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Electron Spin Resonance Studies of Oxidation. Part V.¹ Reactions of Lead Tetra-acetate. (IV.)² Iminoxy-radicals Derived from Oximes

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Ketoximes have been oxidised by lead tetra-acetate to give (comparatively stable) iminoxy-radicals whose electron spin resonance spectra have been studied. The radicals are of σ -type and the modes of interaction between the unpaired electron and the protons in the radical are markedly different from those in π -radicals. In particular, longrange couplings are observed which are strongly dependent on the stereochemistry of the bonds joining the proton concerned to the iminoxy-function. By studying the radicals from alicyclic oximes of known stereochemistry, it has been possible to make a number of deductions about the variation in the coupling with the geometry of the system, although the mechanism of transmission of spin-density, and the underlying reasons for the stereochemical dependence of the couplings, are not yet clear.

ELECTRON spin resonance spectra of iminoxy-radicals, RR'C=N-O, have been observed by irradiating dimethylglyoxime,³ oxidising oximes with ceric ammonium nitrate in a fast-flow system,⁴ and oxidising oximes with lead tetra-acetate in methylene dichloride ⁵ and in benzene.^{6,7} We now describe and discuss the spectra obtained from a number of ketoximes of various structural types, elaborating on our preliminary report⁵ and drawing attention in particular to the evidence which is now available about the long-range interactions which occur in these radicals.

We have generated the iminoxy-radicals by preparing deoxygenated solutions of the oxime and lead tetraacetate, each in methylene dichloride, mixing the solutions under nitrogen at room temperature, and rapidly transferring the resulting solution to the cavity of the spectrometer. In most cases the spectrum contains lines due to secondary nitrogen-containing radicals 5-7 (which have been wrongly ascribed, in one report, to the corres-

ponding iminoxy-radicals⁸). We shall subsequently discuss the spectra and origin of these secondary radicals.

Many iminoxy-radicals are surprisingly stable, although less so than their saturated analogues, nitroxide radicals, RR'N-O. We investigated the decay of four radicals, generated from equimolar concentrations $(5 \times 10^{-3} M)$ of the oxime and lead tetra-acetate in methylene dichloride in the absence of oxygen, and found the kinetics to be first-order with respect to the iminoxy-radical, with the following half-lives (min.): biacetyl monoxime, 10.5; fluorenone oxime, 5.5; 4,4'-dinitrobenzophenone oxime, 3.0; benzophenone oxime, 0.5. Some other iminoxy-radicals (e.g., those from cyclopentanone and cyclohexanone oximes) proved to be too short-lived to be examined in a static system. It was possible to examine the spectra of some of these radicals by employing a flow-system⁹ in which solutions of lead tetra-acetate and the oxime, each in

¹ Part IV, W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1964, 4857.

² Part III, W. A. F. Gladstone and R. O. C. Norman, J. Chem. Soc., 1965, 5177. ^a I. Miyagawa and W. Gordy, J. Chem. Phys., 1959, **30**, 1590.

⁴ J. R. Thomas, J. Amer. Chem. Soc., 1964, 86, 1446.

⁵ B. C. Gilbert, R. O. C. Norman, and D. C. Price, Proc. Chem. Soc., 1964, 234.

H. Lemaire and A. Rassat, Tetrahedron Letters, 1964, 2245. 7 M. Bethoux, H. Lemaire, and A. Rassat, Bull. Soc. chim. France, 1964, 1985.

⁸ M. Fedtke and H. Mitternacht, Z. Chem., 1964, 4, 389.

⁹ W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1963, 3119.

methylene dichloride or benzene, were mixed about 0.02seconds before entering the cavity of the spectrometer; but although three lines due to nitrogen, with the characteristic a_N of iminoxy-radicals (see below), were obtained, no further hyperfine splitting was observed. For the oximes from cyclohexanone and some of its derivatives, the use of a static system with dimethyl sulphoxide as solvent gave weak spectra with fairly well resolved hyperfine splitting.

