text{N}\)); \(1735 \text{ cm}^{-1}\) (strong, C=O); \(1670 \text{ cm}^{-1}\) (medium, C=O); no absorption at \(2200 \text{ cm}^{-1}\)

d) **Attempted Preparation of N-Nitroso-2,2,2-trifluoroacetanilide**

(i) **Method A.** - On pouring the colourless reaction mixture into iced water no precipitate was formed.

(ii) **Method C.** - Evaporation of the filtrate from the reaction mixture yielded a white precipitate, identified as unnitrosated
amide by its infrared spectrum.

e) Other Acylarylnitrosamines

The results for the preparation of other acylarylnitrosamines are given in Table 5. No attempt was made to purify these unstable compounds. The absence of an N-H absorption (3400-3100 cm\(^{-1}\)) and the shift of the C=O absorption from 1690-1640 cm\(^{-1}\) to 1750-1720 cm\(^{-1}\) in the infrared spectrum was taken as an indication of the complete nitrosation of the amide.

Samples of 4-chloro-\(\text{N}\)-nitrosobenzanilide and \(\text{p}\)-methoxy-\(\text{N}\)-nitrosoacetanilide were prepared by J. Cook and had melting points (decomp.) 76-77\(^{\circ}\) (lit. 75\(^{\circ}\)) and 70-71\(^{\circ}\) respectively.

f) Storage of Acylarylnitrosamines

At room temperature acylarylnitrosamines discolor in a matter of hours and turn to a brown tar after several days. During this period the infrared spectrum may show the absorption of a diazonium salt (2300 cm\(^{-1}\)).

It was found that samples of various nitrosamides, kept in stoppered tubes, wrapped in foil and surrounded by cardice remained untarnished for as long as six weeks. The infrared and e. s. r. spectra from these samples were indistinguishable from those of the freshly prepared compounds.
TABLE 5

Preparation of $R^{-} N(NO)COR'$

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Method</th>
<th>Yield (%)</th>
<th>m.p. (decomp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>A</td>
<td>46</td>
<td>45-46° (lit., 42 45-46°)</td>
</tr>
<tr>
<td>Bu$t$</td>
<td>H</td>
<td>B</td>
<td>78</td>
<td>30-32°</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>A</td>
<td>86</td>
<td>73° (lit., 40b 73°)</td>
</tr>
<tr>
<td>Bu$t$</td>
<td>Me</td>
<td>A</td>
<td>92</td>
<td>57-57.5° (lit., 63 57°)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Me</td>
<td>B</td>
<td>72</td>
<td>70° (lit., 42 68-70°)</td>
</tr>
<tr>
<td>CO$_2$Et</td>
<td>Me</td>
<td>A</td>
<td>90</td>
<td>53°</td>
</tr>
<tr>
<td>H</td>
<td>Et</td>
<td>A</td>
<td>83</td>
<td>49-50° (lit., 42 53°)</td>
</tr>
<tr>
<td>H</td>
<td>Pr$^i$</td>
<td>B</td>
<td>58</td>
<td>32-33° (lit., 42 35°)</td>
</tr>
</tbody>
</table>
IV MISCELLANEOUS REACTIONS

a) Preparation of Nitrosyl Chloride

Nitrosyl chloride was prepared as described in "Inorganic Syntheses" by allowing an aqueous solution of sodium nitrite to react with concentrated hydrochloric acid. It was dissolved in acetic anhydride (or anhydrous ether) to give a 25% w/v solution, which was stored at -10°.

b) Preparation of Phenylazotriphenylmethane

Phenylhydrazotriphenylmethane was prepared by the method of Gomberg, in which phenylhydrazine (2 moles) was treated with triphenylmethyl chloride (1 mole) in ether. Oxidation, by the method of Wieland, with alkaline potassium ferricyanide gave phenylazotriphenylmethane (61%), m. p. 109° (lit. 111°).

c) Preparation of Benzenediazonium Acetate

Aniline (2.5 g., 0.027 mole) in glacial acetic acid (6 ml.) and ethanol (3 ml.) at 0° was diazotised with pentyl nitrite (2.9 g., 0.027 mole) to give a red solution. On cooling the flask with cardice a precipitate formed, which remained on warming to -10° in an ice-acetone bath. The mixture was filtered through cold apparatus to give a slushy solid, which was washed with petroleum, but not purified further. On adding a small portion of the solid
to cold alkaline β-naphthol an intense red precipitate was formed. The infrared spectrum of the solid showed absorption at 2300 cm. \(^{-1}\) (-\(\text{N} \equiv \text{N}\)).

d) **Preparation of 3, 3', 5, 5'-Tetramethylbibenzyl and 2, 4, 6-Trimethylbibiphenyl**

Recrystallised dibenzoyl peroxide (6.0 g., 24.8 mmoles) in freshly distilled mesitylene (45.1 g., 0.376 mole) was maintained at 70-80\(^{\circ}\) under nitrogen for 15 min. and then boiled under reflux for 12 hr. The reaction mixture was washed with saturated potassium bicarbonate solution (3 x 25 ml.) and dried over anhydrous magnesium sulphate.

The bulk (22.2 mmoles dibenzoyl peroxide) of the solution was concentrated and chromatographed on alumina (500 g.). Elution with petroleum gave 2, 4, 6-trimethylbibiphenyl (crude 1.54 g., 7.9 mmoles, 28.2m/100m) as a pale yellow oil, b. p. 60-62\(^{\circ}\)/0.08 mm. (lit.,\(^{115}\) 124.3-124.9\(^{\circ}\)/6 mm.).

N. m. r. (CDCl\(_3\)): \(\tau\) 2.40-3.00 (complex, 5H, Ph), 3.03 (2H, Ph), 7.66 (3H, Me) and 7.99 (6H, Me).

Elution with petroleum-benzene (10:1) gave 3, 3', 5, 5'-tetramethylbibenzyl (crude 0.90 g., 3.8 mmoles, 17.1m/100m), m. p. and mixed m. p. 73-74\(^{\circ}\) (lit.,\(^{116}\) 72-73\(^{\circ}\)) after recrystallisation from ethanol.
N. m. r. (CDCl₃): 7 3.17 (6H, Ph), 7.19 (4H, methylene), and 7.72 (12H, Me).

The infrared spectrum was indistinguishable from that of the authentic compound.

A sample of the reaction mixture was examined by g. l. c. (2% NPGS; 90 to 220⁰, linear temperature programme 10⁰/min.) with bicumyl as internal standard, and was found to contain 2, 4, 6-trimethylbiphenyl (31.7 m/100m) and 3, 3', 5, 5'-tetramethylbibenzyl (20.7m/100m).

V REACTIONS OF ACYLARYL NITROSAMINES

a) Decomposition of N-Nitrosoacetanilide in Benzene

The effect on product yields of varying the concentration of N-nitrosoacetanilide in benzene was studied. The following molar ratios of nitrosamide to benzene were used: - A, 1:13.7; B, 1:137; C, 1:13.7; D, 1:1370; E, 1:137; F, 1:4.22; G, 1:2.95.

The reactions were carried out in the presence of air and protected by a calcium chloride tube, using benzene which had been redistilled and dried over sodium wire. For the first hour of the decomposition the reaction flask was surrounded by water to prevent overheating.
A. 1:13.7

N-Nitrosoacetanilide (5.0 g., 30.5 mmoles) was allowed to decompose in benzene (37.5 ml., 0.423 mole) at room temperature for 137 hr.

The reaction mixture was treated with sodium hydroxide (200 ml. of 0.207 M solution), followed by water (3 x 100 ml.) and then dried over anhydrous magnesium sulphate. The aqueous layers were combined and the acid content (92 m/100 m) determined by back-titration against standard hydrochloric acid solution using bromothymol blue as indicator.

The major part (27.8 mmoles nitrosamide) of the reaction mixture was concentrated and chromatographed on alumina (500 g.). Elution with petroleum-benzene (10:1) gave (i) biphenyl (crude 1.71 g., 11.1 mmoles, 39.9 m/100 m), m.p. 68° (lit., 105° 71°) and mixed m.p. 68-69° after recrystallisation from ethanol. The infrared spectrum was indistinguishable from that of authentic biphenyl.

Further elution with petroleum-benzene (10:1) yielded (ii) a yellow solid (0.04 g.), (iii) an orange solid (0.17 g.) and (iv) a yellow solid (0.17 g.). Elution with petroleum-benzene (8:1) gave (v) an orange solid (0.05 g.), and with petroleum-benzene (5:1) (vi) a red solid (0.04 g.). Elution with methanol and washing
the alumina with acetone yielded black tars (1.40 g.).

Fraction (iv) was recrystallised from ether to give p-diphenylbenzene, m. p. 211-212° (lit., 105 213°), mixed m. p. 211-213°. The infrared spectrum was indistinguishable from that of an authentic sample.

Fractions (ii) and (iii) and the mother liquors from fractions (i) and (iv) were examined by g. l. c. (2% NPGS, 184°).

The mother liquor from (i) contained biphenyl and o-diphenylbenzene, and was chromatographed on alumina (220 g.). Elution with petroleum gave biphenyl and then p-diphenylbenzene.

Fraction (ii) contained mostly p-diphenylbenzene. The o-diphenylbenzene fractions from (i) and (ii) were combined and recrystallised from methanol to give the white solid, m. p. and mixed m. p. 55-56° (lit., 105 58°). The infrared spectrum was indistinguishable from that of an authentic sample.

Fraction (iii) contained mostly azobenzene and some o-, m- and p-diphenylbenzenes. The orange solid was dissolved in petroleum and cooled to -20°. Precipitated diphenylbenzenes were filtered off and the filtrate evaporated to dryness. The solid was recrystallised twice from boiling ethanol to give azobenzene, identified by its m. p. and mixed m. p. 67° (lit., 105 68°) and from its infrared spectrum.
A sample of the reaction mixture was examined by g. l. c. (Table 6, p. 61) with naphthalene and 2-methylandanthracene as internal standards.

B. 1:137

N-Nitrosoacetanilide (5.0 g., 30.5 mmoles) was allowed to decompose in benzene (375 ml., 4.23 mole) at room temperature for 96 hr.

The reaction mixture was treated as in part A to give:

acid content 107m/100m, (i) biphenyl (crude 2.33 g., 15.1 mmoles, 51.2m/100m), (ii) a red oil (0.07 g.), (iii) a red solid (0.05 g.) and (iv) black tars (0.42 g.).

C. 1:13.7

N-Nitrosoacetanilide (3.0 g., 18.3 mmoles) was allowed to decompose in benzene (22.5 ml., 0.251 mole) at room temperature for 137 hr.

The acid content (104m/100m) was determined by titration.

The aqueous extract (16.1 mmoles nitrosamide) not used for acid content analysis, was neutralised with excess hydrochloric acid and the solution was continuously extracted with ether for 37 hr. On evaporation of the solvent there remained a pink
solid (0.13 g.) with an odour of phenol. The solid was
dissolved in 10% sodium hydroxide solution and shaken with
benzoyl chloride (1 ml.) for 20 min. The resulting brown solid
was recrystallised from methanol to give phenyl benzoate,
identified by its infrared spectrum and m. p. and mixed m. p. 69°
(lit. 105 69°). Yield of crude phenol: 8.4m/100m.

G. 1. c. analysis - Table 6, p. 61.

D. 1:1370

N-Nitrosoacetanilide (2.5 g., 15.2 mmoles) was allowed to
decompose in benzene (1875 ml., 21.15 mole) at room temperature
for 140 hr.

The acid content (101m/100m) was found by titration.

G. 1. c. analysis - Table 6, p. 61.

E. 1:137

N-Nitrosoacetanilide (3.0 g., 18.3 mmoles) was allowed to
decompose in benzene (225 ml., 2.51 mole) at room temperature
for 137 hr.

The acid content (104m/100m) was found by titration.

G. 1. c. analysis - Table 6, p. 61.
F.  1:4.22

\[ N\text{-Nitrosoacetanilide} \ (4.9 \text{ g.}, \ 29.7 \text{ mmoles}) \] was allowed to decompose in benzene \((11 \text{ ml.}, \ 0.128 \text{ mole})\) at room temperature for 134 hr.

The acid content \((103m/100m)\) was found by titration.

G. 1:2.95

\[ N\text{-Nitrosoacetanilide} \ (2.46 \text{ g.}, \ 15.0 \text{ mmoles}) \] was allowed to decompose in benzene \((3.8 \text{ ml.}, \ 0.043 \text{ mole})\) at room temperature for 134 hr.

The acid content \((96m/100m)\) was found by titration.

G. l. c. analysis - Table 6, p. 61.

b) Decomposition of \(N\text{-Nitrosoacetanilide} \) in Mesitylene

\[ N\text{-Nitrosoacetanilide} \ (5.0 \text{ g.}, \ 30.5 \text{ mmoles}) \] was allowed to decompose in mesitylene \((50.0 \text{ g.}, \ 0.417 \text{ mole})\) at room temperature for 6 days.

The acid content \((105m/100m)\) was found by titration.

The bulk \((24.2 \text{ mmoles nitrosoamide})\) was distilled to give:

(i) a liquid, b. p. \(55-65^\circ/10\text{mm.}\), and (ii) an orange oil \((2.74 \text{ g.}), \) b. p. \(50-130^\circ/0.04\text{mm.}\), leaving a black residue \((0.49 \text{ g.})\).
<table>
<thead>
<tr>
<th>Reaction</th>
<th>moles benzene/ moles nitrosamide</th>
<th>Yields (m/100m nitrosamide)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>biphenyl</td>
</tr>
<tr>
<td>A</td>
<td>13.7</td>
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<td>C</td>
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<td>1370</td>
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</tr>
<tr>
<td>G</td>
<td>2.95</td>
<td>23.6</td>
</tr>
</tbody>
</table>

**TABLE 6**

N-Nitrosoacetanilide in Benzene
The orange oil (ii) was chromatographed on alumina (500 g.). Elution with petroleum gave a colourless liquid and a white solid: the liquid was identified as mesitylene from its infrared spectrum; the white solid (0.05 g.) was recrystallised from ethanol, m.p. 54-55°, b.p. 118-120°/0.04 mm.

I. r. (Nujol): 740 cm. \(^{-1}\); 730 cm. \(^{-1}\) (aromatic CH).

Further elution with petroleum yielded 2, 4, 6-trimethylbiphenyl (crude 1.00 g., 5.10 mmoles, 16.7m/100m), b.p. 62-63°/0.10 mm., identified by comparison of its infrared and n.m.r. spectra with those of the authentic compound.

Elution with petroleum-benzene (10:1) gave 3, 3', 5, 5'-tetramethylbibenzyl as a pale yellow solid (crude 0.08 g., 0.34 mmoles, 1.4m/100m), m.p. and mixed m.p. 73-74° after recrystallisation from ethanol, identified by its infrared and n.m.r. spectra.

Elution with methanol gave an orange oil (0.58 g.).

A sample of the reaction mixture was examined by g.l.c.
(2% NPGS; 90-220°, linear temperature programme 10°/min.) with bicumyl as internal standard, and was found to contain 2, 4, 6-trimethylbiphenyl (30.3m/100m) and 3, 3'5, 5'-tetramethylbibenzyl (2.4m/100m).
VI E.S.R. STUDY OF THE DECOMPOSITION OF ACYLARYLNITROSAMINES

a) General Technique

Unless otherwise stated, the procedure used was as follows: a measured volume of solvent was added to a known weight of nitrosamide in a small beaker. The solution was then transferred to a sample tube, and the tube placed in the cavity of the e.s.r. spectrometer. The time taken between the mixing of solid and solvent and recording of the first spectrum was about two minutes.

In general no attempt was made to exclude air from the system, or to control the temperature of the solution.

The sample tubes used were of quartz or pyrex and were of 3 or 5 mm. internal diameter. As the use of the 5 mm. tubes provided more intense signals, they were used whenever possible, but were only suitable for non-polar solvents; for polar solvents in the wider tubes complete tuning of the spectrometer cavity was not possible, with a resultant decrease in sensitivity.

b) Determination of Splitting Constants and g-Values

Measurements were made by comparison with a saturated sodium carbonate solution of Fremy's salt (potassium nitroso-disulphonate) for which \( g_N = 13.091 \pm 0.004 \) gauss and
Fig. 1 Superimposed signals of PAPN and Fremy's salt
A sealed capillary tube containing this solution was either placed inside or attached to the outside of the sample tube.

The concentration of the reference solution was chosen so as to facilitate accurate determination of the separation of the hyperfine lines of both standard and sample. A typical example is shown in Fig. 1; the 1:1:1 triplet of the Fremy's salt spectrum is clearly distinguishable superimposed on the signal resulting from the decomposition of N-nitrosoacetanilide in benzene.

**Splitting Constants.** - The spectrum was calibrated by measuring the distance "x" separating the centres of the high and low field lines of the Fremy's salt signal.

Thus "x" is equivalent to 26.18 gauss.

For the (N-phenylacetamido)phenylnitroxide (PAPN) signal the larger $a_N$ value was found by measuring "y" and "z", the distances separating corresponding lines of the high and low field groups. Whenever possible lines were chosen on both sides of the Fremy's salt signal; in this way errors arising from any nonlinearity in the magnetic field sweep were minimised.

Thus $a_N = 26.18 \times \frac{y + z}{4x}$ gauss.
Using this technique a reproducibility of ± 0.02 gauss was achieved, and the resulting error in the hyperfine coupling constants was estimated as < 0.05 gauss.

Measurements were made sweeping upfield only. On several test runs there was no measurable discrepancy between the results from sweeping up and down.

The other coupling constants were either found for the same trace, or from one with no superimposed standard, in which case the larger $a_N$ value was used as reference. Each time corresponding distances were measured for both high and low field groups, and the mean value determined. Particular attention was paid to the intergroup portion of the spectrum, as small changes in the values of the coupling constants were most easily detected in this region.

The same principle was used in the measurement of the coupling constants of all the other signals.

The $g$-values were calculated from the relationship:

$$ g = \frac{h\nu}{\beta H_c} = \frac{h\nu}{\beta(H_{FS} + \Delta F)} $$

where $H_c$ and $H_{FS}$ are the centres of the sample and Fremy's salt signals respectively, and $\Delta F$ is the separation of these in gauss.

$H_{FS}$ was computed from its $g$-value thus:
\[ H_{FS} = \frac{\hbar \nu}{\beta g} = \frac{6.6252 \times 10^{-27}}{0.92732 \times 10^{-20}} \times \frac{9270.4 \times 10^{6}}{2.00550} = 3302.52 \text{ gauss} \]

\( \Delta F \) was measured from the superimposed signals using the same calibration as for the determination of \( a_N \). It was defined as positive when the centre of the sample signal was at higher field than that of the standard. A positive value of \( \Delta F \) implied a \( g \)-value less than 2.00550 and vice versa.

Although the middle of the sample signal was frequently masked by the middle line of the standard, its position could be accurately determined from the nearest unhidden hyperfine lines: thus for the spectrum shown in Fig. 1 the centre is at point \( X \) midway between the centres of the arrowed hyperfine lines.

The accuracy with which the \( g \)-value could be measured depended on the errors involved in measuring \( \Delta F \) and in the known \( g \)-value for Fremy's salt. The former was estimated as \( \pm 0.02 \text{ gauss} \), while the latter was stated\(^{118}\) as \( \pm 0.00005 \). Thus, while absolute \( g \)-values are quoted with an error of \( \pm 0.0001 \), the difference \( \delta g \) between those of sample and Fremy's salt \( (\delta g = 2.00556 - g \text{ sample}) \) has an estimated accuracy of \( \pm 0.00002 \).

**Linewidths.** - The peak to peak linewidths were measured
only from the outside lines of the spectrum, as the inner ones consisted of a number of partially resolved hyperfine components.

c) **Purification of Solvents**

Benzene was distilled and dried over sodium. Toluene, ethylbenzene, cumene, mesitylene, p-xylene and t-butylbenzene were distilled, dried over sodium and passed down an alumina column immediately before use. Alcohols were boiled under reflux over calcium hydride, fractionally distilled and stored over molecular sieve. Pyridine was distilled and dried over potassium hydroxide pellets. Ethers were distilled and dried over sodium. Furan was distilled and passed down an alumina column immediately before use. 2,6-Dimethylfuran was treated similarly and stored at -10°. Carbon tetrachloride was dried over calcium chloride and fractionally distilled.

There follows a description of the e. s. r. signals observed during the decomposition of the acylaryl nitrosamines in solution. The coupling constants and g-values were measured with reference to Fremy's salt as described in part (b). The intensities of the signals are classified by the following qualitative scale: intense, medium, weak, very weak, nil.

The various signals observed are summarised on page 99.
Fig. 2  N-Nitrosoacetanilide in benzene
d) N-Nitrosoacetanilide

(i) In Aromatic Hydrocarbons

Benzene. - Using a concentration of 130mg. /ml. and
modulation amplitude (mod.) of between 0.23 and 0.023 gauss,
the intense signal reported by Rüchardt,⁵², ⁵⁶, ⁵⁹ and assigned
by Perkins⁶¹ to the (N-phenylacetamido)phenylnitroxide (PAPN)
radical, was observed.

The signal, which was still detectable after two days, is
shown in Fig. 2, and was analysed to give the following splitting
constants in gauss: (1) a_N = 11.62, (1) a_o-H = 2.73, (2) a_o, p-H = 2.60,
(1) a_N = 1.67 and (2) a_m-H = 0.89. Also measured were:
linewidth = 0.18 and ΔF = 0.29 gauss.

Hence g = 2.0053 and 8 g = 18 x 10⁻⁵.

When a more concentrated solution (250 mg. /ml.) and a
modulation amplitude (mod.) of 1.27 gauss were used a second
weak signal, not reported by previous workers, was observed
superimposed on the first. This signal, which decayed rapidly
until it was undetectable after 30 min., can be seen in Fig. 3,
straddling the intense (N-phenylacetamido)phenylnitroxide
(PAPN) signal.
Fig. 4  N-Nitrosoacetanilide in mesitylene
Mesitylene. - Using a concentration of 250 mg./ml. and mod. 1.27 gauss the PAPN signal was very weak, while that of the second signal was weak, but now entirely discernable. Fig. 4 shows that the second signal consists of nine lines arranged as a 1:1:1 triplet of 1:1:1 triplets, suggesting two nitrogen nuclei with splitting constants of about 30 and 2 gauss. For mod. 0.23 gauss no signal was detected.

During the course of the decomposition a gelatinous precipitate was formed: after 20 min. this had occurred sufficiently to trap bubbles of the nitrogen gas evolved in the reaction. The resultant detuning of the spectrometer prevented further study.

Toluene, Ethylbenzene and p-Xylene. - For a concentration of 250 mg./ml. and mod. 1.27 gauss the PAPN signal intensities for the three solvents were weak, very weak and very weak, while in each case the triplet of triplets signal was weak. Using mod. 0.23 gauss no signal was detected. As for mesitylene the precipitation of solids prevented the recording of spectra after about 20 min.

Cumene. - For a concentration of 250 mg./ml. and mod. 1.27 gauss the spectrum (Fig. 5) consisted of a weak triplet of triplets
and superimposed another weak signal, consisting of three lines of relative intensities 1:1:1 and with a splitting constant of about 15 gauss. On changing to mod. 0.23 gauss the triplet of triplets was undetectable, while the new 1:1:1 triplet remained.

The precipitation of solid products limited the examination to 30 min.

**t-Butylbenzene.** - The spectrum observed was indistinguishable from that found for benzene as solvent (Figs. 2 and 3). For a concentration of 250 mg./ml. and mod. 1.27 gauss the PAPN signal was intense and the triplet of triplets weak, while for mod. 0.23 gauss only the intense, well resolved PAPN signal was detected. For this signal $a_N = 11.51$ gauss and $\Delta F = 0.29$ gauss.

