Electron Spin Resonance Studies of some Radicals

formed from Substituted Hydroxylamines

A Thesis submitted to the University of London

for the Degree of Doctor of Philosophy

by

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May, 1965

Battersea College of Technology

London, S.W.11.
Abstract

The Electron Spin Resonance spectra of radicals prepared from compounds derived from N-aryl substituted hydroxylamines have been studied. The preparative details together with certain analytical evidence in favour of the proposed structures are given.

The coupling constants have been obtained and show that, in one series of compounds, hyperconjugative coupling between remote parts of the molecule takes place. A steric effect has been observed from radicals derived from N-ortho-methylphenylhydroxylamines while the effect of other ring substituents has also been considered. The effect of the second N-substituent on the coupling constants has been studied and is seen to have little effect on the relative spin densities of the aromatic proton and nitroxide nitrogen nuclei.

After an introductory section and one devoted to the basic theory, a section is included which describes the construction and use of a spectrometer.
Preface

The work described in this thesis was carried out in the laboratories of the Department of Spectroscopy and Chemical Physics, Battersea College of Technology, under the supervision of the Head of Department, Professor V.S. Griffiths.

The author wishes to express his appreciation of the continual encouragement and help received from Professor Griffiths during the course of the work and to many of his colleagues for their useful help and advice.

A Scholarship from the Governors of Battersea College of Technology and a subsequent Research Assistantship are gratefully acknowledged.

Thanks are also due to Mrs. S.J. McCann for typing the script.
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SECTION 1

INTRODUCTION
This thesis includes an account of work undertaken to investigate the electron spin resonance (ESR) spectra of various organic free radicals. The work is conveniently considered in three parts: (a) the construction of an ESR spectrometer, (b) the preparation of the free radicals, and (c) the interpretation of the ESR spectra. The thesis also includes a section giving some of the basic theory of ESR.

The construction and use of an ESR spectrometer is reported, the design being that of a conventional radio-frequency field modulated instrument. Certain simplifications in design are described, which were made possible by the restricted nature of all the radicals investigated, while a high field homogeneity for a small (4 inch) magnet was made necessary due to the narrowness of the hyperfine structure in many of the spectra. Detailed descriptions of the circuits constructed are given, together with brief accounts of some of the commercial equipment obtained and built into the spectrometer. Nearly all the ESR spectra considered were run on this equipment. It is stated in the text where another instrument was used.

The preparation of the various free radicals followed similar routes in each case. N,N disubstituted hydroxylamines with the general formula ArN(OH)R were prepared from various N-arylhydroxylamines ArNH₂OH. Oxidation removed the labile hydroxyl hydrogen to produce nitroxide free radicals ArNOR with one unpaired electron per molecule located classically in the oxygen. Conjugation with
the aromatic ring ensures the stability of these species. All the radicals studied were of this form, the group R depending on the compounds used to condense with the aromatic hydroxylamines.

The condensing compounds were: acetone and deuterated acetone, aromatic iso-cyanates, phenyl-chloroformate and benzoic anhydride. With the first three of these, aromatic hydroxylamines with ring substituents as well as the basic phenyl compound were used while in the latter cases only the basic phenyl compounds were prepared.

As all the preparations involved the initial formation of one of twelve N-arylhdroxylamines, a section on the preparation of these rather unstable compounds is given. The preparations of the subsequent 'condensation products' are dealt with under separate sections together with certain analytical evidence in support of the various proposed structures.

The related free radicals were all formed by the mild oxidation of the condensation products in chloroform solution with ammoniacal silver nitrate. The only radicals previously reported and studied by ESR were some of those prepared from acetone.

The final part of the work is the investigation of the ESR spectra. These are considered under different sections, the divisions being dictated by the various condensing agents used to give the different N-substituent groups, R. However, the
spectra all had some similarities in that their hyperfine structures indicated a strong coupling of the unpaired electron to one nitrogen nucleus with a smaller coupling to the attached aromatic ring protons. A section is devoted to comparing the results from the various different compounds.
SECTION 2

E.S.R. THEORY
1. GENERAL

The theory of electron spin resonance (ESR) has been extensively treated in review form (1, 2) - only those parts of it which are essential for the understanding of the systems under consideration will be given in the present section.

2. PRINCIPLES OF ESR

In all paramagnetic materials there exist one or more unpaired electrons per molecule in addition to the more 'normal' paired electrons of the bonding, 'covalent' or 'ionic' type, as well as the closed shell electrons and the non-bonding p and \( \pi \) systems.

In ESR, only transitions involving the energy states of the unpaired electrons are directly observable, and consequently only paramagnetic materials may be studied by the technique. Among the many classes of such compounds are organic and inorganic free radicals, some inorganic crystalline materials, the products of irradiation of solids and semisolids, conduction electrons in metals, triplet state molecules and some biological systems. Of these, only the first, namely organic free radicals, will be considered in the present thesis.

A free electron has a spin angular momentum \( S = \sqrt{s(s+1)} \frac{h}{2 \pi} \), where \( s = \frac{1}{2} \) is the spin quantum number and \( h \) is Planck's constant. Associated with this is a magnetic moment \( \mu_s = -g \beta \sqrt{s(s+1)} \), where \( g \) is the spectroscopic splitting
factor which for the free electron has the value 2.0023 (3) and $\beta$ is the Bohr Magneton which takes the value of $0.92732 \times 10^{-20}$ erg per gauss (4).

In an applied field $H$ gauss (this unit should, strictly, be the oersted, however the less accurate but more usual 'gauss' will be used in the present work for the magnetic field strength), the magnetic moment orients itself such that its component in the field direction $\mu_H$ takes up the value $-g\beta m_s$, where $m_s$ is the magnetic spin quantum number and which for a single electron can only take the values $\pm \frac{1}{2}$. The energy $\mu_H^2$ associated with the magnetic moment in the field is given by $-\mu_H^2 H$ and can only take the two values $\pm \frac{1}{2}g\beta H$.

The direction of the spin angular momentum and the magnetic moment $\mu_s$ will precess about the field direction with the Larmor frequency

$$\gamma_L = \frac{eH}{4\pi mc} = \left( \frac{g\beta}{h} \right) H \quad ---- (1)$$

The energy difference $\Delta E$ between the two orientations of the magnetic moment in the field is clearly $2\sqrt{\mu_s^2} = g\beta H$ and transitions between these two states will be associated with the emission or absorption of radiation of frequency $\gamma$, such that

$$h \gamma = g\beta H \quad ---- (2)$$

which is seen to be the same as that of the Larmor precession.
If, to the electron in the magnetic field, radiation is applied with its magnetic vector polarised perpendicular to the field direction, it is possible to induce transitions between the two energy states.

These transitions, in the 'up' and in the 'down' direction, will take place with equal probability. However, due to the normal Boltzmann distribution of populations in different energy levels, the number of transitions actually taking place in the up direction - that is from lower to higher energies - will predominate and a net absorption of energy from the incident radiation will take place. This net absorption will continue until the populations in the two levels are equal when the system is said to have become saturated. If, however, by some means the thermal equilibrium for non-saturation can be maintained, then the absorption of energy could continue indefinitely. The excess population in the higher energy state loses its energy by various non-radiative transitions back to the ground state, thus enabling absorption of incident radiation to continue. Mechanisms for these relaxation processes are described later in this section.

If the applied radiation has frequency $\nu$ and the field magnitude is lower than is required for equation (2) to be satisfied then no resonance will be observed. On slowly raising the value of the field, the Larmor frequency increases until, at the resonant value of $H$, the applied radiation couples with the precessing magnetic dipoles and transitions take place, being observed in practice as an absorption of radiation.
It is convenient to work with magnetic field strengths of about 3, 200 gauss; the corresponding radiation frequencies are about 9, 300 Mc/s in the microwave region of the spectrum.

The main parameters which may be extracted from ESR spectra are:

(a) Fine structure
(b) g value
(c) Hyperfine structure
(d) Line shapes and widths

3. **FINE STRUCTURE**

The fine structure is the term given to the spectral lines produced by the splitting of the electronic spin levels in the molecule in the absence of an applied field. This is observable only when there are more than one unpaired electrons per molecule and is therefore unimportant in free radical studies. It will not be considered further.

4. **g VALUE**

The spectroscopic splitting factor, or g-value, determines the centre of the resonance in terms of the ratio of the microwave frequency \( \nu \) and the magnetic field \( H \). In inorganic compounds, large variations in the g-value are obtained resulting from variations in spin/orbit coupling. However, its magnitude lies
within 1\% of the free electron value of 2.0023 in all organic free radicals containing only first-row elements. It is therefore a rather non-specific and unimportant parameter in the present work. The details of a determination of g are given in Appendix I for one radical and it is confirmed here that all others lie within the above mentioned range.

5. HYPERFINE STRUCTURE

The hyperfine structure and splitting is by far the most important parameter in this work and will be considered in some detail.

In the second part of the present section it was shown that the basic ESR phenomenon could be expressed by the equation $h \gamma = g \beta H$. This gives rise to a spectrum consisting of one line and examples of this may be observed, in particular with stable free radicals in the solid phase, e.g. diphenyl picryl hydrazyl (DPPH).

Hyperfine splitting in molecules arises from the interaction of the unpaired electron with neighbouring magnetic nuclei, a table of the more important is given (Table 1), and may be observed if the free radicals are studied in dilute solution, the solvent being diamagnetic.

There are two main hyperfine effects which may be described as the 'dipole-dipole' or anisotropic hyperfine interaction and the 'Fermi contact' or isotropic hyperfine interaction.
Table 1
Table of Some Magnetic Nuclei

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance (%)</th>
<th>Spin Quantum Number</th>
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<tr>
<td>$^1\text{H}$</td>
<td>99.98</td>
<td>1/2</td>
</tr>
<tr>
<td>$^2\text{D}$</td>
<td>$1.56 \times 10^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>1.1</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{14}\text{N}$</td>
<td>99.3</td>
<td>1</td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td>0.36</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>$3.7 \times 10^{-2}$</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{33}\text{S}$</td>
<td>0.76</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{35}\text{Cl}$</td>
<td>74.5</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{37}\text{Cl}$</td>
<td>24.6</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{79}\text{Br}$</td>
<td>50.6</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{87}\text{Br}$</td>
<td>49.4</td>
<td>3/2</td>
</tr>
</tbody>
</table>
The first, the anisotropic interaction, arises from the effect over space of
the magnetic moment of the nucleus under consideration upon the magnetic moment of the unpaired electron. The energy of interaction may be given in the form
\[ \mathcal{H} = B(3\cos^2 \Theta - 1), \]
where \( \Theta \) is the angle between a fixed direction in space and an axis joining the two dipoles within the molecule and \( B \) is directly proportional to \( 1/r^3 \), \( r \) being the distance between the two dipoles.

The mean value of \( 3\cos^2 \Theta - 1 \) may be shown to be zero, so that if the molecule is randomly tumbling in all directions for a sufficient period the axis will point through all equal surface elements of a unit sphere with equal probability. In this event, the Hamiltonian interaction energy \( \mathcal{H} \) reduces to zero in value.

This is the situation which arises in solutions of sufficiently low viscosity to allow the tumbling motion of the paramagnetic molecules to average the Hamiltonian function to zero during the relaxation time of the unpaired electron. In order to simplify the effects due to hyperfine interaction nearly all the present work has been carried out using solutions in low viscosity solvents at room temperature.

The second hyperfine effect - the Fermi contact or isotropic interaction - arises from the direct contact of the unpaired electron with the various nuclei in the molecule. For this contact to be made the unpaired electron must have a finite probability of being in the \( s \) atomic orbitals of the nuclei in question, this being due to the fact that only \( s \) orbitals have finite electron densities at the nuclear site.
The interaction of electron and nucleus by this contact process is direction-independent and does not therefore average to zero with rapid molecular tumbling. It is this isotropic hyperfine interaction which is directly observable in the ESR spectra of organic free radicals in solution, and is used to provide information about the magnetic environment of the unpaired electron’s orbital.

The interaction energy is written as

\[ \mathcal{H} = \frac{8\pi g_\text{E} \beta}{3} \left( \frac{\mu_n}{I} \right) \sum SI \delta(r) \]

where \( \delta(r) \) is the Dirac delta function of the distance \( r \) between the electron and the nucleus and has zero value when \( r \) is non-zero, \( S \) is the electron spin quantum number and \( I \) the nuclear spin quantum number.

The equation may be rewritten as

\[ \mathcal{H} = \frac{8\pi g_\text{E} \beta}{3} \gamma \psi_0^2 S \cdot I \]

where \( \gamma \) is the magnetogyric ratio of the nucleus and \( \psi_0^2 \) is the probability of finding the electron at the nucleus, this being the property of chemical interest.

Writing this equation as

\[ \mathcal{H} = A S \cdot I \]

then in a magnetic field the values of \( S \) and \( I \) which are relevant to the present
problem are given by $m_s$ and $m_I$. For an ESR transition $|\Delta m_s| = 1$, that is from a state $m_s = +\frac{1}{2}$ to $-\frac{1}{2}$ and $|\Delta m_I| = 0$, the total spin Hamiltonian (ignoring anisotropy) is

$$\mathcal{H}_{\text{Total}} = g \beta H_0 m_s + A m_s m_I$$

and

$$\Delta E = \mathcal{H}(+) - \mathcal{H}(-) = g \beta H_0 (+\frac{1}{2} - (-\frac{1}{2})) + A (+\frac{1}{2} - (-\frac{1}{2}))m_I = g \beta H_0 + Am_I$$

The effect of a magnetic nucleus with spin $= I$ can now be seen.

Taking one nucleus with $I = \frac{1}{2}$, i.e. $m_I = \pm \frac{1}{2}$, it can be seen that there will be two values of $\Delta E$ — that is two transitions with energies given by

$$\Delta E_1 = g \beta H_0 + \frac{1}{2} A$$

and

$$\Delta E_2 = g \beta H_0 - \frac{1}{2} A$$

It was seen (equation 2) that the microwave frequency and the magnetic field strength were directly proportional and hence we can rewrite these equations as

$$\Delta E = h \gamma \omega = g \beta H^+ - \frac{1}{2} A$$
and therefore the two values of magnetic field corresponding to a resonance at constant frequency \( \gamma_o \) are

\[
H = \frac{1}{g \beta} \left( h \gamma_o \mp \frac{1}{2} A \right)
\]

This is convenient due to the relative ease with which the field may be varied and the frequency kept constant.

For free radical species, \( A = g \beta \left( \frac{8 \pi X \Psi (0)}{3} \right) \) is considerably smaller than \( h \gamma_o \) - i.e. about 1% or less - and consequently the magnetic fields in the two cases are similar which means that the Boltzmann distribution in the two cases is also the same - hence the probabilities of the transitions and their intensities will be equal.

The separation between the two components of the doublet so formed is \( \frac{A}{g \beta} \) and it is seen to be directly proportional to \( \Psi (0)^2 \).

For two equivalent nuclei with \( I = \frac{1}{2} \) there will be three ways of writing the total \( \sum m_I \) value - that is +1 (spins ++), 0 (spins + - or - +) and -1 (spins --).

Thus three different values of \( \Delta E \) and \( H \) may be written, viz

\[
\Delta E = g \beta H_o \mp A \quad \text{or} \quad g \beta H_o
\]

and

\[
H = \frac{1}{g \beta} \left( h \gamma_o \mp A \right) \quad \text{or} \quad \frac{1}{g \beta} \left( h \gamma_o \right)
\]
Once more the $\Delta E$ values are separated from each other by $A$ the contact interaction constant, or when considering a changing magnetic field by $A/g\beta$, but in this case the central transition is twice as probable and hence results in a line twice as intense as the outer two. This is due to there being two ways of combining the spins for $\sum m_1 = 0$ but one way only for the values $\pm 1$.

In this manner it may be shown that for $n$ equivalent spin $I = \frac{1}{2}$ nuclei, there will be $n + 1$ hyperfine components, separated from each other by $A$ the interaction constant centred on the original unperturbed $(g\beta H_0)$ position and with intensity distributions following the binomial series.

It may also be shown that for one nucleus per molecule with $I = 1$ there will result three equal intensity hyperfine components with separations equal to their interaction constants. In general there will be $(2nI + 1)$ components resulting from $n$ equivalent nuclei with spins $= I$.

When there are two or more groups of non-equivalent nuclei the Hamiltonian has to include components from each group. Thus

$$\mathcal{H} = g\beta H_0 + A_1 \sum m_{I(1)} + A_2 \sum m_{I(2)} + \ldots$$

from which it is clear that for every hyperfine component of nucleus (1) there will be $2nI_1 + 1$ components from nucleus (2) and so on. The total number of hyperfine lines (neglecting accidental degeneracies) is $\prod_i (2nI_i + 1)$ for $i$ sets of different nuclei.
Having described the effect hyperfine interactions have on the spectra, a short account of the mechanisms of these interactions is now given.

**Configurational Interaction**

In a highly conjugated free radical such as an aromatic anion where there is a large degree of electronic delocalisation within a $\pi$ system, an unpaired electron should, in principle, be able with ease to spread itself over a considerable number of atoms within that molecule. If the unpaired electron orbital extends to the $\pi$ system and is delocalised within it, there is no direct way in which it may interact with nuclei to give isotropic hyperfine structure, due to there being a node in the $\pi$ orbital along the nuclear plane. However, it is well known (5) that in such molecules a large isotropic hyperfine interaction with the ring protons is observed. The mechanism used to explain this is configurational interaction.

Assume an unpaired electron to be situated in a $p$ orbital of an $sp^2$ carbon atom. The ground-state wave function of the $p$ electron will not be capable of mixing with those bonding $sp^2$ electrons. However, if the excited-states are considered, admixing of the various wave functions becomes possible and a part of the unpaired electron's orbital wave function is present in the carbon $s$-atomic
orbital. This has a finite density at the carbon nucleus and explains how the observed hyperfine coupling to the ring $^{13}$C nuclei (3) may take place. Coupling to the attached ring protons is also possible due to the overlap of the hydrogen s-orbital with the carbon sp$^2$ lobe to form a σ bond. This has a finite electron density at the hydrogen nucleus and, due to the admixing of ground and excited states mentioned above, this configurational interaction does enable the unpaired electron to interact isotropically with the various ring protons.

According to the now widely accepted equation $a_H = Q \rho$ (7) the isotropic proton hyperfine interaction ($a_H$), known also as the coupling constant, is seen to be directly proportional to the unpaired electron spin density ($\rho$) at the carbon atom. $Q$ is an approximate constant with a value lying between about 22 and 28 gauss for most aromatic hydrocarbons.

This coupling constant, measured in gauss, is related to the hyperfine interaction energy ($A$) by the equation $a_H = A/g\beta$ and is the parameter measured and quoted in this present work.

In the case of radicals containing hetero atoms, the relation between the coupling constant ($a$) and the spin density ($\rho$) on any particular nucleus is not so simple as with hydrocarbons. However the coupling constant to a nucleus is still directly proportional to $\psi^2(o)$ and therefore has meaning if the values to corresponding nuclei in related compounds only are compared.
Hyperconjugation

The effect on the ESR spectrum of a methyl group as an aromatic ring substituent is now considered.

In practice there is ample evidence (9, 9 and 10) to show that the coupling constants of such \( \beta \) protons is comparable to those of the replaced \( \alpha \) ring protons and any proposed mechanism must take into account the magnitude of the empirical values of the coupling constants.

The concept assumes an overlap of the planar \( \pi \) orbital (2p\( \pi \) of the contiguous carbon atom) with a pseudo \( \pi \) orbital consisting of the three methyl proton 1s orbitals. Any unpaired electron spin density in the carbon p-orbital is therefore able to delocalise onto the methyl proton system where it is able to interact magnetically with the protons by the Fermi contact process mentioned above. This produces an isotropic interaction which does not average to zero either by the molecule's tumbling or by the methyl group's rotating relative to the rest of the molecule.