Iminoxy-radicals are characterised by a large splitting due to nitrogen; $a_N \sim 30$ gauss. This indicates that there is significant spin-density on nitrogen in an orbital of s-containing type, and calculations based on the data for the radical from dimethylglyoxime indicate that about 45% of the unpaired spin is on nitrogen in an orbital whose p: s ratio is 6.6:1, the CNO bond angle being 140° ; ¹⁰ there is thus a marked similarity to NO₂.¹¹ The radicals are best represented as hybrids of the structures (I) and (II); the unpaired electron is in a π -type orbital which is derived from a nitrogen sp^2 orbital and an oxygen p-orbital which lies in the nodal plane of the C-N π -bond. This π -type orbital is orthogonal to the molecular π -system, so that the radicals are described as σ -radicals.^{7,12}



Experimental evidence for the assignment of these radicals as σ -radicals will be apparent from all the data in this Paper, but one observation is quoted here in illustration. Both syn- and anti-benzaldoxime give a mixture of the same two iminoxy-radicals⁴ (i.e., the radicals, unlike the oximes, are interconvertible in the reaction medium); in one [assigned ⁷ structure (III)] the splitting due to the aliphatic proton $(a_{\rm H})$ is 26.9 gauss and in the other [assigned structure (IV)] it is 6.2 gauss.



The marked stereochemical discrimination between the two protons is similar to that between the somewhat analogous pairs in the well substantiated o-radicals, 1-methylvinyl¹³ and vinyl.¹⁴ In the latter (V), the $a_{\rm H}$ values are 68 and 34 gauss,¹⁴ and Karplus and Adrian calculated that the larger coupling is with the proton trans to the unpaired electron.¹⁵

The spectral patterns and splitting constants for the iminoxy-radicals which we have studied are in Table 1.

1962, 2873.

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TABLE 1

Coupling constants (gauss) of iminoxy-radicals (in methylene dichloride unless stated otherwise)

			No. of inter- acting
Radical from	$a_{ m N}$	$a_{\rm H}$	protons
Benzophenone oxime	31.4	1.4	2
2.3.4.5.6-Pentadeutero	(i) 31.6	1.4	2
benzophenone oxime *	(ii) 31.6		
4.4'-Dinitrobenzophenone oxime	31.6	1.4	2
4.4'-Dimethylbenzophenone oxime	31.5	1.4	2
3.3'-Dimethoxybenzophenone oxime	31.5	1.4	2
Benzil a-monoxime	(i) 32·65	1.4	2
Benzil β -monoxime	(ìi) 29·95		
Fluorenone oxime	`´ 30 ∙85	2.7	1
Anthraquinone monoxime	$29 \cdot 8$	2.5	1
Anthraquinone dioxime	30.6	2.5	1
2,3:6,7-Dibenzosuberone oxime	32.0	$2 \cdot 1$	1
Camphor oxime	$29 \cdot 8$	2.35	3
3-Deuterocamphor oxime	29.9	2.35	2
1-Methylnorcamphor oxime	30.3	$2 \cdot 4$	3
Norcamphor oxime	32.0	$2 \cdot 4$	3
Isonitrosocamphor ‡	$28 \cdot 15$	—	
Isonitrosonorcamphor ‡	28.3	1.7	I
Fenchone oxime	$29 \cdot 95$	$2 \cdot 3$	1
		1.12	6
Cyclohexanone oxime §	31.0	$2 \cdot 9$	2
2		1.45	2
4-t-Butylcyclohexanone oxime §	31.2	4·3	1
		2	2
4-t-Butyl-2,2,6,6-tetradeuterocyclo-			
hexanone oxime §	$31 \cdot 2$	$2 \cdot 3$	1
2-Methylcyclohexanone oxime§	30.7	$4 \cdot 2$	1
		$2 \cdot 0$	2
4-Methylcyclohexanone oxime §	31.0	$4 \cdot 2$	1
		$2 \cdot 0$	2
Tropinone oxime	30.8	4.4	1
		$2 \cdot 0$	2
		0.5	1
Bicyclo[3,2,1]octan-3-one oxime	30.7	4.4	1
		$2 \cdot 0$	2
		0.62	1
1,2,3,4-Tetrahydro-4-oxophenanthr-	$32 \cdot 4$	3.6	1
ene oxime §		1.8	3
Cycloheptanone oxime	$31 \cdot 2$	3.50	2
		1.75	2
Cyclo-octanone oxime	30·5	28	1