As with all the other aromatic hydrocarbon solvents except benzene, the precipitation of solids caused rapid detuning after about 30 min.

(ii) **In Alcohols**

**Methanol.** - With concentration 130 mg./ml. and mod. 0.23 gauss a well resolved PAPN signal of medium intensity was observed. For this signal $a_N = 11.90$ gauss and $\Delta F = 0.44$ gauss, giving $g = 2.0052$ and $\xi g = 27 \times 10^{-5}$. 
Ethanol. - With concentration 130 mg./ml. and mod. 0.23 gauss a weak PAPN signal was observed, for which $a_N = 11.84$ gauss.
\[
\Delta F = 0.40 \text{ gauss giving } g = 2.0053 \text{ and } g_s = 24 \times 10^{-5}
\]

n-Propanol. - With concentration 130 mg./ml. and mod. 0.41 gauss the PAPN signal was very weak, with $a_N = 11.81$ gauss and $\Delta F = 0.39$ gauss: thus $g = 2.0053$ and $g_s = 24 \times 10^{-5}$.

The limited solubility of $N$-nitrosoacetanilide in alcohols prevented the use of more concentrated solutions or of higher homologues.

The triplet of triplet signal was not detected for this series of solvents.

(iii) In Ethers

The e.s.r. signals observed during the decomposition of $N$-nitrosoacetanilide in ether solvents were more complex than those found for alcohols or aromatic hydrocarbons. That the spectra were not symmetrical was caused by the superimposition of at least two signals.

Diethyl Ether. - Using a concentration of 250 mg./ml. the dominant signal was that of the PAPN radical, with a second unidentified signal superimposed on it. When the concentration of nitrosamide was 130 mg./ml. the PAPN signal was weak
and dominated by the second signal, for which three coupling constants could be determined: \( (1) a_N = 15.4 \text{ gauss}, \) 
\( (1) a_H = 5.8 \text{ gauss} \) and \( (1) a_N = 1.4 \text{ gauss}. \) This signal was similar to the one found for \( p-t\)-butyl-\( N\)-nitrosoacetanilide in diethyl ether, described elsewhere (p.77) in this thesis and illustrated in Fig. 7.

**Dimethoxyethane and Tetrahydrofuran.** - As with diethyl ether as solvent, the spectra were a complex mixture of the PAPN and other unidentified signals.

**(iv) In Halogenated Solvents**

**Carbon Tetrachloride.** - Using a concentration of 130 mg./ml. and mod. 0.23 gauss no signal was detected. When the concentration was increased to 200-400 mg./ml. and for mod. 1.27 gauss a 1:1:1 triplet of 1:1:1 triplets, indistinguishable from that found for the aromatic hydrocarbon solvents, was observed. The signal was weak and lasted about 30 min. At the outset there was no sign of the PAPN signal, but after about 15 min. a very weak 1:1:1 broad triplet appeared superimposed on the triplet of triplets: the separation of the broad lines was about 12 gauss, but the signal could not be resolved further.

The precipitation of solids during the course of the decomposition prevented spectra being recorded after about 30 min.
Bromotrichloromethane. - The only signal observed was the triplet of triplets, which was weak and of 30 min. duration.

Methylene Chloride. - For a concentration of 400 mg./ml. and mod. 1.27 gauss weak signals of both PAPN and the triplet of triplets were observed. The former lasted several hours, while the latter was not detectable after 15 min.

Ethyl Bromide. - Using a concentration of 330 mg./ml. and mod. 1.27 gauss two signals were observed: the weak triplet of triplets, lasting about 15 min., and an intense PAPN signal. For the latter (at mod. 0.23 gauss) the following measurements were made in gauss: (1) $a_N = 11.72$, (1) $a_{o-H} = 2.74$, (2) $a_o, p-H = 2.62$, (1) $a_N = 1.69$ and (2) $a_{m-H} = 0.89$. Also $\Delta F = 0.37$ giving $g = 2.0053$ and $\xi_g = 23 \times 10^{-5}$.

1,1,2,2-Tetrabromoethane. - With a concentration of 330 mg/ml. and mod. 1.27 gauss the only signal detected was the triplet of triplets: the signal was weak and of about 5 min. duration.

(v) In Other Solvents

The signals observed for various other solvents are listed below, with the concentration, mod. and coupling constants in gauss.
Acetone. - 800 mg./ml.

Mod. 0.13: PAPN signal well resolved and of medium intensity.

\(a_N = 11.86, \quad (1) a_{o-H} = 2.75, \quad (2) a_{o,p-H} = 2.62, \quad (1) a_N = 1.69\n
and \( (2) a_{m-H} = 0.89 \). Also \( \Delta F = 0.39 \) giving \( g = 2.0053 \) and \( \delta g = 18 \times 10^{-5} \).

Mod. 1.27: weak triplet of triplets superimposed on PAPN signal.

Furan. - 750 mg./ml.

Mod. 0.074: intense well resolved PAPN signal. \( a_N = 11.82, \)
\( a_{o-H} = 2.75, \quad (2) a_{o,p-H} = 2.62, \quad (1) a_N = 1.69 \) and \( (2) a_{m-H} = 0.89 \).

Also \( \Delta F = 0.38 \) giving \( g = 2.0053 \) and \( \delta g = 24 \times 10^{-5} \).

Mod. 1.27: triplet of triplets signal very weak with lifetime less than 5 min.

For a concentration of 400 mg./ml. the PAPN signal was of medium intensity - noticeably weaker than for the same concentration in benzene.

2,6-Dimethylfuran. - 400 mg./ml.

No signal was detected.

Pyridine. - 400 mg./ml.

Mod. 0.13: intense PAPN signal. \( a_N = 11.77, \quad (1) a_{o-H} = 2.74, \)
\( (2) a_{o,p-H} = 2.61, \quad (1) a_N = 1.68 \) and \( (2) a_{m-H} = 0.89 \). Also
\[ \Delta F = 0.34 \text{ giving } g = 2.0053 \text{ and } \delta g = 21 \times 10^{-5}. \]

The triplet of triplets was not observed.

**Hexafluorobenzene.** - 300 mg./ml.

Mod. 1.27: medium intensity PAPN and weak triplet of triplets, both signals lasting about 30 min., when they were replaced by an intense single line of width 15 gauss, which could not be resolved.

e) \textit{p-t-Butyl-N-nitrosoacetanilide}

(i) \textbf{In Aromatic Hydrocarbons}

The e.s.r. spectra observed during the decomposition of \textit{p-t-butyl-N-nitrosoacetanilide} in aromatic hydrocarbons were comparable with those found for the unsubstituted nitrosamide. However, no solids were formed, so study over a longer period of time was possible.

**Benzene.** - Both the (N-arylacetamido)arylnitroxide and triplet of triplets signals were detected in similar intensities to those found for N-nitrosoacetanilide in benzene.

The (N-arylacetamido)arylnitroxide spectrum was as observed by Rüchardt,\(^{59}\) with \(a_N = 11.73 \text{ gauss} \) and \(\Delta F = 0.43 \text{ gauss};\)

thus \(g = 2.0052 \) and \(\delta g = 26 \times 10^{-5}.\) As reported by Rüchardt,\(^{59}\) the linewidth was 0.32 gauss: he attributed the increase from
the value of 0.18 gauss found for the unsubstituted nitrosamide to long range coupling with the protons of the t-butyl group.

**Ethylbenzene.** - With a concentration of 270 mg. /ml. and mod. 1.27 gauss the PAPN type signal was very weak and short-lived, while the triplet of triplets was weak, but detectable for 45 min. The coupling constants for this signal were measured and found to be: \((1) a_N = 30.5 \text{ gauss} \) and \((1) a_N = 2.35 \text{ gauss}\). The linewidth was 1.14 gauss.

After 1 hr. a weak unsymmetrical six line spectrum appeared. This mixture of at least two signals persisted for several hours, but was not resolved further.

**Cumene.** - The spectra observed were similar to those found for N-nitrosoacetanilide itself. The triplet of triplets was weak and lasted about 30 min. The 1:1:1 triplet, with \(a_N = 15 \text{ gauss}\), was weak at the start, but its intensity increased over several hours. In addition a weak unidentified signal appeared after 1 hr. superimposed on the 1:1:1 triplet, but was not studied further.

(ii) **In Alcohols**

In order to study the dependence of the splitting constant and \(g\)-value on the polarity of the solvent, the larger \(a_N\) value
Fig. 6  p-t-Butyl-N-nitrosoacetanilide in methanol (top) and t-butanol (bottom)
and $\Delta F$ were measured for a series of alcohols. The results are listed in Table 7, together with three polarity parameters for comparative purposes.

$p$-t-Butyl-$N$-nitrosoacetanilide proved more suitable for this study than the unsubstituted nitrosamide, because of its greater solubility in this series of solvents.

The intensity of the (N-arylacetamido)aryl nitroxide signal decreased in the order: $\text{MeOH} > \text{EtOH} > \text{Pr}^n\text{OH} > \text{Bu}^n\text{OH} > n-C_5H_{11}\text{OH} > \text{Pr}^i\text{OH}$. However, for t-butanol as solvent the signal was similar in strength to that found for methanol.

The resolution of the high field group of lines decreased with increasing viscosity of the solvent. This is illustrated by the spectra observed in methanol and t-butanol shown in Fig. 6.

(iii) **In Diethyl Ether**

For a concentration of 33 mg./ml. the PAPN type signal was very weak and short-lived. On the other hand a signal, similar to that found for $N$-nitrosoacetanilide in diethyl ether, was of medium intensity and remained detectable for several hours.

Fig. 7 shows the spectrum observed after 15 min., using mod. 0.13 gauss, with a reconstruction of the spectrum assuming
Fig. 7  $\text{t-Bu-N-nitrosocyanilide in diethyl ether}$ with reconstructed spectrum

$\tilde{a}_m \quad \tilde{a}_N$

$\tilde{a}_H \quad \tilde{a}_N$
TABLE 7

The (N-Arylacetamido)arylnitroxide E. S. R. Signal observed during the Decomposition of p-t-Butyl-
N-nitrosoacetanilide in Alcohols

Variation of $a_N$ and $\delta g$ with Solvent Polarity

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$a_N$ (in gauss)</th>
<th>$\delta g \times 10^5$</th>
<th>$E_T$</th>
<th>$K$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>12.02</td>
<td>32</td>
<td>55.5</td>
<td>83.6</td>
<td>33.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.91</td>
<td>29</td>
<td>51.9</td>
<td>79.6</td>
<td>25.7</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>11.88</td>
<td>29</td>
<td>50.7</td>
<td>78.3</td>
<td>21.8</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>11.86</td>
<td>29</td>
<td>50.2</td>
<td>77.7</td>
<td>17.8</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>11.86</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-Butanol</td>
<td>11.82</td>
<td>28</td>
<td>43.9</td>
<td>71.3</td>
<td>11.4</td>
</tr>
</tbody>
</table>

a) $E_T$: Reichardt's $E_T$ - value\textsuperscript{119}
b) $K$: Kosower Z factor\textsuperscript{120}
c) $\varepsilon$: Dielectric constant\textsuperscript{121}
the following coupling constants in gauss: \( (1) a_N = 15.30 \),
\( (1) a_H = 5.77 \) and \( (1) a_N = 1.35 \). Also measured were:
linewidth = 0.63 gauss and \( \Delta F = -0.39 \) gauss, giving
g = 2.0057 and \( \delta g = -24 \times 10^{-5} \). It can be seen from the
figure that the signal is distorted by another unidentified signal
for which \( a_N \approx 16 \) gauss.

(iv) In Halogenated Solvents

**Carbon Tetrachloride.** - Using a concentration of 200 mg. /ml.
no solids were precipitated during the decomposition. The
only signal detected was the triplet of triplets, which remained
for about 20 min. The following measurements were made:
\( (1) a_N = 30.5 \) gauss, \( (1) a_N = 2.39 \) gauss, linewidth = 0.94 gauss
and \( \Delta F = 6.47 \) gauss - hence \( g = 2.0016 \) and \( \delta g = 392 \times 10^{-5} \).

**Bromotrichloromethane.** - The spectra observed were
similar to those observed for carbon tetrachloride as solvent:
\( (1) a_N = 30.6 \) gauss and \( \Delta F = 6.53 \) gauss - hence \( g = 2.0015 \)
and \( \delta g = 396 \times 10^{-5} \).

For both carbon tetrachloride and bromotrichloromethane,
spectra were recorded for the first 30 min. of the reaction:
during that time there was no PAPN type signal.
Fig. 8  p-Methoxy-N-nitroscocetanilide in benzene
(iv) **In Pyridine**

For a concentration of 400 mg./ml. and mod. 0.41 gauss, the only signal observed was that of the PAPN type radical. The following measurements were made in gauss: \(a_N = 11.88\), \(a_{o-H} = 2.73\), \(a_{o-H} = 2.59\), \(a_N = 1.71\), \(a_{m-H} = 0.90\) and \(\Delta F = 0.51\) giving \(\delta g = 2.0052\) and \(\delta g = 31 \times 10^{-5}\).

f) **p-Methoxy-N-nitrosoacetanilide**

(i) **In Benzene**

The solubility of p-methoxy-N-nitrosoacetanilide in benzene was much less than that of the unsubstituted nitrosamide. Only by using a saturated solution, with undissolved solid at the bottom of the tube, was the concentration sufficient to give well resolved e.s.r. spectra, and then only the PAPN type signal and not the triplet of triplets was observed. Fig. 8 shows the spectrum observed on mixing 130 mg. nitrosamide with 1 ml. benzene. Coupling of the unpaired electron with the protons of the methoxy group results in an increase in the number of hyperfine lines in each group from 16 to 30 compared with the signal from the unsubstituted nitrosamide.

The coupling constants for the major nitrogen and the methoxy protons were measured accurately as: \(a_N = 12.30\) gauss
Fig. 9  p-Methoxy-N-nitrosoacetanilide in benzene with reconstructed spectrum
and (3) $a_H = 0.39$ gauss. In addition the following were determined:
linewidth = 0.18 gauss and $\Delta F = 0.53$ gauss giving $g = 2.0052$
and $\delta g = 34 \times 10^{-5}$.

Without the aid of a spectra simulation computer programme,
extact analysis of the remaining coupling constants was less
certain. Taking into account the number of lines per group (30)
and by measuring the separation of the lines in the intergroup
portion, the most likely assignment was: (2) $a_{o-H} = 2.75$ gauss,
(1) $a_N = 1.60$ gauss and (2) $a_{m-H} = 0.78$ gauss.

Fig. 9 shows the low field group at mod. 0.13 gauss, with the
reconstructed spectrum assuming the above analysis.

(ii) **In Pyridine**

The decomposition in pyridine was fast, and as a result the
signal intensity dropped rapidly. However, the following
measurements were made: (1) $a_N = 12.44$ gauss and $\Delta F = 0.60$ gauss,
giving $g = 2.0051$ and $\delta g = 37 \times 10^{-5}$.

(iii) **In Cumene**

Using a saturated solution (160 mg. /ml.) and mod. 1.27 gauss,
a weak triplet of triplets signal was observed for about 20 min.
The 1:1:1 triplet ($a_N = 15$ gauss), always found for cumene as
solvent, was again present, its intensity reaching a maximum
after about 1 hr. There was no sign of the PAPN type signal.
Fig. 10 4-nitro-4-nitrosoacetanilide in pyridine
For the triplet of triplets: $(1) a_N = 30.6$ gauss and $(1) a_N = 2.36$ gauss.

g) p-Nitro-N-nitrosoacetanilide

(i) In Benzene

p-Nitro-N-nitrosoacetanilide was sparingly soluble in benzene. Even using a saturated solution (100 mg. /ml.) the PAPN type signal was weak and poorly resolved. In addition the precipitation of solids caused rapid detuning of the spectrometer.

(ii) In Pyridine

For a concentration of 300 mg. /ml. and mod. 0.074 gauss, the intense well resolved signal of the PAPN type, shown in Fig. 10, was observed. Coupling with the nitrogen nucleus of the nitro group accounts for the extra complexity of this spectrum compared with the signal from the unsubstituted nitroamide.

Fig. 11 shows the low field group of lines with the reconstructed spectrum assuming the following analysis in gauss: $(1) a_N = 10.59$, $(2) a_{O-H} = 2.59$, $(1) a_N = 1.57$, $(2) a_{m-H} = 0.94$ and $(1) a_N = 0.63$. Also $\Delta F = -0.12$ giving $g = 2.0056$ and $\delta g = -7 \times 10^{-5}$.

(iii) In Cumene

Using a saturated solution (200 mg. /ml.) and mod. 1.27 gauss
Fig. 11  p-Nitro-N-nitrosoacetanilide in pyridine
with reconstructed spectrum
Fig. 12  p-Nitro-N-nitrosoacetanilide in cumene

5 gauss
the triplet of triplets signal was observed for about 20 min. The signal was analysed as follows: \( (1) a_N = 31.0 \text{ gauss}, \)
\( (1) a_N = 2.41 \text{ gauss and } \Delta F = 6.71 \text{ gauss}, \) giving \( g = 2.0014 \) and \( \delta g = 357 \times 10^{-5}. \)

The 1:1:1 triplet was weak in the early stages of the decomposition, but its intensity increased rapidly during the first hour: by this time the satellite lines due to \(^{13}\text{C}\) and \(^{15}\text{N}\) in natural abundance could be detected. Fig. 12 shows, for mod. 0.23 gauss, that there are three pairs of \(^{13}\text{C}\) lines for each of the main component lines of the 1:1:1 triplet \((a_{14N} = 15.0 \text{ gauss}).\) These splitting constants were measured and found to be 8.8, 5.2 and 2.9 gauss.

The expected positions of the \(^{15}\text{N}\) satellites were calculated from the \( a_{15N} \) value, which could be found from the nuclear g-values of the two isotopes.

\[
\text{Thus } a_{15N} = a_{14N} \times \frac{g_{15N}}{g_{14N}} = 15.0 \times \frac{-0.567}{0.403} = 21.2 \text{ gauss}
\]

The lines of this doublet are thus found to coincide with two of the \(^{13}\text{C}\) lines as shown in the figure. Evidence for this overlap is provided by a study of the intensities of this set of \(^{13}\text{C}\) lines. Fig. 13 shows, at mod. 1.27 gauss, the low
Fig. 13

p-Nitro-N-nitrosoacetanilide in cumene
Fig. 14  p-Methyl-M-nitrosoacetanilide in benzene
field group for which the $^{13}\text{C}$ line on the high field side is more intense than that on the low field side. As no such effect is found for middle group, the difference in the two intensities can be assigned to the $^{15}\text{N}$ satellite.

h) p-Methyl-N-nitrosoacetanilide

(i) In Benzene

Using a concentration of 150 mg./ml. and mod. 0.73 gauss, a weak, very short-lived signal of the PAPN type was observed. The spectrum, part of which is shown in Fig. 14, was not sufficiently resolved to permit complete analysis, but the following measurements were made: $a_N = 11.94$ gauss and $\Delta F = 0.44$ gauss, giving $g = 2.0052$ and $\delta g = 27 \times 10^{-5}$.

(ii) In Pyridine

Using a concentration of 600 mg./ml. and mod. 0.41 gauss, the PAPN type signal, while more intense than that found for benzene, was complex and only partially resolved. Only $a_N = 12.05$ gauss and $\Delta F = 0.51$ gauss (giving $g = 2.0052$ and $\delta g = 31 \times 10^{-5}$) could be measured accurately. The most likely assignment of the other coupling constants was:

$1. a_{\text{N}} = 1.7$ gauss and $a_{\text{Me-H}} = 3.0$ gauss, $a_{\text{o-H}} = 3.0$ gauss, $a_{\text{Me-H}} = 1.7$ gauss and $a_{\text{m-H}} = 0.95$ gauss. The linewidth was 0.28 gauss.
Fig. 15
p-Carboxy-A-nitrosoacetanilide in pyridine

5 gauss
(iii) In Cumene

For a concentration of 150 mg./ml. and mod. 1.27 gauss the triplet of triplets signal was weak and only detectable for 10 min. For this signal \( (1) a_N = 30.7 \) gauss.

The 1:1:1 triplet \( (a_N = 15 \) gauss) was also observed.

\[ \text{i) p-Carbethoxy-N-nitrosoacetanilide} \]

(i) In Benzene

For a concentration of 400 mg./ml. and mod. 1.27 gauss, both the PAPN type and triplet of triplets signals were observed. The signals were of similar intensity, the triplet of triplets being noticeably more intense than for the unsubstituted nitrosamide, while the PAPN type signal was much weaker. At mod. 0.23 gauss the PAPN type signal was too weak to be analysed.

(ii) In Pyridine

For a concentration of 600 mg./ml. and mod. 0.074 gauss the PAPN signal, shown in Fig. 15, was intense and long-lived. The spectrum consisted of 3 groups of 13 lines and was very similar to that found for \( p-t \)-butyl-N-nitrosoacetanilide in benzene. The analysis was as follows: \( (1) a_N = 11.04 \) gauss, \( (2) a_{o-H} = 2.53 \) gauss, \( (1) a_m-N = 1.66 \) gauss and \( (2) a_{m-H} = 0.92 \) gauss.
Also $\Delta F = 0.11$ gauss giving $g = 2.0054$ and $\delta g = -6 \times 10^{-5}$.

The linewidth was 0.34 gauss.

(iii) In Cumene

For a concentration of 350 mg./ml. and mod. 1.27 gauss, the triplet of triplets signal was of medium intensity and of 40 min. duration, while the 1:1:1 triplet intensity, as before, increased over the first hour.

The comparatively high intensity and stability of the triplet of triplets allowed a more detailed study than previously possible. The signal was still detectable when the mod. was reduced to 0.13 gauss. The linewidth was consequently reduced from 0.90 gauss (mod. 1.27 gauss) to 0.62 gauss. In spite of this no further hyperfine structure was resolved. The other measurements made were: $(1) a_N = 30.9$ gauss, $(1) a_N = 2.33$ gauss and $\Delta F = 6.70$ gauss. Hence $g = 2.0014$ and $\delta g = 406 \times 10^{-5}$.

j) N-Nitrosoformanilide

(i) In Benzene

Both Huisgen$^{43c}$ and Hey$^{42}$ reported that the rate of decomposition of N-nitrosoformanilide was slower than that for N-nitrosonicotanilide. This was also evident from the intensities of the respective e.s.r. spectra. For N-nitroso-
Fig. 16  N-Nitrosoformanilide in benzene
acetanilide the signal was strongest during the first hour of the reaction and then slowly decreased, while for a similar concentration of \(N\)-nitrosoformanilide the signal was weak at the outset but built up gradually before decreasing.

In order to create a sufficiently high stationary state concentration of radicals to give the best resolved spectra a solution of 400 mg./ml. was used. The resultant signal consisted of 3 overlapping groups of at least 20 lines. This hyperfine structure was more complicated and less well resolved than that found for \(N\)-nitrosoacetanilide itself. The use of pyridine as solvent provided better resolved signals, so the attempted analysis was left for that system. However, the following measurements were made for \(N\)-nitrosoformanilide in benzene: \(1 \) \(a_N = 11.65 \) gauss, \(2 \) \(a_{m-H} = 0.89 \) gauss and \(\Delta F = 0.33 \) gauss. Hence \(g = 2.0053\) and \(\delta g = 20 \times 10^{-5}\).

It was also noted that the low field group of lines was unsymmetrical. Fig. 16 shows that the lines at the low field side of this group were broader and less resolved than those at higher field. This effect was not observed for pyridine as solvent or for \(N\)-nitrosoacetanilide in any solvent.

(ii) In Pyridine

Using a concentration of 200 mg./ml. and mod. 0.041 gauss
Fig. 17  N-Nitrosoformanilide in pyridine
the intense signal shown in Fig. 17 was observed. The resolution was better than for benzene as solvent.