Unhindered methyl groups rotate rapidly \((10^9 \text{ c/s is normal at room temperature})\) and this time averages the coupling to each proton of the group and all become equivalent. The effect is to produce a hyperfine splitting and a 1:3:3:1 quartet is produced in place of the aromatic proton's doublet.
The coupling constant for a given nucleus was shown earlier in this section to obey an equation of the form \( A = \frac{3\beta}{2} \gamma \psi^2(\phi) \). On substituting deuterium for hydrogen in a molecule it is reasonable to assume that the wave function \( \psi^2(\phi) \) of the unpaired electron at the nucleus remains the same. Likewise the spin orbit coupling remains constant and ensures that the g value is unaltered. The ratio of the coupling constants of deuterium and hydrogen at equivalent molecular sites is therefore given by:

\[
\frac{A_D}{A_H} = \frac{\gamma_D}{\gamma_H} \frac{I_D}{I_H} \frac{1}{1.0 \times 2.79} = 0.154
\]

Substitution with deuterium thus reduces the coupling constant by a factor of greater than six. The number of components, on the other hand, increases from two to three due to the difference in the value of I, causing a reduction in the spectral intensity of individual components.

This is a convenient way of identifying an assignment for a given coupling constant and has been used frequently.

6. **LINE WIDTHS AND LINE SHAPES**

The shape of an ESR line arising from a free-radical in solution is Lorentzian (11) and is described by a plot of absorption intensity \( g(\nu - \nu_0) \) against frequency \( \nu \) satisfying the equation:

\[
g(\nu - \nu_0) = \frac{T_2}{\pi (1 + (\nu - \nu_0)^2 T_2^2)}
\]
where $T_2$ is the line width parameter which has the dimensions of time. The line width at half height is $2/T_2$. (It is convenient to use frequency ($\nu$) rather than magnetic field ($H$) in this context, it was seen earlier that they are equivalent).

Instrumentally, the first derivative of the absorption intensity is displayed and the width between the extrema (the points of maximum and minimum slope on the absorption-frequency curve) is $2/\sqrt{3} T_2$ being the dimension referred to as the line width in the present work.

The line width parameter has two main components, $T_1$ and $T'_2$ related by the equation $\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T'_2}$. $T_1$ is known as the spin-lattice relaxation time and is a measure of the rate at which the system reapproaches the Boltzmann distribution of spin populations, after its having been disturbed.

In practice this means that for narrow lines (large values of $T_1$) there is a tendency to saturate the system if too large a microwave power is used, because the rate at which the energy levels are forced towards a state of equal populations is only opposed by the spin lattice relaxation time.

The second component of the line width parameter is the transverse relaxation time $T'_2$, which is a measure of any fluctuations in the positions of the energy levels involved. It measures the rate at which the electron magnetic dipoles,
precessing about the field, lose their phase relationship and is greatly affected by the homogeneity of the applied magnetic field. The greater the variation of instantaneous field strength over the volume of the sample within the absorption cavity, the smaller will be the value of \( T'_2 \) (and hence \( T_2 \)), \( T_1 \) being constant, and the greater will be the line width. One attempts, therefore, to make the field homogeneity sufficiently uniform for other line broadening mechanisms to predominate.

It has just been shown that the homogeneity of the applied magnetic field may have an important broadening effect on ESR lines, however other factors do contribute and may broaden the lines sufficiently for resolution of the individual components to be lost completely.

It has been shown (12) that the effect of dissolved oxygen on the line widths is most marked, broadening the component hyperfine structure many hundred times. The mechanism by which oxygen (a triplet state molecule with two unpaired electrons) broadens the hyperfine components is via an exchange process between the magnetic dipoles. This is complex and affects both \( T_1 \) and \( T'_2 \). Exchange broadening of the hyperfine components of an ESR spectrum for a free radical in solution is also to be seen when the concentration of the radical is increased to the point when the dipole–dipole interaction between unpaired electrons in neighbouring molecules becomes sufficiently great.
These two effects must be avoided if well resolved spectra are to be studied, hence it is essential that the radical solutions be thoroughly deoxygenated and be sufficiently diluted with a diamagnetic solvent to reduce the exchange effects.

The effect of a viscous solution slowing down the Brownian movement of the radicals and so exhibiting some anisotropic hyperfine structure has been described. Any anisotropic structure present will have the effect of smearing out the isotropic lines and result in a net broadening of the spectrum. At room temperature most of the common organic solvents are sufficiently non-viscous for the anisotropic effect to be negligible.

The last process that can affect the broadness of the lines and hence the resolution of finely spaced hyperfine components is 'modulation broadening'. This arises due to the experimental convenience of modulating the static magnetic field at a frequency of the order of 100 kc/s. If the amplitude of the modulation exceeds about one third of the line width then a broadened line will result. Likewise, if the line width (measured in frequency units) is comparable to 100 kc/s then broadening due to unresolved sidebands at that frequency will result. As this corresponds (in field units) to about 35 milligauss it has an insignificant effect on the lines compared with other processes, e.g. inhomogeneities in the field.
It is seen that a compromise between high sensitivity (large modulation) and high resolution must be found in each individual case. A compromise is also found between sensitivity and resolution in the optimum concentration of the radical solution (see above).

Having considered how the relaxation times affect the line width, it is now worth examining the practical effect on spectra of line widths which are comparable to the line separations.

Instrumentally the derivative of the absorption curve is displayed giving a plot of the slope of the absorption envelope. Fig. 1 shows the relation between a Lorentzian shaped line and its first derivative. In Fig. 2 three cases with different line width/line separation ratios have been illustrated with their corresponding derivative curves. It is clear that it is only when the separation (a) is very nearly the same as the width (w) that resolution is completely lost. In the cases where a is less than w but greater than zero, the resultant line is broader than the components but does not have the gross distortion seen when a approximately equals w.
Fig. 1 Lorentzian Line and First Derivative
Fig. 2  Line Width/Line Separation Variations
SECTION 3

EXPERIMENTAL PROCEDURE
1. **SAMPLE PREPARATION**

**Purification of Solvents**

The solvent used in nearly all the ESR sample preparations was dioxan, which was purified carefully. The procedure was as follows:

Into a 250 ml flask was placed 150 - 200 ml of dioxan (B.D.H. Laboratory Reagent quality) and about 3 - 5 g of sodium. The mixture was heated and the solvent refluxed for about 30 - 45 minutes when it was allowed to cool. The liquid was filtered off from a brown resin into another flask and the refluxing repeated with fresh sodium for a further 15 - 30 minutes. In general no further formation of resin was observed. The pure dioxan was distilled off directly from the mixture, the apparatus having been flushed through with nitrogen, and stored in a dark bottle under nitrogen. The last 20% of liquid was not distilled to avoid concentrating any peroxides which may have been present.

The dioxan so prepared was used without any further purification.

Other solvents that have been used are chloroform, tetrahydrofuran and dimethoxy-ethane. These solvents were of the standard 'Laboratory Reagent' quality and were purified as required.
Solution Preparation

Due to the small volume of sample required for ESR and due to the low concentration of radicals necessary for the good resolution of the hyperfine structure, the actual quantity of free radical that was required for any sample was minute, i.e. a few milligrams at most.

For all the radicals which were stable in the solid phase, the solution preparation followed the same procedure.

About 5 milligrams of the purified condensation compound was dissolved in about 3 - 5 ml of chloroform and the solution shaken with ammoniacal silver nitrate solution for a period of five minutes to several hours, according to the rate of oxidation of the particular compound. When no further darkening of the solution was observed, a portion of the non-aqueous layer was pipetted out, filtered and evaporated to dryness at room temperature.

The red residue, either in the form of minute crystals or an oil, was then placed in a vacuum desiccator and dried for a period of half an hour. It was dissolved in a small quantity of the purified dioxan and was then ready to be deoxy­ genated.

For those radicals which were unstable in the solid phase, the procedure was modified; a solution of the free radical in chloroform was prepared as before,
pipetted off and filtered. This solution was then shaken with anhydrous sodium sulphate and refiltered. The solution, depending on its concentration, was partially evaporated and a portion of it diluted with the pure dioxan. This solution was then ready for deoxygenation.

Cleaning of Specimen Tubes

The specimen tubes used and described later in the section were made of fused silica. Their thorough cleaning was essential and the procedure used is described below. Even new tubes were cleaned before use and, in their case, 'blank' runs were carried out in the $g = 2$ region to ensure there were no highly absorbing radical species trapped in the silica.

The tubes were rinsed four or five times with chloroform and a further three times with acetone and twice with distilled water. They were then heated to red-heat in a Bunsen flame, more especially in the region to be inserted in the cavity, and allowed to cool in a desiccator.

When the rinsing with water had not been adequate or when some organic species, free radical or otherwise, was left in the tube before heating, breakdown occurred forming an opaque layer of carbon on the inside of the tubes. This glows brightly at red heat where a perfectly clean tube glows red only at the bubbles and other small flaws in the silica.
When a layer of carbon formed it was removed by adding a few drops of concentrated nitric acid and heating to red-heat. After rinsing thoroughly with water and drying as above, these tubes were found to be completely radical-free.

**Deoxygenation of Solutions**

A diagram of the apparatus used for the deoxygenation of the samples is shown in Fig. 3. The quartz specimen holder was attached via a short piece of PVC tubing to a length of 7 - 8 cm of 'pyrex' glass tube. This, in turn, was connected to a 'Quickfit' tube with a B.7 cone via another piece of PVC. To ensure that the connections were completely air-tight, the glass and quartz tubes were gently heated before being pushed into the PVC. The whole of this specimen tube assembly was then attached to the rest of the apparatus by a B.7 socket on the head piece, which fitted into a boiling tube shaped container by a B.19/26 connection. Also from the headpiece ran a connection via a length of pressure tubing to a tap, a trap and a vacuum pump.

The free radical solution in dioxan prepared above was placed in the apparatus, and, with the tap shut, the pump was turned on. The tap was carefully opened until small bubbles within the solution first appeared when it was immediately closed again. With the tap shut, the whole apparatus was gently shaken, inducing the solution to boil. After it had settled down, the tap was carefully opened once more and the process repeated two or three times. With a little experience and care it was possible to avoid the solution 'bumping'.
Fig. 3  Deoxygenation Equipment
The apparatus was then tipped with the tap shut so that the solution was able to run down into the specimen tube assembly. Further boiling of the solution at the junctions of the various tubes in general occurred, but as this helped the de-oxygenation no attempt was made to reduce it. When the solution in the specimen tube reached a height of four to five cm, the 'pyrex' tube was flame sealed. The specimen was then ready to be placed in the ESR spectrometer.

In the design of the apparatus, a detachable bulb was fitted to enable the de-oxygenation of the solvent to be completed before the addition of the solid free radical. This was felt necessary by analogy with work done on D.P.P.H. which scavenges the paramagnetic oxygen in the solution and holds it firmly enough to make deoxygenation by the above procedure impossible. However, with all the species examined, the scavenging effect was clearly small and deoxygenation of the solutions directly proved to be perfectly adequate.

2. THE USE OF 'FREMY'S SALT' AS A REFERENCE

It was decided that, for the purposes of determining hyperfine splitting constants and approximate 'g' values, a reference should be run before and after the actual spectrum. However, it was found more convenient to seal a reference radical, in a capillary tube, in with the deoxygenated sample solution. The filled and sealed capillaries, their length being about seven cm, were placed in the specimen tubes before deoxygenation of the sample. As only the lower 3 cm of
the specimen actually enters the microwave cavity, it was found quite simple to shake the capillary containing the reference to the top of the specimen tube where it was held by 'surface tension' and, by this means, it was possible to obtain spectra of the sample unaffected by the presence of the reference. Having obtained these spectra, the capillary could be shaken down to the bottom of the tube and the sample and reference spectra run together.

The choice of a suitable reference radical depended on several factors. These are listed below.

The ESR lines of the reference should be:

(i) sharp

(ii) well separated and not too numerous

(iii) easily made and at least moderately stable

(iv) the 'g' value approximately equal to 2

(v) strongly absorbing.

The reference decided upon was Fremy's Salt – the trivial name for potassium peroxyamine disulphonate, $K_2(SO_3)_2NO$. The aqueous solution of this gives three sharp, equal intensity lines centred at $g = 2.0054 \pm 0.0004$ (13) with line widths of about 0.3 gauss for air-saturated solutions of concentration about $10^{-3}$ moles/litre and separations of $13.05 \pm 0.03$ gauss (14).
This radical satisfied the five conditions set out above, but has the slight disadvantage that, being in an aqueous solution, it tends to decrease the Q of the spectrometer cavity. However, by using a sufficiently narrow capillary to contain it, this effect is small and tubes with inside diameters of about 0.5 mm were used with success.

It was found that the aqueous solution required potassium carbonate (about 0.1 Molar) to stabilise the radical. Such solutions were found to be quite suitable as reference solutions for a period of several days, or weeks even, when prepared in the presence of air.

3. THE SPECTROMETER

General

The ESR spectrometer, a 100 kc/s field modulated instrument, followed a conventional design which was found to be adequate for the free radical systems which were studied. The design of the X-band microwave bridge and electronics is illustrated in Fig. 4.

As was seen in the section devoted to theoretical ESR considerations, to exhibit the isotropic hyperfine structure, one requires the sample to be in a dilute low viscosity solution. This almost completely limits one to work at room temperature or above and, because the radicals were all stable, for at least a few
Fig. 4  Spectrometer - Block Diagram
hours, no irradiation or 'flow-through' techniques were necessary. These considerations greatly simplified the design of the cavity.

The relatively small size of the cavity that was found to be adequate enabled a rather narrower magnetic gap width than is normal to be used, with consequently improved field homogeneity.

As all the samples had total hyperfine structures not exceeding about 40 to 50 gauss, a fairly simple magnetic field sweep generator was found quite satisfactory.

The detection and display units were kept as simple as possible which necessarily led to a slightly lower sensitivity. However, as nearly all the spectra had sharp and intense lines, this was found to be not a crucial limitation in most cases.

The final simplification that was made was the elimination of a microwave frequency stabiliser. The klystron used had a good short-term stability and it was found, in practice, that, over the period required for the average spectrum run, the frequency was essentially constant.

A more detailed discussion of the spectrometer design follows.
Microwave Bridge

It is seen that a cavity tuned klystron (E.M.I. Ltd., type CV 3246) in a Wayne Kerr Ltd. cavity oscillator (type S381) coupled microwave power in both directions along the waveguide. The total power available was between 15 and 35 milliwatts. To cool the klystron a small mains operated blower with a tube one foot, six inches in length and one inch in diameter attached was used, the latter being necessary as a 50 c/s magnetic modulation of the microwave power appeared when the blower was positioned too close to the klystron.

The power supply for the klystron was the 'Decca Universal Klystron Power Supply', type MW 59. This was set up to give stabilised voltages of between 185 - 200 V on the reflector plate and a resonator voltage of 300. The heater voltage was also stabilised and set to 6.3 V.

The specification of stability for these supplies is given as:- less than 0.1V variation on the reflector, less than 0.5 V variation on the resonator, and less than 0.25 V on the heater, for a ± 10% mains supply change.

Following the klystron was a Mullards tuneable isolator, type L 324 with a reverse attenuation of about 21 dB and a Wayne Kerr Ltd. variable attenuator. The former was added to prevent the klystron frequency from being 'pulled' when tuning the bridge and the attenuator was added to avoid any saturation effects which may occur. In practice saturation was seldom, if ever, observed.
The power then entered a 'Magic-tee' where it divided equally along the E- and H-arms. In the H-arm was a tuneable stub and the sample reflection cavity. The latter was designed to work in the \( H_{012} \) mode at a frequency of 9300 Mc/s.

A more detailed consideration of the design of the cavity is given later in the section.

The purpose of the stub was to give a degree of variation in the coupling of the bridge with the cavity. The iris diaphragm was made with a coupling hole and its corresponding coupling constant, which was slightly too large. An approximate optimum size of hole was determined experimentally by making a series of irises and soldering them, in turn, onto the cavity.

When correctly tuned and coupled, no power should be reflected back to the Magic-tee. This condition was achieved by modulation of the klystron output with a saw-tooth waveform of 900 c/s applied to the reflector plate. The output mode from the klystron was displayed by connecting the output crystal directly to the video amplifier of a Mullard type L101/3 double beam oscilloscope. With the attenuation in the bridge-balance arm at a maximum (20 dB) the oscilloscope thus displayed the klystron mode as reflected from the cavity and iris only and, by tuning the klystron cavity, it was possible to bring the sample cavity absorption to the centre of the displayed mode. The appearance of the oscilloscope display should resemble Fig.5a at this stage.
(a) Correctly tuned

(b) Coupling too large

(c) Coupling too small

(d) Incorrect phasing

Fig. 5  Klystron Modes
Figs. 5b and c show the appearance when the cavity coupling was too large or too small. It is seen that, at the frequency of cavity resonance, there is no microwave power at the detector crystal and the optimum condition of coupling is achieved.

It is necessary to allow a small microwave power to be incident on the detector crystal to bias it at the point on its working curve where there is maximum conversion efficiency. The D.C. current passing through the crystal, under these conditions, and with a load of 500 ohms should be about 50 micro amps. The current depends on the type of crystal used and with an E.M.I. Ltd., type CV 2155, the above value is found to give the best results.

To achieve this biasing condition it was necessary firstly to reduce the amplitude of the source modulation to zero, keeping the minimum of the cavity absorption in the middle of the oscilloscope screen by small adjustments of the reflector voltage, and then to reduce the attenuation in the balance arm of the bridge, until the current in the detector crystal rose to the required value.

By switching on the source modulation again, the klystron mode - cavity absorption display on the oscilloscope was, in general, distorted (see Fig. 5d). Adjustment of the phase in the bridge balance arm re-established the symmetry of the display and, in so doing, brought the spectrometer to the correct condition to give pure absorption spectra. The phase adjustment was made by terminating
the arm with a tuneable short circuit. By reducing the amplitude of modulation to zero once more and keeping the cavity absorption dip in the centre of the trace as before, the bridge was then set up correctly.

Electronics

The block diagram of the spectrometer in Fig. 4 shows the various units that are necessary outside the microwave bridge. These are conveniently considered in four groups:

(a) Field modulation supply
(b) Detection and display
(c) Field supply and sweep unit
(d) Magnet

The power supplies used were three Racal Engineering Ltd. Stabilised Power Units, type FV 156. These gave 300 volts with a regulation of ± 0.1%.

(a) Field Modulation Supply

The field modulation supply consists of three units - the 100 kc/s oscillator generator, the phase shifter and the power amplifier.

The circuit for the 100 kc/s generator is shown in Fig. 6 and is seen to consist of a standard crystal regulated 'Colpitts' oscillator.
Fig. 6  100 kc/s Oscillator
No attempt was made to temperature-stabilise the crystal as the frequency band pass of all the units but the phase sensitive detector were sufficiently broad for no effect to be observed and, as both the signal and reference to the detector arrive indirectly from the oscillator, any small frequency changes affecting both inputs have no effect on the final D.C. output.

The output from the 'Colpitts' valve (peak to peak about 1 volt) fed the grids of a 12AT7 double triode, set up as two independent cathode-following circuits. The signals were then fed into 75 ohm coaxial cables, one leading directly to the phase sensitive detector as the reference, the other to the second unit of the modulation supply - the phase shifter.

The circuit for the phase shifter is shown in Fig. 7.

The input from the master oscillator (which should not exceed about 0.75 V peak to peak) was fed to the EF 91, connected to provide two signals with a phase difference of 180°. A potentiometer (50 Kohm) in the anode line enabled the relative amplitude of the signals to be varied, and both were fed through 1000 pF capacitors to the grids of a 12AT7.

In the initial setting-up procedure the variable capacitor C on one cathode of the double triode was replaced by a resistor whose value (33 Kohms) was the same as that of the one connected to the opposite cathode. An A.C. valve voltmeter was attached to point 'A' midway between the cathodes and earth and the
Fig. 7 Phase Shifter
potentiometer in the anode line of the EF 91 adjusted to give a zero (in practice a minimum) reading. The variable capacitor \( C \) (500 pF) was then replaced and, depending on its setting, gave any phase from \( 0 - 90^\circ \) between 'A' and earth. Theoretically, the capacitance equivalent to an impedance of about 33 Kohms at a frequency of 100 kc/s is only 50 pF, but, in practice, it was found that it gave rather less than \( 90^\circ \) phase change, hence the larger capacitance was inserted.