* Mixture of radicals with identical g-factors. † Each gave the same mixture of iminoxy-radicals. ‡ Weak signals from the isomeric radicals $(a_N \sim 31 \text{ gauss})$ were also observed. § In dimethyl sulphoxide. Attempts to observe iminoxy-radicals in this solvent from cyclopentanone, a-tetralone, and indan-1one were unsuccessful.

DISCUSSION

Thomas's observation that the interaction with protons in iminoxy-radicals has stereochemical requirements⁴ receives confirmation and further elaboration from the results for aromatic ketoximes. The 1:2:1 hyperfine splitting $(a_{\rm H} \ 1.4 \ {\rm gauss})$ in the spectrum from benzophenone oxime indicates coupling to two protons; and since the spectrum from 2,3,4,5,6-pentadeuterobenzophenone oxime does not contain a doublet splitting from one proton but consists of the superimposition of a singlet (intensity 4) on the central line of a 1:2:1triplet $(a_{\rm H} \ 1.4 \text{ gauss})$, the two interacting protons must

¹⁰ M. C. R. Symons, J. Chem. Soc.; 1963, 1189; M. C. R. Symons, Adv. Phys. Org. Chem., 1963, 1, 283. ¹¹ P. W. Atkins, N. Keen, and M. C. R. Symons, J. Chem. Soc.,

¹² M. C. R. Symons, J. Chem. Soc., 1965, 2276.

¹³ R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 1963, **39**, 2147.

¹⁴ E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys., 1964, 40, 213.

¹⁵ M. Karplus and F. J. Adrian, J. Chem. Phys., 1964, 41, 56.

both be on one of the two aromatic rings. Since 4,4'-dinitro-, 4,4'-dimethyl-, and 3,3'-dimethoxy-benzophenone oxime give spectra identical with that from benzophenone oxime, the two interacting protons are in each case the two ortho-protons of one ring. These results are not compatible with the radicals' being of π -type, for, if that were the case, not only would we expect no differentiation between the protons on the two rings but also we should expect the *para*-protons in benzophenone oxime to couple more strongly than the ortho-protons, by analogy with the results for benzyl and related radicals.¹

It is not clear from these results whether the interacting protons are those on the aromatic ring which is *cis* to the iminoxy-oxygen (VI) or trans to it (VII). The former is inferred from the following argument. Under our oxidising conditions, benzil α -monoxime and benzil β -monoxime give the same mixture of radicals, in one of which there is an interaction between the unpaired electron and two protons of the same magnitude as in the radical from benzophenone oxime, whereas in the other no interaction with protons can be discerned; therefore, the protons of the benzoyl group do not couple significantly. In the conditions employed by Rassat and his co-workers, benzil α -monoxime gives only one radical, in which there is coupling to two protons.⁷ Evidently, under the latter conditions the isomeric radicals are not interconvertible, so that the radical observed has the same geometry as the α -monoxime, *i.e.*, it has structure (VIII), the interacting protons (from our results for benzophenone oxime and related compounds) being those depicted.