Without the aid of computer simulation an exact and unambiguous analysis was not possible. However, the following measurements were made with certainty:

(1) $a^N = 11.76$ gauss, (2) $a^\text{m-H} = 0.89$ gauss and $\Delta F = 0.32$ gauss.

Hence $g = 2.0053$ and $\delta g = 20 \times 10^{-5}$. The complexity of the structure prevented the accurate determination of the $a^o, p^\text{H}$ and smaller $a^N$ values. However, two other coupling constants could be measured: the outside lines revealed a splitting of 1.25 gauss, while from the centre of each group a doublet of 3.12 gauss was obtained. This extra $a^\text{H}$ value was provisionally assigned to the proton of the formyl group: the use of deuterium substitution to confirm this is reported later in this thesis (p. 91).

Fig. 18 shows the low field group of lines with the formyl proton splitting marked.

(iii) In Cumene

Three e.s.r. signals were observed during the decomposition of N-nitrosoformanilide in cumene. Fig. 19a shows the spectrum, at mod. 0.23 gauss, 5 min. after mixing solute and solvent.
Fig. 18
N-Nitrosoformanilide in pyridine
Fig. 19  N-Nitrosoformamidine in cumene after 5 min. (top)  
             after 3 hr. (bottom)
Fig. 20  N-Nitrosoformanilide in cumene (24 hr.)

with reconstructed spectrum
Two signals are present: the 1:1:1 triplet observed for all cumene systems, and superimposed a new 1:1:1 triplet of 1:1:1 triplets, suggesting two nitrogen nuclei with coupling constants of 18.1 and 1.4 gauss. Comparison with Fig. 5 shows that this was not the usual triplet of triplets: instead of the centre of the spectrum being well upfield of that of the 1:1:1 triplet, the lines in this case symmetrically straddle it.

Fig. 19b was recorded, at mod. 0.23 gauss, 3 hr. later: the only signal present is the 1:1:1 triplet. After 15 hr. another new signal appeared. It was analysed to give the following in gauss: (1) $a_N = 11.38$, (3) $a_H = 2.43$, (2) $a_H = 0.88$ and linewidth = 0.21. Also $\Delta F = -0.39$ giving $g = 2.0057$ and $\delta g = -24 \times 10^{-5}$. This signal, which lasted for several days, is illustrated in Fig. 20, together with a reconstruction of the spectrum assuming the above analysis.

k) **p-t-Butyl-N-nitrosoformanilide**

(1) **In Pyridine**

The PAPN type signal observed during the decomposition of a 400 mg./ml. solution, and shown in Fig. 21, had hyperfine structure much simpler than that for the unsubstituted nitrosamide. However, the broad linewidth (0.37 gauss) due to coupling with
the t-butyl protons prevented an accurate analysis. The following measurements were made in gauss: (1) $a_N = 11.85$, (2) $a_{m-H} = 0.89$ and $\Delta F = 0.42$. Hence $g = 2.0053$ and $\delta g = 24 \times 10^{-5}$.

(ii) In Cumene

The spectra observed during the decomposition of a 400 mg./ml. solution of the nitrosamide in cumene paralleled those found for N-nitrosoformanilide itself. For the first half hour two signals were present: the new 1:1:1 triplet of 1:1:1 triplets had (1) $a_N = 18.10$ gauss, (1) $a_N = 1.36$ gauss and $\Delta F = -0.58$ gauss. Hence $g = 2.0058$ and $\delta g = -36 \times 10^{-5}$. Spectra recorded after 1 hr. showed only the second signal, the 1:1:1 triplet for which $a_N = 15.00$ gauss and $\Delta F = -0.67$ gauss. Hence $g = 2.0059$ and $\delta g = -41 \times 10^{-5}$. The linewidth was 0.52 gauss at mod. 0.041 gauss. Also observed were the $^{13}$C satellite lines for which the splittings were 8.8, 5.1 and 3.0 gauss. After 12 hr. the spectrum showed the third signal superimposed on the 1:1:1 triplet. It consisted of 3 groups of 9 lines, each group being a 1:2:1 triplet of 1:2:1 triplets: the following measurements were made in gauss: (1) $a_N = 11.69$, (2) $a_H = 2.47$ and (2) $a_H = 0.90$. Also $\Delta F = -0.12$ giving $g = 2.0056$ and $\delta g = -7 \times 10^{-5}$. 
1) N-Nitrosoformanilide-1-d

(i) In Benzene

Although the nitrosamide could not be prepared in a pure state, the e.s.r. spectra were not affected. In a test run with undeuterated N-nitrosoformanilide, prepared by the same technique, the signals observed were indistinguishable from those reported earlier for the pure compound.

Using a concentration of 330 mg./ml. and mod. 0.041 gauss the spectrum illustrated in Fig. 22 was observed. From this intense signal the following were determined: (1) $a_N = 11.65$ gauss, (2) $a_{m-H} = 0.89$ gauss and (1) $a_D = 0.48$ gauss. Also $\Delta F = 0.33$ gauss giving $g = 2.0053$ and $\delta g = 20 \times 10^{-5}$.

The use of deuterium substitution confirmed the assignment of the extra coupling to the formyl hydrogen. The doublet splitting of 3.12 gauss was replaced by a 1:1:1 triplet of 0.48 gauss, in accordance with the change of nuclear spin from $1/2$ to 1 and the ratio of the nuclear $g$-factors of 6.5 for the proton and the deuteron. This triplet is illustrated in Fig. 23 for the low field group of lines.

(ii) In Pyridine

The e.s.r. signals observed on mixing the already partially decomposed nitrosamide with pyridine were too short-lived for
Fig. 23  N-Nitrosoformanilide-1-d
in benzene
Fig. 24
1-Nitrosoacrylonilide in benzene at 10°
accurate analysis. However, it was clear that the spectra differed from those found for the unsubstituted nitrosamide.

m) **N-Nitrosopropionanilide**

(i) **In Benzene**

Both Huisgen$^{43c}$ and Hey$^{42}$ reported that the rate of decomposition of N-nitrosopropionanilide was faster than that of N-nitroacetanilide. This meant that at room temperature the evolution of nitrogen gas for concentrated solutions (450 mg./ml.) was too fast to allow e.s.r. spectra to be recorded, while for more dilute solutions (50 mg./ml.) the rate was slower, but the signals were too weak. However, by maintaining the temperature of the spectrometer cavity fixed at $10^\circ$ the rate of reaction was slowed and intense signals were obtained.

Using mod. 1.27 gauss the spectra were very similar to those found for N-nitroacetanilide in benzene. The (N-phenylpropionamido)phenylnitroxide signal was intense, while the triplet of triplets was weak. For mod. 0.23 gauss the triplet of triplets was just detectable, while the PAPN type signal, shown in Fig. 24, had hyperfine structure similar to that found for N-nitroacetanilide in benzene. However, the
intensities of the component lines and the linewidths were quite different. The following measurements were made for this signal in gauss: (1) $a_N = 11.64$, (2) $a_{o-H} = 2.74$, (2) $a_{o,p-H} = 2.61$, (1) $a_N = 1.67$ and (2) $a_{m-H} = 0.89$. Also $\Delta F = 0.32$ giving $g = 2.0053$ and $\delta g = 20 \times 10^{-5}$. The large linewidth of 0.35 gauss probably conceals a small coupling, either with acyl group protons or ones in the second phenyl ring.

(ii) **In Pyridine**

By maintaining the cavity temperature at $10^0$ and using a concentration of 400 mg./ml., the PAPN type signal was observed and the following measurements made in gauss:

(1) $a_N = 11.80$, (1) $a_{o-H} = 2.75$, (2) $a_{o,p-H} = 2.62$, (1) $a_N = 1.68$ and (2) $a_{m-H} = 0.90$. Also $\Delta F = 0.39$ giving $g = 2.0053$ and $\delta g = 24 \times 10^{-5}$.

(iii) **In Cumene**

For a 150 mg./ml. solution at room temperature two signals were observed. The 1:1:1 triplet with $a_N = 15$ gauss and the triplet of triplets: the latter signal was much stronger than that observed for N-nitrosoacetanilide in cumene, and was detectable for mod. as low as 0.041 gauss. However, the rapid evolution of nitrogen prevented spectra from being
Fig. 25  N-Nitroscisobutyranilide in benzene at 5° (15 min.)
recorded after 20 min.

n) N-Nitrosoisobutyranilide

(i) In Benzene

The increase in the rate of the decomposition, resulting from changing the acyl group from acetyl through propionyl to isobutyryl, made an e.s.r. study at room temperature impossible. Only by maintaining the cavity at 5°C could spectra be recorded. Using a concentration of 450 mg./ml. both the PAPN type signal and the triplet of triplets were observed during the first half hour of the reaction. The PAPN type signal, illustrated in Fig. 25, had hyperfine structure similar to that found for N-nitrosoacetanilide and N-nitrosopropionanilide, with only slight differences in the widths and intensities of the lines. Due to the instability of the signal the only measurements made were: (1) $a_N = 11.70$ gauss and $\Delta F = 0.33$ gauss. Hence $g = 2.0053$ and $\delta g = 20 \times 10^{-5}$.

After leaving the sample to decompose at room temperature for 12 hr. the PAPN spectrum was replaced by another signal, which is illustrated in Fig. 26, and which was identified as diphenylnitrooxide from its hyperfine coupling constants. These were measured in gauss as: (1) $a_N = 9.84$, (6) $a_o, p-H = 1.86$.
Fig. 26  DPN0 from N-nitrosoisobutyranilide in benzene at 25° (7 days)
Fig. 27  DPNO from N-Nitrosoisobutyranilide in benzene
with reconstructed spectrum
and \( (4) a_{m-H} = 0.80 \). Also \( \Delta F = -0.28 \) giving \( g = 2.0057 \) and 
\[ \delta g = -17 \times 10^{-5}. \] The values for the splitting constants fall 
below those found by other workers for DPNC in benzene.

Thomas\(^{77,122}\) found \( (1) a_N = 10.9 \) gauss, \( (6) a_{o,p-H} = 1.97 \) gauss 
and \( (4) a_{m-H} = 0.77 \) gauss, while Strom, Bluhm and Weinstein\(^{123}\) 
found \( (1) a_N = 9.70 \) gauss, but did not report \( a_H \) values. Fig. 27 
shows the low field group of hyperfine lines, with a 
reconstruction of the spectrum assuming the above analysis.

(ii) \textbf{In Pyridine}

The decomposition in pyridine was too fast to allow spectra 
to be recorded.

(iii) \textbf{In Cumene}

For a 160 mg./ml. solution at room temperature the 
triplet of triplets was detected for about 30 min. and had 
\( (1) a_N = 30.7 \) gauss, while the 1:1:1 triplet intensity increased 
over several days. The \( ^{13}C \) and \( ^{15}N \) satellite lines were 
observed as shown in Figs. 12 and 13, and two of the coupling 
constants were measured as 8.3 and 5.2 gauss. Variation of 
the temperature from \(-50^\circ \) to \(25^\circ \) produced no improvement in 
the resolution of the main or satellite lines.
Fig. 28  
N-Nitrosobenzanilide in pyridine at 0°C
N-Nitrosobenzanilide

(i) In Benzene and Cumene

The precipitation of solids during the decomposition prevented the recording of any spectra.

(ii) In Pyridine

No solids were formed during the decomposition of a 400 mg./ml. solution at 0°C. The spectrum observed at mod. 0.074 gauss is shown in Fig. 28, the basic pattern for this (N-phenylbenzamido)phenylnitrooxide signal differing slightly from the PAPN signal found for N-nitrosoacetanilide in benzene. Each group of lines was analysed and found to consist of 9 main components with relative intensities 1:1:4:3:6:3:4:1:1, each of these lines being further split 1:2:1. Fig. 29 shows the low field group of lines with a reconstruction of the spectrum assuming the following analysis: (1) \( a_N = 12.08 \) gauss, (2) \( a_m = 0.94 \) gauss, and (3) \( a_o, p-H \) (mean value) = 2.79 gauss. Also measured were: linewidth = 0.18 gauss and \( \Delta F = 0.46 \) gauss, giving \( g = 2.0052 \) and \( \delta g = 28 \times 10^{-5} \).

Close examination of the outside lines of the spectrum (Fig. 30a) revealed an additional doublet splitting of 0.38 gauss. The most likely assignment of this splitting is to a proton in the para-
Fig. 29  N-Nitrosobenzanilide in pyridine at $0^\circ$ with reconstructed spectrum
Fig. 30a

N-Nitrosobenzanilide
in pyridine

Fig. 30b

4-Chloro-N-nitrosobenzanilide
in pyridine

Fig. 30c

p-t-Butyl-N-nitrosobenzanilide
in pyridine

2 gauss
position of either the benzoyl group or the second phenyl ring in the formula below:

These alternatives were examined by studying the PAPN type signal resulting from the decomposition of \( N \)-nitroso-benzanilides with these positions substituted.

p) 4-Chloro-\( N \)-nitrosobenzanilide

In Pyridine

E. s. r. spectra observed during the decomposition of a 120 mg. /ml. solution were indistinguishable from those found for the unsubstituted nitrosamine. Fig. 30b shows the outside lines of this spectrum.

q) \( p \)-t-Butyl-\( N \)-nitrosobenzanilide

In Pyridine

Using a concentration of 160 mg. /ml. the PAPN type signal was weak and short-lived. The groups of lines were analysed and found to consist of 7 main lines with intensities 1:1:3:2:3:1:1, with each of these lines split 1:2:1. The following measurements
were made: \((1) a_N = 12.11\, \text{gauss, (2) } a_{m-H} = 0.94\, \text{gauss}\)

and \(\Delta F = 0.52\, \text{gauss}\). Hence \(g = 2.0052\) and \(\delta g = 32 \times 10^{-5}\).

The extra doublet splitting, found for both 4-chloro-\(N\)-nitrosobenzanilide and the unsubstituted nitrosamide, was not observed (Fig. 30c). It was thus provisionally assigned to the \(p\)-proton of the second aryl ring.

r) The Use of Degassed Solvents

The effect of dissolved oxygen in nitrosamide solutions has been studied by Simamura.\(^{124}\) He found an increase in the formation of tarry residues at the expense of arylation products on bubbling oxygen through the solution.

It has also been established that the presence of dissolved oxygen in solution can effect the resolution of e. s. r. spectra. For example, Deguchi\(^{125}\) found that for a solution of diphenyl-picrylhydrazyl open to the atmosphere the signal consisted of a quintet of broad lines with intensities 1:2:3:2:1, due to coupling with the two nitrogen nuclei. However, after removal of the dissolved oxygen, many additional hyperfine lines were observed, due to coupling with the aryl ring nuclei.

In order to examine the effect of dissolved gasses on the e. s. r. spectra observed during the decomposition of nitrosamides
the following procedure was employed. The solvent to be used was degassed by the standard vacuum line procedure of successive cycles of freezing, evacuation and melting. A small flask containing the nitrosamide, and fitted with an e.s.r. tube sidearm, was attached to the vacuum system and evacuated. The degassed solvent was then distilled into the reaction vessel and the resultant nitrosamide solution kept at liquid air temperature until required. The solution was then tipped into the sidearm, which was placed in the cavity of the spectrometer.

Using this technique solutions of N-nitrosoacetanilide in benzene and carbon tetrachloride were examined. For neither the PAPN nor the triplet of triplets signals was there an improvement in the intensity, linewidth or resolution: in view of this no attempt was made to exclude air from other nitrosamide solutions.

s) Summary of E. S. R. Signals Observed during the Decomposition of Acylarylnitrosamines in Solution

Signals corresponding to that first reported by Rüchardt, and assigned by Perkins to the (N-arylacetamido)arylnitroxide radical, were observed for all the nitrosamides studied.
Variation of the acyl group, or the p-substituent of the aryl ring, of the nitrosamide altered the hyperfine structure of the spectrum. It was also noted that the use of a number of solvents produced, not only small changes in the $a_N$ and $g$-values (Table 7), but also quite different signal intensities.

In addition a hitherto unreported signal consisting of a 1:1:1 triplet of 1:1:1 triplets was also detected during the decomposition in a number of solvents, particularly the aromatic hydrocarbons. This signal was characterised by a large $a_N$ value of about 30 gauss and a g-factor of 2.0015 - less than the free spin value of 2.0023. The splitting constants were insensitive to variations of the acyl and aryl groups of the nitrosamide.

A number of other signals were also observed.

For all the nitrosamides in cumene a 1:1:1 triplet, with $a_N = 15.00$ gauss and $g = 2.0059$ was detected.

When diethyl ether was used as solvent there was a signal for which $(1) a_N = 15.3$ gauss, $(1) a_H = 5.8$ gauss, $(1) a_N = 1.35$ gauss and $g = 2.0057$.

The decomposition of N-nitrosoisobutyranilide produced a signal attributed to diphenylnitroxide, in addition to the one
assigned to \( \text{N-phenylisobutyramido} \)phenylnitroxide.

The decomposition of \( \text{N-nitrosoformanilide} \) in cumene produced two previously undetected signals. The first was a 1:1:1 triplet of 1:1:1 triplets with \((1) \alpha_N = 18.1 \text{ gauss}, \)
\((1) \alpha_N = 1.4 \text{ gauss} \) and \( g = 2.0058. \) The second appeared after 1 day and had coupling constants of \((1) \alpha_N = 11.4 \text{ gauss}, \)
\((3) \alpha_H = 2.4 \text{ gauss} \) and \((2) \alpha_H = 0.9 \text{ gauss}, \) and \( g = 2.0057. \)

Each of these signals is discussed later in this thesis in terms of its variation with solvent and substituent group, and the information that they give in determining the mechanism of the reaction is assessed.

VII E.S.R. STUDY OF RELATED SYSTEMS

a) Decomposition of Phenylazotriphenylmethane

On warming a 100 mg./ml. solution of phenylazotriphenylmethane in benzene to 50° and allowing to cool, a very intense e.s.r. signal was detected. For mod. 0.013 gauss the linewidth was 0.053 gauss and the spectrum (Fig. 31) was well resolved. After study of the hyperfine structure, the signal was assigned
to the triphenylmethyl radical\(^{126}\) \(((3) a_{p-H} = 2.78 \text{ gauss,} \)
\((6) a_{o-H} = 2.55 \text{ gauss and } (6) a_{m-H} = 1.115 \text{ gauss}\) formed\(^8\) during the decomposition.

\[
\text{Ph. N:N. CPh}_3 \rightarrow \text{Ph}^\cdot + \text{N}_2 + \cdot \text{CPh}_3
\]

No other signal was detected.

b) **Reaction of Aniline and Pentyl Nitrite**

Aniline (800 mg.) and pentyl nitrite (800 mg.) were dissolved in benzene (1 ml.) and the solution maintained at 40\(^\circ\) in the cavity of the spectrometer.

Using mod. 2.3 gauss a weak 1:1:1 broad triplet was observed during the reaction, and lasted for about 3 hr. On decreasing the mod. to 0.23 gauss the triplet was partially resolved to give the signal shown in Fig. 32. The groups of lines were separated by about 12 gauss and the hyperfine structure of each group consisted of about 15 lines separated by about 1 gauss. The instability of the signal and the low signal to noise ratio prevented an accurate analysis of the spectrum.

c) **The Isolation and Study of Solids Precipitated during the Decomposition of AcylarylNitrosamines**

(i) **The Solid from N-Nitrosobenzanilide in Carbon Tetrachloride**

The solid formed during the decomposition of N-nitroso-
benzanilide (0.5 g.) in carbon tetrachloride (3 ml.) was collected and washed with petrol. The infrared spectrum (Nujol) showed absorption at 2300 cm.\(^{-1}\) (weak, \(-\mathbf{N}\equiv\mathbf{N}\)) and at 1700 cm.\(^{-1}\) (medium, \(\mathbf{C}=\mathbf{O}\)).

The solid was dissolved in pyridine and, after the subsidence of the initial evolution of gas, the solution was transferred to an e.s.r. tube. The signal, which was intense and well resolved for mod. 0.041 gauss, was indistinguishable from that shown in Fig. 26 for \(\mathbf{N}\)-nitrosoisobutyranilide in benzene, and was thus assigned to diphenyl nitroxide (DPNO).

The following measurements were made in gauss: (1) \(a_N = 9.88\), (2) \(a_o, p-H = 1.87\) and (4) \(a_m-H = 0.81\). Also linewidth = 0.16 and \(\Delta F = -0.19\), giving \(g = 2.0056\) and \(\delta g = -11 \times 10^{-5}\).

(ii) The Solid from \(\mathbf{N}\)-Nitrosobenzanilide in Mesitylene

The solid formed during the decomposition of \(\mathbf{N}\)-nitrosobenzanilide (0.5 g.) in mesitylene (3 ml.) was collected and washed with petrol. The infrared spectrum (Nujol) showed absorption at 2300 cm.\(^{-1}\) (medium, \(-\mathbf{N}\equiv\mathbf{N}\)) and at 1720 cm.\(^{-1}\) (intense, \(\mathbf{C}=\mathbf{O}\)).
The intense e. s. r. signal observed on dissolving the solid in pyridine was indistinguishable from that found for the solid from N-nitrosobenzanilide in carbon tetrachloride.

(iii) The Solid from N-Nitrosoacetanilide in Carbon Tetrachloride

The solid isolated from the decomposition of N-nitrosoacetanilide (0.5 g.) in carbon tetrachloride (2 ml.) was dissolved in pyridine. The e. s. r. signal observed consisted of a weak broad 1:1:1 triplet, which could be partially resolved to give structure similar to that found for the other solids.

(iv) The Solid from N-Nitrosoacetanilide in Cumene

It was reported earlier in this thesis that solids were precipitated during the decomposition of concentrated solutions of N-nitrosoacetanilide in all the aromatic hydrocarbon solvents used, with the exception of benzene. As this was most apparent when cumene was used, this solvent was selected for more detailed study.

N-nitrosoacetanilide (1.0 g.) was dissolved in cumene (4 ml.) and the solution allowed to decompose at room temperature. After 30 min. the solid deposited was collected and washed with petroleum in the water and oxygen free atmosphere of a dry box.
On filtering the reaction mixture in the presence of air one sample of the solid exploded.

The infrared spectrum (Nujol) showed absorption at 2300 cm.\(^{-1}\) (medium, \(\tilde{\text{N}}=\text{N}\)) and at 1710 cm.\(^{-1}\) (medium, C=O).

Dissolving the solid in acetone-\(d_6\) resulted in rapid evolution of gas. The n.m.r. spectrum showed absorption at \(\tau\ 2.0-3.0\) (complex) and at \(\tau\ 8.0\).

The e.s.r. signal observed on dissolving the solid in pyridine was the same as that found for the other solids and was thus assigned to DPNO.