The output from point 'A' in the phase shifter was taken directly, by coaxial cable to the power amplifier, the circuit of which is shown in Fig. 8.

The circuit consisted of a buffer amplifier with a 50 Kohm attenuator to set the modulation level at any convenient value, and a power amplifier valve (type 807). In order to limit the valve current in the 807 to reasonable levels, it was found necessary to bias the grid with a 90 V dry cell battery. A 50 Kohm potentiometer enabled the biasing voltage to be varied and an R - C network isolated the battery from the modulation level potentiometer.

An L - C circuit in the anode line of the 807 was tuned to 100 kc/s, the coil being a standard long-wave radio detector type with about 800 turns in the primary. Round the outside of this was coiled 11 turns of multistranded bell wire in which was induced the relatively large radio-frequency current required for the field modulation. An r.f. thermocouple type ammeter was wired in series with the secondary coil, the current being taken from this to the modulation coil inside
Fig. 8  Power Amplifier
the microwave cavity by about 3 ft. of 75 ohm coaxial wire. The braiding of the coaxial wire provided the return path for the current. It was important to prevent any earth loops, the only place at which this circuit was grounded being the coaxial socket in the front panel of the power amplifier console.

It was felt desirable to prevent any r.f. signal leaking from the power amplifier onto the H.T. line and to prevent this a choke was inserted above the tuned circuit. A switching device was included which enabled the anode current to be monitored while adjusting the bias voltage. The valve worked in its most linear characteristic when the anode current was 25 m.A. with zero modulation level; this drops to about 16 m.A. when the level is at its maximum value. The maximum radio frequency current output was about 2.5 amps, which would correspond to a little over 3 gauss modulation amplitude; with capacitive losses this probably reduces to about 2 gauss.

(b) Detection and Display

The units included in the second group of the spectrometer are the 100 kc/s amplifiers and phase sensitive detector, the D.C. amplifier and the chart recorder and oscilloscope display units.

The preamplifier used in the initial experiments was replaced by one made by Hilger & Watts Ltd. and used by them in their 'Microspin' ESR spectrometer. This had a larger gain (67 dB) and a bandwidth of about 2.5 kc/s but, more
important, a higher signal/noise ratio. To prevent any spurious effects from other parts of the equipment a separate 'Racal' power supply was used for this unit alone.

The D.C. crystal current could be monitored continually through an external circuit (500 ohms impedance). This was also used with the crystal video display when connected to the Mullard oscilloscope as previously described.

The circuit for the subsequent amplifier (maximum gain about 65 dB) and 9.0 ke/s band width is given in Fig. 9 and consists of 2 simple EF 91 tuned stages in series. To prevent feedback along the H.T. line some demodulation was included in the first stage. To prevent the amplifier from self-oscillating the two stages had to be well screened from each other; they were capacity coupled and a potentiometer enabled the gain to be varied. The output, taken directly to the phase sensitive detector could be monitored continuously by a connection to a coaxial socket on the front panel of the amplifier. For this a Tel-equipment oscilloscope, type D 31, was used and was only disconnected while running very weak absorption spectra. This was necessary as there was some loss of power from the output of the amplifier by the oscilloscope.

The circuit diagram for the phase sensitive detector (P.S.D.) is given in Fig. 10. The design was based on a Schuster circuit (15) and was found to work satisfactorily.
Fig. 9 Amplifier
A reference 100 kc/s signal was taken directly from the oscillator and amplified, the second stage being a 6BR7 pentode with a tuned inductive anode load. This was the primary of an iron dust radio frequency transformer, the tuned secondary enabling two signals with a phase difference of 180° to be fed onto the grids of a double triode (12AU7). It was essential that the transformer used had the primary and secondary coils wound over separate parts of the core. It was found that, if the secondary was wound over the primary, capacitive coupling gave a very large difference in the amplitudes of the two out-of-phase signals. The difference in amplitude with the coils separated was not too large, and to adjust them to the same amplitude a one megohm potentiometer was placed across the grids with its sliding contact connected to the two cathodes. This point (D') was taken to a coaxial socket on the front panel of the P.S.D. console. A reversing switch enabled the phases to be changed, a procedure used only infrequently.

A resistor network in the anode lines allowed the gains of the two sides of the double triode to be equated, thus balancing the detector.

The signal input from the 100 kc/s tuned amplifiers was taken through a coaxial lead directly onto the grids of an ECC 81 valve, both halves of which were connected in parallel, there being a grid leak of 47 Kohms to earth. The anodes of this signal valve were connected to the cathodes of the 12AU7 (point 'D'), thus completing the detector.
The gating circuits through the 12AU7 pass only signals of exactly the same frequency as the reference and so provide a potential difference between 'A' and 'B', the sense and amplitude of this difference depending on the phase and amplitude respectively of the signal. The phase shifter was adjusted to give a maximum output from the P.S.D. The r.f. at the anodes is shorted to earth through 0.01 μF capacitors, leaving a D.C. or slowly changing potential which is taken to a D.C. amplifier.

The initial setting up of the P.S.D. requires one to know the waveform at the point 'D'. A coaxial socket was provided so that an oscilloscope could be connected with ease.

A 100 kc/s signal from the crystal oscillator was fed into the reference input, the reference level being set to a maximum. The primary of the r.f. transformer was tuned to give a maximum amplitude of the signal at 'D'. The secondary was then tuned similarly, then the primary again, and so on to an optimum. A slightly greater amplitude at 'D' was obtained when the 'Reference Level' was set at an intermediate position, this being due, presumably, to saturation in the 6BR7. The 'Reference Level' was then left at that point and did not have to be re-adjusted.

The waveform was, in general, as illustrated in Fig. 11a. By alternate alterations of the 'Reference Balance' and 'Balance' potentiometers, the waveform was brought to a symmetrical shape, illustrated in Fig. 11b, the apparent frequency being, of course, 200 kc/s. The P.S.D. was then set up correctly and it was found in practice hardly necessary to alter any of the settings subsequently.
Fig. 11  P.S.D. Waveform

(a) General
(b) Balanced
Fig. 12  D.C. Amplifier
The circuit diagram for the D.C. amplifier is shown in Fig. 12.

The D.C. signal from the P.S.D. was fed through an R-C filtering circuit (a range of capacitors from 1000 p.F. to 4 µF were included to vary the time constant) onto the grids of a cathode following, double triode (12AX7). The low impedance output was taken through a potential dividing chain (Recorder Sensitivity') to a 1/2 second' Honeywell Controls Ltd. Potentiometer Recorder. This was a centre-zero recorder with full-scale deflection given by ± 5 millivolts.

With the 'Recorder Sensitivity' set to the desired value, the potentiometer in the resistor chain across the grids of amplifier was adjusted to centralise the recorder pen. This 'Zero Centreing' control counter balanced any asymmetry in the circuit from the P.S.D.

(c) Field Supply and Sweep Unit

The unit supplying power to the electromagnet was a Belix Co. power unit, type TSS 127, giving 0 - 60 volts and up to 6 amps continuously variable. Random fluctuations are quoted as better than 1 in 5000 for the normal voltages (about 25 V) used.

As the supply is voltage, rather than current stabilised, it is necessary to allow the magnet to warm up to an equilibrium temperature before reproducible spectra can be obtained.
The supply has both thermal and overload cut outs and so, to protect the transistors from dangerously high 'back E.M.F.s' in the event of sudden power failure, a Mullard diode (type SX75IN) was placed across the output.

In addition to supplying the main coils of the magnet with a constant current, the power unit was also used to provide the necessary current for the field sweep unit, the circuit of which is shown in Fig. 13.

A 50 Kohm precision wound potentiometer (P.X. Fox Ltd., type B 355) connected across the supply of about 25 volts was turned by one of four slow speed asynchronous electric motors, provided by Crouzet England Ltd. - their speeds range from 8 revolutions per minute to 1 revolution in 10 minutes. This had the effect of applying to the base of an OC 71 transistor a saw-tooth voltage waveform. With the collector grounded, the circuit provided a similar waveform in the lower impedance emitter circuit. This, in turn, fed onto the base of an OC 29 which also had a grounded collector; the sweep coils, approximately 24 ohms each, connected in series provided the emitter load. The voltage across the load followed the same saw-tooth waveform with a slight reduction in the amplitude. In the range from 0 to 0.5 amps the voltage against time variation of linearity was 3.0% (expressed as % RMS deviation of total sweep), as measured by sampling a fraction of the voltage and applying to a potentiometer recorder.
Fig. 13  Field Sweep Unit
(d) Magnet

The electromagnet used in the spectrometer was a Newport 4 inch type A.* Each coil had about 3650 turns of copper wire with resistances about 20 ohms each.* These were connected in parallel and required about 25 volts to produce a magnetic field (about 3400 gauss) suitable for ESR at X-band.*

The pole tips were made of polished iron with adjustable Rose shims and supplied by Newport Instruments Ltd.*

In order to check the parallelism of the pole tips, a pair of brass, internal callipers were constructed. The field was turned on and any wedge shaping observed was removed by placing small slithers of copper foil under one or other of the pole pieces.

Once parallel, the Rose shims had to be checked. The optimum position for these was calculated by Rose (16) who showed that the degree of correction was a function not only of the thickness of the shims but also of the gap dimension between the tips. For a gap of 3.5 cm and with a shim thickness of 0.10 cm, the best homogeneity is given by the shims 0.10 cm above the pole tip surfaces.*

To obtain a measurement of the homogeneity of the field, a proton magnetometer was constructed (see below for a description of the circuit).
With the proton sample at the geometric centre of the gap and the shims set to their theoretical position, a small amplitude 50 c/s field modulation was applied to the sweep coils. The D.C. field was set to about 3400 gauss - the working value for ESR and the frequency of the magnetometer varied until an absorption peak appeared on the oscilloscope. The field was then reduced to zero and one of the shims rotated by about $10^\circ$. The field was then turned on once more and the appearance of the absorption peak observed. By continuing this, the peak was narrowed until a few wiggles appeared on one side of it; further improvement of the field resulted in a larger number of wiggles. Once the optimum position for one shim had been found, i.e. symmetry had been obtained, then both could be varied by about $20^\circ$ each, while maintaining the symmetry. The improvement in the homogeneity was not greatly increased once the initial symmetry had been achieved.

A check on the homogeneity was made by running an ESR spectrum of perylene dissolved in concentrated sulphuric acid. The lines are 460 milligauss apart (17) and were found to be completely resolved.

The magnetometer was constructed with two objectives in mind.

1. To measure 'g' values and line splittings
2. To give a measure of field homogeneity.
Fig. 14 Magnetometer

Diagram of a magnetometer circuit with various components such as resistors (e.g., 47K, 22K, 6.8K, 1.8K), capacitors (e.g., 0.1, 0.001, 500pF), and transformers (RFC). Specific components include a 150B2 valve, an audio frequency O.P., and a 10 turns 1/4" diam. coil.
'g' value and line splitting measurements were found to be too cumbersome by this method for general use but one determination of 'g' is reported in Appendix I. Its use in improving the field homogeneity is described in detail above.

The circuit for the magnetometer is shown in Fig. 14. It consists of a capacity feedback, L - C tuned oscillator - the coil being wound around a proton sample (a glass tube, o.d. 0.55 cm and i.d. 0.45 cm containing liquid paraffin was used). The coil was wound with 10 turns of 23 S.W.G. copperwire, directly onto the glass proton sample tube and an air spaced variable 500 p.F. capacitor enabled the system to be tuned over the required frequency range, i.e. from about 11 to 15 Mc/s. A 1000 ohm potentiometer in the cathode circuit of the oscillator valve allowed the r.f. level at the tank coil to be varied and so avoided saturation effects from becoming too large.

Various stages of demodulation in the anode line removed the r.f. and a 0.1 microfarad capacitor coupled the audiofrequency component to an a.f. amplifier. The output from this was taken directly to an oscilloscope.

In order to observe the NMR absorption a small amplitude 50 c/s magnetic field modulation had to be applied. The minimum output from a mains supplied Variac connected directly to the sweep coils had an amplitude which was too large for convenient g value measurements. To reduce it, a 40 to 1 transformer was used, the level being set when the line width was about one quarter of the x dimension on the oscilloscope screen.
For field homogeneity checks, the transformer was not necessary.

Cavity Design

The cavity (see Fig. 15) consisted of a length of waveguide (4.53 cm), coupled to the H-arm of the microwave bridge by a diaphragm of thin copper sheet (0.03 cm thick) carefully soldered on both sides, into which was cut a hole 0.95 cm in diameter, the edges of which were rounded. On to the other end of the cavity was soldered a polished piece of brass sheet which acted as a total reflector. This construction was designed to give a cavity resonating at 9300 Mc/s. The experimental frequency, at room temperature and with a dioxan sample, was found to be 9306 Mc/s. This value varies slightly with the coupling conditions, with the size and nature of the sample, and the ambient temperature.

At the mid-point of the cavity on the narrow side was drilled a hole 0.6 cm in diameter, above which was soldered about 6.5 cm of brass tubing, the inside diameter being the same as the drilled hole. This arrangement enabled the sample tubes to be placed in the cavity in the position of maximum amplitude of the H-microwave field. The amount of slack that was possible was very small and, with the cavity arranged so that the brass tubing was vertical, no difficulty was experienced positioning sample tubes which varied slightly in size.

In order to modulate the magnetic field at 100 kc/s it is necessary to place coils carrying the modulation current close to the sample. There are two poss—
Fig. 15  Absorption Cavity
ibilities. The first is to fix the coils to the outside of the cavity and make the wall thickness such that it exceeds the skin depth at the microwave frequency and is less than the skin depth at 100 kc/s. This thickness is calculated to be about 0.2 mm for brass at room temperature (18, 19).

The second possibility, the one that was chosen, is to place the coils inside the cavity itself. Here the thickness of the walls is immaterial and hence the equipment can be made from brass waveguide. The coils were constructed of four straight lengths of 23 S.W.G. wire, being as close to the sample tube as possible. The wires passed through both of the narrow sides of the waveguide, insulated from it, at the corners of squares with sides of about 0.6 cm in size. They were fixed to the waveguide with small amounts of 'Durafix' and soldered together so that the modulation magnetic field was parallel to the externally applied constant field.

A simpler system uses only two wires but the method described above produces a more uniform modulation field over the sample volume and a consequent increase in the effective sensitivity.

The field strength produced by such a system is given by

\[ H_{\text{mod}} = 0.4 \frac{i_{\text{mod}}}{r} \]

where \( H_{\text{mod}} \) is the modulation field in gauss, \( i_{\text{mod}} \) is the current in amperes and \( r \) is half the distance between the parallel wires. For the system used therefore

\[ H_{\text{mod}} = 1.3 i_{\text{mod}}. \]
To exhibit spectra with no modulation broadening $H_{\text{mod}} (r.m.s.)$ must be less than about 0.3 of the line width at points of maximum slope. This means that, for lines 200 milligauss in width and separation, one requires $H_{\text{mod}}$ to be about 60 mg and consequently $i_{\text{mod}} (r.m.s.)$ to be only about 45 milli-amps.

When searching for weak signals, however, it is sometimes necessary to use modulation fields of about 2.5 gauss resulting from a current of about 2 amps (r.m.s.) which is the reason for using the rather thick wire for the modulation coils.
SECTION 4

PREPARATION OF N-ARYLHYDROXYLAMINES
1. **REVIEW**

Considerable difficulty in the preparation of some of the substituted N-aryhydroxylamines was experienced, and several different methods for their preparation were tried.

All the methods used depended on the reduction of the corresponding aryl nitro compounds, the different methods employed being attempts to reduce the rate of the various side reactions which may take place giving unusable yields of the hydroxylamines.

The more important of these side effects are:-

**The Action of Mineral Acids**

In the presence of mineral acids, N-aryhydroxylamines rearrange to form amino phenols.

\[
\text{NHOOH} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \text{NH}_2\text{OH}
\]

The para-amino phenol is formed unless the hydroxylamine is already para-substituted, in which case the hydroxyl group migrates to the ortho position.
Sulphuric acid in alcohol can induce the formation of several side products such as p-phenetidines and p-aminodiphenyl amines (20).

Clearly these reactions are far from simple and some work has been attempted to determine the precise nature of the stages involved (21).

Hydrochloric acid will form ortho and para chloramines.

It is of course well known that the reduction of nitro compounds in the presence of dilute acids gives a good yield of the corresponding amine.

**Oxidation Effects**

Saturated solutions of N-arylhydroxylamines in benzene slowly darken over a period of 3 – 4 days in the presence of air and droplets of a brown oil are
formed. This is due to the formation of the corresponding nitroso compound,

\[
\text{ArNH} + \text{O} \longrightarrow \text{ArNO} + \text{H}_2\text{O}
\]

and the subsequent condensation of this with further hydroxylamine to give an azoxy compound,

\[
\text{ArNH} + \text{ArNO} \longrightarrow \text{Ar} - \text{N} = \text{N} - \text{Ar} + \text{H}_2\text{O}
\]

**Action of Dilute Alkali**

A number of side reactions take place when the reduction of nitro compounds is attempted in the presence of dilute alkali. Azoxy-, hydrazo- and azo compounds may all be formed (22).

It is seen therefore that the best conditions for the preparation of hydroxylamines is in 'neutral' solutions. However, even in the presence of dilute ammonium chloride solution, the yield of some substituted hydroxylamines can be very low.

Nearly all the methods involved the reduction of the corresponding nitro aryl compound by zinc in the presence of water: \(\text{ArNO}_2 + 2\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ArNH} + 2\text{ZnO}\).

Some hydroxylamines, e.g. \(p\)-diphenyl, appear to self condense before isolation and recrystallisation can be completed. In these cases an improvement is noted if the reduced solution is filtered into glacial acetic acid before isolation of the hydroxylamine is attempted.
Some hydroxylamines are more easily oxidised, e.g. p-phenetyl and p-anisyl, and their preparation therefore has to be more rapid than other more stable compounds.

Many hydroxylamines are most susceptible to slightly acid or basic conditions. In these cases, e.g. N-m-nitro phenylhydroxylamine, (22) the standard zinc-ammonium chloride-ethanol-water reducing medium has to be modified to overcome the inhomogeneity in the pH of the reacting medium. A small quantity of acetic acid added before the reaction commences improves the efficiency of the preparations of these more difficult hydroxylamines to usable values. This method is generally applicable and has been used whenever there was any doubt about the best method.

In general N-arylhydroxylamines are unstable compounds and decompose on standing over a period of a few days or weeks. It was most convenient, therefore, to use them in the preparation of their various condensation products immediately after recrystallisation had been completed, while a small portion was kept by for analysis by infra-red spectrophotometry.

On occasion, it was necessary to attempt to store a portion of the hydroxylamine for a short period. It was found that much longer storage times could be expected for pure compounds which had been vacuum dried, to remove recrystallisation solvents, and which were kept in a refrigerator. A factor of two in
improvement was noted when just the latter precaution was attempted. Darkening was always observed when crystals of the hydroxylamines were kept for a few days or longer but repurification was easily carried out when necessary, i.e., just before the next stage of a preparation, by washing the compound with a small quantity of benzene and subsequently recrystallising from hot benzene.

The presence of a reducing group in the products was tested in each case by the action of their chloroform solutions on ammoniacal silver nitrate. Rapid reduction was taken as proof of the existence of the hydroxylamine.

In most cases a sample of the hydroxylamine was tested by infra-red analysis. The characteristic N - H and O - H stretching bands in the 2.9 to 3.2 μ region were used to confirm the presence of hydroxylamine.

2. PURIFICATION OF NITRO-ARYL COMPOUNDS

The various nitro-aryl compounds used in the preparation of their corresponding hydroxylamines were mostly of the 'Laboratory Reagent' grade and supplied by B.D.H. Ltd. Others were supplied by Koch-Lights Ltd.

All the compounds, solid at room temperature, were purified by recrystallisation from boiling ethanol then filtered and dried at the pump. The compounds which were liquid at room temperature were purified by low pressure distillation. The materials so prepared were reduced directly to form the hydroxylamines, but small samples were kept for infra-red analyses.
3. **PREPARATIVE DETAILS**

**N-Phenylhydroxylamine**

The preparation of this compound followed the method of Kamm (23).