The interaction of the unpaired electron with the two ortho-protons of an adjacent aromatic ring depends not only on whether the iminoxy-oxygen is cis or trans to the ring but also on the geometry of the H-C-C-C-N-O fragment. The data for the iminoxyradicals from benzophenone, fluorenone, anthraquinone, and 2,3:6,7-dibenzosuberone help to delineate the stereochemical dependence of the interaction. In the first, a variety of conformations is possible as a result of the rotation about the C(aliphatic)-C(aromatic) bond, and the observed $a_{\rm H}$ of 1.4 gauss represents the average value of these various situations. The coupling (presumably to the proton shown) in the radical (IX) from fluorenone oxime, which should be coplanar or almost so, is approximately twice as great $(a_{\rm H} 2.7 \text{ gauss})$, as it is also in the geometrically similar radicals from anthraquinone monoxime and dioxime, and the coupling in the radical from 2,3:6,7-dibenzosuberone oxime, where the tendency towards coplanarity is somewhat less, is smaller $(a_{\rm H} 2.1 \text{ gauss})$. It appears that maximal inter-

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action is associated with the coplanar arrangement in which the iminoxy-oxygen and the interacting proton are close together, suggestive of there being a direct penetration involving interaction between the wave-functions of the unpaired electron and the hydrogen 1s-orbital. However, in the light of the long-range interactions elucidated below, alternative or additional mechanisms cannot be ruled out, especially since calculations indicate that, at least for a CNO bond-angle of 140° as suggested by Symons,¹⁰ the magnitude of coupling as a result of spatial interaction should be very small.¹⁶

The dependence of the magnitude of the coupling in these σ -radicals on the molecular geometry of the radical led us to study next iminoxy-radicals derived from alicyclic ketones of fixed, or known, stereochemistry. Our observation of 1:3:3:1 quartets in the spectra of the iminoxy-radicals (X, XI) from camphor oxime and 1-methylnorcamphor oxime suggested that coupling occurs with three equivalent protons of the bridgehead methyl group,⁵ but the observation that the radical (XII) from norcamphor oxime gives the same spectrum invalidates this conclusion. We therefore substituted deuterium for one of the two protons on the methylene group adjacent to the oxime function in camphor oxime; the resulting radical showed a 1:2:1 triplet hyperfine splitting, so that, of the three protons responsible for the 1:3:3:1 hyperfine splitting, two are on the α -methylenic carbon. The third, which fortuitously couples to the same extent as the first two, appears to be the bridgehead proton. This conclusion is supported by the fact that in the radical from isonitrosonorcamphor (XIII) there is an interaction with one proton $(a_{\rm H} 1.7)$ gauss) whereas in that from isonitrosocamphor (XIV) there is not.



It is to be noted that in all these radicals from boatshaped cyclohexane derivatives interactions are observed only with protons on one side of the iminoxy-function, which is analogous to the results for the aromatic systems. That it is again those protons which are on the same side of the C-N double bond as the iminoxy-oxygen is less easy to prove rigorously but is indicated by the following. The monoximes of certain α -diketones give a mixture of isomeric radicals, regardless of which of the two isomeric oximes is oxidised. One is always characterised by a larger a_N and larger ¹³C-splittings (where the latter can be observed); the data for benzil monoxime are reported in Tables 1 and 2 and those for other oximes which behave in this way will be reported subsequently.

¹⁸ J.-P. Malrieu, J. Chim. phys., 1964, 61, 1587.

Evidence has already been given that the radical from benzil monoxime in which the two ortho-protons of the adjacent ring are coupling is that in which the iminoxyoxygen is cis to the ring concerned. This radical has the larger a_N and a_{C-13} , and it is reasonable to infer that the lower values for these parameters are associated in other cases with the isomeric radical in which the iminoxyoxygen is cis to the carbonyl group. On this basis, examination of a_N and a_{C-13} for the single radicals observed clearly from isonitrosocamphor and isonitrosonorcamphor leads to the stereochemical assignments for these radicals shown in structures (XIII) and (XIV), *i.e.*, with the iminoxy-oxygen *cis* to the carbonyl group. Consequently, the interacting bridgehead proton in the radical (XIII) and the three interacting protons in the camphor derivatives are almost certainly cis to the iminoxy-function.