No other signal was detected for any of these systems.

d) Decomposition of Benzenediazonium Acetate

The preparation of this unstable solid is described elsewhere in this thesis. Using a concentration of about 25 mg./ml. in benzene and mod. 1.27 gauss a weak broad 1:1:1 triplet was detected. On reducing the mod. to 0.41 gauss the hyperfine components of the broad peaks were resolved and showed the typical structure of the DPNO spectrum and the following measurements were made in gauss: \(1) a_N = 10.07\), \(6) a_o, p-H = 1.88\) and \(4) a_{m-H} = 0.84\). Also \(\Delta F = -0.12\), giving \(g = 2.0057\) and \(\delta g = -7 \times 10^{-5}\).
## THEORETICAL CALCULATIONS

### I McLACHLAN MOLECULAR ORBITAL CALCULATIONS

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<td>(iii) (N-Phenylacetamido)phenylNitroxide</td>
<td>120</td>
</tr>
</tbody>
</table>

### II CNDO SELF-CONSISTENT FIELD THEORY CALCULATIONS

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<td>--------</td>
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</tr>
<tr>
<td>(iii)</td>
<td>H_3C=O</td>
</tr>
<tr>
<td>(iv)</td>
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<td>(v)</td>
<td>C_6H_5^*</td>
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<td>(vi)</td>
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</tr>
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<td>(viii)</td>
<td>HN=NO^*</td>
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<tr>
<td>(ix)</td>
<td>PhNO^*</td>
</tr>
<tr>
<td>(x)</td>
<td>PhNO^+</td>
</tr>
<tr>
<td>(xi)</td>
<td>PhCH=NO^*</td>
</tr>
<tr>
<td>(xii)</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
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<th>Page</th>
</tr>
</thead>
<tbody>
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</tr>
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</table>
McLACHLAN MOLECULAR ORBITAL CALCULATIONS

a) Introduction

It is now well established that the hyperfine splitting from a ring proton in the e. s. r. spectrum of most aromatic free radicals in solution is related to the unpaired spin density in the $\pi$-orbital at the adjacent carbon atom by the McConnell equation

$$a_H = Q \rho_c$$

Among several methods developed to account for the spin distribution over the carbon atoms in a radical, two in particular have found widespread use.

The first is the simple Hückel molecular orbital method, which neglects the $\sigma$-orbitals as being localised and non-interacting, and regards the $\pi$-orbitals as a linear combination of the available $2p_z$ atomic orbitals. The resultant unpaired electron spin distribution gives a successful account of the spectra of many alternant hydrocarbon ions. However, because the molecular orbital wave function makes no allowance for the correlation of electrons the method is unable to account for the negative spin densities which n.m.r. studies have shown to occur in radicals such as the pyrene negative ion.
The second method is the Valence Bond theory, which, although allowing for negative spin densities, is also both laborious and inflexible.

The McLachlan\textsuperscript{57} theory combines the best of both these methods to provide a straightforward technique for predicting spin density distributions, the basis of which is outlined below.

In a radical the conventional single determinant wave function with one unpaired electron and 2n other electrons paired in n molecular orbitals is less useful than for a closed shell system, because the motions of the electrons of $\alpha$ and $\beta$ spins are affected in different ways by the odd electron. To allow for this effect and the resultant negative spin densities, two types of wave function can be used. One type uses the conventional determinant with a small admixture of excited configurations, while the other uses a single determinant with different orbitals for $\alpha$ and $\beta$ spins. McLachlan\textsuperscript{57} was able to show that the former leads to nearly the same $\pi$-electron spin distribution as the latter, if the small admixture of excited states is regarded as a perturbation of the Hückel molecular orbitals.

Thus the spin density in McLachlan's method is given by

$$\rho_T = C_{r0}^2 - \lambda \sum_s \prod_{rs} C_{s0}^2$$
where $C_{r}^{2}$ is the Hückel spin density on atom $r$, $\Pi_{rs}$ is the mutual polarisability of atoms $r$ and $s$, and $\lambda$ is a numerical constant which can be adjusted to give the best fit with experiment, but is often set at 1.2.

The perturbation can be regarded as a small additional attractive term acting, within the Hückel framework, on those electrons with spin parallel to the odd electron.

The calculation thus produces spin densities approximating to those from the more rigorous self-consistent field theory. Identical densities are predicted for positive and negative ions, and the approximation holds for neutral alternant radicals giving negative spin densities where the Hückel densities are zero or small. Although not contained in the original theory, the spin density distributions for radicals containing heteroatoms have been successfully calculated using the McLachlan method.

b) **Computer Programme**

The calculations were performed on an IBM 1620 computer, using a programme written by D. H. Levy in Fortran II, for an IBM 7090 and modified for the 1620 by Dr. C. Thomson. The programme calculates both Hückel and McLachlan spin densities from input data consisting of the constant $\lambda$ and the non-zero
elements of the initial secular determinant.

c) **Choice of Molecular Orbital Parameters**

It is usual to express the Coulomb \( (\alpha_i) \) and resonance \( (\beta_{ij}) \) integrals in terms of the values appropriate to benzene.\(^{130, 131}\)

\[
a_x = a_c + h_x \beta_{c-c'}
\]

\[
\beta_{xy} = k_{xy} \beta_{c-c'}
\]

where \( h_x \) and \( k_{xy} \) are the MO parameters in the Pauling approximation.

For the Ph-N-O* fragment of arylnitroxides the parameters required are \( h_N, h_O, k_{NO} \) and \( k_{CN} \). The normal ranges of these have been listed by Streitweiser\(^{131}\) as follows: \( h_N = 1.5, 1.0 < h_O < 2.0, 0.6 < k_{NO} < 0.8 \) and \( 0.7 < k_{CN} < 1.2 \). In addition the effect of steric hindrance preventing planarity in the radical can be taken into account by considering the resonance integral as a term \( \beta_0 \cos \Theta \), where \( \Theta \) is the angle of twist and \( \beta_0 \) is the resonance integral between the planar system and the substituent.

Two quite different sets of values have been used for McLachlan calculations on nitroxide radicals with equal success.

Deguchi et al.,\(^{132}\) and also Kikuchi and Someno\(^{133}\) used the following values for calculations performed on phenylnitroxide (PNO) and diphenylnitroxide (DPNO): \( \lambda = 1.0-1.2, h_N = 1.5, h_O = 1.2, \)
\[ k_{\text{NO}} = 0.7, k_{\text{CN}} = 0.8-1.0. \]

On the other hand Ayscough and Sargent\textsuperscript{134} found it necessary to employ a value of \( k_{\text{NO}} \) outside the limits mentioned by Streitweiser. The parameters they used are as follows:

\[ \lambda = 1.2, \ h_N = 1.5, \ h_O = 1.0-1.8, \ k_{\text{NO}} = 1.6, \ k_{\text{CN}} = 1.05-1.2. \]

In view of this disagreement in the choice of \( k_{\text{NO}} \), it was decided to carry out calculations on both phenylnitroxide (PNO) and diphenylnitroxide (DPNO) in an attempt to find a common set of parameter values for the \( \text{Ph-N-O}^\cdot \) fragment, which could then be used for the (N-phenylacetamido)phenylnitroxide (PAPN) radical.

**Phenylnitroxide**

Below are listed the hyperfine coupling constants for PNO found by Kikuchi and Someno,\textsuperscript{133} together with the experimental spin densities for the protons assuming a \( Q_{\text{CH}}^H \) value of 23.7 gauss.

\[
\begin{align*}
  a_N &= 8.81 \text{ gauss} \\
  a_{N-H} &= 11.71 \text{ gauss} \\
  a_{o-H} &= a_{p-H} = 2.92 \text{ gauss} \quad \sigma (\text{exp.}) = 0.123 \\
  a_{m-H} &= 1.01 \text{ gauss} \quad \sigma (\text{exp.}) = 0.043
\end{align*}
\]
Table 8 shows the calculated spin density distribution in the PNO radical for values of $k_{NO}$ ranging from 0.6 to 2.0, with the remaining parameters fixed at the following values:

$\lambda = 1.2$, $h_N = 1.5$, $h_O = 1.0$, $k_{CN} = 1.2$.

From this table and from Fig. 33, which shows the change in the ratio $o(\text{para})/o(\text{ortho})$ with variation of $k_{NO}$, it is clear that the experimentally observed equivalence of the ortho and para positions is predicted for $k_{NO}$ values of about 0.5 and 1.6.
Fig. 33

\[ \rho_{\text{para}} / \rho_{\text{ortho}} \] versus \( k_{\text{NO}} \) for PNO
MCLACHLAN SPIN DENSITIES FOR PHENYLNITROXIDE

VARIATION WITH $k_{NO}$

<table>
<thead>
<tr>
<th>$k_{NO}$</th>
<th>1, 5</th>
<th>2, 4</th>
<th>3</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-1.611</td>
<td>-0.0633</td>
<td>1.550</td>
<td>0.0111</td>
<td>0.3427</td>
<td>0.3178</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.423</td>
<td>-0.0646</td>
<td>1.144</td>
<td>0.0484</td>
<td>0.3534</td>
<td>0.4252</td>
</tr>
<tr>
<td>0.8</td>
<td>-1.136</td>
<td>-0.0642</td>
<td>0.610</td>
<td>-0.0971</td>
<td>0.3648</td>
<td>0.5723</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.967</td>
<td>-0.0611</td>
<td>0.406</td>
<td>-0.1131</td>
<td>0.3584</td>
<td>0.6427</td>
</tr>
<tr>
<td>1.1</td>
<td>-0.926</td>
<td>-0.0590</td>
<td>0.407</td>
<td>-0.1110</td>
<td>0.3483</td>
<td>0.6547</td>
</tr>
<tr>
<td>1.2</td>
<td>-0.912</td>
<td>-0.0567</td>
<td>0.462</td>
<td>-0.1036</td>
<td>0.3343</td>
<td>0.6541</td>
</tr>
<tr>
<td>1.4</td>
<td>-0.956</td>
<td>-0.0527</td>
<td>0.699</td>
<td>-0.0774</td>
<td>0.2976</td>
<td>0.6240</td>
</tr>
<tr>
<td>1.6</td>
<td>-1.065</td>
<td>-0.0498</td>
<td>1.034</td>
<td>-0.0424</td>
<td>0.2557</td>
<td>0.5699</td>
</tr>
<tr>
<td>1.7</td>
<td>-1.130</td>
<td>-0.0488</td>
<td>1.219</td>
<td>-0.0230</td>
<td>0.2345</td>
<td>0.5383</td>
</tr>
<tr>
<td>1.8</td>
<td>-1.194</td>
<td>-0.0480</td>
<td>1.409</td>
<td>-0.0026</td>
<td>0.2135</td>
<td>0.5053</td>
</tr>
</tbody>
</table>
Diphenylnitroxide

The hyperfine coupling constants found by Baird and Thomas are listed below, with the experimental spin densities assuming $Q_{CH}^H = 23.7$ gauss.

- $a_N = 10.9$ gauss
- $a_{o-H} = a_{p-H} = 1.97$ gauss, $\rho_{(exp.)} = 0.083$
- $a_{m-H} = 0.77$ gauss, $\rho_{(exp.)} = 0.033$

Table 9 shows the calculated spin densities for the DPNO radical for values of $k_{NO}$ ranging from 0.5 to 1.8, with the other parameters fixed at the following values: $\lambda = 1.2$, $h_N = 1.5$, $h_O = 1.0$, $k_{CN} = 1.05$.

The change in the ratio of $\rho_{(para)}/\rho_{(ortho)}$ with variation of $k_{NO}$ is plotted in Fig. 34. As for PNO the experimentally observed equivalence of the ortho and para-positions is predicted for $k_{NO}$ values of 0.5 and 1.6.
Fig. 3A

$\frac{\rho_{(\text{para})}}{\rho_{(\text{ortho})}}$ versus $k_{NO}$ for DPNO
### TABLE 9
McLachlan Spin Densities for Diphenylnitroxide

Variation with $k_{NO}$

![Structure of Diphenylnitroxide](image)

<table>
<thead>
<tr>
<th>$k_{NO}$</th>
<th>1, 5, 9, 13</th>
<th>2, 4, 10, 12</th>
<th>3, 11</th>
<th>6, 8</th>
<th>7</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.1109</td>
<td>-0.0410</td>
<td>0.1119</td>
<td>-0.0184</td>
<td>0.3177</td>
<td>0.2157</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1033</td>
<td>-0.0407</td>
<td>0.0973</td>
<td>-0.0312</td>
<td>0.3192</td>
<td>0.2983</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0897</td>
<td>-0.0396</td>
<td>0.0741</td>
<td>-0.0503</td>
<td>0.3178</td>
<td>0.4340</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0798</td>
<td>-0.0378</td>
<td>0.0609</td>
<td>-0.0585</td>
<td>0.3074</td>
<td>0.5199</td>
</tr>
<tr>
<td>1.1</td>
<td>0.0764</td>
<td>-0.0368</td>
<td>0.0580</td>
<td>-0.0587</td>
<td>0.2984</td>
<td>0.5446</td>
</tr>
<tr>
<td>1.2</td>
<td>0.0740</td>
<td>-0.0358</td>
<td>0.0574</td>
<td>-0.0565</td>
<td>0.2869</td>
<td>0.5586</td>
</tr>
<tr>
<td>1.4</td>
<td>0.0719</td>
<td>-0.0330</td>
<td>0.0615</td>
<td>-0.0464</td>
<td>0.2581</td>
<td>0.5590</td>
</tr>
<tr>
<td>1.6</td>
<td>0.0728</td>
<td>-0.0321</td>
<td>0.0711</td>
<td>-0.0308</td>
<td>0.2242</td>
<td>0.5329</td>
</tr>
<tr>
<td>1.8</td>
<td>0.0750</td>
<td>-0.0305</td>
<td>0.0840</td>
<td>-0.0117</td>
<td>0.1889</td>
<td>0.4886</td>
</tr>
</tbody>
</table>
As a result of this examination it was decided to select two sets of parameters, which, giving satisfactory agreement between the calculated and experimental spin densities for both PNO and DPNO, could then be used for other nitroxides. After systematic variation of the parameters the following common sets were chosen.

**Set A.** \( \lambda = 1.1, \ h_N = 1.5, \ h_O = 1.6, \ k_{NO} = 0.7; \) the value of \( k_{CN} \) could be chosen between 0.6 and 0.9 depending on the degree of twist between the aryl ring and the N-O group.

**Set B.** \( \lambda = 1.2, \ h_N = 1.5, \ h_O = 0.95, \ k_{NO} = 1.6; \) \( k_{NO} = 1.0-1.35 \) depending on the angle of twist.

d) **Calculated Spin Density Distributions for Nitrooxide Radicals**

(i) **PhenylNitroxide**

The distribution of spin density in the PNO radical was calculated using the parameters of sets A and B, the \( k_{CN} \) value being varied to give the best fit with experiment. The results are listed and compared with the experimental values in Table 10.

(ii) **DiphenylNitroxide**

The calculated spin density distribution for DPNO, using both set A and set B and after optimisation of \( k_{CN} \), are listed in Table 11, and compared with the experimental values.
TABLE 10

McLachlan Spin Densities for Phenylnitroxide

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho$ (calc.)</th>
<th>$\rho$ (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set A</td>
<td>Set B</td>
</tr>
<tr>
<td>1, 5</td>
<td>.1241</td>
<td>.1229</td>
</tr>
<tr>
<td>2, 4</td>
<td>-.0484</td>
<td>-.0543</td>
</tr>
<tr>
<td>3</td>
<td>.1227</td>
<td>.1241</td>
</tr>
<tr>
<td>6</td>
<td>.0074</td>
<td>-.0362</td>
</tr>
<tr>
<td>7</td>
<td>.4968</td>
<td>.2223</td>
</tr>
<tr>
<td>8</td>
<td>.2216</td>
<td>.5527</td>
</tr>
</tbody>
</table>

a) For key to position numbers, see Table 8 on p. 114.
b) With $k_{CN} = 0.82$.
c) With $k_{CN} = 1.33$.
d) The sign of $\rho$ (exp.) is not determined from the spectrum.
<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_{\text{calc.}}$</th>
<th>$\rho_{\text{exp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>Set B</td>
<td></td>
</tr>
<tr>
<td>1, 5, 9, 13</td>
<td>0.0824</td>
<td>0.0823</td>
</tr>
<tr>
<td>2, 4, 10, 12</td>
<td>-0.0311</td>
<td>-0.0350</td>
</tr>
<tr>
<td>3, 11</td>
<td>0.0845</td>
<td>0.0829</td>
</tr>
<tr>
<td>6, 8</td>
<td>-0.0066</td>
<td>-0.0291</td>
</tr>
<tr>
<td>7</td>
<td>0.4589</td>
<td>0.1909</td>
</tr>
<tr>
<td>14</td>
<td>0.1801</td>
<td>0.5103</td>
</tr>
</tbody>
</table>

a) For the position numbers, see Table 9 on p. 116.

b) With $k_{\text{CN}} = 0.73$.

c) With $k_{\text{CN}} = 1.18$. 
(iii) (N-Phenylacetamido)phenylnitroxide

The hyperfine coupling constants determined for this radical (R=Me) are listed below. There was no resolvable coupling with the protons attached to positions 10-14 on the second phenyl ring, nor with the methyl protons of the acyl group: thus these splitting constants were assumed to be less than 0.1 gauss. The experimental spin densities are also tabulated, their values being computed from the $a_H$ values assuming $\Omega_{CH}^H = 23.7$ gauss and $\Omega_{CCH_3}^H = 28.0$ gauss.

- $a_N(7) = 11.62$ gauss
- $a_N(8) = 1.67$ gauss
- $a_H(5) = 2.73$ gauss
- $a_H(1) = a_H(3) = 2.60$ gauss
- $a_H(2) = a_H(4) = 0.89$ gauss
- $a_H(10-14) < 0.1$ gauss
- $a_H(\text{Me, 16}) < 0.1$ gauss

$\rho (\text{exp.}) = 0.115$

$\rho (\text{exp.}) = 0.110$

$\rho (\text{exp.}) = 0.038$

$\rho (\text{exp.}) < 0.005$

$\rho (\text{exp.}) < 0.004$
Preliminary calculations of the theoretical spin density distribution were performed using the parameters of sets A and B as a basis, and estimating the remainder from the geometry of the system with the aid of molecular models.

**Set A.** \[ \lambda = 1.1, \quad k_{N(7)} = 1.5, \quad h_{O(15)} = 1.6, \quad k_{NO(7-15)} = 0.7. \]

In addition the Streitweiser\(^{131}\) values of \[ h_{N(8)} = 1.5, \quad h_{O(17)} = 1.0 \]

and \[ k_{C=O(16-17)} = 1.0 \] were used. With the molecular models the twists of the CN(6-7), NN(7-8) and NC(8-9) bonds were judged to be similar to those found for the CN bonds in DPNO, while the acyl group was clearly well out of the radical plane. On this assumption the following were chosen:

\[ k_{CN(6-7)} = k_{NN(7-8)} = k_{NC(8-9)} = 0.7 \text{ and } k_{NC(8-16)} = 0.5. \]

**Set B.** \[ \lambda = 1.2, \quad h_{N(7)} = 1.5, \quad h_{O(15)} = 0.95, \quad k_{NO(7-15)} = 1.6. \]

The remaining values were chosen in a similar manner to those of set A, but allowing for the slightly greater steric strain in the NN(7-8) and NC(8-9) than in the CN(6-7) bonds. Thus

\[ h_{N(8)} = 1.5, \quad h_{O(17)} = 1.0, \quad k_{C=O(16-17)} = 1.0, \quad k_{CN(6-7)} = 1.1, \quad k_{NN(7-8)} = k_{NC(8-9)} = 1.0 \text{ and } k_{NC(8-16)} = 0.7. \]

The results of this preliminary investigation, listed in Table 12, show that the essential assumptions of the assignment of the e. s. r. spectrum to the PAPN radical are justified. Even for
these arbitrarily chosen parameters the predicted proton hyperfine coupling constants are in the correct order of magnitude, there being low spin density at positions where no splitting is resolved. Also, for both sets A and B the $\rho(7)$ value is greater than that for $\rho(3)$ as required, but it was noted that while set A predicts $\rho(8) > 0$, set B gives $\rho(8) < 0$. 
<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_{\text{calc.}}$</th>
<th>$\rho_{\text{exp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set A</td>
<td>Set B</td>
</tr>
<tr>
<td>1, 5</td>
<td>0.0833</td>
<td>0.1084</td>
</tr>
<tr>
<td>2, 4</td>
<td>-0.0279</td>
<td>-0.0391</td>
</tr>
<tr>
<td>3</td>
<td>0.0809</td>
<td>0.1251</td>
</tr>
<tr>
<td>6</td>
<td>-0.0179</td>
<td>-0.0057</td>
</tr>
<tr>
<td>7</td>
<td>0.5599</td>
<td>0.2428</td>
</tr>
<tr>
<td>8</td>
<td>0.1886</td>
<td>-0.0377</td>
</tr>
<tr>
<td>9</td>
<td>-0.0646</td>
<td>0.0005</td>
</tr>
<tr>
<td>10, 14</td>
<td>0.0033</td>
<td>-0.0058</td>
</tr>
<tr>
<td>11, 13</td>
<td>-0.0224</td>
<td>-0.0026</td>
</tr>
<tr>
<td>12</td>
<td>-0.0309</td>
<td>-0.0043</td>
</tr>
<tr>
<td>15</td>
<td>0.1849</td>
<td>0.4695</td>
</tr>
<tr>
<td>16</td>
<td>0.0004</td>
<td>0.0759</td>
</tr>
<tr>
<td>17</td>
<td>0.0261</td>
<td>0.0123</td>
</tr>
</tbody>
</table>

a) For key to position numbers, see p. 120.

b) For parameter values, see text p. 121.
These preliminary results showed that the distribution of unpaired electron spin density could be predicted by this type of calculation. Those values of $h_x$ and $k_{xy}$ which had been estimated from the molecular models were systematically varied and the following amended sets of parameters were produced.

**Set A.** - $\lambda = 1.1$, $h_N(7) = h_N(8) = 1.5$, $h_O(15) = 1.6$, $h_O(17) = 1.0$, $k_{NO(7-15)} = 0.7$, $k_{CN(6-7)} = 0.88$, $k_{NN(7-8)} = 0.8$, $k_{NC(8-9)} = 0.7$, $k_{NC(8-16)} = 0.6$ and $k_{C=O(16-17)} = 1.0$.

**Set B.** - $\lambda = 1.2$, $h_N(7) = h_N(8) = 1.5$, $h_O(15) = 0.95$, $h_O(17) = 1.0$, $k_{NO(7-15)} = 1.6$, $k_{CN(6-7)} = 1.1$, $k_{NN(7-8)} = 0.7$, $k_{NC(8-9)} = 0.8$, $k_{NC(8-16)} = 0.5$ and $k_{C=O(16-17)} = 1.0$.

The results using these values, listed in Table 13, show better agreement than the first preliminary guess, in that both sets predict, not only lower spin densities on positions 10-14 and 16, but also the correct magnitude and ratios for the o,m, and p-protons of the main phenyl ring.

<table>
<thead>
<tr>
<th></th>
<th>Set A</th>
<th>Set B</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$(para)/$\rho$(ortho)</td>
<td>1.02</td>
<td>1.11</td>
<td>0.98</td>
</tr>
<tr>
<td>$\rho$(meta)/$\rho$(ortho,para mean value)</td>
<td>0.32</td>
<td>0.38</td>
<td>0.34</td>
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</table>
These ratios were improved still further by a systematic variation of all the parameters, from which it was found that a $k_{\text{NO}}$ value of 1.2, while unsuitable for PNO and DPNO, was most satisfactory for PAPN. A further sophistication was provided by the inclusion of an additional Coulomb parameter of approximately -0.05 to position No. 1. In this way the spin density on the aryl ring was redistributed, reproducing the non-equivalence of the $\alpha$-protons, in a similar manner to that found by Fraenkel\textsuperscript{135} for the acetophenone anion.

As a result of these refinements, the following set C was chosen, and the results shown in Table 13 obtained.

Set C. - $\lambda = 1.0$, $h_{\text{N}(7)} = h_{\text{N}(8)} = 1.5$, $h_{\text{O}(15)} = h_{\text{O}(17)} = 1.0$, $h_{\text{C}(1)} = -0.063$, $k_{\text{NC}(7-15)} = 1.2$, $k_{\text{CN}(6-7)} = 1.11$, $k_{\text{NN}(7-8)} = 1.02$, $k_{\text{NC}(8-9)} = 0.6$, $k_{\text{NC}(8-16)} = 0.45$ and $k_{\text{C}=\text{O}(16-17)} = 1.5$.