Purified nitrobenzene (62 g) was placed in a Winchester bottle with water (1 litre) and ammonium chloride (30 g). The mixture was well shaken while zinc dust (75 g) was added in 1 - 2 g portions over a period of 30 minutes.

The temperature of the mixture rose but, with a little cooling, it was kept to a value of 45 - 50°C. The shaking was continued for a further period of 15 minutes. A mass of white zinc oxide formed which sank to the base of the mixture and was finally filtered off from the warm liquid. The precipitate was washed with two portions of warm water (100 ml), the washings being added to the filtrate. The solution was then saturated with salt and cooled to 0°C, at which temperature it was kept for a period of 20 - 30 minutes. The yellow crystals (30 - 40 g) thus formed were filtered off, extracted from salt and brine with ether, then recrystallised from hot benzene.

As this was the most used of the hydroxylamines, being the easiest and cheapest to prepare, the relatively large quantities quoted above were felt to be necessary. If all of it was not used within a day, the remainder was recrystallised an additional time from benzene and, as described earlier, thoroughly dried and stored in a refrigerator.
Within two weeks the colour had darkened to a light brown - purified crystals being recoverable by recrystallisation from benzene.

Within two months the crystals had decomposed to a dark brown oil.

N-p-Tolylhydroxylamine

This compound was prepared by two methods, both of which were successful.

Method A. The p-nitrotoluene was reduced by sodium hydrogen sulphide by the method of Haworth and Lapworth (24).

P-nitrotoluene (10 g) in benzene (20 ml) was shaken with a solution containing sodium sulphide (Na$_2$S•9H$_2$O, 68 g) water (50 ml) and hydrochloric acid (24.2 ml). Also added was a concentrated solution of calcium chloride (10 g) in water. The mixture resulted in an emulsion which was maintained by occasional shaking. After twenty four hours, solid ammonium chloride (15 g) was added, the whole mixture shaken thoroughly and filtered. The ammonium chloride had the effect of breaking down the emulsion and dissolving any solid calcium salts present. The solid residue from the filtration consisted mainly of the N-p-tolylhydroxylamine which was purified by recrystallisation from benzene.

Method B. The second method employed for this compound was based on that described by Brand and Modersohn (25) for the preparation of N-nitroarylhydroxylamines.
P-nitrotoluene (9.1 g) was dissolved in ethanol (93% 70 ml) and water (30 ml) to which was added calcium chloride (anhydrous 2.0 g) and glacial acetic acid (about 40 drops). The mixture was heated, just to boiling, when zinc dust (10 g) was added in 1 g portions with continuous shaking. The zinc was added at such a rate that the boiling was able to be maintained without the aid of a steam bath. After the addition was complete, the mixture was boiled and agitated for a further fifteen minutes and then filtered hot. The precipitated zinc oxide was washed with two portions (20 ml) of hot ethanol which was added to the filtrate. The excess ethanol in the filtrate was then distilled off, under reduced pressure, until the solution became cloudy when the required hydroxylamine was filtered from the cold liquid, dried, and recrystallised from benzene.

A further crop of crystals was obtained by further reduction of the filtrate under reduced pressure.

N-m-Tolylhydroxylamine

Attempts were made to prepare N-m-tolylhydroxylamine by the sodium hydrogen sulphide method of Haworth and Lapworth (24) but without success.

It was prepared by the method of Kamm (23) as described above for N-phenylhydroxylamine, the quantities used being m-nitro-toluene (5.2 g), ammonium chloride (2.3 g), water (75 ml) and zinc dust (5.6 g).
N-o-Tolyhydroxylamine

The reduction of o-nitrotoluene by Kamm's method (23) was successful but a slight modification of procedure was necessary due to the liquid nature of the product.

O-nitrotoluene (6.9 g) and ammonium chloride (3.0 g) in water (100 ml) were shaken for 30 minutes while zinc dust (7.5 g) was added in small portions. The temperature rose rapidly, but was kept to about 45°C by occasional cooling. Shaking was continued for a further 15 minutes after the zinc had been added and the mixture then filtered warm. The filtrate was cooled to 0°C and saturated with salt when a yellow oil was seen to be floating on the surface. This was collected by ether extraction and dried over anhydrous sodium sulphate before removal of the solvent. No purification of the product was carried out.

This was one of the hydroxylamines, liquid at room temperature, which was encountered (see also N-2,4-dimethyl-phenylhydroxylamine later in this section). It rapidly reduced ammoniacal silver nitrate and gave the characteristic infra-red band at 3.0 µ due to the OH stretching mode. No sharp NH stretching band was seen which was assumed to be due to the influence of an ortho substituent.

N-p-Ethyl-Phenylhydroxylamine

The reduction of p-nitro-ethylbenzene to form the N-hydroxylamine was attempted by two methods.
The first method, which proved to be unsuccessful, was that of Kamm using zinc dust, ammonium chloride and water. The second was that derived from Brand and Modersohn (25), described in detail for the preparation of N-p-tolyldihydroxylamine (Method B), and gave a yield of nearly 70% of the pure hydroxylamine. The quantities used were p-nitroethylbenzene (10 g) in ethanol (70 ml) with water (30 ml), calcium chloride (2 g) and 40 drops of glacial acetic acid. To the boiling mixture zinc dust (10 g) was added over a period of half an hour.

N-p-Methoxy and p-Ethoxy-Phenylhydroxylamines

These two compounds were prepared identically by a method described by Rising (26).

p-Methoxy nitrobenzene (7.7 g) (or p-ethoxy nitrobenzene (8.3 g)) was dissolved in ethanol (30 ml) with ammonium chloride (1 g) in water (25 ml). The mixture was warmed to 65°C and, after a few minutes, zinc dust (7.5 g) was added. The temperature rose rapidly but violent boiling was suppressed by cooling the reaction vessel. For three minutes the mixture was shaken and then quickly filtered and the precipitate washed with hot ethanol (25 ml). The filtrate was cooled in a freezing mixture and the resulting precipitate filtered and washed with cold benzene to give pure white crystals, which proved to be the respective hydroxylamines.
N-2,4-Dimethyl-Phenylhydroxylamine

2,4-dimethyl nitro benzene was reduced by a modified Brand and Modersohn's method (25).

2,4-dimethyl nitro benzene (10 g) in ethanol (70 ml) and water (30 ml) with calcium chloride (2 g) was heated to boiling with 40 drops of glacial acetic acid. Zinc dust (10 g) was added portion wise for 30 minutes and shaken for another 15 minutes. After being filtered hot and the precipitate washed with hot ethanol, the excess solvent was distilled off, under reduced pressure, until the filtrate became cloudy. On cooling in a freezing mixture no crystalline product would form and it was concluded that, in common with N-o-tolylhydroxylamine, the product was liquid at these temperatures.

The hydroxylamine was obtained from the cloudy cold liquid by ether extraction, the solution being dried over anhydrous sodium sulphate. Evaporation of the ether yielded a yellow-orange coloured oil which would not crystallise.

The hydroxylamine was not further purified. It reduced ammoniacal silver nitrate and gave the characteristic IR band at 3.05 μ due to the OH stretching mode. As with N-o-tolylhydroxylamine, no sharp NH peak was seen.

N-p-Diphenylhydroxylamine

The reduction of p-diphenyl-nitro-benzene was carried out by the method described by Gilman and Kirby (27).
P-nitro diphenyl (5 g) in ethanol (96%, 250 ml) was mixed with ammonium chloride (3 g) in water (30 ml) and zinc dust (5 g) added. The mixture was shaken while the containing vessel was cooled under water. This was continued until no further heat was evolved (about 10 minutes) and further shaken for another 30 minutes. The mixture was suction-filtered directly into glacial acetic acid (15 ml) and refiltered into water (300 ml); the resulting yellow precipitate was collected by further filtration (this was difficult owing to the small particle size) and dried.

It was reported (Gilman and Kirby) that the above procedure was necessary due to the unusual sensitivity of this hydroxylamine to oxidation. Initial filtration into glacial acetic acid seems to repress this sensitivity.

The infra-red spectrum of the product showed the broad OH and sharp NH bands, while its solution in chloroform reduced ammoniacal silver nitrate.

N-1-Naphthylhydroxylamine

Considerable difficulty was experienced in the preparation of this compound and several different methods were attempted.

The method of Haworth and Lapworth (24) gave a brown solid residue, but any hydroxylamine present decomposed rapidly on recrystallising from benzene, forming a dark brown oil. A further attempt by this method, using a larger bulk of benzene in the recrystallisation gave a low yield of pale brown crystals. These very rapidly darkened in air.
The reduction of 1-nitronaphthalene was also attempted by zinc dust - ammonium chloride - ethanol methods but with the same result. The most successful method was based on that of Wacker (28).

1-nitronaphthalene (10 g) dissolved in ethanol (96%, 80 ml) and water (12 ml) was heated to boiling with ammonium chloride (15 g). Zinc dust (15 g) was added and the mixture kept boiling for 15 minutes before being filtered hot. The precipitate was washed with hot ethanol, and the filtrate diluted with water (200 ml) and cooled. The resulting precipitate was filtered off and washed with a little cold water, dried and weighed. This was taken up in ethanol (10 ml) and filtered to remove 1-azoxynaphthalene, the filtrate being poured into water (20 ml) and kept at 0°C for 30 minutes. After this time the hydroxylamine had formed and was filtered off and dried between filter papers. As the white crystals were visibly darkening it was decided not to recrystallise but to proceed immediately with the next stage in the preparation of the condensation product.

A small portion of the hydroxylamine was checked chemically and gave a positive reduction to the ammoniacal silver nitrate test.

N-m-Bromo and m-Chloro Phenylhydroxylamines

These two hydroxylamines were prepared similarly, using the following method.
M-bromo nitro benzene (20 g) or m-chloro nitro benzene (16 g) was dissolved in ethanol (96%, 60 ml) and mixed with ammonium chloride (2 g) in water (50 ml). The mixture was heated and zinc dust (15 g) added in small quantities, sufficient to keep the solution boiling, with constant stirring and shaking. After half an hour the hot mixture was filtered, the precipitated zinc oxide washed with hot ethanol (added to filtrate), cooled and small lumps of ice added to precipitate the respective hydroxylamines. These were filtered off, dried, and recrystallised from hot benzene.

N-p-Chloro Phenylhydroxylamine

The reduction of p-chloronitrobenzene to form the corresponding N-hydroxylamine was carried out by the method described by Bamberger and Baudisch (29).

A solution of p-chloronitrobenzene (19 g) in ethanol (96%, 100 ml) was added to a solution of ammonium chloride (2 g) in water (25 ml) and brought to boiling point. Zinc dust (about 35 g) was added in 1 g portions, with continuous shaking, keeping the solution boiling, until the initial brown colour of the liquid had been removed. The precipitated zinc oxide was filtered off from the hot solution and was washed with a little hot ethanol. Water (100 ml) was added to the filtrate which was then rapidly distilled, under slightly reduced pressure, to remove excess ethanol, until the liquid became cloudy. While hot it was quickly filtered, the precipitate being washed with hot water which was added to the filtrate.
This was quickly cooled and white plate shaped crystals formed which were collected and dried.

The hydroxylamine was collected and recrystallised from ethanol. It had the characteristic infra-red spectrum in the 3.0 μ region and reduced ammoniacal silver nitrate.

**N-m-Nitro-Phenylhydroxylamine**

This compound was prepared by the reduction of m-dinitrobenzene by the method described by Brand and Modersohn (25). The details of the method have already been described (see under the preparation of N-p-tolylhydroxylamine). The quantities used were as follows:

m-dinitrobenzene (10 g) in ethanol (96%, 70 ml) with calcium chloride (2 g) in water (30 ml) and glacial acetic acid (40 drops). The quantity of zinc dust was 14 g added over a period of 30 minutes.

Infra-red and chemical evidence showed that the product was N-m-nitrophenylhydroxylamine.
SECTION 5

REVIEW OF THE N-HYDROXYLAMINE/ACETONE CONDENSATION PRODUCTS
1. **CHEMICAL EVIDENCE FOR COMPOSITION**

The condensation between N-phenylhydroxylamine and acetone was first recorded by Bamberger and Rudolf (30) who suggested the structure for the crystalline product was

![Structure Diagram](image)

However, on molecular weight grounds alone, this was shown to be incorrect (31) and, in 1926, Banfield and Kenyon (32) investigating the structure of the compound, showed that it was a substituted hydroxylamine with one of the two following possible structures:-

![Structure Diagram](image)

The name given to structure I was $\beta$-phenylhydroxylamino-$\beta$-methylpentane-$\delta$-phenylimine oxide, and to II, $\beta$-phenylhydroxylamino-$\beta$-methylpentan-$\delta$-oneoxime N-phenyl ether. The compound will hereafter be referred to as the
Kenyon condensation product or compound and substances with aromatic or aliphatic substituents, as the relevant Kenyon type compounds.

The more important evidence put forward in support of these possibilities is given below:

(i) On oxidation of the product with moist silver oxide, only one hydrogen atom per molecule is removed.

(ii) The mono-acetyl and mono-benzoyl derivatives form from the condensation product but do not form from the oxidised product above.

The mono-acetyl derivative is not oxidised by silver oxide.

Both of these results indicate that there is only one reactive hydrogen atom in the molecule.

(iii) A potassium derivative, $\text{C}_{18}\text{H}_{21}\text{O}_{2}\text{N}_{2}\text{K}$, is formed which

(a) on standing yields the red oxidation compound above and

(b) reacts with benzoic anhydride to give the benzoyl derivative above.

This indicates the existence of an active hydroxyl group.
(iv) A chloro-base is formed by the action of cold dilute hydrochloric acid on
the condensation product. Small quantities of N-phenylhydroxylamine, azobenzene
and p-chloroaniline are also produced, the latter two being decomposition pro-
ducts of the hydroxylamine. This base, \( \text{C}_{12} \text{H}_{16} \text{ONCl} \) decomposes into molecular
proportions of p-chloroaniline and mesityl oxide and forms equivalent proportions
of p-chloroacetanilide and mesityl oxide by the interaction of acetic anhydride.

The constitution of the chloro-base is consequently given as
\( \text{C}_6\text{H}_4\text{Cl},\text{NH},\text{CM}_{2}\cdot\text{CH}_2\cdot\text{CO}\text{Me} \) and is confirmed by its synthesis from N-
phenylhydroxylamine, mesityl oxide and hydrochloric acid.

2. THE ADDITION OF THE 'CONденSATION PRODUCT' WITH PHENYL ISO-
CYANATE

It is reported (33) that the condensation product forms, under the appropriate
conditions, an addition compound with phenyl iso-cyanate.

The suggested reaction is

\[
\text{PhN}^\text{R} \quad + \quad \text{Ph-N = C = O} \quad \rightarrow \quad \text{PhN}^\text{R} \quad \text{CO} \quad - \quad \text{N(CH)Ph}
\]

which, it is stated, is analogous to the condensation of N-phenylhydroxylamine
with phenyl iso-cyanate,
If the reaction is by a nucleophilic attack

\[
\begin{align*}
\text{PhN} & + \text{Ph-N}=\text{C}=\text{O} \rightarrow \text{PhN} \text{CO-N(OH)}\text{Ph} \\
\text{Ph} & \quad \text{N} \quad \text{H} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

then, by taking a substituted hydroxylamine PhNR(\text{OH}), the analogous reaction would yield the compounds

\[
\begin{align*}
\text{Ph-N}=\text{C}=\text{O} & \quad \text{Ph-N}=\text{C}-\text{O} \\
\text{Ph-N-H} & \rightarrow \text{Ph-N-H} \\
\text{OH} & \rightarrow \text{OH}
\end{align*}
\]

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

Lactam/Lactim type tautomeration

Tautomeration will not take it to the final stage corresponding to

\[
\begin{align*}
\text{Ph-N}=\text{C}=\text{O} & \quad \text{Ph-N}=\text{C}-\text{O} \\
\text{Ph-N-C} & \rightarrow \text{Ph-N-C} \\
\text{Ph} & \quad \text{R} \quad \text{OH}
\end{align*}
\]
The only way in which the compound

\[
\begin{array}{c}
\text{OH} \\
\text{Ph - N - C = O} \\
\text{N} \\
\text{R} \quad \text{Ph}
\end{array}
\]

could form is, therefore, by some mechanism other than nucleophilic attack, and/or by the formation of OH\(^-\) ions. The latter is highly unlikely because

(i) the hydroxylamine nitrogen is almost certain to take a positive charge and hence oppose the formation of OH\(^-\) and

(ii) in the medium considered, i.e., dry ether or dry benzene, the ions have little chance to be stabilised by highly polar solvent molecules.

It seems, therefore, that either the mechanism is via some other route or there is not, in fact, an analogous reaction.

As was mentioned earlier in this section (33) an addition compound has been reported; however, in trying to repeat this preparation, it has been found completely unsuccessful. Even by following more detailed experimental conditions (34) the only product formed was a tar.
NOTE: Evidence from the ESR spectra of free radicals formed from the addition compound of N-arylhydroxylamines and aryl iso-cyanates indicates that it is the hydrogen and not the hydroxyl group which migrates from the hydroxylamine to the iso-cyanate. This is dealt with in more detail in a later section.

3. EVIDENCE FROM MODERN INSTRUMENTAL METHODS OF ANALYSIS

There are several techniques available today, which enable the determination or confirmation of the structure of compounds which were not available to Banfield and Kenyon when they presented their paper on the constitution of the condensation product. It was felt that, before studying the electron spin resonance spectra of the related free radical, some attempt should be made to confirm or to modify the structure that was proposed on purely chemical grounds.

Possibly the most precise methods applied are Nuclear Magnetic Resonance (NMR) and Infra-Red Spectrophotometry (IR).

Other instrumental measurements that may be made include bulk magnetic susceptibility. This has been measured (35) on the free radical. The results, $\mu = \text{1.73 B}$ for the solid and $\mu = \text{1.68 B}$ for the benzene solution, are very close to the theoretical value for one unpaired electron per molecule ($\mu = \text{1.73 B}$) and confirm, at least, that the species is not a bi-radical.
Nuclear Magnetic Resonance

It was felt that the nuclear magnetic resonance spectrum of the condensation product would yield an almost unequivocal confirmation of its structure. This proved to be correct, but the results, Table 2, in addition had some interesting features which were found to be consistent with the electron spin resonance spectra of the related free radicals.

Three spectra were obtained for the phenyl condensation compound and for those with ortho and para tolyl groups.

The spectra were run on a Varian HA100 instrument, the \( \tau \) values of the various peaks are given.

The lines and groups have been listed in order from high to low field, i.e. in decreasing \( \tau \) values.

At this stage it should be noted that the analysis is in the form of a critical appraisal of the given structure in the light of the NMR information. It is not intended to be an absolute analysis. The alternative structure (I) given earlier in this section is considered, although the two would hardly be distinguishable by the NMR technique.

By inspection of Table 2, it will be seen that the three peaks at highest \( \tau \) values are virtually identical in position in both the phenyl compound and that
### Table 2
Kenyon Compounds γ Values

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Phenyl</th>
<th>p-Tolyl</th>
<th>o-Tolyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me (1)</td>
<td>9.07</td>
<td>9.05</td>
<td>8.88</td>
</tr>
<tr>
<td>Me (2) A</td>
<td>8.63</td>
<td>8.64</td>
<td>8.69</td>
</tr>
<tr>
<td>Me (2) B</td>
<td>8.59</td>
<td>8.57</td>
<td>8.63</td>
</tr>
<tr>
<td>Me (3) A</td>
<td>-</td>
<td>7.72</td>
<td>7.65</td>
</tr>
<tr>
<td>Me (3) B</td>
<td>-</td>
<td>7.69</td>
<td>7.65</td>
</tr>
<tr>
<td>CH₂ A</td>
<td>7.84</td>
<td>7.77</td>
<td>7.67</td>
</tr>
<tr>
<td>CH₂ B</td>
<td>6.88</td>
<td>6.76</td>
<td>6.60</td>
</tr>
<tr>
<td>Aryl H</td>
<td>2.3</td>
<td>2.9</td>
<td>2.8 &amp; 2.4</td>
</tr>
<tr>
<td>CH</td>
<td>2.06</td>
<td>2.09</td>
<td>1.65</td>
</tr>
</tbody>
</table>

| CH₂              | Spin/spin coupling constant = 13.0 c/s in all compounds |
with para methyl groups. As the three have equal intensities they are assigned as follows:- Me(1), \( \xi \) methyl group, Me(2)A and Me(2)B, \( \alpha \) and \( \beta \) methyl groups. The \( \tau \) values for the latter peaks (around 8.8) are in close agreement with the values quoted (\( \tau =8.82 \)) (36) for two equivalent methyls on carbon with one \( \beta \)-nitrogen and one \( \beta \)-methylene.