Apart from the preferential transmission of spindensity to the groups *cis* to the iminoxy-oxygen, it is also clear that the magnitude of the coupling has an angular-dependence. Thus, the bridgehead proton in the radical from camphor oxime couples as strongly as the two methylene protons which are one bond nearer to the iminoxy-group, whereas an attenuation would certainly otherwise be expected. Indeed, an attenuation occurs in other cases, for $a_{\rm H}$ for the six methyl protons in the radical (XV) from fenchone oxime is 1.15gauss, compared with 2.4 gauss for the two methylene protons in the radicals (X) and (XI). It is perhaps relevant that the interacting system in the case of the bridgehead proton is coplanar (XVI) and resembles in some respects the "W"-shaped geometry (XVII) which seems particularly significant for long-range spin-spin coupling observed in nuclear magnetic resonance spectra,17,18 as already pointed out.7



Further evidence for long-range coupling, and its stereochemical dependence, was obtained by studying cyclohexanone oximes fixed in a particular chair conformation. In the radical (XVIII) from 4-t-butylcyclohexanone oxime, coupling occurs to three protons $[a_{\rm H} 4.3 \text{ gauss (1)}, \text{ and } ca. 2 \text{ gauss (2)}].$ The substitution of deuterium for the hydrogen atoms at the two carbon atoms adjacent to the iminoxy-function leads to a radical in which there is still coupling with one proton $(a_{\rm H})$ 2.3 gauss), which must be an equatorial or axial C₃-proton or the axial C_4 -proton. To distinguish between these, the radicals (XIX) and (XX), from tropinone oxime and bicyclo[3,2,1]octan-3-one oxime, were studied. Each gives a spectrum similar to that of the radical (XVIII) in showing coupling of similar magnitude to three ¹⁷ A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 1964, 232; N. S. Bhacca, J. E. Gurst, and D. H. Williams, J. Amer. Chem. Soc., 1965, 87, 302. protons $[a_{\rm H} 4.4$ gauss (1), and 2.0 gauss (2)], as well as a further very small splitting which may have been masked by the line-widths in the spectrum of the radical (XVIII). It is therefore an equatorial C_3 -proton which is observed in each of the radicals (XVIII)—(XX).



Reference to the arguments presented earlier for the iminoxy-radicals from aromatic ketoximes and boatconformation cyclohexanone oximes indicates that the three protons whose interactions are observed in the spectrum of the radical (XVIII) and the corresponding protons in the spectra of the radicals (XIX) and (XX) are on the same side of the C-N double bond as the iminoxyoxygen, as depicted in structure (XVIII). The interacting equatorial C₃-proton is then in the same stereochemical position with respect to the iminoxy-function as the interacting bridgehead proton in the radical from camphor oxime. It is not possible unambiguously to assign the remaining splittings in the spectrum of the radical (XVIII) to the axial and equatorial C₂-protons, but our other observations that a coplanar structure is particularly favourable to the interaction of the unpaired electron with a proton suggests that the larger of the two splittings is due to the equatorial proton. The fourth, very small, splitting observed in the spectra of the radicals (XIX) and (XX) is then probably due to the second equatorial C_2 -proton, *i.e.*, that *trans* to the iminoxy-oxygen.