The results of these calculations are analysed in more detail in the Discussion later in this thesis.
TABLE 13

McLachlan Spin Densities for (N-Phenylacetamido)phenylnitroxide

Using optimised Parameters

<table>
<thead>
<tr>
<th>Position a)</th>
<th>( \rho(\text{calc.}) )</th>
<th>( \rho(\text{exp.}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set A b)</td>
<td>Set B b)</td>
</tr>
<tr>
<td>1</td>
<td>.1145</td>
<td>.1072</td>
</tr>
<tr>
<td>2</td>
<td>-.0367</td>
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</tr>
<tr>
<td>3</td>
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<td>.1194</td>
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<tr>
<td>4</td>
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<td>-.0418</td>
</tr>
<tr>
<td>5</td>
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<td>.1072</td>
</tr>
<tr>
<td>6</td>
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<td>-.0148</td>
</tr>
<tr>
<td>7</td>
<td>.5030</td>
<td>.2555</td>
</tr>
<tr>
<td>8</td>
<td>.1580</td>
<td>-.0330</td>
</tr>
<tr>
<td>9</td>
<td>.0448</td>
<td>-.0016</td>
</tr>
<tr>
<td>10, 14</td>
<td>.0055</td>
<td>-.0046</td>
</tr>
<tr>
<td>11, 13</td>
<td>-.0161</td>
<td>-.0017</td>
</tr>
<tr>
<td>12</td>
<td>-.0155</td>
<td>-.0045</td>
</tr>
<tr>
<td>15</td>
<td>.1396</td>
<td>.5284</td>
</tr>
<tr>
<td>16</td>
<td>.0055</td>
<td>.0292</td>
</tr>
<tr>
<td>17</td>
<td>.0331</td>
<td>.0033</td>
</tr>
</tbody>
</table>

a) For key to position numbers, see p. 120.

b) For parameter values, see text pp. 124 and 125.
II  CNDO SELF-CONSISTENT FIELD THEORY CALCULATIONS

a) Introduction

One of the basic assumptions of the simple Hückel and McLachlan\textsuperscript{57} theories is the neglect of the electrons in the $\sigma$-framework. Although these $\pi$-electron calculations give satisfactory estimates of the spin density distribution for many $\pi$-radicals, they cannot be used for $\sigma$-radicals such as phenyl (18), vinyl (19) and iminoxy radicals (20).

Recent advances in computer technology have allowed more sophisticated calculations to be performed. The resultant extension of molecular orbital theory to include all valence electrons, but neglecting the inner shells, has taken two forms.

The first of these is the extended Hückel theory (EHT), developed by Mulliken\textsuperscript{136} and by Hoffmann,\textsuperscript{137} based on an independent electron model neglecting electron-electron Coulomb
These calculations give a reasonable account of \( \sigma \)-radicals and have been used by Drago et al.\textsuperscript{138} to calculate spin densities for iminoxy radicals with notable success.

The second method is the approximate self-consistent field (SCF) theory developed by Pople,\textsuperscript{139-142} which, as it depends on the inclusion of some inter-electron repulsion terms can be regarded as one step more sophisticated than the independent electron model.

The SCF procedure starts with a set of molecular orbitals, which are expanded in terms of the valence shell atomic orbitals, and to which the electrons are assigned in the usual Aufbau manner. Energy minimisation with respect to electronic repulsion for the single configuration antisymmetric wave function leads to a new set of orbitals. The electrons are assigned to these and the process repeated until self-consistency is reached.

For closed-shell species the standard SCF theory gives doubly occupied orbitals. However, for radicals the different exchange interactions of the \( \alpha \) and \( \beta \) spins is best treated using the Unrestricted Hartree-Fock (UHF) theory, which results in different singly occupied orbitals for the \( \alpha \) and \( \beta \) spins.

The major approximations in Pople's method involves the
extent to which the less important electron repulsion integrals are neglected. One-electron integrals are evaluated with reference to experimental data, while electron repulsion integrals are neglected for all overlap charge distributions, leaving only a limited number of Coulomb repulsion terms to be calculated. Thus for complete neglect of differential overlap (CNDO) the terms of the form $\phi_\mu (1) \phi_\nu (1)$ of different atomic orbitals $\phi_\mu$ and $\phi_\nu$ are neglected in all electron interaction integrals.

The CNDO approximation has been used by Atherton and Hinchliffe in their unrestricted Hartree-Fock calculations on a number of $\sigma$-radicals, though they did not include any nitrogen containing species.

CNDO calculations are unsuitable for the direct calculation of the coupling constants of $\pi$-radicals, as inherent in the approximation is neglect of the very one-centre atomic exchange integrals on which the spin density at the nuclei of the system depends.

It was the purpose of this examination to establish whether the CNDO method of Pople is capable of predicting whether a radical will be $\sigma$ or $\pi$, and whether it can be used for
estimating the spin densities, and hence hyperfine coupling constants of \( \sigma \)-radicals.

b) **Computer Programme**

The calculations were performed on an IBM 360/44 computer, using a programme, written by Segal\(^{139}\) in Fortran IV for an IBM 7090, obtained through the Quantum Chemistry Program Exchange, and modified for the 360 series by Dr. C. Thomson. The input data for the calculation consists of the geometry of the radical, specified as the atomic numbers and cartesian coordinates of the atoms, and the multiplicity of the state. The output includes the interatomic distances and matrices describing overlap, SCF eigenvalues and eigenvectors, and bond order, there being separate listings for the \( \alpha \) and \( \beta \) electrons for an open-shell system.

The spin density for a given orbital can be calculated from the bond order matrices for the \( \alpha \) and \( \beta \) electrons by use of the expression

\[
\rho = P(\alpha) - P(\beta)
\]

where \( P(\alpha) \) and \( P(\beta) \) are the diagonal elements of these matrices, representing the probability density of the electron in that atomic orbital.
Also included in the output is the electronic energy after each self-consistent field iteration, and the total energy.

c) Variation of Radical Geometry to Find the Minimum Energy

There follow details of calculations performed on a number of radicals, for each of which the geometry was varied to give a minimum total energy.

The general procedure was to start with an estimate of the bond angles and lengths based, either on X-ray studies of related molecules, or on the values listed by Pople. These were then varied systematically to find the arrangement corresponding to minimum total energy. From this optimised geometry the spin densities for each orbital were calculated, and are listed in Tables 14-22. All bond lengths are quoted in Angstroms, and, unless otherwise stated, the radical is assumed to be planar.

(i) $\ce{H_2NO^-}$

As a first approximation the bond lengths and angles suggested by Pople were used: $\ce{N-O} = 1.36$, $\ce{N-H} = 1.01$ and $\ce{ONH} (\text{sp}^2) = 120^\circ$.

The N-O bond length and the angle ONH were the varied to find the minimum energy and the following optimised geometry
obtained: N-O = 1.24, N-H = 1.01 and ONH = 120°.

The spin densities are listed in Table 14 (p. 137).

(ii) \( \text{H}_2\text{C}=\text{N} \)

First approximation: C-N = 1.05, C-H = 1.08 and NCH (sp\(^2\)) = 120°.

Optimised geometry: C-N = 1.26, C-H = 1.11 and NCH = 122°.

Spin density distribution: Table 14 (p. 137).

(iii) \( \text{HC}=\text{O} \)

First approximation: C-O = 1.22, C-H = 1.08 and OCH (sp\(^2\)) = 120°.

Optimised geometry: C-O = 1.22, C-H = 1.11 and OCH = 130°.

Spin density distribution: Table 14 (p. 137).

(iv) \( \text{H}_2\text{C}=\text{CH} \)

First approximation: C-C = 1.34, C-H = 1.08, CCH (sp\(^2\)) = \( \alpha = 120° \) and HCC (sp\(^2\)) = \( \beta = 120° \). The ratios of the calculated spin densities were found to be very sensitive to the variation of the angle \( \alpha \), while the total energy was not. Therefore the geometry selected was that which best fitted the ratios of the observed hyperfine coupling constants: C-C = 1.29, C-H = 1.08, \( \alpha = 145° \) and \( \beta = 120° \).

Spin density distribution: Table 14 (p. 137).
(v) $\text{C}_6\text{H}_5^-$

The following values for bond lengths and angles were used without variation: $\text{C}-\text{C} = 1.40$, $\text{C}-\text{H} = 1.08$ and $\text{CCC} = \text{CCH} = 120^\circ$.
The spin density distribution is listed in Table 15 (p. 138).

(vi) $\text{H}_2\text{NC}=\text{O}$

First approximation: $\text{C}-\text{O} = 1.22$, $\text{C}-\text{N} = 1.40$, $\text{N}-\text{H} = 1.01$, $\text{OCN} = 130^\circ$ (by comparison with $\text{OCH}$ of formyl) and $\text{HNC} (\text{sp}^2) = 120^\circ$.

Optimised geometry: $\text{C}-\text{O} = 1.25$, $\text{C}-\text{N} = 1.34$, $\text{N}-\text{H} = 1.01$, $\text{OCN} = 134^\circ$ and $\text{HNC} = 122^\circ$.

Spin density distribution: Table 15 (p. 138).

(vii) $\text{H}_2\text{C}=\text{NO}^-$

First approximation: $\text{N}-\text{O} = 1.41$, $\text{C}-\text{N} = 1.32$, $\text{C}-\text{H} = 1.08$, $\text{CNN} (\text{sp}^2) = \alpha = 120^\circ$ and $\text{HCN} (\text{sp}^2) = \beta = 120^\circ$.

Optimised geometry: $\text{N}-\text{O} = 1.25$, $\text{C}-\text{N} = 1.30$, $\text{C}-\text{H} = 1.08$, $\alpha = \beta = 120^\circ$.

Spin density distribution: Table 16 (p. 139).

(viii) $\text{HN}=\text{NO}^-$

First approximation: $\text{N}-\text{O} = 1.41$, $\text{N}-\text{N} = 1.25$, $\text{N}-\text{H} = 0.99$, $\text{NNO} (\text{sp}^2) = \alpha = 120^\circ$ and $\text{HNN} (\text{sp}^2) = \beta = 120^\circ$. 
Optimised geometry: There were two configurations of similar energy corresponding to the trans and cis-isomers.

**Trans:** N-O = 1.24, N-N = 1.25, N-H = 0.99, \( \alpha = 110^\circ \) and \( \beta = 115^\circ \).  

**Cis:** N-O = 1.22, N-N = 1.25, N-H = 0.99, \( \alpha = 240^\circ \) and \( \beta = 120^\circ \). The spin densities for both isomers are given in Table 16 (p. 139).

(ix) PhNO

For the first approximation the bond lengths and angles reported by Webster\(^ {144} \) were used for the nitroso group, while the phenyl ring values were as for \( \text{C}_6\text{H}_5 \): N-O = 1.24, C-N = 1.28, C\( \hat{C} \)C = 120° and C\( \hat{C} \)NO = \( \alpha = 125^\circ \). The bond lengths were kept constant, but the angle \( \alpha \) and the twist between the NO group and the phenyl ring were varied, and the following values found for minimum energy: \( \alpha = 125^\circ \) and twist = 5°. The spin density distribution is listed in Table 17 (p. 140).

(x) PhNO\(^ + \)

The initial approximation used the same geometry as for PhNO\(^ - \). The bond lengths and angles of the nitroso group and the angle of twist were varied, and the following values found for minimum energy: N-O = 1.20, C-N = 1.33, \( \alpha = 125^\circ \) and twist = 5°. The spin density distribution is shown in Table 18 (p. 141).
(xi) \( \text{PhCH}=\text{NO}^- \)

First approximation: the bond lengths and angles found for the \( \text{H}_2\text{C}=\text{NO}^- \) radical were used, together with the standard values for the phenyl ring: \( \text{N}-\text{O} = 1.25 \), \( \text{C}-\text{N} = 1.30 \), \( \text{C}-\text{H} = 1.08 \), \( \text{C}-\text{C} = 1.46 \), \( \text{CNNO} = \alpha = 120^\circ \) and \( \text{CCN} = \beta = 120^\circ \).

Optimised geometry: there were two configurations of similar energy, corresponding to the \text{syn} and \text{anti}-isomers. Also the angle of twist between the phenyl ring and the iminoxy group was varied between 0° and 90°, the planar arrangement being the most stable for both isomers. 

- **Syn**: \( \text{N}-\text{O} = 1.25 \), \( \text{C}-\text{N} = 1.30 \), \( \text{C}-\text{C} = 1.46 \), \( \alpha = 120^\circ \), \( \beta = 120^\circ \) and twist \( = 0^\circ \).
- **Anti**: \( \text{N}-\text{O} = 1.25 \), \( \text{C}-\text{N} = 1.30 \), \( \text{C}-\text{C} = 1.46 \), \( \alpha = 240^\circ \), \( \beta = 125^\circ \) and twist \( = 0^\circ \). The spin densities are listed in Tables 19 and 20 (pp.142 and 143).

For this species and the phenyldiazotate radical which follows, the progress of the iterative phase of the calculation to self-consistency was found to be erratic, and in some cases no electronic energy minimum could be attained. This phenomenon has been found for other radicals and has been attributed to the mathematical failure of the matrix diagonalisation routine of the programme to cope with some open-shell systems.
In view of this an accurate optimisation of the geometries of both these types of radicals was not possible.

(xli) PhN=NO·

First approximation: the bond lengths and angles used were based on those found for HN:NO; but with the sp² hybrid angle of 120° and the standard values for the phenyl ring:

N-O = 1.24, N-N = 1.25, C-N = 1.40, NNO = α = 120° and CNN = β = 120°.

Optimised geometry: the two configurations, corresponding to the trans and cis-isomers, had similar total energy.

Trans: N-O = 1.24, N-N = 1.25, C-N = 1.38, α = β = 120° and twist = 0°. Cis: N-O = 1.24, N-N = 1.25, C-N = 1.38, α = 240°, β = 120° and twist = 0°. The spin densities for both isomers are given in Tables 21 and 22 (pp.144 and 145).
TABLE 14

CNDO Spin Densities

<table>
<thead>
<tr>
<th>Radical</th>
<th>Orbital</th>
<th>1s</th>
<th>2s</th>
<th>2p_x</th>
<th>2p_y</th>
<th>2p_z</th>
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</thead>
<tbody>
<tr>
<td>H₂NO⁻</td>
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<td>0</td>
<td>0</td>
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<td>-</td>
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<td>0</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂C=NO⁺</td>
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<td>-</td>
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<td>-.0023</td>
<td>.8422</td>
<td>0</td>
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<tr>
<td></td>
<td>C</td>
<td>-</td>
<td>-.0210</td>
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<tr>
<td></td>
<td>H</td>
<td>.1385</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>.0724</td>
<td>.2959</td>
<td>.4138</td>
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<td>-.0348</td>
<td>-.0227</td>
<td>0</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>H(5)</td>
<td>.0375</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Radical</td>
<td>Orbital</td>
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<td>2s</td>
<td>2p_x</td>
<td>2p_y</td>
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<td>C_6H_5</td>
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<tr>
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<td>-.0026</td>
<td>-.0007</td>
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<tr>
<td></td>
<td>H(7)</td>
<td>.0380</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(8)</td>
<td>.0127</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(9)</td>
<td>.0064</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>H_2NC=O</td>
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<td>.1001</td>
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<td>.2927</td>
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<td>-</td>
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<td>H(5)</td>
<td>.0048</td>
<td>-</td>
<td>-</td>
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</table>
### TABLE 16

**CNDO Spin Densities**

<table>
<thead>
<tr>
<th>Radical</th>
<th>1s</th>
<th>2s</th>
<th>2pₓ</th>
<th>2pᵧ</th>
<th>2pₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2C=NO^+ )</td>
<td>O</td>
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<td>.0033</td>
<td>.8491</td>
</tr>
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<td></td>
<td>N</td>
<td>-</td>
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<td>.0097</td>
<td>.0716</td>
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<tr>
<td></td>
<td>C</td>
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<td></td>
<td>H(4)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>H(5)</td>
<td>.0061</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( HN=NO^+ ) (trans)</td>
<td>O</td>
<td>-</td>
<td>-.0002</td>
<td>-.0013</td>
<td>.8753</td>
</tr>
<tr>
<td></td>
<td>N(2)</td>
<td>-</td>
<td>.0185</td>
<td>-.0045</td>
<td>.0421</td>
</tr>
<tr>
<td></td>
<td>N(3)</td>
<td>-</td>
<td>.0023</td>
<td>.0053</td>
<td>.0530</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>.0004</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( HN=NO^+ ) (cis)</td>
<td>O</td>
<td>-</td>
<td>-.0005</td>
<td>.6977</td>
<td>.1479</td>
</tr>
<tr>
<td></td>
<td>N(2)</td>
<td>-</td>
<td>.0212</td>
<td>.0758</td>
<td>-.0102</td>
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<tr>
<td></td>
<td>N(3)</td>
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<tr>
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<td>Radical</td>
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**CNDO Spin Densities**

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**CNDO Spin Densities**

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TABLE 20

CNDO Spin Densities

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<td>-</td>
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<tr>
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## TABLE 22

### CNDO Spin Densities

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<th>2p_x</th>
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<th>2p_z</th>
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<td>.0123</td>
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<td>.0021</td>
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<td>-.0001</td>
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</table>
d) **Calculation of Coupling Constants.**

The hyperfine coupling constants found for the $\sigma$-radicals are listed in Tables 23-25 (pp. 148 - 150). They were calculated from the atomic orbital spin densities as follows.

The $a_H$ values were computed from the relationship

$$a_H = Q \rho_H$$

where $\rho_H$ is the spin density in the 1s orbital of the hydrogen and $Q$ is a scaling parameter. Using the same formula for calculations involving the CNDO approximation, Atherton and Hinchliffe estimated the value of $Q$ to be 508 gauss. In view of the similarity of their calculations to the ones reported here, it was decided to use their value of $Q$, and not to attempt a separate estimate with the limited number of radicals studied.

The $a_N$ values were calculated from the relation

$$a_N = A(\rho_{2s}) + B(\rho_{2p_x} + \rho_{2p_y} + \rho_{2p_z})$$

The empirical constants $A$ and $B$ are scaling factors, $A$ representing the direct Fermi contact term, and $B$ representing an additional spin polarisation term for the electrons in 1s and 2s orbitals by unpaired electrons in the nitrogen 2p orbitals. $B$ was evaluated from the calculation on methyleneimino ($H_2C:N$).
the unpaired electron being placed in an orbital containing negligible $N_{2s}$ spin density for symmetry reasons. Hence, for this radical the equation simplifies to one unknown, and using the nitrogen coupling constant measured by Cochran et. al., we find $B = 13.6$ gauss. Then using this calculated value of $B$, and the experimental value for the nitrogen coupling constant for syn-benzaldoxime, the value of $A$ was calculated as $1507$ gauss.

These values of $A$ and $B$ compare with those (12.01 and 1425) found by Drago for his extended Hückel calculations.

The results of these CNDO calculations are dealt with in more detail in the Discussion of this thesis.
**TABLE 23**

Coupling Constants for δ-Radicals

<table>
<thead>
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<th>a_x (calc.)</th>
<th>a_x (exp.)</th>
<th>Reference</th>
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</table>

a) Used to calculate parameter B.
b) No splitting resolved.
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<th>a (_x) (exp.)</th>
<th>Reference</th>
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<tr>
<td>H(5)</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HN}=\text{NO}^-) (trans)</td>
<td>23.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>28.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(3)</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HN}=\text{NO}^-) (cis)</td>
<td>32.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>32.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{PhNO}^+)</td>
<td>27.2</td>
<td>37.0</td>
<td>103</td>
</tr>
<tr>
<td>H(9)</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(10)</td>
<td>0</td>
<td>(1)a (_x) = 3.8</td>
<td></td>
</tr>
<tr>
<td>H(11)</td>
<td>0</td>
<td>and (1) or (3)a (_x) = 1.3</td>
<td></td>
</tr>
<tr>
<td>H(12)</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(13)</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 25

**Coupling Constants for PhCH: NO- and PhN: NO-**

<table>
<thead>
<tr>
<th>Radical</th>
<th>( a_x ) (calc.) synthesis</th>
<th>( a_x ) (exp.) synthesis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH=NO-</td>
<td>N 29.2</td>
<td>28.5</td>
<td>29.2 (^a) 31.6 95</td>
</tr>
<tr>
<td></td>
<td>H(10) 0</td>
<td>0</td>
<td>- b) 1.4</td>
</tr>
<tr>
<td></td>
<td>H(11) 0.05</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(12) 0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(13) 0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(14) 0.05</td>
<td>1.4</td>
<td>- 1.4</td>
</tr>
<tr>
<td></td>
<td>H(15) 3.3</td>
<td>0.2</td>
<td>2.6 9.4</td>
</tr>
<tr>
<td>PhN=NO-</td>
<td>N(2) 36.3</td>
<td>25.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N(3) 6.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(10) 0.05</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(11) 0.1</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(12) 0.2</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(13) 0.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(14) 0.05</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Used to calculate parameter A.
\(^b\) Represents a splitting too small to be resolved.
\(^c\) Oxygen trans to phenyl ring - corresponding to syn-benzaldoxime.
## DISCUSSION

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The continued interest in the mechanism of the decomposition of acylaryl nitrosamines in organic solvents has been described in the Introduction to this thesis.

The homolytic nature of the arylation process, with a free phenyl radical as reactive intermediate, was established more than thirty years ago. Since then the inclusion of heterolytic side reactions, the conception and final rejection of the "cage" process, anomalous observations such as the apparent participation of arynes and the still unsolved problem of the decomposition in halogenated solvents has led to numerous additions and refinements to the mechanism originally proposed.

1964 saw the introduction of a new dimension to the search for experimental evidence: the observation of an intense, long-lived e. s. r. signal during the decomposition in benzene led to controversy about the identity of the radical involved, and thus to conflicting schemes for the mechanism.

The first section of this Discussion deals with the schemes proposed by Rüchardt and by Perkins, and then with the evidence leading to an unambiguous assignment of the e. s. r. signal.
SCHEME 1

Rüchardt 1964

Ph. N(NO). Ac $\rightarrow$ Ph. N:N. OAc $\leftrightarrow$ PhN$_2^+$ -OAc

Initiation: Ph. N(NO). Ac + "OAc $\rightarrow$ Ph. N:N. O" + Ac$_2$O

Chain Process:

PhN$_2^+$ $\rightarrow$ AcOH

Ph. N:N. O$^-$ $\rightarrow$ AcO$^-$

Ph. N:N. O$^-$ $\rightarrow$ Ph. N:N. OH

Ph. N:N. OH $\rightarrow$ PhPh

Ph$^.$ N$_2$ O. N:N. Ph

PhH $\rightarrow$ H Ph

(3)
I ASSIGNMENT OF THE INTENSE LONG-LIVED E. S. R.
SIGNAL OBSERVED DURING THE DECOMPOSITION
OF N-NITROSACETANILIDE IN BENZENE

The mechanism proposed by Rüchardt and Freudenberg in 1964 (Scheme 1) overcame two of the major objections to previous schemes. Acetic acid is formed, not via the unstable acetoxy radical, but from the acetate ion, and there is present a high stationary state concentration of phenylidiazotate radicals capable of abstracting a hydrogen atom from the phenylcyclohexadienyl radical, thus preventing the formation of quaterphenyls and dihydrobiaryls.

The e. s. r. signal, which they observed when the decomposition took place in the cavity of an e. s. r. spectrometer, was claimed as further support for their proposed mechanism. The spectrum (Fig. 2) was analysed and the hyperfine structure found to be due to two nitrogen and five hydrogen nuclei, and was thus assigned to the phenylidiazotate radical.