The high \( \tau \) value for the \( \xi \) methyl group would seem to be due to its proximity to the \( \pi \) system of the adjacent \( C=N \). However, in acetone 2,4 dinitrophenylhydrazone (37) the two methyl groups \( \beta \) to a \( C=N \) have \( \tau \) values of 7.90 and 7.82 respectively. Also the adjacent methylene protons (see below) do not have abnormally high \( \tau \) values, so that some other explanation has to be sought.

The high value recorded for the \( \xi \) methyl group can be explained if the group lies above the plane of the aromatic ring (attached to the nitrogen on the \( \beta \) carbon) on the remote side of the molecule. In this position it would experience a high degree of shielding from the aromatic ring current and would be expected therefore to have the observed high \( \tau \) value. (It should be noted that, sterically, this position for the \( \xi \) methyl group is quite possible. It will be referred to later in the section on the interpretation of the electron spin resonance spectra of the related free radical).
Furthermore, the shielding would be expected to drop if the aromatic system is twisted, by some means, so that the \( \epsilon \) methyl group no longer lies immediately above the ring. This is just the situation which is observed in the spectrum of the compound with ring ortho methyl groups. The \( \tau \) value for the \( \epsilon \) methyl is seen to be smaller than in the other two cases while that for the \( \alpha \) and \( \beta \) methyils is essentially constant.

In those compounds with ring substituents two additional close lines are observed (degenerate in the ortho substituted case) at about \( \tau = 7.7 \). This value is normal for ring methyl groups (38).

The next part of the NMR spectrum consists of four small lines in the form of two doublets, the two inner lines being slightly more intense than the outer ones. The centre of the group lies at about \( \tau = 7.4 \) and is attributed to the methylene group in the \( \gamma \) position. There seems to be no comparable NMR spectrum recorded for a similarly placed methylene but its position is typical.

Four lines of this kind are formed by an AB spin coupled system and indicate that the two methylene hydrogens are non-equivalent. In the proposed structure, as well as its alternative, this is clearly the case.

With a spin-spin coupling constant of 13 c/s and \( \tau \) values for the two protons of about 7.8 and 6.7, the ratio of \( \Delta \) \( \tau \) (110 c/s) to \( J_{AB} \) is about 8.5. This
means that the system is more nearly AX than AB and justifies the measuring of the values at the points at the centres of the doublets.

As additional confirmation, the $J_{AB}$ value of 13 c/s is typical for geminal protons separated by roughly the tetrahedral angle. ($J$ passes from 0 c/s at $125^\circ$ to 32 c/s at $100^\circ$ (39) with $J$ for methane calculated to be (40) 12.4 c/s).

The next feature in the spectrum is the large, rather complex group found at values of between 2.9 and 2.4. This is normal for phenyl groups and its intensity is consistent with the ten protons on the two phenyl rings.

The lowest field line is found at $\tau = 2.09 - 1.65$. From its intensity it originates from one proton and may be attributed to the hydroxyl group attached to nitrogen. It is seen to be very sharp and is, therefore, not likely to be intramolecular hydrogen-bonded. The chemical shift is normal for hydroxyl hydrogen but no values are recorded in the literature for similar hydroxylamine groups.

From this analysis it is seen that nothing has emerged which is inconsistent with either of the two constitutions proposed by Banfield and Kenyon.
Infra-red Analysis

Reproductions of the infra-red spectra of the phenyl compound and most of the aromatic substituted and deuterated homologues are given in Appendix 2 (Figs. 33 to 39) together with those of other types of condensation products. A key to the figures is given at the beginning of the appendix.

The IR spectra were all rather complex and only a limited amount of information regarding the composition of the compounds was extracted with any ease from them. A short account of the more important features is given below.

In all the compounds a broad, sometimes rather intense, band is to be found in the 3.1 - 3.3 μ region and is assigned to the hydroxylamine, OH stretching mode.

In order to check this, the phenyl compound dissolved in chloroform was shaken with D₂O for five minutes and evaporated to dryness under vacuum.

The resulting crystals were quickly ground up in Nujol and the infra-red spectrum run (Fig. 34a). This shows clearly that the OH band has almost completely disappeared compared with the parent compound (Fig. 33a) but that a strong band at 4.3 μ has formed. The ratio of the wavelengths for OH to OD is 0.72 which compares favourably with the root of ratio of the reduced masses (0.768). It may also be noted that the IR spectra of two radicals (Figs. 33c and d) are completely lacking in these bands.
In the case of those compounds deuterated in their alkyl chain (Figs. 33b, 34d and 35b) a band at 4.48 μ is to be seen and is assigned to C – D stretching. The C – H stretching mode in the undeuterated compounds is hidden in the strong 'Nujol' absorption at 3.4 to 3.5 μ.

The next feature is a sharp band at 6.25 μ with a slightly weaker one at 6.3 to 6.35 μ assigned to aromatic quadrant stretching (41). An interesting feature is that with para substituted compounds the low frequency band disappears and with meta substitution the relative intensity of the two bands is larger than in the other cases.

The strong bands in the 12 to 14.5 μ range due to C – H out-of-plane deformation, are seen and in general correspond to their respective aromatic types.
4. PREPARATION OF KENYON TYPE COMPOUNDS

The chemistry of the condensation of N-phenylhydroxylamine with acetone has been described (32) in detail and a discussion of the reaction and product has just been given. The method of preparation described was used throughout the present work for the various substituted and unsubstituted compounds, it being found successful in many cases. A list of those compounds prepared is given in Table 3 with their melting points.

In common with the findings of Banfield and Kenyon (32) the best yields obtainable arose from the use of perfectly dry components. (The presence of drying agents in the condensing solution did not improve the yield).

The acetone was of the 'Analar' grade and before use was stored, for one or two weeks, over anhydrous sodium sulphate. In the preparation of the solutions equimolecular proportions of acetone were filtered from the sodium sulphate directly onto the hydroxylamines. The solutions thus formed were, in general, perfectly clear but those cases which were cloudy were filtered.

The bottled solutions, usually straw-yellow in colour, were stored in a refrigerator and daily agitation normally resulted in a small crop of white crystals appearing after about one week. However, if none had appeared within about ten days, the bottle was opened for a few seconds, seeding the solution and resulting
Table 3

Substituted Kenyon Compounds

<table>
<thead>
<tr>
<th>Aromatic Group</th>
<th>Alkyl Substituent</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl</td>
<td>H</td>
<td>132.1</td>
</tr>
<tr>
<td>Phenyl</td>
<td>D</td>
<td>132.6</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>H</td>
<td>149.8</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>D</td>
<td>149.8</td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>H</td>
<td>143.6</td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>D</td>
<td>144.0</td>
</tr>
<tr>
<td>o-Tolyl</td>
<td>H</td>
<td>105.2</td>
</tr>
<tr>
<td>p-Ethylphenyl</td>
<td>H</td>
<td>119.3</td>
</tr>
<tr>
<td>2,4-Dimethylphenyl</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>p-Diphenyl</td>
<td>H</td>
<td>148-149</td>
</tr>
<tr>
<td>1-Naphthyl</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>p-Methoxyphenyl</td>
<td>H</td>
<td>125.3</td>
</tr>
<tr>
<td>m-Bromophenyl</td>
<td>H</td>
<td>130.0</td>
</tr>
<tr>
<td>m-Nitrophenyl</td>
<td>H</td>
<td>-</td>
</tr>
</tbody>
</table>
in the precipitation of hard rhomb shaped crystals. Once the crystals had appeared further agitation was unnecessary.

The precipitated crystals grew in size, over the following months, to 0.5 cm or more and were, with a few exceptions, almost completely colourless. Formation of the condensation products continued for about two to three months by which time the colour of the solution had darkened to a deep brown, indicating that decomposition of the original hydroxylamine or the condensation product or both was taking place.

At this point, or earlier if necessary, the crystals were filtered off, washed with two or three small portions of acetone and recrystallised twice from ethanol.

The products so formed were used, without further purification, in the preparation of the oxidised radicals and also for those samples used for IR and NMR analyses. Samples to be prepared for elemental analyses were further purified by recrystallising once from carbon tetrachloride and finally once more from ethanol. Table 4 gives the results of these analyses.

It was noted that, in common with the observation of Banfield and Kenyon on the phenyl compound, the large rhombs appeared completely stable but the smaller crystals, resulting from the recrystallisation from alcohol, in general darkened slightly over the period of a few months.
Table 4

Kenyon Compound Analyses

<table>
<thead>
<tr>
<th>Aromatic Group</th>
<th>Theory %</th>
<th>Found % *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Phenyl</td>
<td>72.45</td>
<td>7.43</td>
</tr>
<tr>
<td>Phenyl **</td>
<td>69.88</td>
<td>10.74</td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>73.53</td>
<td>8.03</td>
</tr>
<tr>
<td>p-Tolyl **</td>
<td>71.17</td>
<td>11.05</td>
</tr>
<tr>
<td>p-Ethylphenyl</td>
<td>74.54</td>
<td>8.53</td>
</tr>
<tr>
<td>p-Methoxyphenyl</td>
<td>67.02</td>
<td>7.31</td>
</tr>
<tr>
<td>m-Bromophenyl</td>
<td>47.39</td>
<td>4.42</td>
</tr>
<tr>
<td>p-Diphenyl</td>
<td>79.97</td>
<td>6.71</td>
</tr>
</tbody>
</table>

* Results from Alfred Bernhardt of the Max-Planck-Institut für Kohlenforschung - Müllheim.

** Compounds deuterated in their alkyl chain.
Some compounds were formed from D-6 acetone and were prepared in an identical way, the deuterated acetone used having an isotopic purity greater than 99.5% (CIBA).

In the preparation of the partially deuterated compounds, it was noted that the formation of the crystalline product, as judged by its first appearance, was some two and one half times slower than with the corresponding fully protonated species. It seems that little information of importance regarding the mechanism of the condensation can be gained from this observed isotopic effect as there would be three separate factors affecting the rate of the reaction:

(i) A Primary Effect is due to the rate depending on a C - D cleavage.

(ii) A Secondary Effect would be present as there are deuterated groups in the end product.

(iii) A Solvent Effect. The rate will be affected due to the solvent's being deuterated.

It is clear that, with so many factors influencing the rate of formation of the product, any evidence for a possible mechanism would be a major undertaking.

It is interesting to notice that Beckmann and Scheiber (42) prepared only the phenyl, p- and m-tolyl and 1-naphthyl compounds, other aryl hydroxylamines
were either not attempted or did not form. It was felt that a worthwhile project would be to investigate the effect an ortho-methyl group has on the condensation.

Also prepared and examined were those compounds with para-methoxy and meta-bromo substituents on the phenyl rings. The compound derived from para-chloro phenylhydroxylamine was prepared, hard glassy rhombs appearing mixed with yellow needles, but it decomposed on recrystallisation. This was not pursued further though Tudos et al (43) report that they were successful in recrystallising the compound by first mechanically sorting the glassy condensation product from the yellow needles of p-chloroazoxybenzene.

As mentioned in an earlier section, considerable difficulty was experienced in the synthesis of the 1-naphthyl hydroxylamine. However, enough of the 1-naphthyl condensation product was made to obtain ESR spectra.

Preparation of the Free Radicals

All the radicals were prepared in the following identical way:-

A solution (about 0.1 Molar but this was not critical) of the recrystallised condensation product in chloroform was added to an ammoniacal silver nitrate solution in a conical flask. The mixture was shaken continuously for twelve hours, by which time the non-aqueous layer had become a deep orange red colour. A portion of this was pipetted off, shaken once with distilled water
from which it was subsequently separated, and allowed to evaporate. The resulting material which was either in the form of a red oil or minute red crystals was then dried under vacuum for half an hour before being dissolved in 1:4 dioxan. The resulting solution was then ready for deoxygenation in the preparation of the ESR samples. This was described in greater detail in a previous section under "Experimental Procedure".
SECTION 6

E.S.R. STUDIES OF KENYON COMPOUNDS
1. **A REVIEW OF THE ESR SPECTRA**

In the initial stages while the subject of ESR was developing, the Kenyon radical was one of the first paramagnetic organic substances to be studied (44) and until diphenyl-picryl-hydrazyl (DPPH) was examined (45) the Kenyon radical was the most highly absorbing species known.

In 1957 van Roggen, van Roggen and Gordy(46) examined the benzene solution of the radical and reported a hyperfine structure of three, broad, equally intense lines arising from the interaction of the unpaired electron with one $^{14}$N nucleus and having a coupling constant of 13.5 gauss.

The present work was commenced with this background in mind and it was decided to attempt to examine any proton hyperfine structure which had previously not been reported.

Two papers have, subsequently, been published with details of the proton hyperfine structure and it is the purpose of this work to show that the interpretation of the spectra in these papers is not entirely correct.

The first report of the proton hyperfine structure of the (unsubstituted) Kenyon radical was given by Buchachenko (47) who interpreted the structure in terms of the five aromatic protons attached to the nitroxide group, but also to the eight closest alkyl protons. The analysis was inconsistent within itself, the
number of hyperfine components reported being too few for the number of protons said to be involved.

The only other reported work on the proton hyperfine structure is that of Tudos, Heidt and Ero (43) who have examined eleven related compounds with different ring substituents. The ESR data was only given for the one (unsubstituted phenyl) compound, and was substantially the same as that given later in this section. The assignments were, once more, only partially correct. The main structure, a quartet, was assigned to the equivalent ortho and para aromatic protons; this, it is seen later in this section, is in line with work on other aromatic nitroxides. However, the 'superhyperfine' structure was assigned to the meta aromatic protons and to five equivalent aliphatic protons. Limited rotation of a methyl group was given as the reason for the non equivalence of all eight closest protons but this is hard to understand on two counts:-

(i) Intuitively it is felt that the methylene, not the methyl group, is more likely to be limited in its rotation.

(ii) Coupling of the unpaired electron to these protons, by what mechanism is not disclosed, would not be completely eliminated by any limitation of the rotation. Indeed, any coupling to these protons seems unlikely by comparison with work on t-butyl substituted nitroxides (see later in this section).
2. **ESR SPECTRA**

The ESR spectra of the Kenyon type compounds are given in this section (Figs. 16 - 24), a key to the figures (Table 5) indicating those spectra which were run on an instrument other than that described in Section 3. To distinguish them, the symbol '100X' is used for the latter instrument, while 'M.S.' is used for the commercial instrument, the Hilger and Watts Ltd. Microspin, which was employed in certain cases. The spectra are all presented with the magnetic field decreasing from left to right and, to indicate the scale in each case, 5 gauss markers are included.

Table 6 presents the coupling constants in gauss for the relevant magnetic nuclei and once more the instrument used in each case is indicated. Also included in Table 6 is the ratio, for each determination, of the coupling constants of nitrogen to those of the ortho and para aromatic protons.
### Table 5

Key to Spectra of Kenyon type Radicals

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Aromatic Group</th>
<th>Alkyl substituents</th>
<th>Instrument used</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Phenyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>17</td>
<td>Phenyl</td>
<td>D</td>
<td>100X</td>
</tr>
<tr>
<td>18</td>
<td>Phenyl</td>
<td>H</td>
<td>100X *</td>
</tr>
<tr>
<td>19a</td>
<td>p-Tolyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>19b</td>
<td>p-Tolyl</td>
<td>D</td>
<td>100X</td>
</tr>
<tr>
<td>20a</td>
<td>m-Tolyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>20b</td>
<td>m-Tolyl</td>
<td>D</td>
<td>M.S.</td>
</tr>
<tr>
<td>21a</td>
<td>1-Naphthyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>21b</td>
<td>o-Tolyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>22</td>
<td>2,4 Dimethylphenyl</td>
<td>H</td>
<td>M.S.</td>
</tr>
<tr>
<td>23a</td>
<td>p-Ethylphenyl</td>
<td>H</td>
<td>M.S.</td>
</tr>
<tr>
<td>23b</td>
<td>p-Methoxyphenyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>24a</td>
<td>m-Bromophenyl</td>
<td>H</td>
<td>100X</td>
</tr>
<tr>
<td>24b</td>
<td>p-Diphenyl</td>
<td>H</td>
<td>100X</td>
</tr>
</tbody>
</table>

* one-sixth of spectrum shown with theoretical reconstruction
Table 6

Coupling Constants of Kenyon Radicals

<table>
<thead>
<tr>
<th>Aryl Group</th>
<th>Alkyl</th>
<th>$a_N$ (gauss)</th>
<th>$a_{op}$ (gauss)</th>
<th>$a_m$ (gauss)</th>
<th>$a_{CH_3}$ (gauss)</th>
<th>Width (gauss)</th>
<th>Instrument</th>
<th>$\frac{a_N}{a_{op}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>12.26 ± 0.09</td>
<td>2.36 ± 0.04</td>
<td>-</td>
<td>0.42 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>a</td>
<td>5.20</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>12.27 ± 0.08</td>
<td>2.37 ± 0.06</td>
<td>-</td>
<td>0.42 ± 0.02</td>
<td>-</td>
<td>b</td>
<td>5.18</td>
</tr>
<tr>
<td>Eth</td>
<td>D</td>
<td>12.21 ± 0.14</td>
<td>2.35 ± 0.05</td>
<td>0.87 ± 0.02</td>
<td>-</td>
<td>0.40 ± 0.01</td>
<td>a</td>
<td>5.20</td>
</tr>
<tr>
<td>Ph</td>
<td>D</td>
<td>12.25 ± 0.21</td>
<td>2.37 ± 0.13</td>
<td>0.96 ± 0.02</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>5.17</td>
</tr>
<tr>
<td>p-To</td>
<td>H</td>
<td>12.47 ± 0.16</td>
<td>2.43 ± 0.06</td>
<td>-</td>
<td>0.42 ± 0.02</td>
<td>-</td>
<td>b</td>
<td>5.13</td>
</tr>
<tr>
<td>p-To</td>
<td>H</td>
<td>12.48 ± 0.13</td>
<td>2.52 ± 0.07</td>
<td>-</td>
<td>0.42 ± 0.02</td>
<td>-</td>
<td>b*</td>
<td>4.95</td>
</tr>
<tr>
<td>p-To</td>
<td>D</td>
<td>12.39 ± 0.10</td>
<td>2.48 ± 0.01</td>
<td>0.90 ± 0.04</td>
<td>-</td>
<td>0.58 ± 0.04</td>
<td>a</td>
<td>4.99</td>
</tr>
<tr>
<td>p-To</td>
<td>D</td>
<td>12.33 ± 0.14</td>
<td>2.42 ± 0.10</td>
<td>0.89 ± 0.03</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>5.09</td>
</tr>
<tr>
<td>m-To</td>
<td>H</td>
<td>12.27 ± 0.07</td>
<td>2.33 ± 0.02</td>
<td>-</td>
<td>0.40 ± 0.01</td>
<td>-</td>
<td>b</td>
<td>5.16</td>
</tr>
<tr>
<td>m-To</td>
<td>D</td>
<td>12.32 ± 0.03</td>
<td>2.41 ± 0.06</td>
<td>0.83</td>
<td>-</td>
<td>-</td>
<td>a</td>
<td>5.12</td>
</tr>
<tr>
<td>m-To</td>
<td>D</td>
<td>12.28 ± 0.12</td>
<td>2.37 ± 0.04</td>
<td>0.78 ± 0.02</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>5.18</td>
</tr>
<tr>
<td>o-To</td>
<td>H</td>
<td>13.99 ± 0.14</td>
<td>0.79 ± 0.02</td>
<td>0.79 ± 0.02</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>17.7</td>
</tr>
<tr>
<td>2,4-Di-Me-Ph</td>
<td>H</td>
<td>13.37 ± 0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.88±0.15</td>
<td>a</td>
<td>-</td>
</tr>
<tr>
<td>p-Et-Ph</td>
<td>H</td>
<td>12.22 ± 0.04</td>
<td>2.41 ± 0.06</td>
<td>-</td>
<td>0.42 ± 0.01</td>
<td>0.2</td>
<td>a</td>
<td>5.07</td>
</tr>
<tr>
<td>p-Me-O-Ph</td>
<td>H</td>
<td>12.8 ± 0.10</td>
<td>2.65 ± 0.08</td>
<td>-</td>
<td>∇ 0.37</td>
<td>-</td>
<td>b</td>
<td>4.84</td>
</tr>
<tr>
<td>m-Br-Ph</td>
<td>H</td>
<td>12.1 ± 0.4</td>
<td>2.6 ± 0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>4.66</td>
</tr>
<tr>
<td>p-Di-Ph</td>
<td>H</td>
<td>11.82 ± 0.01</td>
<td>2.68 ± 0.18</td>
<td>∇ 0.47</td>
<td>-</td>
<td>-</td>
<td>b</td>
<td>4.41</td>
</tr>
<tr>
<td>i-Naphth</td>
<td>H</td>
<td>13.65 ± 0.10</td>
<td>-</td>
<td>-</td>
<td>∇ 2.3</td>
<td>-</td>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>m-Nitro</td>
<td>H</td>
<td>11.59 ± 0.11</td>
<td>2.53 ± 0.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>a</td>
<td>4.59</td>
</tr>
</tbody>
</table>

* in Tetrahydrofuran  \( a = M.S. \) \( b = 100X \)  \( Ph = Phenyl \)

To = Tolyl  Me = Methyl  Et = Ethyl  Br = Bromo
Fig. 16  ESR Spectrum of Phenyl Kenyon Radical
Fig. 17  ESR Spectrum of Partially Deuterated Phenyl Kenyon Radical
Fig. 18 Part of ESR spectrum of Phenyl Kenyon Radical, and reconstructed spectrum.