The spectrum of the radical from cyclohexanone oxime has hyperfine splitting due to four protons $[a_{\rm H} 2.9]$ gauss (2), and $a_{\rm H} 1.45$ gauss (2)]. This radical is evidently interconverting rapidly between the two possible chair conformations, so that the observed couplings are, respectively, the average values for the axial and equatorial C₂-protons and the axial and equatorial C₃-protons. The frequency of interconversion must be greater than the larger of the two differences in coupling constants (expressed in frequency units), *i.e.*, $>6 \times 10^6$ sec.⁻¹

The radicals from 2-methylcyclohexanone oxime and 4-methylcyclohexanone oxime give spectra similar to that from 4-t-butylcyclohexanone oxime. It is probable that, in each, two chair conformations are rapidly interconverting, but the free-energy difference between the two conformations could lead to there being present more than 90% of that conformer with the alkyl group in the equatorial position.* The coupling observed

* Data are not available. However, the enthalpy difference between the two conformers of 2-methylcyclohexanone is 1.6 kcal. mole⁻¹, in favour of the equatorial compound.¹⁹

¹⁸ N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Part I, Holden-Day, San Francisco, 1964, ch. 5.

Francisco, 1964, ch. 5.
¹⁹ E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, p. 240.

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for the rapidly flapping systems will be a weighted average of all conformations, and, if one is dominant, the spectrum observed will be similar to that obtained if the chair-chair interconversion is prevented.

The spectrum of the radical from 1,2,3,4-tetrahydro-4-oxophenanthrene oxime has a 1:3:4:4:3:1 hyperfine splitting $[a_{\rm H} 3.6 \text{ gauss (1)}, \text{ and } 1.8 \text{ gauss (3)}]$. In this cyclohexenone-like system (XXI) the two C3protons are equivalently placed with respect to the iminoxy-function and should therefore couple equivalently; that $a_{\rm H}$ (1.8 gauss) is less than the value for the equatorial proton in the radicals from 4-t-butylcyclohexanone and related oximes follows because the protons are not in the C₃-C-C-N-O plane. Likewise, the pseudo-equatorial C2-proton is not in the C2-C-N-O plane, and the C-H bond of the pseudo-axial C2-proton is at a smaller angle to this plane (nearer to 90°) than that of the axial C_2 -proton in the cyclohexanone (120°); the smaller couplings in the cyclohexenone-like radical $(a_{\rm H} 3.6 \text{ and } 1.8, \text{ compared with } 4.3 \text{ and } 2.0 \text{ gauss})$ are understandable. The spectra of the radicals from cycloheptanone oxime and cyclo-octanone oxime (Table 1) can be similarly interpreted, although detailed information is lacking about the conformational preferences in these systems.

¹³C-Splittings.—It was possible to observe ¹³C-splittings in the spectra of some of the more stable iminoxy-radicals by using rigorously deoxygenated solutions (Table 2). Satellite lines due to ¹⁵N in natural abundance were also observed, the ratio $a_{N-15}: a_{N-14} = 1.40$ being in accord with the ratio of g_N for the two nuclei.

TABLE 2

Carbon-13 splittings (gauss) of iminoxy-radicals

Iminoxy-radical from	$a_{\mathrm{C-13}}$
Fluorenone oxime	26·6 , 9·6
4,4'-Dinitrobenzophenone oxime	24 ·2, 10·0
Camphor oxime *	$25 \cdot 2$
Benzil α -monoxime *	∫ (i) 22·0
Benzil β -monoxime	l (ii) 15.0
Isonitrosocamphor	16·2, 6·8
Isonitrosonorcamphor	16 ·1, 6·4

* The second ¹³C-splitting is obscured by the line-width of the spectrum.

In four cases, two ¹³C-splittings were observed, the smaller probably being due to the carbon attached to the iminoxy-carbon which is cis to the iminoxy-oxygen, by analogy with the more favourable transmission of spindensity to protons in this direction.

g-Factors.—The g_{av} -factors of iminoxy-radicals are significantly greater than the free-spin value. Radicals from typical parent oximes have the following g-factors: fluorenone oxime, 2.0063; camphor oxime, 2.0065; isonitrosocamphor 2.0052; benzil α - and β -oximes, 2.0047 and 2.0054.

Summary.—The following are the main conclusions about the transmission of spin in the σ -type iminoxy-radicals.

(i) Spin is more effectively transmitted to one side of the iminoxy-function than the other.