As a result of McLachlan molecular orbital calculations carried out on the $\pi$-electron system of the radical the larger of the two nitrogen splittings (11.6 gauss) was assigned to position 3 and the smaller to position 2.

However, further investigation by the same group established,
TABLE 26

Coupling Constants and Spin Densities for the Phenyl Diazotate

\( Ti \)-Radical

\[
\begin{align*}
&\begin{array}{|c|c|c|c|}
\hline
\text{Atom} & a_x & \rho(\text{exp.}) & a_x & \rho(\text{exp}) & \rho(\text{calc.}) \\
\hline
1 & & & & .5442 \\
2 & \pm 1.67 & \pm 11.61 & & & -.0244 \\
3 & \pm 11.61 & \pm 1.67 & & & .2179 \\
4 & & & & .0264 \\
5 & -2.60 & .110 & -2.60 & .110 & .0944 \\
6 & 0.89 & -.038 & 0.89 & -.038 & -.0407 \\
7 & -2.73 & .115 & -2.60 & .110 & .1286 \\
8 & 0.89 & -.038 & 0.89 & -.038 & -.0407 \\
9 & -2.60 & .110 & -2.73 & .115 & .0944 \\
\hline
\end{array}
\end{align*}
\]
by isotopic labelling, that this assignment should be reversed. The original (1966) \(^{56}\) and amended (1967) \(^{59}\) hyperfine coupling constants and experimental spin densities, together with the McLachlan spin densities, are listed in Table 26.

Rüchardt and Binsch \(^{59}\) carried out further calculations and found that no variation of the resonance and Coulomb parameters, within accepted limits, could reverse the magnitudes of the nitrogen spin densities. The explanation they put forward depended on large contributions to the \(a_N\) value for nitrogen No. 2 from spin density on the neighbouring oxygen and nitrogen No. 3 atoms. This was based on an extension of the Karplus-Fraenkel \(^{147}\) theory, developed to explain \(^{13}\)C hyperfine coupling constants, to fit this diazotate \(\pi\)-radical.

\[
\begin{align*}
\alpha_{N(2)} &= \left[ S_{N(2)}^{N(2)} + \Omega_{N(2)O}^{N(2)} + \frac{\Omega_{N(2)N(3)}}{\rho_{N(2)}} \right] \rho_{N(2)} + \frac{\Omega_{ON(2)}}{\rho_{N(2)}} \rho_{N(2)} + \Omega_{N(3)N(2)}^{N(2)} \rho_{N(3)} \\
\alpha_{N(3)} &= \left[ S_{N(3)}^{N(3)} + \Omega_{N(3)N(2)}^{N(3)} + \frac{\Omega_{N(3)C(4)}}{\rho_{N(3)}} \right] \rho_{N(3)} + \frac{\Omega_{N(3)N(2)}}{\rho_{N(2)}} \rho_{N(3)} + \Omega_{C(4)N(3)}^{N(3)} \rho_{C(4)}
\end{align*}
\]

where \(\rho_x\) stands for the \(\pi\)-electron spin density at atom \(x\), \(S\) is the contribution of the s electrons, and the \(\Omega\)s are a measure
of the contributions due to spin polarisation of the various
\( \sigma \)-bonds, e.g., \( \Omega_{\text{ON}(2)} \) represents the contribution to the
unpaired spin at the nitrogen atom No. 2 due to polarisation of
the N-O bond by unit unpaired spin at the oxygen atom. As a
result of the high positive spin densities on the oxygen and on
nitrogen No. 3 the terms \( \Omega_{\text{ON}(2)} \frac{\rho_{\text{O}}}{\rho_{\text{O}}} \) and \( \Omega_{\text{N}(3)\text{N}(2)} \frac{\rho_{\text{N}(3)}}{\rho_{\text{N}(3)}} \) give
large negative contributions to the expression for \( a_{\text{N}(2)} \)' which
can then be added to the first term. On the other hand the
corresponding terms for \( a_{\text{N}(3)} \) are small and, moreover,
counterbalance each other because of the opposite signs of the
spin densities \( \rho_{\text{N}(2)} \) and \( \rho_{\text{C}(4)} \). Although the numerical values
of the \( \Omega \) parameters are not accurately known, it is clear from
the above reasoning that the sign of \( a_{\text{N}(2)} \) must be negative.

Further argument as to whether this was an acceptable
explanation was cut short by Chalfont and Perkins, assignment of the spectrum to a completely different radical.

A study of the scavenging of phenyl radicals by \( \text{C} \)-nitroso
compounds led Perkins to suggest that the e. s. r. signal reported
by Rüchardt was in fact the result of a phenyl radical adding across
the nitroso group of \( \text{N} \)-nitrosoacetanilide to give the
\((\text{N-phenylacetamido})\text{phenylnitroxide (PAPN) radical} \). Independent
generation of an identical spectrum by mixing benzene solutions
SCHEME 2

Perkins 1967

Ph. N(NO). Ac $\rightarrow$ Ph. N:N. OAc

Initiation:  Ph. N:N. OAc $\rightarrow$ Ph$^\cdot$ + N$_2$ + OAc

Chain Process:

\[
\begin{array}{ccc}
\text{Ph. N:N, OAc} & \text{Ph-N-OH} & \text{Ph-N-Ac} \\
\downarrow & \downarrow & \downarrow \\
\text{Ph-N-O-} & \text{Ph-N-Ac} & \text{PhPh} \\
\downarrow & \downarrow & \downarrow \\
\text{AcOH + N$_2$ + Ph$^\cdot$} & \text{PhH} & \text{PhH}
\end{array}
\]
of nitrosobenzene and N-bromoacetanilide, and also later, by the oxidation of N-acetylhydrazobenzene by t-butylhydroperoxide provided strong evidence for this new interpretation.

Perkins then proceeded to adapt Rüchardt's mechanism to include the nitrooxide (4) and not the diazotate (3) in the chain process. His scheme is reproduced opposite.

The McLachlan calculations on radical (4) are described elsewhere in this thesis (pp. 120-126). Using sets of parameters, which have been well established for other nitroxides, the two main features of Perkins' assignment are borne out.

The experiments already cited still require the nitrogen adjacent to the oxygen to have the larger coupling. The calculations indicate that the spin densities on the two nitrogen atoms are in a similar ratio to their observed splitting constants: so neighbouring atom effects need no longer be the dominating factor.

The second requirement is that the spin density on the N-phenylacetamido ring be low enough for there to be no measurable coupling with the ring protons. The calculated spin densities for these positions are small and give values $< 0.1$ gauss - less than the linewidth of the spectrum.
In addition to the preceding argument, there is the observation that different e.s.r. signals result from variation of the acyl group of the initial nitrosamide. The hyperfine structure of the spectrum detected during the decomposition of N-nitrosoformanilide (Fig. 17) was more complex than that found for N-nitrosoacetanilide (Fig. 2), there being an extra doublet splitting of 3.12 gauss. In order to test whether this was due to coupling of the unpaired electron with the proton of the formyl group, N-nitrosoformanilide-1-d was synthesised and the e.s.r. spectra observed during its decomposition studied. Comparison of Fig. 18 with Fig. 23 shows that the doublet \( a_H = 3.12 \text{ gauss} \) has been replaced by a 1:1:1 triplet \( a_D = 0.48 \text{ gauss} \). This is in accordance with the change of nuclear spin from \( 1/2 \) to 1 and the ratio of 6.5 for the nuclear g-factors for the proton and the deuteron. Therefore the presence of the acyl group in the radical is firmly established.

Thus there seems little doubt that Perkins is correct in his assignment of the intense long-lived e.s.r. signal, observed during the decomposition of N-nitrosoacetanilide in benzene, to the PAPN radical.
### TABLE 27

$a_N$ and $a_H$ Values (in gauss) for Nitroxides $RR'NO$

<table>
<thead>
<tr>
<th>Radical</th>
<th>$R$</th>
<th>$R'$</th>
<th>$a_N$</th>
<th>$a_{o,p-H}$</th>
<th>$a_{m-H}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>NPhAc</td>
<td></td>
<td>11.6</td>
<td>2.7</td>
<td>0.9</td>
<td>*</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td></td>
<td>9.1</td>
<td>3.0</td>
<td>1.0</td>
<td>148</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td></td>
<td>10.9</td>
<td>2.0</td>
<td>0.8</td>
<td>77, 122</td>
</tr>
<tr>
<td>Ph</td>
<td>$Bu^t$</td>
<td></td>
<td>13.4</td>
<td>1.9</td>
<td>0.8</td>
<td>91</td>
</tr>
<tr>
<td>Bu$^t$</td>
<td>$Bu^t$</td>
<td></td>
<td>15.4</td>
<td>-</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>Ph</td>
<td>O-CH</td>
<td></td>
<td>15.1</td>
<td>3.1</td>
<td>1.1</td>
<td>149</td>
</tr>
<tr>
<td>Bu$^t$</td>
<td>O$Bu^t$</td>
<td></td>
<td>28.0</td>
<td>-</td>
<td>-</td>
<td>89</td>
</tr>
</tbody>
</table>

* This work
II  THE (N-ARYLACETAMIDO)ARYLNITROXIDE RADICAL

\[ \text{Ar-N-O} \]
\[ \text{Ar-N-Ac} \]

The previous discussion dealt with the evidence that established (N-phenylacetamido)phenylnitroxide as the radical responsible for the e.s.r. signal. This section of the investigation shows that it is a typical nitroxide by considering the effects on its e.s.r. spectrum caused by variation of the solvent, acyl and aryl groups, and by examining the results of the McLachlan molecular orbital calculations performed on this and related species.

a) The Size of the Hyperfine Coupling Constants

The magnitude of the coupling of the unpaired electron with the various magnetic nuclei in the radical gives a clear indication of its delocalisation throughout the \( \pi \)-system. That PAPN is a typical nitroxide can be seen from Table 27, which compares its \( a_N \) and phenyl ring \( a_H \) values with those of other well-established radicals of this class.

The relative sizes of the \( a_N \) and ring \( a_H \) values for nitroxides depend on the extent to which the spin density is delocalised from the NO group throughout the radical. So the
near planar phenylnitroxide (Ph-NH-O·) has small $a_N$ and large $a_H$, while the more sterically hindered t-butylphenyl-
nitroxide has higher $a_N$ and lower $a_H$.

From the table it can also be seen that the presence of an
electronegative heteroatom next to the nitrogen increases its
splitting constant. In view of this the $a_N$ value for PAPN
might be expected to be higher than the 11.6 gauss recorded and
fall between those of RO-N(O·)-R and $R_2C-N(O·)-R$.

The explanation lies in the presence of the acyl group
attached to the second nitrogen. This will tend to delocalise
the lone pair of electrons of the nitrogen, leaving a partial
positive charge.

\[
\begin{align*}
\text{Ph-N-O·} & \quad \text{Ph-N-O·} \\
\text{Ph-N-C-R} & \quad \text{Ph-N=C-R}
\end{align*}
\]

The result would be a reduction in the importance of the
resonance structure $R_2^{+}N-O^-$ by coulombic repulsion of like
charges, and a corresponding reduction in the nitrogen coupling
constant.

Thus the values of $a_N$ and $a_H$ for PAPN are consistent with
those of a $\Pi$-nitroxide.
b) Variation of $a_N$, $g$-Value and Linewidth with Solvent

The remarkable changes in intensity of the PAPN e. s. r. signal with change of solvent will be discussed elsewhere. Here the variations of $a_N$ and $g$-values will be compared with those of other nitroxides.

$\overset{\frown}{a_N}$ - That the nitrogen splitting constants of nitroxide and nitroanion radicals are sensitive to variation of the solvent polarity has been observed by a number of workers.

Gendell, Freed and Fraenkel$^{150}$ suggested that this effect was due to a redistribution of the $\pi$-electron spin density in the N-O bond, caused by the formation of local complexes between polar solvents and polar groups in the radical, or of a hydrogen bond between solvent and radical. In other words, mesomeric structure (B) becomes more important in the resonance of the N-O bond, and the $a_N$ value increases.

$$R_2N-O \leftrightarrow R_2\overset{\frown}{N}-O^-$$

(A) \hspace{1cm} (B)

A number of solvent polarity parameters have been used for comparative purposes, all with a certain degree of success.

Deguchi$^{151}$ in his early work plotted $a_N$ versus dielectric constant,
while Lemaire, Rassat et al. chose the Kosower Z factor, and de Boer used the Reichardt $E_T$ value.

Deguchi, in a more critical examination decided that there must be a distinction between the effects due to electrostatic interaction and those due to hydrogen bonding.

For solvents containing no OH or NH groups he found a linear relationship between coupling constant and dipole moment $\mu$. 

$$a_N = \text{constant} + \text{constant} \times \mu$$

This did not hold for alcohols and amines, where hydrogen bonding with the following structures could take effect:

$$R_2N-O \cdots H-O \leftrightarrow R_2N^+O-H \cdots O^- \leftrightarrow R_2N-OH^- \cdots H-O^-$$

Thus, while the variation of $a_N$ is still dependent on solvent polarity, the effect is much greater when hydrogen bonding is possible.

The variation of the $\Upsilon$-electron spin densities on the nitrogen and oxygen atoms was put on a quantitative basis in independent theoretical studies by Ayscough and Sargent, and by Kikuchi and Someno, both groups using McLachlan calculations. By varying the Coulomb integral parameter of the oxygen atom, they were able to achieve the required redistribution of spin density in the N-O bond, thus imitating the
## Table 28

\[ a_N \] Values for Nitroxides in Alcohols

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DPNO</th>
<th>PAPN</th>
<th>p-Bu(^t)-PAPN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>10.45</td>
<td>11.90</td>
<td>12.02</td>
</tr>
<tr>
<td>Ethanol</td>
<td>10.21</td>
<td>11.84</td>
<td>11.91</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>10.21</td>
<td>11.81</td>
<td>11.88</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>10.22</td>
<td></td>
<td>11.86</td>
</tr>
<tr>
<td>n-Pentanol</td>
<td>10.18</td>
<td></td>
<td>11.86</td>
</tr>
<tr>
<td>t-Butanol</td>
<td></td>
<td></td>
<td>11.82</td>
</tr>
</tbody>
</table>
effect of solvent polarity variation. Comparison with the experimental coupling constants then allowed them to estimate some of the $\sigma-\pi$ Q values.

Table 7 (p. 78) in the Experimental section listed the variation of $a_N$ and $\delta g$ with solvent polarity for a series of alcohol solvents, while the $a_N$ values for the PAPN radicals, formed from N-nitrosoacetanilide and $p$-t-butyl-N-nitrosoacetanilide, are compared with those for diphenylnitrooxide (DPNO) in Table 28.

From the table it can be seen that the $a_N$ variation is similar, but not notably smaller than that for DPNO. Thus for DPNO: $a_N$(MeOH) - $a_N$(C$_5$H$_{11}$OH) = 0.27 gauss

while for PAPN: $a_N$(MeOH) - $a_N$(C$_5$H$_{11}$OH) = 0.16 gauss.

This slight difference can again be attributed to the partial positive charge on the second nitrogen. As before the importance of the mesomeric form $R_2\dot{N}^-O^-$ is reduced, and with it the likelihood of hydrogen bonding.

$g$-Value. - Solvent effects on the $g$-value of nitroxides have been studied by Kawamura et al. They found that for DPNO and di-$t$-butyl nitroxide the $g$-value decreased with increasing solvent polarity. The $g$-value is dependent, according
to Stone's theory, on the unpaired electron on the oxygen and the lone pair on the nitrogen of the nitroxide. The more polar the solvent is, the less likely are structures containing this nitrogen lone pair and unpaired spin on the oxygen, and thus the lower becomes the g-value.

The g-values for the p-t-butyl-PAPN radical were measured as $\delta g$ with reference to the standard Fremy's salt signal for which $g = 2.00550$, and are listed in Table 7 on p. 78. Below Kawamura's $\delta g$ values for DPNO in methanol and ethanol are compared with the corresponding values for the PAPN signals.

DPNO: $\delta g \times 10^5 = 4$ in MeOH and $O$ in EtOH
PAPN: $= 27$ 24
p-But-PAPN: $= 32$ 29

While the g-values are different for the two types of nitroxide, the changes in g with variation of solvent are very similar.

Linewidths. - The solvation of nitroxides by alcohols also has a noticeable effect on the resolution of the hyperfine lines of their e.s.r. spectra. The resultant reduction in solute motion causes changes in the relaxation times, and the
164.

lines of the higher magnetic field group become strongly
broadened compared with those of the lower one. This
observation leads to the determination of the sign of the
\( a_N \) value, by use of the following expression relating linewidth
to magnetic quantum number:

\[
T_2^{-1}(m) = A + Bm + Cm^2 + \ldots
\]

The linewidth theory developed by Kivelson\textsuperscript{17a} shows that
\( B < 0 \), assuming the positive value for \( a_N \) which theoretical
calculations indicate. Thus only when \( a_N > 0 \) and \( m=1 \) and \(-1\)
for the low and high field groups will the observed linewidth
effects take place. Fig. 6 shows that this phenomenon is
greater in t-butanol than in methanol, the higher viscosity of
the former reducing radical tumbling and thus increasing
anisotropy.

c) Variation of the para-Group

As the hyperfine splitting constant is related to the unpaired
electron densities, e. s. r. spectroscopy offers a convenient
method of measuring substituent effects. Since the Hammett
\( \sigma^+ \) constant is interpreted as a measure of the substituent effect
on electron densities several workers have compared variations
in the \( a_N \) value with changes in \( \sigma^+ \). The criterion for determining
whether an aromatic radical will follow a Hammett relationship

has been stated by Walter\textsuperscript{157} as follows. For a functional group $F$

\[
\begin{align*}
\text{(A)} & \quad X-\text{F}^* \\
\text{(B)} & \quad X-\text{F}^* 
\end{align*}
\]

with a substituent $X$, if the resonance structures can be drawn with an unpaired electron (A) and an unshared pair (B) on the atom \textit{para} to the site of substitution, then the system will exhibit Hammett behaviour. By this criterion arylnitroxides should show a Hammett relationship.

Lemaire and Rassat\textsuperscript{91} considered aryl-t-butylnitroxides and successfully plotted $a_N$ versus $\sigma$, while Strom, Bluhm and Weinstein,\textsuperscript{123} and Fischer and Neugebauer\textsuperscript{92b} independently examined the same relationship for DPNO.

In Table 29 the latter group’s results are compared with those found in this investigation for \textit{para}-substituted (N‐arylacetamido)aryl nitroxides. The plot of $a_N$ versus $\sigma$ is shown in Fig. 35 with the corresponding least squares line. From this the $a_N$ value can be expressed in terms $\sigma$ by the following
equation:

\[ a_N = 11.301 - 1.621 \sigma \text{ (gauss)} \]

for which the standard deviation is 0.159 gauss. This is very similar to the one Fischer found for DPNO, once again emphasising the typical nitroxide behaviour of PAPN.

\[ a_N = 9.655 - 1.602 \sigma \text{ (gauss)} \]

Standard deviation 0.103 gauss.

d) **Variation of the Acyl Group**

One of the features of the e. s. r. spectrum of PAPN is the accidental coincidence of hyperfine lines, resulting from some of the splitting constants being multiples of others. While alteration of the para-substituent had little effect on the appearance of the signal, changing the acyl group destroyed much of this precise overlap, giving rise to more complex spectra.
Fig. 35

Hammett plot of \( a_N \) versus \( \sigma \)
for para-substituted PAPN
TABLE 29

Variation of $a_N$ with para-Substituent for DPNO and PAPN

![Diagram](image)

<table>
<thead>
<tr>
<th>R</th>
<th>$\sigma$</th>
<th>DPNO/xylene</th>
<th>PAPN/pyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>-.268</td>
<td>10.07</td>
<td>12.44</td>
</tr>
<tr>
<td>Me</td>
<td>-.170</td>
<td>9.79</td>
<td>12.05</td>
</tr>
<tr>
<td>Bu^t</td>
<td>-.151</td>
<td></td>
<td>11.88</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>9.66</td>
<td>11.77</td>
</tr>
<tr>
<td>CO_2Et</td>
<td>.45</td>
<td>8.89</td>
<td>11.04</td>
</tr>
<tr>
<td>NO_2</td>
<td>.778</td>
<td>3.38</td>
<td>10.59</td>
</tr>
</tbody>
</table>


### TABLE 30

**Variation of Coupling Constants with Acyl Group**

<table>
<thead>
<tr>
<th>R</th>
<th>9(^{aN(7)})PhH</th>
<th>9(^{aN(7)})pyridine</th>
<th>9(^{aN(8)})</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>11.65</td>
<td>11.76</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>11.65</td>
<td>-</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>11.62</td>
<td>11.77</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>11.64</td>
<td>11.77</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Pr(^i)</td>
<td>11.70</td>
<td>-</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>-</td>
<td>12.08</td>
<td>1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>p-Cl, C(_6)H(_4)</td>
<td>-</td>
<td>12.07</td>
<td>1.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

![Chemical Structure](image)
Although accurate measurement of all the splitting constants was not possible, some significant changes are clear from the results listed in Table 30. These variations can be related to the twist around the \( N_7 - N_8 \), \( N_8 - C_9 \), and \( N_8 - C_{16} \) bonds, caused by the different steric requirements of the acyl groups (COR).

(i) \( R = \text{Me} \). - For the protons of a methyl group the hyperfine splitting, arising from hyperconjugative and exchange polarisation effects, is given by the relationship

\[
a_H = \omega_{CCH_3}^H \omega_C
\]

where \( \omega_C \) is the \( \pi \)-electron spin density at the carbon to which the methyl group is attached and \( \omega_{CCH_3}^H \) is the \( \Omega \) parameter, having values between +18 and +38 gauss.

As no splitting was observed from the methyl protons in this case there must be low spin density on the acyl carbon atom (No. 16). This situation can be visualised if the acyl group is forced out of the plane of the rest of the radical by rotation around the \( N_8 - C_{16} \) bond. The McLachlan calculations estimate the angle of the twist as 70°.

(ii) \( R = \text{Et and Pr}^i \). - Figs. 24 and 25 show that the only variation observed when \( R \) is changed from Me to Et and \( \text{Pr}^i \)
is in the intensity of the component lines. The increase in
the size of the acyl group will tend, not only to force the group
further out of the radical plane, but also to increase the twist
around the \( N_7 - N_8 \) bond, thus causing slight changes in the two
nitrogen coupling constants.

(iii) \( R=\text{Ph} \). - The basic pattern of each group of lines
is now quite different (Fig. 28). The accidental coincidence of
lines is removed by the reduction of the second \( a_N \) value from
1.7 to 1.4 gauss. This change, and the increase of the major
\( a_N \) value from 11.77 to 12.08 gauss, can be rationalised in
terms of further twisting of the \( N_7 - N_8 \) bond reducing the
spin density on \( N_8 \) and increasing that on \( N_7 \). Also observed
(Fig. 30) was an additional proton coupling of 0.3 gauss: as
this was also present for \( R=\text{p-Cl-C}_6\text{H}_4 \), but not for the signal
resulting from the decomposition of \( \text{p-t-butyl-N-nitroso-}
benzanilide} \), it seems reasonable to assign it to the proton
attached to \( C_{12} \) in the radical.

(iv) \( R=\text{H and D} \) (Figs. 17, 18, 22 and 23). - Molecular
models show that instead of the acyl group being almost
completely out of the radical plane, as in the case of \( R=\text{Me} \),
the system can be almost coplanar. A measure of the spin
density, which is now found on the acyl group can be computed from the size of the acyl proton coupling constant. Using McConnell's equation, with a standard \( \Omega_{\text{CH}} ^{23.7} \) value of 23.7 gauss:

\[
\rho = \frac{3.1}{23.7} = 0.131
\]

Thus this coplanarity produces greater spin density on the acyl group C\(_{16}\) atom than on any of the aryl ring positions.

d) McLachlan Molecular Orbital Calculations

The results of the McLachlan calculations, described in the Theoretical section of this thesis, provide further confirmation of Perkins' assignment of the e.s.r. signal to the PAPN \( \Pi \)-radical. Using parameters that had been found satisfactory for the well established \( \Pi \)-nitroxides DPNC and PNC, the agreement between the calculated and experimental spin densities was good.