↑ indicates centre of quartet.

\[ a_{op} = 2.37 \, g \]

\[ a_{m} = 0.87 \, g \]

\[ a_{CH_{3}} = 0.42 \, g \]

1 cm = 0.91 g
Fig. 19  ESR Spectrum of
(a) p-Tolyl Kenyon Radical
(b) Deuterated p-Tolyl Kenyon Radical
Fig. 20  ESR spectrum of
(a) m-Tolyl Kenyon Radical
(b) The Partially Deuterated Radical
Fig. 21 ESR Spectrum of
(a) 1-Naphthyl Kenyon Radical
(b) o-Tolyl Kenyon Radical
Fig. 22 ESR Spectrum of 2,4 dimethylphenyl Kenyon Radical
Fig. 23  ESR Spectrum of
(a) p-Ethylphenyl Kenyon Radical
(b) p-Methoxyphenyl Kenyon Radical
Fig. 24  ESR Spectrum of
(a) m-Bromophenyl Kenyon Radical
(b) p-Diphenyl Kenyon Radical
3. DISCUSSION OF COUPLING CONSTANTS

It was seen in the previous section that the instrumental investigations of these condensation compounds confirms the structure that was proposed by Banfield and Kenyon (32) on purely chemical grounds. The results of the elemental analyses, where attempted, of the substituted compounds is also seen to agree throughout.

It is the intention of this discussion to show that the ESR results are also consistent with the work that has gone before and lead as well to a hitherto unrealised feature of the molecular structure of this group of compounds.
Nitrogen Hyperfine Structure

From a qualitative viewpoint, all the compounds exhibit a basic three line ESR pattern. By analogy with other papers dealing with nitroxides (48) there is little doubt that this main structure arises from the interaction of the unpaired electron with one $^{14}$N nucleus. The measured values of the nitrogen coupling constant ($a_N$) are given in Table 6.

Numerically, nearly all the $a_N$ values are seen to lie within the range $12.4 \pm 0.4$ gauss, their differences being considered too small to be significant. The main exceptions, however, are those with ortho methyl, 1-naphthyl, meta nitro, and para phenyl substituents, where the values (13.99, 13.65, 11.59 and 11.82 gauss respectively) show significant changes in the nitrogen coupling constant.

Recent work on phenyl-t-butyl nitroxide (49) shows that its $a_N$ value (13.3 gauss) is intermediate between that of diphenyl nitroxide (10.5 gauss) and di-t-butyl nitroxide (15.5 gauss) while a subsequent paper (50) quotes amended values for these compounds, $a_N = 12.50$ gauss for phenyl-t-butyl NO and 15.25 gauss for di-t-butyl NO. The values of $a_N$ for the compounds under consideration, as expected, are all very close to this; the small difference ($a_N = 12.25$ gauss for the phenyl compound) may be explained by one or more of three different effects.

(i) It is possible that the unpaired electron orbital may extend to a more remote part of the molecule by a hyperconjugative mechanism.
This is considered in more detail later in this section when dealing with the proton hyperfine structure, but suffice it to say at this point that the difference in $a_N$ (a reduction of about 0.3 gauss from phenyl-t-butyl NO) would seem reasonable if the assumption is made and there is a slight increase in the delocalisation of the unpaired electron.

(ii) A small inductive effect caused by an aliphatic substituent γ to the nitrogen atom may cause a small difference in the electronic distribution within the molecule.

The effect of a similar γ substitution is seen (50) when CH$_3^-$ is replaced by C$_6$H$_5^-$, $a_N$ for Ar-t-butyl NO = 13.22 gauss and for Ar-C$_6$H$_5$C(CH$_3$)$_3$NO = 13.19 gauss, where Ar = 2,6 di methoxy phenyl), though it is ten times smaller than that observed.

(iii) The third possible reason for the variation in $a_N$ is due to a solvent effect. Plots of nitrogen splittings in substituted nitroxides and in nitrobenzene anions measured in one solvent against those in another give straight lines for each series of radicals (51).

Rieger and Fraenkel (52) show that the spin density on nitrogen in nitroxides increases with the polarity of the solvent. However, the value (12.50 gauss) reported by Hoffman (50) for phenyl-t-butyl NO
was obtained from a solution in benzene which is hardly different from 1:4 dioxan in its polarity.

The conclusion is that, in the absence of more detailed quantitative evidence, the \( a_N \) value is such as could have been predicted.

Meta and para methyl substituents have only very small effects on the \( a_N \) values (an increase of 100 - 200 milligauss) and are not considered significant.

However, a very much larger effect is observed when an ortho position substituent is added. The ortho methyl, 2,4 dimethyl and 1-naphthyl compounds all have \( a_N \) values about 1.5 gauss larger than the para substituted or unsubstituted homologues and cannot be explained by either inductive or hyperconjugative reasoning, as any effects by the former would be identical in both the ortho and para substituted compounds, and by the latter would produce the opposite effects.

Steric hindrance may well produce these differences which closely correspond to the observations of Geske, Ragle, Bambenek and Balch (53) when studying substituted aromatic nitro anions. They found that the \( a_N \) values of nitrobenzene and mono and di methyl nitro benzenes vary only slightly and it was only when the substituents were di-ortho to the nitro group that a large increase in the value was seen. Associated with the increase in \( a_N \) was a corresponding decrease in coupling to the aromatic ring and substituent protons - this was also observed with the subject compounds and is dealt with in more detail below. The difference in
the two cases is interesting. Geske et al found that methyl substituents increase the \( a_N \) value from 10.32 gauss in nitrobenzene to 11.7 in 2,3 dimethyl nitrobenzene - see Table 7. It was only when an ortho-t-butyl or two ortho-methyl groups were added that much larger effects occurred. (14.9 and 17.8 gauss for \( a_N \) respectively). As seen from Table 6, a large increase in \( a_N \) and decrease in a aromatic occurred in substituted nitrooxides when only one ortho methyl group was added.

Geske (53) reported that the effect was caused by the two ortho substituents twisting the nitro group out of the aromatic plane and hence decoupling it from the benzene ring with a consequent localization of charge onto the nitro group. It was stated that electronic charge was not the same as spin density but that as a working principle, subject to further experience, the ring charge and spin densities were similar and behave in a similar fashion on perturbation of the \( \Pi \)-electron system under discussion.

The theoretical work of Colpa and Bolton (54) on hydrocarbon anion and cation radicals supports the above intuitive argument - arriving at the relation for the coupling constant \( a = -(Q + Kq) \rho \) where \( \rho \) and \( q \) are the spin density and excess charge density respectively.

Geske continues by stating that the simultaneous decrease of hyperfine coupling at all ring positions makes it likely that the effect observed is related to a
Table 7

Coupling Constants of some Substituted Nitrobenzene Anions *

<table>
<thead>
<tr>
<th>Parent Compound</th>
<th>$a_N^{\text{gauss}}$</th>
<th>$a_{o1}^{\text{gauss}}$</th>
<th>$a_{m1}^{\text{gauss}}$</th>
<th>$a_p^{\text{gauss}}$</th>
<th>$a_{m2}^{\text{gauss}}$</th>
<th>$a_{o2}^{\text{gauss}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>10.32</td>
<td>3.39</td>
<td>1.09</td>
<td>3.97</td>
<td>1.09</td>
<td>3.39</td>
</tr>
<tr>
<td>4-Methylnitrobenzene</td>
<td>10.79</td>
<td>3.39</td>
<td>1.11</td>
<td>3.98</td>
<td>1.11</td>
<td>3.39</td>
</tr>
<tr>
<td>3-Methylnitrobenzene</td>
<td>10.4</td>
<td>3.30</td>
<td>1.07</td>
<td>3.88</td>
<td>1.07</td>
<td>3.30</td>
</tr>
<tr>
<td>2-Methylnitrobenzene</td>
<td>11.0</td>
<td>3.12</td>
<td>1.04</td>
<td>3.91</td>
<td>1.04</td>
<td>3.12</td>
</tr>
<tr>
<td>2,3 Dimethylnitrobenzene</td>
<td>11.7</td>
<td>2.91</td>
<td>0.99</td>
<td>3.3</td>
<td>0.99</td>
<td>2.91</td>
</tr>
<tr>
<td>2,6-Dimethylnitrobenzene</td>
<td>17.8</td>
<td>0.85</td>
<td>0.88</td>
<td>1.41</td>
<td>0.88</td>
<td>0.85</td>
</tr>
<tr>
<td>2-t-butylnitrobenzene</td>
<td>14.9</td>
<td>-</td>
<td>1.1</td>
<td>2.5</td>
<td>1.1</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* See Ref. 53
charge transfer from the ring to the nitro group rather than a charge redistribution
taking place on the nitro group. He suggests that a small in-plane deflection
takes place with one ortho methyl next to the nitro group and only with two ortho
substituents does a twist about the N - C bond take place.

At this point it is worth comparing nitroxide radicals with aromatic nitro
anions.

The difference in charge means that coupling constants at corresponding
nuclei in nitro and nitroxide compounds cannot be directly compared as the wave
functions in the two cases will, in general, be completely different, though it
should be possible to compare the effects of similar substituents on the two dif-
ferent series.

The second difference, that nitro anions have in general a higher symmetry
than the nitroxides, is of more importance in the interpretation of the ESR re-
sults.

The substituted nitroxides under investigation all have a bulky t-butyl group
α to the nitrogen and there is little doubt that it would take up the position anti to
a ring ortho methyl substituent, leaving the \( \chi \) -bonded oxygen in the syn position.
Contrary to the ortho nitro toluene anion where a small in-plane deflection is
thought to take place (see above), the large t-butyl group would preclude this and
the only steric effect possible would be a twist about the N - (aromatic) C bond.
This then reduces the $\Pi$-electron overlap and increases the nitrogen coupling constant. It requires one large or two small ortho groups to produce the same result with aromatic nitro anions where there is no such large t-butyl group.

The observed differences are thus accounted for but will be mentioned again when dealing with the proton hyperfine splitting.

The coupling constants for the nitrogen nuclei in the para-phenyl and meta nitro substituted compounds are the only ones with values less than that of the unsubstituted material (11.32 and 11.59 gauss compared with 12.25 gauss). The difference is not large - of the same order as the effect due to a para methoxy group but of opposite sign - however it is the first known para-di-phenyl substituted nitroxide and the change in $a_N$ is worth comparing with that from the 1-naphthyl compound.
Proton Hyperfine Structure

The material which has been studied in most detail is the unsubstituted phenyl compound and it was the investigation of the proton hyperfine structure of this which led to a rather unexpected result.

The spectrum, Fig. 16 clearly shows that each of the nitrogen lines is split into four groups of lines equally separated and with relative intensities of 1:3:3:1. There is little doubt that this structure originates from the closely similar coupling constants of the para and ortho protons. Diphenyl nitrooxide and radicals arising from diphenylamines have coupling constants such that $a_o = a_p$ to within about 1% (55) and further proof of this equality is not felt necessary. Likewise, in every case where ring substituents have been added, the assumption has been further justified.

The values of $a_{op}$ for all the substituted compounds are given in Table 6 and are seen to vary only slightly, increasing from 2.35 gauss for the unsubstituted phenyl to 2.52 gauss for the para tolyl compound. A larger value of 2.82 gauss is seen for the para-diphenyl compound which would seem consistent with its low value of $a_N$. The structure for this is a 1:2:1 triplet arising from two equivalent ortho protons. The other large value of $o-p$ coupling constant (2.6 gauss) is found in the m-bromo compound. This was the only halogenated material studied and, due to the rather broad lines obtained, the precise value of the coupling constant was somewhat in doubt.
Exceptionally small coupling constants are found with ortho-methyl substituted compounds where the value for $a_{op}$ is seen to drop to 0.79 gauss. The 2,4 dimethyl compound has lines too numerous and close to be resolved but by inspection of the spectra for the three compounds reproduced in Fig. 21 and Fig. 22 the coupling constants are clearly similar. The line width, between points of maximum slope, is 2.9 gauss.

The other radical with a similar spectrum is that derived from N-1-naphthyl-hydroxylamine. Here again the proton structure is too close to be resolved, the line width of the three 'nitrogen' lines being 2.3 gauss.

Comparison of the ortho-para coupling constants of these mono-ortho methyl substituted nitroxides with the corresponding aromatic nitro anions (53) shows a larger discrepancy even than their nitrogen coupling constants. In the latter compounds no very large deviation of $a_o$ from 3.39 gauss (nitro benzene anion) is found until the di-ortho methyl substituents are added when the value drops to 0.85 gauss. In particular, the $a_o$ value for the o-methyl nitro benzene anion is 3.12 gauss, only 8% below that of nitro benzene. The $a_{op}$ values for the nitroxide radicals, however, are seen to drop by a factor of about three with the same substituent.

Another difference in the two classes of compounds is seen in the non equality of $a_o$ and $a_p$ in aromatic nitro anions. It is seen from Table 7 where the
coupling constants for some of the nitro anions are quoted, that the values vary by more than just a few percent. This has not been observed in the nitrooxides.

The argument put forward above to explain the observed differences in $a_N$ between ortho substituted nitrooxides and nitro anion compounds applies equally to the observed differences in $a_o$. The percentage differences in the proton coupling constants, however, are much larger than those for nitrogen but that is not inconsistent with the generally accepted notions of conjugation and configurational interaction. Hence the delocalisation of the unpaired electron from the nitrooxide or nitro groups onto the aromatic ring takes place through the overlap of the nitrogen $p$ atomic orbital with the aromatic $\pi$-orbital. The nitrogen will be nearly $sp^2$ in the nitrooxides as the $N-O$ bond will have a large double bond character. It is probable, therefore, that the nitrooxides, like the nitro anions, will be planar or near planar.

When the groups are made to twist out of the aromatic plane by ortho substituents the $p-\pi$ overlap is reduced and the spin density in the ring diminished. The spin density on the nitrogen, however, need not necessarily increase by a corresponding amount as this depends not only on the electron density, but also on the degree of configurational interaction admixing $s$ and $p$ orbitals and giving a finite electron density at the nuclear site.

Substituents, other than ortho-substituents, behave 'normally' as there is no steric effect.
The para-tolyl compound has a six line structure resulting from five equivalent spin $\frac{1}{2}$ nuclei, consistent with the spin density on the protons of the methyl group being the same as that of the replaced ring proton and being equivalent to the two ortho position protons. This is in agreement with previous observations (53, 56) on the para methyl nitro benzene anion and with the predicted theory (57) of hyperconjugation of aromatic methyl substituents.

The spectra from the meta tolyl and para ethyl compounds are also consistent with the above remarks - a note being made that only the methylene protons have an observable spin density in the ethyl substituent, giving a five line structure, assigned to the two methylene and two ortho ring protons all being equivalent.

Considering once more the spectrum of the unsubstituted phenyl compound Fig. 16 it is seen that each of the twelve groups of lines consists of about six components. However, the only aromatic protons unaccounted for in the part of the molecule containing the unpaired electron are two in the meta-positions. These, of course, are only expected to split the lines into 1:2:1 triplets so that there must be a more extensive delocalisation involved than might at first have been considered. Consistent with theoretical predictions, there is ample evidence to show that no measureable spin density reaches the protons of a tertiary butyl group $\mathcal{A}$ to a nitroxide (49, 50) and it is clear that the eight alkyl protons closest to the NO group are in environments very nearly the same as t-butyl. It is to be expected, therefore, that the observed hyperfine splitting cannot be assigned to
coupling with these protons but must be sought elsewhere. Also, if these protons were involved, they would give rise to nine components (or thirteen if one counts the aromatic meta protons with twice the coupling constants as well) which is contrary to the observed facts.

A close inspection of the spectrum (Fig. 16) of the phenyl compound shows that the six lines in the wing components of the 1:3:3:1 quartets do not follow a binomial intensity pattern. Indeed the two inner lines (four and five) appear more intense than the other four.

To explain the observed splitting, delocalisation of the unpaired electron onto a more remote part of the molecule had to be postulated. Either the aromatic imine oxide group or the remaining (E) methyl group would have to be involved and, to resolve this, the preparation of the compound from D-6 acetone was undertaken. The spectrum (Fig. 17) for the phenyl compound prepared in this way is seen in its main structure to be the same as that from the fully protonated counterpart - the \( a_N \) and \( a_{op} \) values remaining the same, the only difference is that each of the twelve groups of lines, with six components, reduces to triplets on deuteration. This evidence clearly shows that coupling takes place with some of the alkyl hydrogens, most likely the E methyl group and not with the aromatic imine oxide group which, of course, remained undeuterated. The coupling constants for the meta-protons can be obtained from the spectra of the deuterated
compounds and are quoted in Table 6. The more narrow splittings arising from the protonated compounds are also given in Table 6 and are seen to be a little less than half the \( a_m \) values.

In order to ascertain whether the foregoing discussion was consistent with the detailed structure of the spectrum, a reconstruction was undertaken using the empirical coupling constants and assigning them as follows: three equivalent protons, \( a_{op} = 2.37 \), two equivalent protons \( a_m = 0.87 \) and three equivalent (methyl) protons \( a_{CH_3} = 0.42 \).

The reconstruction, showing the first one-sixth of the complete spectrum, is given in Fig. 18.

It is clear from this that lines three to six (counting from the wing) consist of two almost degenerate components each. The difference between the components \( (a_m - 2a_{CH_3}) \) is only 30 milligauss which is too close to be resolved and leads to the first six lines having effective intensities of 1:3:5:7:7:5. As the measured line widths are about 200 milligauss (see Table 6) little broadening in these lines would be expected.

However, lines seven and eight are separated from each other, and from lines six and nine, by 210 milligauss each (the difference between six and seven is \( a_{op} - 2a_m - a_{CH_3} \)). Having line widths equal to the separation, they will cancel each other out and also modify the appearance of the neighbouring lines.
This is exactly the effect observed, even down to the detail that the last line of the first group (number six) is asymmetric. An enlarged one-sixth of the spectrum is shown in Fig. 18 by way of a comparison with the reconstructed spectrum.