(iii) The interaction with both β - (*i.e.*, O-N=C-C-H) and γ -protons (*i.e.*, O-N=C-C-H) is angular-dependent and is strongest when the interconnecting σ -bond system is coplanar [compare, *e.g.*, $a_{\rm H}$ for the γ -(bridgehead)-proton with the β -protons in camphor oxime, and fluorenone oxime with benzophenone oxime].

(iii) There is a marked fall-off in coupling constants as between α - and β -protons, but relatively small attenuation between β - and γ -protons (a factor of about 2) (compare, for example, camphor and fenchone oximes, and the β - and γ -protons in 4-t-butylcyclohexanone oxime). This result may be compared with the attenuation between the ortho- and meta-protons in the (σ -)phenyl radical.²⁰

(iv) In aromatic-substituted radicals, interaction is observed only with *ortho*-protons, in contrast to π -type radicals, and is not affected by substituents such as p-nitro which interact with the π -system.

EXPERIMENTAL

A Varian V4500 electron spin resonance spectrometer was used. Hyperfine splitting constants were measured with the Varian "Fieldial" attachment and by comparison with Frémy's salt ($a_N = 13.0$ gauss). g-Factors were measured by attaching a capillary tube containing an aqueous solution of Frémy's salt (g = 2.0055) to the outside of the Varian aqueous solution cell. The flow system was described previously.⁹

Solutions of the reactants were deoxygenated by bubbling nitrogen through them before mixing. Electron spin resonance spectra were recorded at room temperature under nitrogen.

Proton magnetic resonance spectra were recorded on a Perkin-Elmer 60 Mc. spectrometer.

Materials.—Dimethyl sulphoxide was refluxed over calcium hydride and fractionally distilled under reduced pressure. Methylene dichloride was refluxed over phosphorus pentoxide and fractionally distilled. Commercial lead tetra-acetate, moist with acetic acid, was used.

Oximes were prepared by standard methods and, where previously reported, had the appropriate physical constants. 1-Methylnorcamphor oxime, m. p. 85–86° (from light petroleum, b. p. 60–80°) (Found: C, 68·1; H, 9·0; N, 10·45. C₈H₁₃NO requires C, 69·0; H, 9·4; N, 10·1%). Bicyclo[3,2,1]octan-3-one oxime, m. p. 87–88° (from light petroleum, b. p. 60–80°) (Found: C, 68·4; H, 9·3; N, 10·3. C₈H₁₃NO requires C, 69·0; H, 9·4; N, 10·1%).

2,3,4,5,6-Pentadeuterobenzophenone oxime, from benzoyl chloride and hexadeuterobenzene followed by oximation, was shown to contain approximately five aromatic protons by comparison of the integrated proton magnetic resonance with that of an added standard.

4-t-Butylcyclohexanone was deuterated by refluxing the ketone (1 g.) with deuterium oxide (5 ml.) and sodium hydrogen carbonate (0.75 g.), cooling the mixture, and filtering off the solid ketone. After three successive treatments, the p.m.r. spectrum of the resulting oxime showed that replacement of the four α -protons by deuterium was more than 90% complete.

3-Deuterocamphor was prepared by the method of

²⁰ J. E. Bennett, B. Mile, and A. Thomas, *Chem. Comm.*, 1965, 265.

House and Kramar.²¹ The electron spin resonance spectrum of the resulting iminoxy-radical indicated that deuteration was incomplete; the spectrum consisted of the superimposition of three triplets (1:2:1) on three quartets (1:3:3:1), the two radicals having identical g-factors.

Kinetics.—Solutions in methylene dichloride of the oxime and lead tetra-acetate, each 5×10^{-3} M, were deoxygenated at -78° , mixed under nitrogen, and transferred to the cavity of the spectrometer.

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²¹ H. O. House and V. Kramar, J. Org. Chem., 1963, 28, 3362.