![Chemical Structure]

\[
\begin{align*}
\text{PAPN} & \quad \text{TP-radical}
\end{align*}
\]
Calculations with the parameters of both set A and set B predict greater spin density on N(7) than on N(8), as implied by the observed coupling constants. However, while set A gives positive values for both sites, set B predicts $\rho_{N(7)} > 0$ and $\rho_{N(8)} < 0$.

Two observations can be made from a study of the linewidth variations within the PAPN signals. In every case the high field group lines are broader than those for low field, implying a positive value for $a_{N(7)}$ as discussed earlier (p.164). However, only in the PAPN type signal observed during the decomposition of N-nitrosoformanilide in benzene can any information about $a_{N(8)}$ be deduced. For the low field group the lines on the low field side are broader and less resolved than those at higher field. But as the sign of $\rho_{N(8)}$ cannot be determined with certainty from the theoretical calculations the only conclusion that can be drawn is that $\rho_{N(8)} a_{N(8)} < 0$.

Expressions relating the nitrogen hyperfine coupling constants to the spin densities on that atom and its nearest neighbours can be formulated by extending the Karplus-Fraenkel theory.
\[ a_{N(7)} = [s_{N(7)} + \Omega_{N(7)}^N + \Omega_{N(7)}C(6) + \Omega_{N(7)}N(8)] \rho_{N(7)} \]

\[ + \Omega_{ON(7)}^N \rho_{O} + \Omega_{C(6)N(7)}^N \rho_{C(6)} + \Omega_{N(8)N(7)}^N \rho_{N(8)} \]

\[ a_{N(8)} = [s_{N(8)} + \Omega_{N(8)}C(16) + \Omega_{N(8)}C(9) + \Omega_{N(8)N(7)}^N \rho_{N(8)} \]

\[ + \Omega_{C(16)N(8)}^N \rho_{C(16)} + \Omega_{C(9)N(8)}^N \rho_{C(9)} + \Omega_{N(7)N(8)}^N \rho_{N(7)} \]

While low calculated spin densities on certain sites in the radical mean that some of the terms in the above equations can be neglected, there still remain too many \( \Omega \) parameters of uncertain value for any conclusions to be drawn about the sign of \( a_{N(8)} \). For example, values of \( \Omega_{ON}^N \) between -1 and -14 have been reported \(^{133, 134} \) for nitroxides, while for \( \Omega_{CN}^N \) estimates between +9 and -4 have been used \(^{158} \) and \( \Omega_{NN}^N \) is even less certain.

**Geometry of the PAPN radical.** - Examination of molecular models of the radical shows quite clearly that the system cannot be planar. While the twist around the \( C_6-N_7 \) bond is very similar to that in DPNO, it is less straightforward to estimate the angles for \( N_8-C_9 \) and \( N_8-C_{16} \). However, these can be found from the \( k_{CN} \) resonance parameters used in the McLachlan
calculations. The following values were chosen from set C, as they gave the most satisfactory account of the spin density distribution.

\[ k_{CN(6-7)} = 1.11, \quad k_{NC(8-9)} = 0.60 \quad \text{and} \quad k_{NC(8-16)} = 0.45 \]

Deguchi\textsuperscript{132} calculated the twist of the C-N bonds of DPNO as 22.5°. Assuming the same angle for PAPN, the value of \( k_o \) for a planar system can be found from the equation \( k = k_o \cos \Theta \) to be \( k_o = 1.20 \). Then from the same relationship the twists around the \( N_8 - C_9 \) and \( N_8 - C_{16} \) bonds are approximately 60° and 70° respectively.

The failure to detect coupling constants for the protons of the second phenyl ring and the acetyl group, in the e. s. r. signal of the PAPN radical, can thus be explained by the non-planarity resulting from the steric requirements of the two groups.

III THE IDENTITY OF THE CHAIN CARRIER RADICAL

Section I of this Discussion dealt with the evidence which established the identity of the intense e. s. r. signal observed during the decomposition of N-nitrosoacetanilide in benzene. As neither Rüchardt nor Perkins reported the use of any other
solvents, it was decided to examine the spectra obtained on replacing benzene by other aromatic hydrocarbons. Below are listed the intensities of the PAPN signal for the series of solvents.

Benzene  intense
Toluene  weak
Ethylbenzene  v. weak
Cumene  nil
t-Butylbenzene  intense
Xylene  v. weak
Mesitylene  v. weak

The signal is intense only for benzene and t-butylbenzene, while for solvents containing an easily abstractable \(\pi\)-hydrogen atom it is weak or not detectable.

The stationary state concentration of the radical, on which the intensity of the signal depends, will be determined by the rates of its formation and removal.

To specify the rate of formation of PAPN, the courses open to the phenyl radical must be considered. They are:
(i) Addition across the nitroso group of the nitrosamide.

\[
\text{Ph}^* + \text{N}=\text{O} \quad \text{Ph-N-O}^* \\
\text{Ph-N-Ac} \quad \text{Ph-N-Ac}
\]

(ii) Addition to the solvent to give a phenylcyclohexadienyl radical.

\[
\text{Ph}^* + \text{ArH} \quad \text{[PhArH]}^* 
\]

(iii) Abstraction of an aromatic hydrogen from the solvent.

\[
\text{Ph}^* + \text{ArH} \quad \text{PhH} + \text{Ar}^* 
\]

(iv) Abstraction of an \(\alpha\)-hydrogen from the side-chain of the solvent.

\[
\text{Ph}^* + \text{ArCHR}_2 \quad \text{PhH} + \text{ArCR}_2 
\]

On the other hand, the disappearance of the radical can be due to:

(v) Disproportionation of the radical.

(vi) Coupling with other radicals present.

\[
\text{R}_2\text{N-O}^* + \cdot\text{R} \quad \text{R}_2\text{N-O-R} 
\]

(vii) Abstraction of a hydrogen atom from the phenylcyclohexadienyl radical to give biphenyl.

\[
\text{R}_2\text{N-O}^* + [\text{PhC}_6\text{H}_5\text{H}]^* \quad \text{R}_2\text{N-OH} + \text{PhPh} 
\]

Each of these reactions will now be considered in turn.
Reaction (i) will become more important as the concentration of the nitrosamide is increased. At higher concentration the e. s. r. signal is intensified, not only by the overall faster reaction rate, but also by the higher statistical chance of the phenyl radical meeting a nitrosamide molecule.

Reaction (ii) is the step involved in the major product forming sequence, and will be correspondingly less important at higher concentration.

Reaction (iii) has been shown to be of comparatively minor significance, and has been observed in only a few isolated cases. For example Hey\textsuperscript{159} found that in the preparation of \( \text{p-terphenyl} \) from the decomposition of \( \text{N}_2\text{N'}\text{-diacetyl-N,N'-dinitroso-1,4-phenylenediamine (21)} \) in benzene a trace of biphenyl was formed. The same author\textsuperscript{160} also reported that the decomposition of both \( \chi-3\)- and \( \chi-4\)-N-nitrosoacetamidophenylpyridine (22) in benzene produced a little \( \chi\)-phenylpyridine in addition to the expected pyridylbiphenyls, while Huisgen's study\textsuperscript{38} of the phenylation of

\[
\begin{align*}
\text{Ac(ON)}N & \begin{array}{c}
\text{N(NO)Ac}
\end{array} \\
& \text{(21)}
\end{align*}
\]

\[
\begin{align*}
\text{N} & \begin{array}{c}
\text{N(NO)Ac}
\end{array} \\
& \text{(22)}
\end{align*}
\]
pyridine revealed that the relative rate of abstraction to substitution was about 1:120.

On the other hand, abstraction of hydrogen from the α-position of the side-chain \([\text{reaction (iv)}]\) is far more important. This produces a solvent radical which is sufficiently resonance stabilised to dimerise; thus bicumyl is one of the products of the decomposition of dibenzoyl peroxide in cumene. Hey, Pengilly and Williams\(^{161}\) studied the ratio of side-chain abstraction to nuclear arylation for dibenzoyl peroxide in toluene, ethylbenzene, cumene and t-butylbenzene, and found 13, 55, 60.5 and 0%, these figures indicating the relative stabilities of the solvent radical formed. Although part of the product might be due to the benzoyloxy radical, Dannley and Zaremsky's\(^{162}\) isolation of benzene from the same system indicated that the phenyl radical also abstracted hydrogen.

Rondestvedt and Blanchard\(^{163}\) found that for the decomposition of \(N\)-nitrosoacetonilide in toluene only 4% bibenzyl was formed, while for cumene there was 35% bicumyl. That side-chain abstraction products are formed in lower yield for \(N\)-nitrosoacetonilide than for dibenzoyl peroxide is borne out by the results, reported in this thesis (p.60) for mesitylene as solvent.
In this case, the ratio of 14% abstraction for N-nitrosoacetanilide rises to 57% when dibenzoyl peroxide is used.

Reaction (v). - The reactions of nitroxide radicals have been the subject of intermittent study since their chemistry was first examined by Wieland \(^ {24}\) and Meyer \(^ {3}\) fifty years ago. The relative instability of DPNO in concentrated solution was discussed in the Introduction, together with the probable mechanism of the decomposition to amine and nitrone. A similar disproportionation for PAPN would result in N-acetylhydrazobenzene and quinonimine-N-oxide thus:

\[
\begin{align*}
2 \text{Ph-N-O}^- + \text{Ph-N-H} & \rightarrow \text{Ph-N-Ac} + \text{Ph-N-Ac} \\
\text{Ph-N-Ac} & \rightarrow \text{Ph-N-Ac} + \text{O} = \begin{array}{c}
\text{N} \\
\text{N(Ac)Ph}
\end{array}
\]
\]

When the para-group of diarylnitroxides is methoxy or nitro, this mode of decomposition is no longer possible and the radical is sufficiently stable to be isolated as a crystalline solid. However, the e.s.r. spectrum from p-methoxy-N-nitrosoacetanilide is no more long-lived than that from the unsubstituted compound. Thus reaction (v) appears to be of little consequence in determining the intensity of the signal.

The possibility of coupling of a nitroxide radical with a
radical derived from the solvent [reaction (vi)] has recently been confirmed by Calder, Forrester and Thomson. They studied the oxidation of N-hydroxynaphthalimide with lead tetraacetate in toluene and isolated the coupling product in 53% yield:

\[
\text{N-O-CH}_2\text{Ph} + \cdot\text{CH}_2\text{Ph} \rightarrow \text{N-O-CH}_2\text{Ph}
\]

The analogous product was formed for \( \cdot\text{CCl}_3 \) in yields of 9% from \( \text{CCl}_4 \) and 75% from \( \text{CHCl}_3 \). However, when benzene was used no product corresponding to coupling of a phenyl radical with the nitroxide was found.

So coupling of nitroxides with radicals derived from the solvent is likely only when the latter are resonance stabilised.

Reaction (vii), involving the oxidation of phenylcyclohexadienyl to biphenyl, will be little affected by substituents in the solvent and should have no effect on the intensity of the e.s.r. signal. This reaction finds close analogy with the mechanism proposed for the decomposition of dibenzoyl
peroxide in the presence of diphenylnitroxide.

The conditions used for recording the e. s. r. spectrum are quite different from those at which the highest yields of arylation products are found. In order to obtain an intense, well resolved signal concentrated solutions are used and no precaution need be taken to exclude air from the system, while high yields of biaryl only result from dilute solutions in deoxygenated solvents.

Hey \(^4\) studied the effect of varying the concentration for oxygen-free solutions and found that the biaryl yield dropped from 80% to 40% as the solute to solvent molar ratio increased from 0.011 to 0.180: for the more concentrated solutions he also found small quantities of the secondary products, ter- and quaterphenyls. In a similar investigation Eliel \(^48\) found a tenfold increase in nitrosamide concentration from 0.025 M to 0.25 M reduced the biphenyl yield from 91% to 66.5%.

The effect of dissolved oxygen on the product yields was examined by Simamura: \(^124\) he found that the 91% yield found for dilute degassed samples fell to 5% when air was bubbled through the system: this was paralleled by an increase in the formation of oxidation products such as phenol.
In view of the obvious importance of such effects, a study was made under the conditions used for the e.s.r. experiments. The yield of biphenyl, resulting from the decomposition of N-nitrosoacetanilide in benzene, was found to fall from 59% to 24% as the molar ratio increased from 0.0007 to 0.339. At the same time the yields of terphenyls, resulting from the phenylation of the primary product, rose from <0.1% to 7.5% and the formation of tars increased at the same time. The level of phenol formation remained constant at about 10%.

Hey also found that the yields of products were sensitive to variation of temperature; his recorded yields of biphenyl were 53, 80, 71 and 68% at 10°, 20°, 30° and 40° respectively.

As no precautions were taken to exclude air, or to control the temperature of the reaction, while in the cavity of the spectrometer, it would seem that the conditions under which the e.s.r. spectra were generally recorded are those for which the yields of arylation product are lowest and side reactions leading to tar formation are the dominating factor.

The intensity of the e.s.r. signal for the series of hydrocarbon solvents can now be rationalised in terms of the ease of formation and decay of the PAPN radical. The spectrum is thus
predicted, and observed to be intense for concentrated solutions of the nitrosamide in solvents containing no α-hydrogen atoms: under these circumstances the formation of the radical is favoured by the high probability of addition of phenyl across the nitroso group (i) and by there being no side-chain abstraction (iv), while its decay is minimised by the absence of a coupling reaction (vi). On the other hand there is a low signal level for solvents containing an α-hydrogen atom, when formation is reduced by side-chain abstraction (iv), and decay increased by coupling of the nitroxide with the solvent radical (vi).

The importance of the competition for the free phenyl radical between the nitrosamide and the aromatic solvent to give nitroxide and phenylcyclohexadienyl radicals is illustrated by the e.s.r. spectrum resulting from the decomposition of N-nitrosoacetanilide in furan. In this system the furan is phenylated about twenty times more readily than the corresponding reaction in benzene, at the expense of nitroxide formation. The signal, while still distinct and well resolved, is markedly weaker than when benzene is the solvent.

No signal was detected when N-nitrosoacetanilide decomposed in 2,6-dimethylfuran, thus showing again the importance of
side-chain hydrogen abstraction, which in this reaction accounts for all of the arylation products isolated.

\[
\text{Ph}^- + \text{Ph}^\text{O} \rightarrow \text{Ph}^- + \text{Ph} \\
\text{Ph}^- + \text{Me-} + \text{Me} \rightarrow \text{PhH} + \text{H}_2\text{C-} \rightarrow \text{coupling products}
\]

The effect of the coupling reaction is illustrated by the yields of 3, 3',5, 5'-tetramethylbibenzyl from the decompositions of dibenzoyl peroxide and N-nitrosoacetanilide in mesitylene. In the former reaction the ratio of side-chain abstraction to nuclear arylation is 1.3, but for the latter the figure is 0.3, the reduction being partly due to the absence of the benzoyloxy radical and partly due to coupling of the 3, 5-dimethylbenzyl radical with PAPN.

The mechanism proposed by Perkins (Scheme 2) requires a high stationary state concentration of PAPN radicals to be present to effect the main product forming sequence. Although this is clearly the case when the solvent is benzene or t-butylbenzene, the e.s.r spectrum indicates very low or undetectable
concentrations when toluene, ethylbenzene, cumene, etc. are
used. On the other hand, there is no reason to doubt that the
same mechanism is operable throughout the series. In spite
of the possibility of the abstraction of side-chain hydrogen
atoms, the major products are still due to the arylation of the
solvent.

So, while Perkins' assignment of the e.s.r. signal, shown
in Fig. 2, to the PAPN radical is surely correct, there are
some doubts as to whether his mechanism is the complete
answer.

An observation made for the first time during the course
of this investigation is that of a second weak signal superimposed
on that attributed to PAPN. This signal, which is illustrated
in Figs. 3-5, consists of nine lines arranged as a 1:1:1 triplet of
1:1:1 triplets, indicating two nitrogen nuclei with different coupling
constants. Unlike the PAPN signal this one has the same intensity
throughout the series of aromatic hydrocarbon solvents: thus
in benzene the PAPN signal dominates the triplet of triplets, which
can only be observed at high modulation amplitude: it is probably
for this reason that it has not been reported by previous workers.
However, when the PAPN signal intensity is low (in toluene,
cumene, mesitylene, etc.) the triplet of triplets is the

dominant species. Comparison of Figs. 3 and 4 illustrates the
relative intensities of the two signals in benzene and mesitylene.

In view of the constant concentration of this second radical
compared with PAPN, and the requirement of the same
mechanism throughout this series of solvents, the possibility
that this triplet of triplets is due to the elusive chain carrier
radical is worthy of consideration.

The e.s.r. spectra observed for a number of related systems
were studied in an attempt to detect the triplet of triplets without
success. For phenylazotriphenylmethane in benzene the only
signal (Fig. 31) was that due to the triphenylmethyl radical
formed during the decomposition. During the reaction of
aniline with pentyl nitrite in benzene the weak and very poorly
resolved signal shown in Fig. 32 was observed. The separation
of the hyperfine lines was 1 gauss, while the three groups were
about 12 gauss apart. This reaction has recently been studied
by Levit and Gragerov,\textsuperscript{167} who attributed the signal to the
phenyldiazotate radical on the basis of Rüchardt's original study
of the decomposition of N-nitrosoacetanilide in benzene. This
assignment has become improbable in the light of the work
reported by Perkins, \(^{61}\) Forrester \(^{62}\) and in this thesis, which has firmly established that this latter signal is due to PAPN. That the latter radical contains an acyl group shows that it cannot be formed from aniline and pentyl nitrite and that some other species must be present. In view of the low signal level and poor resolution of the spectrum, further speculation as to the identity of the radical does not seem justified.

The e. s. r. signal of DPNO was detected for solutions of benzenediazonium acetate and of the solid products isolated from various nitrosamide decompositions. As it has been shown\(^ {71}\) that these solids consist, at least in part, of benzene-diazonium acetate, it is likely that the DPNO is formed from the diazonium salt. The mechanism by which the nitrooxide is formed is uncertain, but as it is known to arise from the addition of phenyl to nitrosobenzene\(^ {78a}\) a scheme such as the following is possible:

\[
\begin{align*}
\text{PhN}_2^+ \cdot \text{OAc} & \quad \text{Ph.N=O} \quad \text{Ph} \rightarrow \text{Ph}_2\text{NO} \\
\text{Ph.N=N. OAc} &
\end{align*}
\]

The subsequent decomposition of the diazonium salt in the presence of DPNO is discussed later.
IV THE TRIPLET OF TRIPLETS E. S. R. SIGNAL

In the previous section the suggestion was made that the second weaker signal - the 1:1:1 triplet of 1:1:1 triplets - might be the radical involved in the chain process, and that the PAPN radical was formed in a side reaction, resulting from the use of concentrated solutions, and possibly irrelevant to the production of phenyl radicals from N-nitrosoacetanilide. A more detailed examination of this new signal is thus required in an attempt to identify the radical to which it is due, and hence to clarify the mechanism.

The spectrum (Figs. 3-5) shows two unusual features: the major nitrogen coupling constant of 30.7 gauss is abnormally high for radicals in solution, while the g-factor of 2.0015 is less than the free spin value of 2.0023. This suggests that the radical is not a typical π-nitroxide like DPNO, PNO and PAPN for which $a_N = 9-12$ gauss and $g = 2.0050 - 2.0055$. The same conclusion can be drawn from the insensitivity of the signal to changes in the acyl and aryl groups of the nitrosamide. Identical spectra resulted from the decomposition of N-nitrosoacetanilide, and N-nitrosoisobutyranilide, while on changing the para-substituent of the aryl group from methoxy to nitro the major
a_N value only varied from 30.6 to 31.0 gauss—an increase of 1.3%. This compares with a decrease from 12.44 to 10.49 gauss (17%) for the same substituents in PAPN.

In view of the magnitude of the a_N value, two types of radical are considered. The first is the nitroxide formed by the addition of an alkoxy radical, possibly formed from oxidation of the solvent, across the nitroso group of the nitrosamide. Alkoxyalkynitroxides have been reported to have nitrogen splitting constants in the region of 25-30 gauss, and in this case a nine line spectrum might be expected through unequal coupling of the unpaired electron with the two nitrogen nuclei. However, this assignment can be rejected on the grounds that the g-factor of 2.0015 is inconsistent with the values of about 2.0055 found for nitroxides of all types.

The second type of radical with a_N values of the correct magnitude is the iminoxy radicals derived from the oxidation of oximes. These were considered in the Introduction, their large coupling constants being attributed to the location of the unpaired electron in a σ-orbital with high s:p ratio. Thus
from syn- and anti-benzaldoximes, signals with $a_N = 29.2$ and 31.6 gauss were observed by Thomas.\textsuperscript{95}

The similarity between these radicals and the isoelectronic $\sigma$-phenyldiazotate originally proposed by Rüchardt as a $\pi$-radical is remarkable.

\[
\begin{array}{c}
\text{Ph} & \text{Ph} \\
\text{N=N,} & \text{C=N,} \\
\text{O} & \text{O}
\end{array}
\]

An assignment of the triplet of triplets signal to the PhNNO $\sigma$-radical explains several features of the spectrum by analogy with the results obtained by Thomas\textsuperscript{95} and Gilbert and Norman\textsuperscript{96b} for syn-PhCHNO.

(i) The large $a_N$ value of 30.7 gauss is consistent with the unpaired electron occupying a molecular orbital in the plane of the phenyl ring, with high $s:p$ ratio and comprised of the $sp^2$ hybrid orbitals of the two nitrogen atoms and $a_2p$ atomic orbital of the oxygen.

(ii) The coupling of the unpaired electron with the protons of the phenyl ring is small and remains unresolved, the minimum linewidth for the spectrum being 0.5 gauss. The hyperfine structure thus consists of nine lines arranged as a triplet of triplets.
(iii) For the σ-radical, variation of the para-substituent of the aryl ring has little effect on the $a_N$ values, unlike the \(\widetilde{W}\)-nitrooxide case when Hammett behaviour is exhibited.

In addition the absence of the acyl group in the postulated radical explains why identical signals result from the decompositions of \(\text{N}-\text{nitrosoacetanilide}\), \(\text{N}-\text{nitrosopropionanilide}\) and \(\text{N}-\text{nitrosoisobutyranilide}\).

The g-factor of 2.0015 differs from that of 2.0055 found for iminoxy radicals, but is typical of other well established σ-radicals such as formyl (2.0009)\(^{102c}\), vinyl (2.0022)\(^{24}\), carbamoyl (2.0017)\(^{146}\) and the nitrosobenzene cation (2.0007)\(^{103}\). This inconsistency in the values for PhNNO and PhCHNO probably arises from the additional lone pair of electrons on the second nitrogen atom, the importance of which is stressed in the g-value theory developed by Stone.\(^{156}\)

The essential difference between Rüchardt's original concept of the phenyldiazotate radical and the one now proposed is that while he considered a \(\widetilde{W}\)-radical with delocalisation of the unpaired electron throughout the system, it can now be regarded as a σ-radical.

In order to clarify this ambiguity it is necessary to turn to
theoretical calculations, the conclusions of which are discussed below.