The evidence presented shows conclusively that the $\epsilon$-methyl group in some way shares a part of the unpaired electron density. The mechanism for this is not obvious but one or two observations might usefully be made:

(i) There is little chance of the coupling taking place by a conjugative mechanism along the aliphatic chain. Apart from the improbability of this on chemical grounds, it would lead to coupling onto all the intermediate protons (and nitrogen) as well, and that is clearly not so.

(ii) From a steric point of view the methyl group may easily approach close to either the phenyl or the nitrooxide group. If it does so and is held in close proximity to the π electron system of either group for a sufficiently long time interval, $1.7 \times 10^{-6}$ seconds or longer, then it is conceivable that coupling could take place via a mechanism closely parallel to hyperconjugation.

The weakness of this hypothesis is that there seems little reason why the methyl group should remain preferentially in the neighbourhood of that part of
the molecule retaining the unpaired electron. The only possible cause for the molecule to remain in such a rigid or semi-rigid position would seem to be the repulsive influence of the two aromatic groups on each other, coupled with the effect of the two dipolar N - O groups.

The only recorded case of such a coupling mechanism 'across space' is reported for iminoxy radicals (58) where the coupling is thought to take place between the oxygen atom and the ortho-protons. At no time, however, is it possible for the molecule to bend out of a 'quasi-six-membered' ring structure and large coupling results. Typical coupling constants range from 1.25 to 2.7 gauss.

(iii) Hyperconjugation of methyl groups on aromatic rings is thought to take place (59) by time averaging the overlap of the proton s-orbitals with both positive and negative lobes of the aromatic \( \pi \) -orbital. If this is also the mechanism in this proposed 'long-range' hyperconjugation then it does not quite tie up with the NMR evidence obtained from the parent hydroxylamine (see previous section) which indicated that the \( \epsilon \) methyl group was positioned above and not to the side of the aromatic ring. This is not entirely incompatible as it is quite conceivable that the relative positions of the groups will change on oxidation of the hydroxylamine to the nitroxide.
The compounds derived from m- and p-methyl and p-ethyl phenylhydroxyl-
amine with acetone all exhibit this 'super-hyperfine' structure, the first two
were also prepared with deuterated acetone as well, these only showing a coup-
ing to the aromatic protons.

The para methoxy-phenyl compound exhibited this structure only in the cen-
tral (ortho) line of the central (nitrogen) line. All the other components were
broadened.
SECTION 7

STUDIES OF RADICALS FROM SUBSTITUTED UREAS
1. GENERAL

In the course of other work (the ESR investigation of Kenyon condensation radicals) it became apparent that it should be possible to prepare several different families of radicals from N-aryl, N-substituted hydroxylamines. Depending on the N-substituent, the stability of the radical types would vary from zero (or a very short period) as in the case of oxidised N-phenylhydroxylamine itself to infinite stability for example in the case of the above mentioned Kenyon type radicals. The former of course has an N-proton, the latter a large and complex aliphatic group as its N-substituent.

The radicals formed by oxidation of these various substituted N-hydroxylamines should all be N-di-substituted nitroxides by analogy with diphenyl nitroxide and the Kenyon radical.

Nitroxides other than those with aromatic and simple aliphatic groups are to be found but rarely in the literature; one of the few such compounds studied is diphenylguanidine (47).

The present section is devoted entirely to a study of one class of nitroxides, previously unreported, which are derived from N, N'-di-aryl-N-hydroxy ureas (ArN(OH)CONHAr').
2. PREPARATION AND CHEMICAL EVIDENCE FOR COMPOSITION

The preparation of all the hydroxy-ureas followed the same pattern described originally by Beckmann (50) for the N,N' diphenyl compound.

N-arylhydroxylamines will condense with iso-cyanates according to the formula ArNH(OH) + Ar'N.CO = ArN(CH)2.CO.NHar'.

The method consists of adding to a solution of the appropriate N-arylhydroxylamine in dry benzene, an equimolecular quantity of an aryl iso-cyanate. The latter, diluted with benzene, was added dropwise, with constant stirring and occasional cooling, over a period of about ten minutes. The quantities used were, usually, between 5 and 10 gm of hydroxylamine and between 50 and 100 ml of benzene, depending on the solubility.

The straw-yellow colour of the solution darkened within a few seconds of the addition of just a few drops of iso-cyanate, and about four minutes later, after further addition, the liquid became cloudy and finally started to precipitate a fine white powder. After half an hour, during which time the solution was occasionally stirred, the solid was filtered off and washed with one or two small quantities of dry benzene. After vacuum drying, the powder was recrystallised from aqueous methanol and finally benzene to yield a fine slightly off-white powder.
A list of all the compounds so formed is to be found in Table 8.

That the proton and not the hydroxyl group migrates during the condensation has been shown by Beckmann (60) who used N-benzylhydroxylamine and phenyl iso-cyanate to form the compound \( \text{C}_7\text{H}_7\text{N}\text{(OH)}\text{C} \text{O} \text{N} \text{H}_6\text{H}_5 \).

It was shown that this formed the same compound when benzylated as is formed when O-benzylhydroxylamine is treated with phenyl iso-cyanate and subsequently with benzyl chloride.

With both N-methyl and N-ethyl hydroxylamines and phenyl iso-cyanate, Kjellin (61) showed that the product formed was \( \text{C}_6\text{H}_5\text{NHCON(OH)}\text{Me} \) (or Et) and not \( \text{C}_6\text{H}_5\text{N(OH)CONHMe} \).

Both authors found that only one equivalent of the iso-cyanate reacted with the hydroxylamine and that ferric chloride produced an intense colouration with the compounds. All the di-arylhydroxy ureas prepared in the present work formed with ferric chloride intense blue-green solutions in ethanol.

Additional chemical evidence is afforded from the fact that the compounds are oxidised by ammoniacal silver nitrate yielding of course free radicals, the presence of which is shown by ESR.

Table 8 shows that the \( NN' \) diphenyl-thio-hydroxy urea was prepared. This followed a similar method to that for the oxy-compounds and resulted in
### Table 8

**Substituted Hydroxyureas**

<table>
<thead>
<tr>
<th>Ar¹ *</th>
<th>Ar¹&quot; *</th>
<th>Melting Point °C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl</td>
<td>Phenyl</td>
<td>126.3</td>
<td></td>
</tr>
<tr>
<td>Phenyl</td>
<td>Phenyl</td>
<td>-</td>
<td>Formed from Phenyl isothiocyanate</td>
</tr>
<tr>
<td>Phenyl</td>
<td>o-Tolyl</td>
<td>104 - 106</td>
<td></td>
</tr>
<tr>
<td>Phenyl</td>
<td>1-Naphthyl</td>
<td>122.3</td>
<td></td>
</tr>
<tr>
<td>o-Tolyl</td>
<td>Phenyl</td>
<td>112 - 113</td>
<td></td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>Phenyl</td>
<td>117.3</td>
<td></td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>Phenyl</td>
<td>128.6</td>
<td></td>
</tr>
<tr>
<td>p-Diphenyl</td>
<td>Phenyl</td>
<td>~174</td>
<td>Darkens over long temperature range before melting</td>
</tr>
<tr>
<td>2,4 Dimethylphenyl</td>
<td>Phenyl</td>
<td>128.6</td>
<td></td>
</tr>
</tbody>
</table>

* Ar¹NOHCONH Ar¹"
soft white platelets which were recrystallised from benzene. These crystals decomposed within three weeks to a sticky yellow mass, having been stored in a dark cupboard at room temperature throughout. The nature of the decomposition products is unknown but may be similar to the product formed by boiling the hydroxy urea in alcohol (60), i.e., to form \(N\,N'\) diphenyl urea. However, this was not followed up as the related radical was difficult to prepare and decomposed rapidly. Also, the ESR spectrum when observed had no proton hyperfine structure and the compound was treated somewhat as a curiosity in this context.

The nitroxide free radicals were all prepared in a similar way to those from the Kenyon condensation products.

A solution of the hydroxy urea in chloroform (about 0.1 M) was shaken in the presence of ammoniacal silver nitrate. The colour of the non-aqueous layer darkened to a deep red-brown which, after about half an hour, was removed and washed twice with water. The further preparation of the radical solutions in readiness for ESR measurements is described in more detail in an earlier section.

Judging by the rate of appearance of the coloured component under identical conditions, it would seem that the radicals derived from substituted ureas are formed more easily than those of the Kenyon type. Indeed, though no quantitative measurements on the rate of formation were made, it would seem that there
is greater than a factor of ten difference in the rate of oxidation of the hydroxyl
groups in the two classes of compound.

The stability of these radicals is not so great as those of the Kenyon type,
which is illustrated by their decomposition when the solution in which they are
found is evaporated to dryness.

Elemental analyses of four condensation compounds are given in Table 9.
Table 9

Urea Analyses

<table>
<thead>
<tr>
<th>Ar' *</th>
<th>Ar'' *</th>
<th>Theory %</th>
<th>Found % **</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Phenyl</td>
<td>1-Naphthyl</td>
<td>73.36</td>
<td>5.07</td>
</tr>
<tr>
<td>Phenyl</td>
<td>Phenyl</td>
<td>68.41</td>
<td>5.30</td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>Phenyl</td>
<td>69.40</td>
<td>5.32</td>
</tr>
<tr>
<td>2,4 Dimethylphenyl</td>
<td>Phenyl</td>
<td>70.29</td>
<td>6.29</td>
</tr>
</tbody>
</table>

* Ar' NOHCONHAr''

** Results by Alfred Bernhardt of the Max-Planck-Institut für Kohlenforschung – Müllheim.
3. **INFRA-RED ANALYSIS**

The infra-red spectra of these substituted hydroxy ureas were run and are reproduced (Figs. 37a to 38d) in Appendix 2, the key is to be found at the beginning of the section.

The spectra all have the common feature that, in addition to the OH stretching band (in general broad) there is also a sharp line in the same region (2.9 - 3.0 μ) which is assigned to N - H stretching.

The aromatic double band at 6.25 μ is present in these compounds but is dwarfed in several cases by a stronger and slightly broader band at about 6.1 μ which is assigned to carbonyl stretching.
4. ESR SPECTRA

The ESR spectra of the radicals derived from substituted hydroxyureas are given in this section (Fig. 25 to Fig. 30). As with the spectra of the Kenyon type radicals, these are presented with the magnetic field decreasing from left to right and 5 gauss markers are given in each case to indicate the scale. A key to the spectra is given - Table 10.

Table 11 shows the coupling constants in gauss of the magnetic nuclei for the compounds and also the ratio of the coupling constants of the nitroxide nitrogen and the aromatic ortho and para protons.
Table 10
Key to Spectra of Radicals from Substituted Ureas

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Ar' *</th>
<th>Ar'' *</th>
<th>Instrument Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>25a</td>
<td>Phenyl</td>
<td>1-Naphthyl</td>
<td>100X</td>
</tr>
<tr>
<td>25b</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>100X</td>
</tr>
<tr>
<td>26</td>
<td>Phenyl</td>
<td>o-Toly1</td>
<td>100X</td>
</tr>
<tr>
<td>27a</td>
<td>p-Toly1</td>
<td>Phenyl</td>
<td>100X</td>
</tr>
<tr>
<td>27b</td>
<td>m-Toly1</td>
<td>Phenyl</td>
<td>100X</td>
</tr>
<tr>
<td>28</td>
<td>o-Toly1</td>
<td>Phenyl</td>
<td>100X</td>
</tr>
<tr>
<td>29</td>
<td>2,4 Dimethylphenyl</td>
<td>Phenyl</td>
<td>100X</td>
</tr>
<tr>
<td>30</td>
<td>p-Diphenyl</td>
<td>Phenyl</td>
<td>M.S.</td>
</tr>
</tbody>
</table>

* Ar'NOCONHAr''
### Table 11

**Substituted Urea Coupling Constants**

<table>
<thead>
<tr>
<th>Ar' **</th>
<th>Ar'' **</th>
<th>$a_N$ gauss</th>
<th>$a_{op}$ gauss</th>
<th>$a_m$ gauss</th>
<th>Width gauss</th>
<th>$\frac{a_N}{a_{op}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl</td>
<td>Phenyl</td>
<td>9.14±0.07</td>
<td>1.79±0.01</td>
<td>0.80±0.03</td>
<td>-</td>
<td>5.11</td>
</tr>
<tr>
<td>Phenyl</td>
<td>o-Tolyl</td>
<td>9.09±0.11</td>
<td>1.83±0.01</td>
<td>0.82±0.02</td>
<td>√0.3</td>
<td>4.97*</td>
</tr>
<tr>
<td>Phenyl</td>
<td>o-Tolyl</td>
<td>9.36±0.12</td>
<td>1.82±0.02</td>
<td>0.77±0.03</td>
<td>√0.5</td>
<td>5.13</td>
</tr>
<tr>
<td>Phenyl</td>
<td>l-Naphthyl</td>
<td>9.19±0.06</td>
<td>1.83±0.03</td>
<td>0.85±0.05</td>
<td>-</td>
<td>5.02</td>
</tr>
<tr>
<td>p-Tolyl</td>
<td>Phenyl</td>
<td>9.43±0.09</td>
<td>1.90±0.03</td>
<td>0.93±0.04</td>
<td>-</td>
<td>4.97</td>
</tr>
<tr>
<td>m-Tolyl</td>
<td>Phenyl</td>
<td>9.16±0.03</td>
<td>1.82±0.02</td>
<td>0.70±0.03</td>
<td>-</td>
<td>5.05</td>
</tr>
<tr>
<td>o-Tolyl</td>
<td>Phenyl</td>
<td>9.63±0.10</td>
<td>0.41</td>
<td>0.41</td>
<td>√4.5</td>
<td>23.5</td>
</tr>
<tr>
<td>p-Diphenyl</td>
<td>Phenyl</td>
<td>8.82±0.15</td>
<td>1.89±0.08</td>
<td>0.85±0.02</td>
<td>-</td>
<td>4.87*</td>
</tr>
<tr>
<td>2,4 Dimethyl-phenyl</td>
<td>Phenyl</td>
<td>9.43±0.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 'Microspin' used for these determinations, 100X otherwise

** Ar'NOCO NHAr''
Fig. 25  ESR Spectrum of
(a) Ph NO CO NH 1-Naphthyl
(b) Ph NO CO NH Ph
Fig. 26  ESR Spectrum of PhNOCO NH o-Tolyl
Fig. 27  ESR Spectrum of
(a) p-Tolyl NOCO NH Ph
(b) m-Tolyl NOCO NH Ph
Fig. 28 ESR Spectrum of o-Tolyl NOCO NH Ph
Fig. 29  ESR Spectrum of 2,4(CH₃)₂ Ph NO CO NH Ph
Fig. 30  ESR Spectrum of p-Ph-Ph NOCO NH Ph
5. DISCUSSION OF SPECTRA COUPLING CONSTANTS

Inspection of Figs. 25 to 30 shows that the most general structure of the ESR spectra of these substituted ureas is similar to that from the Kenyon-type radicals and mono-nitro-aryl-anions, in that they take the form of three almost identical groups of lines, the origin of which may be assigned to coupling of the unpaired electron with one $^{14}$N nucleus.

It was pointed out earlier in this section that there was a little chemical evidence to show that the N-proton and not the N-hydroxyl group migrated during the condensation process onto the iso-cyanate nitrogen. The ESR spectra of these compounds has confirmed the limited chemical evidence showing unambiguously that the proton migrates, leaving the hydroxyl group attached to the original nitrogen atom. Thus those compounds formed from N-phenylhydroxylamine and various different aryl-iso-cyanates have spectra which are all almost identical - certainly from a qualitative viewpoint - and are consistent with one phenyl ring attached to the nitrogen on which there is a considerable unpaired spin density. (The radicals resulted from the mild oxidation of hydroxylroreaas and there is little doubt that that process would form nitroxides from the hydroxylamine group rather than from the N - H group).

The phenyl rings in the above mentioned compounds are thus shown to be attached to the nitrogen carrying the hydroxyl group, while additional confirmation
of this is obtained from those compounds prepared from N-hydroxylamines with
substituents on the phenyl ring, with phenyl iso-cyanate. The ESR spectra of
the radicals from these are all consistent with there being a nitrooxide group
attached to the relevant substituted aromatic system and not to the phenyl group.
In none of the compounds studied has any coupling to two nitrogen atoms been ob-
served.

**Nitrogen Hyperfine Structure**

By inspection of Table 11 it can be seen that the coupling constants of all the
compounds lie within the range $9.2 \pm 0.4$ gauss.

The variations are too small for many conclusions to be drawn from them,
however, but it is interesting to note certain trends.

The radical with the lowest $a_N$ value is that prepared from N-p-diphenyl-
hydroxylamine. This would seem to result from an increased delocalisation of
the unpaired electron over the larger conjugated system. The effect is small
and little significance, it is felt, can be drawn from the result.

The rest of the compounds exhibit nitrogen coupling constants which increase
up to a value of $9.63$ gauss in the case of the compound with an ortho-tolyl adjacent
to the nitrooxide group. There is no large difference between this and the
next lowest $a_N$ value ($9.48$ gauss for the para-tolyl compound).
A discussion of these trends is included below together with the proton coupling constants.

**Proton Hyperfine Structure**

An inspection of Table 11 and Figs. 25 to 30 shows that the ortho-para proton coupling constants for nearly all the compounds are almost constant, centring on about 1.85 gauss. The exception to this is the radical derived from N-o-tolylhydroxylamine and phenyl iso-cyanate where the $a_{op}$ value drops to 0.41 gauss. It is worth noting, however, that its homologue, formed by condensing N-phenylhydroxylamine with o-tolyl iso-cyanate is, from the ESR point of view, in no way exceptional.

The greatly reduced $a_{op}$ value for the ortho-tolyl compound is explained by a reduction in the unpaired electron spin density on the ring adjacent to the nitroxide group. The reason for this seems once more (see previous section) to be due to a twist of the nitroxide group relative to the ring and caused by the steric effect of the ortho-methyl protons lying close to the oxygen atom. Also attached to the nitrogen is a carbonyl group which, being larger than oxygen, is most likely to lie in the anti position relative to ortho-methyl. It appears that the carboxyl group is also too large to allow the in-plane bending observed by Geske et al (53) for nitro anions when one ortho substituent is placed in the ring.
That a partial removal of the unpaired electron from the aromatic ring has taken place is shown by the decrease in the proton coupling constant and is presumably due to the uncoupling of the overlapped nitrogen p- and the aromatic \( \pi \)-orbitals.

It is interesting to note that, though the proton coupling constants have decreased by 1.4 gauss (or a factor of 5 - 6 times), the nitrogen coupling has remained almost constant. The reason for this would seem to lie in the conjugated system which includes the carboxyl and nitrooxide groups. Being conjugated, the system is able to accommodate the consequent increased unpaired electron density delocalised over all four atoms but this, as was explained in the previous section, does not necessarily mean that the spin density on any one atom (in particular nitrogen) increases to any large extent.

The coupling constant for the meta-position protons (see Table 11) in nearly all the radicals was found to be practically constant, centring around 0.86 gauss. The compound formed from N-o-tolylhydroxylamine was exceptional.

The compound prepared from N-2,4 dimethylphenylhydroxylamine and phenyl iso-cyanate gave results closely similar to the o-tolyl compound (see Fig. 29 and Table 11).
SECTION 8

STUDIES OF SOME

MISCELLANEOUS CONDENSATION PRODUCTS
As a continuation of some ideas developed during the study of substituted ureas - see previous section - a search was made for other types of compound with the general structure ArN(OH)R. Depending on the nature of R, it was hoped that these would produce, on oxidation, radicals which were stable enough - due to conjugation of the unpaired electron over the aromatic ring - to prepare chemically and to study by ESR. A report on two of these follows.

1. **PREPARATION AND PROPERTIES OF THE N-PHENYLHYDROXYLAMINE/ PHENYL CHLOROFORMATE CONDENSATION**

The condensation of N arylhydroxylamines with aryl chloroformates is reported once only in the literature (62). The reaction is thought to proceed as follows:-

\[
\text{ArNHOH + Ar'O.CCl} \rightarrow \text{ArNOH.CO.OAr' + HCl}
\]

the product being an N-aryl-N-hydroxy-aryl-urethane.

The experimental details for its preparation are given below.