CNDO Calculations

(i) Distinction between $\sigma$- and $\pi$-Radicals

The theoretical method used to test whether the phenyl-
diazotate radical would have $\sigma$- or $\pi$-symmetry was the
CNDO approximate SCF treatment of Pople. In view of the
neglect of $\sigma$-$\pi$ interactions, it was decided to perform
calculations on a number of known $\sigma$- and $\pi$-radicals to
establish that this particular procedure could locate the
unpaired electron in an orbital of the correct symmetry type.
For $\sigma$-radicals the spin density is spread throughout the
$\sigma$-framework in the hydrogen 1s orbital and the 2s, 2p$_x$ and
2p$_y$ orbitals of the other atoms, while for $\pi$-radicals it is only
found in the 2p$_z$ orbital.

The systems reported in this thesis are listed below, the
correct symmetry being predicted in every case.

$\sigma$: $\text{H}_2\text{C}=\text{N}^-$, $\text{H}\text{C}=\text{O}$, $\text{H}_2\text{C}=\text{CH}$, $\text{H}_2\text{N}\text{C}=\text{O}$, $\text{C}_6\text{H}_5^-$

PhNO$^+$ and PhCH=NO$^-$ (syn and anti)

$\pi$: $\text{H}_2\text{NO}^-$ and PhNO$^-$
In addition the following radicals have also been studied with equal success.

\[ \sigma: \quad \text{NO}_2 \]

\[ \pi: \quad \text{N}_2\text{H}_4^+, \text{HOB}^-, \cdot\text{CF}_3, \cdot\text{CH}_3, \text{C}_6\text{H}_5\text{N}^- \text{ and CO}_2^+ \]

Having established that the method is satisfactory for the above examples, the results for the iminoxy and diazotate radicals can be considered.

The parent radicals HCH=NO- and HN=NO- are both predicted to be \( \sigma \); for the latter the cis and trans-isomers are found to be of similar stability. The iminoxy radicals from syn- and anti-benzaldoxime are both \( \sigma \), a planar configuration being the most stable in each case. This is in conflict with the results of the extended Hückel theory calculations reported by Drago, in which the anti-radical was more stable when the phenyl ring was twisted 90° out of the nodal plane.

The results for trans- and cis-phenyldiazotate, listed in Tables 21 and 22 (pp. 144-145) clearly show that the spin density is in the \( \sigma \)-framework. Thus the assumption made earlier that they are \( \sigma \)-radicals is justified on the basis of these calculations.
(ii) **Proton Splitting Constants**

In view of the approximate nature of the method, and the assumption of Atherton and Hinchliffe's $^{143}$ Q value, the agreement between theory and experiment is satisfactory. The errors involved are similar to those found from the extended Hückel method of Drago $^{138}$ and the CNDO calculations of Atherton. $^{143}$ However, for the larger systems, containing phenyl rings, the geometry was not optimised so rigorously, with corresponding inaccuracy in the $a_H$ values. This is particularly marked for syn- and anti-PhCH=NO$^-$, where $a_H(15)$ is very low in each case. The values for the phenyl ring proton splitting constants are in better agreement with experiment. In every case, low densities are predicted when no coupling is resolved, and when one is observed the calculated value is in the correct order of magnitude. In particular the results for syn-PhCH=NO$^-$ are very similar to those found by Drago: however, the planar geometry predicted for the anti-isomer, with non-equivalent o-protons, is less realistic than the 90° conformer used by Drago; only for this latter case are the o-protons equivalent in agreement with the analysis of the e.s.r. spectrum. $^{95, 96b}$

While the calculated proton coupling constants for trans-
phenyldiazotate are all small, and considerably less than
the observed linewidths of the triplet of triplets signal, the
corresponding values for the cis-isomer are notably larger,
and would have been resolved under the experimental conditions.

(iii) **Nitrogen Splitting Constants**

The procedure used to calculate the nitrogen splitting
constants was described on p. 146. The results, listed in
Tables 23-25, show in general only limited agreement between
theory and experiment, the calculated values for PhNO$^+$ and
H$_2$NC=O being particularly inaccurate. On the other hand,
using *syn*-PhCH=NO$^-$ as a calibration, the calculated $a_N$ value
for the anti-isomer is approximately right, and as the phenyldiazo-
ate radicals are so similar, both geometrically and
electronically, estimates of $a_N^{(2)}$ and $a_N^{(3)}$ are possible. The
values of 36.3 and 25.7 gauss for nitrogen No. 2 of the trans-
and *cis*-isomers compare with the observed value of 30.7 gauss
for the triplet of triplets signal, while 6.2 and 6.9 gauss are
predicted for $a_N^{(3)}$ compared with the experimental value of
2.3 gauss. In view of the approximations discussed earlier
better agreement than this is not to be expected.
(iv) **Conclusion**

The results of the CNDO calculations support the assignment of the triplet of triplets signal to the **trans**-phenyldiazoate radical. Not only is the unpaired electron assigned to a molecular orbital of \( \sigma \)-symmetry, but the calculated hyperfine coupling constants are of the correct magnitude. No splitting is predicted or observed for the phenyl ring protons, while the ratio \( a_{N(2)}/a_{N(3)} \) of 5.9 compares with the experimentally observed one of 13.3. The **trans**-isomer is preferred to the **cis** on the basis of the calculated values of the proton hyperfine coupling constants and the ratio \( a_{N(2)}/a_{N(3)} \) for the parent HN=NO\cdot radicals and for PhN=NO\cdot itself.

Kauffmann, Friestad and Henkler\(^{55}\) assigned a **cis**-**cis** configuration to the diphenyldiazoanhydride (23)

\[
\text{Ph}-N=N-O-N=N-\text{Ph}
\]

(23)

from which the phenyldiazoate radical is formed. However, decomposition in solution to give the **trans**-diazoate is probable by analogy\(^{96b}\) with the ready interconversion of iminoxy radical isomers compared with the fixed geometry of the oximes.

The results for all the radicals studied show that the CNDO method is capable of assigning the unpaired electron to an orbital
of the correct symmetry, but that is less valuable for the
determination of splitting constants. The more sophisticated
INDO method (Intermediate Neglect of Differential Overlap)
developed more recently by Pople,\textsuperscript{142b} which includes $\sigma$-$\pi$
interaction, would be more suitable for this purpose, but the
programme is too large to be run on the IBM 360/44 computer
available for this investigation.

V \hspace{1cm} \textbf{THE MECHANISM OF THE DECOMPOSITION}

a) \hspace{1cm} \textbf{In Aromatic Hydrocarbons}

The assignment of the triplet of triplets e. s. r. signal to
the $\sigma$-phenyl diazotate radical adds support to the mechanism
originally proposed by Rüchardt (Scheme 1), but rejected by
Perkins in favour of one (Scheme 2) including the PAPN radical
as chain carrier. Consequently there are present two radicals
in the system, both of which are capable of abstracting a
hydrogen atom, and thus cleanly oxidising the phenylcyclohexadienyl
radical to biphenyl. It is thus necessary to examine the evidence
that can decide which mechanism is operable or whether or not
they are self-excluding.
The most striking feature of the e. s. r. study is the constant concentration of the phenyldiazotate (triplet of triplets) signal compared with that due to PAPN. This lends weight to the argument that the Rüchardt scheme is the primary product-forming sequence, with PAPN being formed in a side reaction.

On the other hand it has been established that nitroxides such as DPNO are capable of acting as the chain carrier radical in the decomposition of diazonium salts. Rüchardt found that the addition of catalytic amounts of hydroxypiperidine to a solution of N-nitrosoacetanilide caused rapid denitrosation of part of the nitrosamide. As the e. s. r. spectrum of DPNO was observed later in the reaction, he considered the following cycle to be in operation.

\[
\begin{align*}
\text{Ph}_2\text{NO}^+ & + [\text{PhC}_6\text{H}_5\text{H}]^+ \rightarrow \text{Ph}_2\text{NOH} + \text{PhPh} \\
\text{Ph}_2\text{NOH} + \text{PhN}_2^+ & \rightarrow \text{Ph}_2\text{NO}^+ + \text{N}_2 + \text{H}^+ + \text{Ph}^- 
\end{align*}
\]

The detection of the same signal during the decomposition of N-nitrosoisobutyranilide in benzene suggests that a similar process is at work, this time the denitrosation of the nitrosamide probably being caused by the bulk of the acyl group.

Perkins also illustrated the chain carrying potential of DPNO by studying the decomposition of benzenediazonium
fluoroborate in the presence of diphenylhydroxylamine in aromatic solvents. The biaryl isomer ratios and the DPNO e. s. r. signal indicated free radical phenylation by the above chain process. He suggested, in support of his scheme (2), that a similar cycle involving PAPN and benzenediazonium acetate was likely to be involved in the N-nitrosoacetanilide reaction.

The two schemes under consideration are in fact very similar, the differences being in the carrier radical and the initiation step. Scheme 2 requires the formation of at least some phenyl radicals from homolysis of the diazoacetate - a process which was earlier rejected in view of the minimal yields of carbon dioxide, but which is conceivable as a purely initiation reaction. The corresponding step in Rüchardt's scheme (1) involves attack by an acetate ion on the phenyl-diazoacetate to give a diazotate anion and acetic anhydride, and subsequent formation of diphenyldiazoanhydride - a compound which has been isolated from the closely related Gomberg reaction. This initiation process is also supported by the formation of carboxylic anhydrides in 0.5-3% yield from the decomposition of acylaryl nitrosamines.
In view of the evidence discussed earlier it is likely that any radical of the nitrooxide type, which is present in sufficient concentration to give an e. s. r. signal, could act as the chain carrier. Thus for the reaction in benzene or t-butylbenzene, when both the phenyldiazotate and PAPN radicals are present, schemes 1 and 2 are both possible, while in cumene, mesitylene etc. only the Rüchardt mechanism is operative.

During the decomposition of all the nitrosamides in cumene a 1:1:1 triplet e. s. r. spectrum (Fig. 5) was observed, for which $a_N = 15.00$ gauss and $g = 2.0059$. In view of the ready formation of cumyl radicals in the system, this signal was assigned to dicumynitroxide $[(\text{PhCM}e_2)_2\NO^-]$, the probable mode of formation being

$$
\text{Ph}^- + \text{PhCHMe}_2 \rightarrow \text{PhH} + \text{PhCM}e_2
$$

$$
\text{PhN(NO)Ac} \rightarrow \nm
$$

$$
\text{PhCM}e_2 + \nm \rightarrow \text{PhCM}e_2\NO
$$

$$
\text{PhCM}e_2\NO + \text{PhCM}e_2 \rightarrow (\text{PhCM}e_2)_2\NO.
$$

The formation of dialkynitroxides by this mechanism is well established, and the e. s. r. spectrum of dicumyl-nitroxide has been observed by de Boer, who found $a_N = 15.1$ gauss in cumene, and by Hoffmann, who found $a_N = 14.9$ gauss in n-heptane. Neither workers reported the detection
of the satellite lines (Fig. 12) due to $^{13}$C in natural abundance.

These splittings of 8.8, 5.2 and 2.9 gauss compare with the values of 4.38 and 4.35 gauss found for the closely related di-t-butyl nitroxide in benzene reported by Faber and by Rassat. By comparison with Rassat's results the most likely assignment is of the largest value (8.8 gauss) to the tertiary carbon atom, the 5.2 gauss to the methyl carbons and the smallest (2.9 gauss) to carbon atoms in the phenyl ring.

The decomposition of N-nitrosoformanilide in cumene proved anomalous in that there was no sign, not only of PAPN, but also of the phenyl diazotate radical. Instead two new signals, in addition to that due to dicumyl nitroxide were observed. The first (Fig. 19) was a triplet of triplets ($a_N = 18.10$ gauss, $a_N = 1.36$ gauss, $g = 2.0059$) very similar to that reported by Perkins for (N-phenylacetamido)-t-butyl nitroxide, and was thus assigned to the (N-phenylformamido)cumyl nitroxide which would result from the addition of a cumyl radical across the nitroso group of N-nitrosoformanilide. The second new signal (Fig. 20) appearing later in the reaction and lasting several days, showed hyperfine structure due to the five protons of a phenyl ring and one nitrogen. The coupling constants of this signal are
identical to those observed for the stable radical formed during
the azobisisobutyronitrile-catalysed oxidation of aniline, the
reaction of t-butylhydroperoxide with phenylhydroxylamine or
triphenylhydrazine, the reaction of nitrosobenzene with
sodium methoxide in methanol and the reaction of sodium
dithionite with nitrosobenzene. Several authors assigned this signal to the radical PhNOH, or to a time average
of PhNOH and PhNHO·. However, Russell considered that
the stability of this ubiquitous species and the absence of a
hydroxyl proton splitting, although such a coupling (a_H = 0.38
gauss) can be detected for PhNO2H, made this assignment
improbable and a more likely structure was PhN(O')OX where
X = PhNH. The a_N value of 14.9 gauss reported by de Boer for PhN(O')OBu is much larger than the value of 11.69 gauss
observed for the N-nitrosoformanilide system and makes the
structure of Ph-N(O')OCMe2Ph unlikely. While the alkylaryl-
nitroxide PhN(O')OCMe2Ph is a possibility, the structure assigned
by Russell seems the most probable.

b) In Diethyl Ether

The e.s.r. spectra observed during the decomposition of
N-nitrosoacetanilide in diethyl ether were characterised by the
absence of the triplet of triplets and the detection of another unreported signal in addition to that due to PAPN. This new signal (Fig. 7) showed hyperfine structure due to coupling with two nitrogen nuclei and one proton, and is assigned to the nitrooxide radical formed by the addition of the 1-ethoxyethyl radical, resulting from the abstraction of a hydrogen atom from the $\alpha$-carbon atom of the ether, across the NO group of the nitrosamide.

\[
\text{MeCHOEt} + \text{N}=\text{O} \quad \rightarrow \quad \text{Me}^\bullet\text{EtO}^-\text{CH-N-O}^\bullet
\]

\[
\text{Ph-N-Ac} \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{Ph-N-Ac}
\]

A similar nitroxide spectrum was detected by Chachaty and Forchioni\textsuperscript{172} during the photolysis of nitroalkanes in tetrahydrofuran, the coupling constants being $a_N = 14.7$ gauss and $a_{H(\text{THF})} = 6.9$ gauss. By analogy the signal observed for N-nitrosoacetanilide-diethyl ether showed coupling with the nitrogen of the nitroxide group ($a_N = 15.4$ gauss), with the nitrogen of the acetamido group ($a_N = 1.4$ gauss) and the $\alpha$-alkoxyalkyl proton ($a_H = 5.8$ gauss). Smaller couplings with the protons of the rest of the solvent residue and of the phenyl ring probably account for the large linewidth of 0.6 gauss. Thus the e. s. r. study of this reaction illustrates the intermediacy of
SCHEME 4

N-Nitrosoacetanilide in Diethyl Ether

\[
\text{PhN(NO)Ac} \rightarrow \text{PhN}_2^+ \cdot \text{OAc}
\]

PhN(NO)Ac

\[
\text{PhN(NO)Ac} \rightarrow \text{PAPN (e. s. r.)}
\]

PhN(NO)Ac

\[
\text{Ph} \leftarrow \rightarrow \text{N}_2 \quad (59\%)
\]

PhH

\[
\text{PhH} \rightarrow \text{MeCHOEt}
\]

(52%)

MeCHO + Et

(50%)

MeCHO Et

Me

\[
\text{EtO} \longrightarrow \text{Ph-N-Ac (e. s. r.)}
\]

Me

\[
\text{CH-N-O}^* \quad (22\%)
\]

Me

\[
\text{CHOEtAcO}^-\cdot
\]

Me
both the phenyl and $\alpha$-alkoxyalkyl radicals, each being detected as a result of the scavenging properties of the nitroso group of the nitrosamide.

Denney, Gershman and Appelbaum\textsuperscript{49} studied the products of the reaction and found benzene (52%), nitrogen (59%), 1-ethoxyethyl acetate (22%) and acetaldehyde (50% as the 2,4-dinitrophenylhydrazone derivative).

The formation of these products and the observation of the e. s. r. signals can be rationalised in terms of the free radical chain process outlined in scheme 4. The mechanism involves the cycle proposed by Rüchardt\textsuperscript{169} for the reaction of diazonium salts with 1, 3-dioxalane, in which there is an electron transfer from the $\alpha$-alkoxyalkyl radical to the diazonium ion to form a carbonium ion and a diazo radical, which then decomposes to give phenyl and nitrogen.

The initiation step providing the first phenyl radical may involve partial homolysis of the phenyldiazoacetate (2.6% carbon dioxide was isolated\textsuperscript{39} from the reaction in dioxan), or proceed via diazoanhydride formation as proposed for aromatic hydrocarbons.
204.
c) **In Alcohols**

The detection of the PAPN e. s. r. signal during the decomposition of N-nitrosoacetanilide in alcohols indicates that a free phenyl radical is also involved in this system. The failure to detect the phenyldiazotate triplet of triplets signal and the formation of the product benzene only by the abstraction of $\alpha$-hydrogen atoms, as indicated by the formation of $<1\%$ $C_6H_5D$ from the reaction in EtOD\textsuperscript{177} suggests a mechanism similar to that proposed for ether solvents. Thus the observed products, benzene, nitrogen, acetic acid and ketone could be formed in the following chain sequence.

\[
\begin{align*}
\text{Ph}^- + R_2\text{CHOH} & \rightarrow \text{PhH} + R_2\text{COH} \\
R_2\text{COH} + \text{PhN}_2^+ & \rightarrow \text{PhN}_2^- + R_2\text{COH} \\
\text{PhN}_2^- & \rightarrow \text{Ph}^- + N_2 \\
R_2\text{COH} + \text{AcO}^- & \rightarrow R_2\text{C}:O + \text{AcOH}
\end{align*}
\]

This scheme receives added support from Huisgen's study of the decomposition of o-methyl-N-nitrosoacetanilide. In chloroform indazole resulted in almost quantitative yield, but in ethanol a high yield of acetaldehyde was given, with negligible formation of indazole: thus oxidation must have been achieved at the expense of cyclisation by some species containing nitrogen.
The electron transfer process outlined above would account for these results.

The variation in the intensity of the PAPN signal for the series of solvents can be rationalised in the same way as for the aromatic hydrocarbons. The intensity decreases with increasing stability of the solvent residue radical, suggesting removal of the nitrooxide by the coupling reaction.

The fact that satisfactory mechanisms can be proposed for the reaction in both ethers and alcohols, which do not involve PAPN as the chain carrier, and yet its e.s.r signal is detected in each case, supports the proposal that its formation may only be a non-product-forming side reaction.

d) In Halogenated Solvents

The anomalous nature of the decomposition of acylaryl-nitrosamines in halogenated solvents was described in the Introduction to this thesis. Despite exhaustive study no mechanism has been proposed which can accommodate all the experimental observations, and it has been in doubt\(^{68}\) whether free radicals were involved in the reaction.

The detection of the phenyldiazotate e.s.r. signal establishes the free radical nature of at least part of the process and suggests
a mechanism similar to that considered for benzene. Also comparable to the aromatic hydrocarbon system is the complete or partial suppression of the PAPN signal summarised in the list below.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PAPN</th>
<th>PhN=NO·</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄, BrCCl₃</td>
<td>nil</td>
<td>weak</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>weak</td>
<td>weak</td>
</tr>
<tr>
<td>CHBr₂·CHBr₂</td>
<td>nil</td>
<td>weak</td>
</tr>
<tr>
<td>C₂H₅Br</td>
<td>medium</td>
<td>weak</td>
</tr>
</tbody>
</table>

The constant intensity of the diazotate signal indicates that this radical is involved in the major product forming sequence, rather than PAPN. The latter is either removed by coupling with the solvent residue radical, thus explaining the failure to

\[
\text{e.g. } \quad \text{Ph}^* + \text{CCl}_4 \rightarrow \text{PhCl} + \cdot \text{CCl}_3
\]
\[
\text{Ph-N-O}^* + \cdot \text{CCl}_3 \rightarrow \text{Ph-N-O-CCl}_3
\]
\[
\text{Ph-N-Ac} \quad \text{Ph-N-Ac}
\]

isolate hexachloroethane, or is only formed in small quantities due to competition for the phenyl radical with the abstraction process.
The detection of the phenyldiazotate e.s.r. spectrum and
the isolation of 0.5 to 3% carboxylic anhydrides strongly
supports an initiation process similar to that proposed for
aromatic hydrocarbons

$$\text{PhN(NO)Ac} \rightarrow \text{PhN:NOAc} \rightleftharpoons \text{PhN}_2^+ - \text{OAc}$$

$$\text{AcO}^- + \text{PhN:NOAc} \rightarrow \text{PhN}_2\text{O}^- + \text{Ac}_2\text{O}$$

$$\text{PhN}_2^+ + \text{PhN}_2\text{O}^- \rightarrow \text{PhN}_2\text{ON}_2\text{Ph}$$

$$\text{PhN}_2\text{ON}_2\text{Ph} \rightarrow \text{Ph}^* + \text{N}_2 + \cdot\text{ON:NP}$$

The observation that in carbon tetrachloride at
room temperature half the total nitrogen is evolved and
benzene diazonium chloride is precipitated, while at higher
temperatures this diazonium salt decomposes to give the
remainder of the nitrogen, suggests that only the first stage
is an entirely radical process.

The production of carboxylic acids has been explained by the abstraction of an acidic α-proton from the diazonium
salt by the carboxylate ion, but the formation of diazonium halides still requires further investigation.
CONCLUSION

The work described in this thesis has been concerned with the e.s.r. spectra observed during the decomposition of acylarylnitrosamines in four series of solvents, and with the information that these provide in the determination of the reaction mechanism.

In aromatic hydrocarbons two signals were observed. The first was that originally detected by Rüchardt and assigned by Perkins to (N-phenylacetamido)phenylnitroxide. This has been confirmed by McLachlan molecular orbital calculations and by studying the effects on the spectrum of varying the aryl and acyl groups of the nitrosamide. It was thus established that the radical behaves as a typical π-nitroxide by comparison with the results of similar studies on phenyl-nitroxide and diphenylnitroxide. The second signal, consisting of a 1:1:1 triplet of 1:1:1 triplets was attributed to phenyl-diazotate (σ) by analogy with the related iminoxy radicals. The results of the CNDO calculations performed on PhN=NO· and PhCH=NO· support this assignment while only approximate estimates of the splitting constants were possible, the location of the unpaired electron in an orbital of σ-symmetry was firmly
established. Further confirmation must await generation of the radical by other means, such as oxidation of the phenyl-
diazotate anion by electrochemical or flow techniques. In contrast to the results for the $\text{TT-PAPN}$ radical, variation of the aryl and acyl groups had little or no effect on the e. s. r.
spectrum of this radical. Although the e. s. r. signals observed in benzene and t-butylbenzene support both the mechanism of Rüchardt (Scheme 1, opposite p.153) and Perkins (Scheme 2, opposite p.156), the failure to detect the signal from the chain carrier radical of the latter scheme for the decomposition in cumene, mesitylene, etc. makes the former the more likely product-forming sequence for the whole series of solvents.

In ethers the e. s. r. study confirmed the presence of phenyl and $\alpha$-alkoxyalkyl radicals by the detection of signals attributable to the nitroxides formed by addition of the radicals across the nitroso group of the nitrosamide. The mechanism proposed, which is also applicable to the reaction in alcohols, involves, in the chain process, an electron transfer step.

$$\text{PhN}_2^+ + \text{RCHO} \rightarrow \text{Ph}^- + \text{N}_2 + \text{RCHO}^+$$

This scheme is supported by the isolation of the ester $\text{RCH(OAc)OR}$
formed by the combination of the carbonium and the acetate ions.

No satisfactory explanation has been found for the decomposition in halogenated solvents, nor for the e. s. r. signal observed during the reaction of aniline and pentyl nitrite. The study of these two systems and of the nitrosamide reactions in the presence of aryne traps will provide scope for investigation for some time to come.
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