N-phenylhydroxylamine (7 g) was dissolved in dry ether (300 ml) into which was placed potassium carbonate (about 10 g). An equimolar quantity of phenyl chloroformate (10 g) was mixed with dry ether (10 - 20 ml) and added slowly to the hydroxylamine solution with continuous stirring and cooling. The mixture was then allowed to stand for 30 minutes when it was filtered and the filtrate
evaporated slowly to dryness. The yellow-brown solid residue was then re-
crystallised from benzene and carbon tetrachloride to form fine needle shaped
white crystals. This was the desired condensation product, the melting point
being 127°C compared with 124°C in Oesper and Broker's reference (62) above.
The analysis results and spectral evidence for its composition are given in a later
part of this section; some chemical evidence is given below:-

(i) A chloroform solution of the product is oxidised readily with
ammoniacal silver nitrate, giving a red coloured solution. This
parallels the reactions of the substituted hydroxy-ureas, the 'Ken-
yon' type compounds and N, N diphenylhydroxylamine which, on
oxidation, give coloured nitroxide free radicals.

(ii) An ethanol solution of the condensation product produces a bright
purple colour on the addition of ferric chloride. This would seem
to indicate the presence of a group - N(OH).CO - (see also the sub-
stituted hydroxy ureas but not the Kenyon type condensation products).

(iii) Some indication of the above preparative reaction proceeding as
stated is given by considering the chemistry of chloroformates to-
wards other compounds.

(a) N-hydroxy urethanes with alkyl substituents have been
prepared (63) with the general formula R"O . CO . N(OH)R′
from $N - R' -$ hydroxylamines and $R'' -$ chloroformate esters.

(b) In a recent review of the chemistry of chloroformates it was shown that, with amino phenols, it is the amino group which is more reactive towards chloroformate than the OH group, this remaining unaffected unless $N -$ acylation becomes impossible due to prior substitution.

The above evidence leads to the conclusion that the product formed by reacting $N$-arylhydroxylamines with aryl chloroformates has the general structure $\text{ArN(OH)CO}_2 \text{Ar'}$.

Analysis result for $N$-phenyl-$N$-hydroxy-phenyl-urethane:-

Theory, $C = 68.11$, $H = 4.84$, $N = 6.11$

Found, $C = 67.58$, $H = 4.66$, $N = 6.20$

Evidence given below, derived from infra-red, NMR and ESR also supports the above conclusion.
2. PREPARATION AND PROPERTIES OF N-PHENYLHYDROXYLAMINE/

BENZOIC ANHYDRIDE CONDENSATION PRODUCT

The reaction of N-arylhydroxylamines with benzoic anhydride is reported
(65, 66) to give (i) an N-aryl-N-benzylohydroxylamine of the form
ArN(OH)COPh and (ii) benzoic acid.

The preparation of the compound was as follows:-

To N-phenylhydroxylamine (4.5 g) in dry ether (30 ml) was added a saturated
solution of benzoic anhydride (9.3 g), also in dry ether. The mixture was shaken
a few times and, after about 10 minutes, during which a slight rise in temperature
was noted, a fine white precipitate formed. It was shaken for a further 20 min-
utes when the precipitate was filtered off and washed with ether.

The product was purified by recrystallisation from carbon tetrachloride
forming fine white needle-shaped crystals melting at $117^\circ$C.

An ethanol solution of this product gave, on the addition of ferric chloride,
an intense purple colouration. The formation of colour under these conditions
suggests, as with the hydroxy-ureas and the compound formed from phenyl
chloroformate, a structure of the form $\text{-N(OH)CO-}$.

A chloroform solution of the product was oxidised by ammoniacal silver
nitrate to a red colour. The presence of a free radical was demonstrated by
ESR, but decomposed on evaporation of its solution to dryness.
Analysis result for N-phenyl-N-benzoylhydroxylamine was:

Theory, C = 73.22, H = 5.20, N = 6.57

Found, C = 73.31, H = 5.25, N = 6.62

The IR and ESR evidence for the proposed composition of this and the chloroformate condensation follows.
3. **INSTRUMENTAL ANALYSIS**

The infra-red spectra of the N-hydroxy-urethane (Fig. 39b) and the N-benzoylhydroxylamine (Fig. 39a) in Appendix 2 supply further evidence in support of the proposed structures.

The spectrum of the N-hydroxy-urethane has a strong band at 3.5 μ assigned to the OH stretching mode. A band (rather weak) at 6.26 μ and two strong bands at 13.28 and 13.47 μ are due to the various aromatic modes.

The NMR spectrum of the N-hydroxy-urethane was run on a Varian HA100 instrument, the only absorptions being found in the γ = 2.5 region due to the two aromatic phenyl rings. No OH absorption was found, it being assumed that it lay in the region of the phenyl protons.
4. **ESR SPECTRA**

Fig. 31 and 32 show the ESR spectra of the two radicals prepared by oxidising the condensation products of N-phenylhydroxylamine with phenyl chloroformate and with benzoic anhydride.

All the evidence given above indicates that the former is

\[ \text{C}_6\text{H}_5\text{NO}\cdot\text{CO}\cdot\text{OC}_6\text{H}_5 \]

(l)

and the latter is

\[ \text{C}_6\text{H}_5\text{NO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5 \]

(II)

It is seen that the ESR spectra are almost identical and they are being treated together in this section, while Table 12 shows the hyperfine coupling constants for the compounds are also very close.

The spectra consist of the familiar three similar groups of lines, arising from a large spin density on one nitrogen atom. The coupling constants \(7.36-7.36\) gauss - are small compared with those of the substituted ureas and Kenyon type compounds but still very much larger than any proton coupling.

The proton hyperfine structure for both compounds is consistent with there being one phenyl ring adjacent to the nitroxide group - giving a quartet \(1:3:3:1\) from the ortho and para hydrogens and triplets \(1:2:1\) from the meta protons.
Table 12
Coupling Constants of Two Radicals

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_N$ gauss</th>
<th>$a_{op}$ gauss</th>
<th>$a_m$ gauss</th>
<th>Width gauss</th>
<th>$a_N/a_{op}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhNOCOPh</td>
<td>7.68±0.04</td>
<td>1.50±0.03</td>
<td>0.65±0.05</td>
<td>$\frac{1}{2} a_m$</td>
<td>5.10</td>
</tr>
<tr>
<td>PhNOCO$_2$Ph</td>
<td>7.28±0.02</td>
<td>1.48±0.01</td>
<td>0.86±0.04</td>
<td>0.37</td>
<td>4.88*</td>
</tr>
<tr>
<td>&quot;</td>
<td>7.45±0.04</td>
<td>1.48±0.03</td>
<td>0.89±0.01</td>
<td>-</td>
<td>5.03</td>
</tr>
</tbody>
</table>

* 'Microspin' used for this determination, 100X otherwise.
Fig. 31 ESR Spectrum of PhNOCO₂Ph
Fig. 32  ESR Spectrum and Reconstruction for PhNOCOPh

\[ a_{op} = 1.50 \text{ g} \]
\[ a_{m} = 0.65 \text{ g} \]
\[ 1 \text{ g} = 0.72 \text{ cm} \]
Due to partial overlap, the number of components is reduced, but it is clear that the assignments given in Table 12 are satisfactory and lead to the empirical spectrum. A reconstruction from the coupling constants for the first one third of the spectrum from compound II is given in Fig. 32 by way of a comparison with the experimental spectrum. It is seen that lines 3 and 4, 6 and 7, and 9 and 10 are much closer to each other than the rest (\( a_{\text{op}} - 2a_{\text{m}} = 200\) milligauss), the linewidths being about 300 milligauss these pairs of lines overlap.

No observable structure from the second aromatic ring has been observed, even though in compound II, the \( \pi \)-system may be considered to extend over the whole molecule. If, in fact, there is any coupling, then it will be less than 300 milligauss overall, i.e. \( a_{\text{op}} \) will be less than 100 milligauss, and, due to the resolving power of the instrument, this would not be observable.

Coupling to the second aromatic system in compound I is less likely as the system is not expected to extend over an ester linkage.

The line widths in the two compounds are almost identical, being about 300 milligauss, one half of the \( a_{\text{m}} \) values.

Coupling to the second aromatic system in compound I might also be expected to take place, by analogy with the radicals formed by oxidation of ethyl and methyl \( N \)-hydroxycarbamates, where the alkoxy-protons possess coupling constants of about 1.0 gauss (37). However, none is observed and it can only be assumed
that the substitution of the N-proton by N-aryl groups drastically affects the electronic distribution so that coupling to the more distant groups is greatly reduced.
GENERAL DISCUSSION OF COUPLING CONSTANTS
A comparative discussion of some of the salient features arising from the coupling constant of all the compounds considered in this thesis was thought to be of importance. Certain features are seen to be common to several of the classes of compound while others are seen to contrast.

Every compound studied was derived from an N-arylhydroxylamine with its N-proton substituted. The compounds of the form ArNOHR, were all converted to substituted nitrooxide radicals, of the form ArNOR and, because of this common structure, the ESR spectra all had certain similarities.

Thus every spectrum consisted of three almost identical groups of lines, in general completely separated from each other, showing that the coupling constant to the $^{14}N$ nucleus was much larger than to any other magnetic nucleus. The coupling constants of the various compounds are given in Tables 6, 11 and 12 and it is seen that, in every case, the ratio for nitrogen to that for the ortho and para aromatic protons (the next largest coupling constant) is 4.3 or greater. It is an interesting fact that the majority of $a_N/a_O$ values lie within only 4% of 5.0, the exceptions depending more on substituents on the aromatic ring than on the N-substituent $R$.

Diaryl-hydroxyureas and Kenyon type compounds were prepared with ring substituents and, in general, the effects on the various coupling constants were parallel in the two classes of compound. Thus the p-diphenyl compounds both
had very low $a_N$ values. Ortho substituents increase the $a_N$ values in both types of compound while, at the same time, markedly decreasing the coupling to ring protons. This, it was seen, was caused by a steric effect, twisting the aromatic ring relative to the nitrooxide group and consequently decreasing the unpaired electron delocalisation through a reduction of the overlap of the $\pi$ systems. It was seen to contrast with observations on aromatic nitro anions where a similar effect only occurs when there are two ortho substituents present.

Both the N-substituents were thus seen to be sufficiently large to prevent the aromatic mono-ortho substituent taking up the position anti to the nitrooxide and also an in-plane tilt was seen to be unlikely due to their size. The twist about the N-aromatic bond becomes necessary to remove the close proximity of the N, and the aromatic ortho, substituents.

The nitrogen coupling constants for the Kenyon type compounds lay between 11.6 and 14.0 gauss while the substituted ureas had values between 8.8 and 9.6 gauss. The two miscellaneous condensation products gave radicals whose $a_N$ values were 7.26 and 7.66 gauss. These differences are explained by variations in the $\pi$-delocalisation of the unpaired electron from the nitrooxide to the carbonyl and other groups. In the Kenyon compounds there is, of course, little delocalisation, there being an almost pure $\sigma$-bond between the nitrogen and the sp3 tert-butyl like carbon. With all the other compounds there is a carbonyl group $\alpha$ to the nitrogen which, due to conjugation, is highly likely to have a
large spin density. This is not directly observable as a hyperfine splitting as neither of the nuclei is magnetic; however, the secondary effect is to reduce the spin density on the rest of the molecule and this is seen as a reduction in both nitrogen and aromatic proton coupling constants.

Further delocalisation onto the more remote parts of the molecules would be expected as there is a considerable double bond character beyond the carbonyl groups. The compounds formed from benzoic acid anhydride and from chloroformate might even be thought to extend their delocalisation onto the second aromatic ring. In no compound, however, has any coupling been observed to groups $\beta$ to the nitrooxide. If indeed any coupling does take place, then it would have to be nearly 100 times smaller than to the nitrooxide nitrogen and, to observe this, an instrument with much greater resolving power would have to be employed.

This comparison with compounds possessing a large delocalisation onto $\alpha$ carbonyl groups - but no observable coupling to magnetic nuclei $\beta$ to the nitrooxide - makes the case for a hyperconjugative coupling to the $\xi$-methyl group in the Kenyon compounds even more convincing. This coupling, seen in nearly all Kenyon radicals with alkyl substituents on the aromatic ring, has in every case a coupling constant of just over 400 milligauss which is only 30 times smaller than to the nitrooxide nitrogen.

The different classes of radical contrast with each other in their stability. Although a detailed study of this subject has not been made, it appears that the
stability of the radicals in solution increases in rough proportion with the time required to oxidise their condensation products in their preparation.

In all the radicals studied, the ortho and para proton coupling constants, where obtainable, had equal values to within the experimental resolution of the instrument. Likewise the coupling constants to ring methyl and ethyl groups were, with the exception of ortho substituents, the same as the replaced protons. This latter effect is consistent with other work (68) where hyperconjugation has been observed, the former seems to apply to uncharged radicals only, c.f. nitro anions (53) where there is reported to be a marked difference between $a_o$ and $a_p$.

An interesting non-equivalence has been reported recently (69) between the ortho-protons in the anions of nitrosobenzene and of azobenzene. This is thought to be due to a restricted rotation of the aromatic rings about the Ar – N bonds.

It was not observed in the neutral nitroxide radicals however - this presenting further evidence for the equivalence of the para with both the ortho protons - and no reason was given for the difference with the anionic species.
Appendix 1

Determination of the g-Value for the Phenyl Kenyon Radical

The absolute determination of g-value invokes the use of the basic ESR equation:

\[ g = \frac{h \omega}{\beta H} \]

(see Section 2) where \( \omega \) (the microwave frequency) may be measured directly and \( H \) (the magnetic field) may be determined using a Proton Magnetometer, the construction and use of which is given in Section 3.3.

The accuracy to which the magnetometer frequency may be measured is set by a heterodyne beat frequency meter (army surplus type BC221-AF) and is 1 part in 13000. However, the limiting accuracy of the technique is set by the measurement of the microwave frequency which is obtained by using a tuneable absorption cavity wave meter (Wayne Kerr Ltd., type SP1) with a micrometer dial. Dial positions can be measured to four significant figures while the discrimination is quoted as being better than 1 part in 2000 of frequency.

The experimental method was as follows:

The spectrometer was set up with the radical in the cavity, the output from the 100 kc/s tuned amplifier being fed directly to an oscilloscope, the time base of which was set to 50 c/s. The 100 kc/s modulation power level was set to its
maximum value and a 50 c/s voltage applied to the magnet modulation coils. The field was manually adjusted until an absorption was observed on the oscilloscope and by alternate manipulations of the 50 c/s voltage amplitude and field strength the absorption was centred and made to fill the oscilloscope screen. Reduction of the 100 kc/s modulation amplitude improved the resolution of the absorption peaks but decreased the amplitude – a compromise had to be found.

Meanwhile the proton magnetometer probe was placed next to the ESR cavity such that the two were positioned along the magnetic field axis. The audio-frequency output from the magnetometer was connected to the second beam of the oscilloscope and the oscillation frequency adjusted until a sharp absorption peak appeared on the screen. Small adjustments of the oscillation frequency allowed the magnetometer peak to coincide with the centre of the ESR absorption.

The amplitude of the 50 c/s modulation had then to be reduced and by small alterations of the field strength and magnetometer oscillation frequency the coincidence of the centres of the two absorptions was maintained. With the minimum 50 c/s modulation (corresponding to a field change of about one gauss) the final adjustments brought the two centres in line once more.

At this point the magnetometer frequency was measured. This was carried out by using a radio receiver (army surplus type R1155) and the beat frequency meter. The receiver was used to pick up the oscillation frequency, detect it
and give an approximate value to the frequency. The precise value was obtained by tuning the frequency meter until it beat with the magnetometer giving an audio frequency on the loudspeaker of the receiver. The frequency value was obtained from a calibrated vernier scale when the beat frequency was reduced to zero.

As soon as possible after the determination of the magnetometer frequency, the microwave frequency was measured by tuning the wave meter.

The magnetometer frequency $\nu_m$, once determined, enabled the magnetic field to be calculated using the relation

$$H = 2.3497 \times 10^{-4} \nu_m$$

which is valid for all proton samples at resonance.

**Results for $g$ determination of a benzene solution of the phenyl Kenyon free radical**

Magnetometer frequency $\nu_m = 13.794$ Mc/s

Microwave frequency $\nu_e = 9097$ Mc/s

Magnetic field $H$ corresponding to $\nu_m$

$$= 2.3497 \times 10^{-4} \times 13.794 \times 10^{-6} = 3239.8 \text{ gauss}$$

$$g = \frac{\hbar \nu_e}{\sqrt{2} \mathcal{H}} = \frac{6.8252 \times 10^{-27}}{9.2732 \times 10^{-21}} \times \frac{9097 \times 10^6}{3239.8} = 2.0061$$

This value of $g$ compares well with $2.0057 \pm 0.0002$ found by Holden et al (45).
Appendix 2

The present section includes only the infra-red spectra of the various condensation compounds referred to earlier in this work. A key to the spectra is included (Table 13).

All the spectra were run as Nujol mulls on sodium chloride plates using a Grubb Parsons spectrophotometer type GS2A. The range covered was 2.5 to 15 μ, the scale being linear in wavelength.
Table 13

Key to Infra-red Spectra

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 a</td>
<td>Phenyl Kenyon compound</td>
</tr>
<tr>
<td>33 b</td>
<td>Phenyl Kenyon compound (alkyl chain deuterated)</td>
</tr>
<tr>
<td>33 c</td>
<td>Phenyl Kenyon radical</td>
</tr>
<tr>
<td>33 d</td>
<td>Phenyl Kenyon radical (alkyl chain deuterated)</td>
</tr>
<tr>
<td>34 a</td>
<td>Phenyl Kenyon compound (hydroxyl group deuterated)</td>
</tr>
<tr>
<td>34 b</td>
<td>Ortho-tolyl Kenyon compound</td>
</tr>
<tr>
<td>34 c</td>
<td>Para-tolyl Kenyon compound</td>
</tr>
<tr>
<td>34 d</td>
<td>Para-tolyl Kenyon compound (alkyl chain deuterated)</td>
</tr>
<tr>
<td>35 a</td>
<td>Meta-tolyl Kenyon compound</td>
</tr>
<tr>
<td>35 b</td>
<td>Meta-tolyl Kenyon compound (alkyl chain deuterated)</td>
</tr>
<tr>
<td>35 c</td>
<td>Para-ethylphenyl Kenyon compound</td>
</tr>
<tr>
<td>35 d</td>
<td>Meta-bromophenyl Kenyon compound</td>
</tr>
<tr>
<td>36 a</td>
<td>Para-methoxyphenyl Kenyon compound</td>
</tr>
<tr>
<td>36 b</td>
<td>Para-ethoxyphenyl Kenyon compound</td>
</tr>
<tr>
<td>36 c</td>
<td>Para-diphenyl Kenyon compound</td>
</tr>
<tr>
<td>36 d</td>
<td>I-Naphthyl Kenyon compound</td>
</tr>
<tr>
<td>37 a</td>
<td>N-phenyl-N-hydroxy-N'-1-naphthylurea</td>
</tr>
<tr>
<td>37 b</td>
<td>N-phenyl-N-hydroxy-N'-o-tolylurea</td>
</tr>
<tr>
<td>37 c</td>
<td>N-p-tolyl-N-hydroxy-N'-phenylurea</td>
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<tr>
<td>37 d</td>
<td>N-m-tolyl-N-hydroxy-N'-phenylurea</td>
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<tr>
<td>38 a</td>
<td>N-p-diphenyl-N-hydroxy-N'-phenylurea</td>
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<td>38 b</td>
<td>N-phenyl-N-hydroxy-N'-phenylurea</td>
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<tr>
<td>38 c</td>
<td>N-2,4-dimethylphenyl-N-hydroxy-N'-phenylurea</td>
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<tr>
<td>38 d</td>
<td>N-ortho-tolyl-N-hydroxy-N'-phenylurea</td>
</tr>
<tr>
<td>39 a</td>
<td>N-phenyl-N-benzoylhydroxylamine</td>
</tr>
<tr>
<td>39 b</td>
<td>N-phenyl-N-hydroxy-phenylurethane</td>
</tr>
</tbody>
</table>
Fig. 35
Fig. 36
Fig. 37
Fig. 39
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