Longuet-Higgins,[10] low-lying excited states enhance molecular paramagnetism, and the relatively high paramagnetism of bicyclopentene is as expected[10,11] for a homo[4n]annulene.

Might the lowest excited state of 1 be involved in its thermal isomerization through a nonadiabatic transition, as has been suggested[12] for certain triatomic molecules?

The different activation energies for [$_\sigma 2_s + {}_\sigma 2_a$] reactions of bicyclopentene and bicyclo[1.1.0]butane (5), 26.9 and 41 kcal mol^{-1},[13] may be compared with the different magnetic susceptibilities: $+3.6 \times 10^{-6}$ (1) and -15.3×10^{-6} (5) erg G^{-2} mol^{-1}.[14] Thus the lack of low-lying excited states in bicyclobutane is reflected in its diamagnetism and its high activation energy for thermal isomerization.

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The correlation observed in Figure 1 makes labeling experiments testing whether the other hydrocarbons, like bicyclopentene (1), may rearrange according to the [$_\sigma 2_s + {}_\sigma 2_a$] mechanistic template seem very worthwhile. The magnetic properties of 1 suggest the possibility of systematic magnetic field effects on thermolysis rates. Low-lying excited states having energies proportionate to the $\pi \rightarrow \pi^*$ spectroscopically accessible singlet state (Figure 1) may be important to the thermal chemistry of [4n]- and homo[4n]annulenes.[10] Experiments designed to probe for further examples of [$_\sigma 2_s + {}_\sigma 2_a$] thermal rearrangements and to gauge the importance of low-lying excited states on unimolecular isomerizations are in progress.

(10) H. C. Longuet-Higgins, Chem. Soc. Spec. Publ., No. 21, 109 (1967).

(11) J. A. Pople and K. G. Untch, J. Amer. Chem. Soc., 88, 4811 (1966).

(12) E. E. Nikitin, "Theory of Thermally Induced Gas Phase Reactions," Indiana University Press, Bloomington, Ind., 1966, pp 65–67.

(13) H. M. Frey and I. D. R. Stevens, Trans. Faraday Soc., 61, 90 (1965); R. Srinivasan, A. A. Levi, and I. Haller, J. Phys. Chem., 69, 1775 (1965).

(14) T. D. Gierke and W. H. Flygare, unpublished observations.

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Reactions of Aromatic Nitrile N-Oxides with Organic Radicals. A New Type of Spin-Trapping Reagent

Sir:

Both nitroso compounds and nitrones react readily with organic radicals to form relatively stable nitroxide radicals.[1,2] This "spin-trapping" technique enables esr spectroscopy to be applied successfully in the di-

(1) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, Tetrahedron, 24, 1623 (1968), and references therein; G. R. Chalfont, M. J. Perkins, and A. Horsfield, J. Amer. Chem. Soc., 90, 7141 (1968), and J. Chem. Soc. B, 401 (1970); S. Forshult, C. Lagercrantz, and K. Torssell, Acta Chem. Scand., 23, 522 (1969); K. Torssell, Tetrahedron, 26, 2759 (1970); E. G. Janzen and B. J. Blackburn, J. Amer. Chem. Soc., 90, 5909 (1968); 91, 4481 (1969); J. G. Pacifici and H. L. Browning, Jr., ibid., 92, 5231 (1970).

(2) E. G. Janzen, Accounts Chem. Res., 4, 31 (1971).

agnosis of free-radical intermediates and is especially valuable when the initial radical is too short lived to reach concentrations detectable by the esr method; the scope of this technique and the relative merits of nitroso compounds and nitrones as spin traps have been summarized.[2] We now report on the utility of aromatic nitrile N-oxides (RCNO) as spin-trapping reagents and certain advantages of these compounds compared with nitroso compounds and nitrones; reactions with radicals (R'·) lead to iminoxy radicals (RR'C=NO·) which are usually sufficiently long lived for esr observation in a static system.[3]

In most of our studies the N-oxides of benzonitrile or p-chlorobenzonitrile have been employed. The latter is thermally the more stable compound and may therefore be preferred; the iminoxy radicals from each have very similar esr spectra (see below), in accord with the observation that para substituents do not significantly affect the hyperfine splitting constants or g factors of aryl-containing iminoxy radicals.[3] The N-oxide was prepared either separately[4] or in situ in a suitable solvent; concentrations of 0.1–0.5 M were usually employed, and all solutions were deoxygenated before irradiation.

In control experiments, there was no esr absorption when solutions of nitrile N-oxides, in a variety of solvents, were irradiated with ultraviolet light in the cavity of an esr spectrometer. However, when dibenzoyl peroxide was included, esr signals were detected soon after irradiation began. With benzonitrile N-oxide, in benzene, chloroform, diethyl ether, or dichloromethane, the spectrum was the same as that obtained by the one-electron oxidation of benzophenone oxime,[3,5] indicating that the phenyl radical had been trapped. An identical spectrum was obtained by the use of p-chlorobenzonitrile oxide, and in neither case was there an appreciable dependence of a^H or a^N on solvent.

The following results illustrate some typical applications of this spin-trapping technique; esr data for some of the radicals observed are in Table I. Mixtures of a nitrile N-oxide and di-tert-butyl peroxide or tert-butyl perbenzoate did not yield a detectable concentration of radicals on irradiation in the absence of a solvent, but esr signals were obtained when either methanol or chloroform was present. In methanol with benzonitrile N-oxide, the spectrum showed the presence of the radicals resulting from the addition of both ·CH$_3$ and ·CH$_2$OH to the trap; the same signals were obtained when a mixture of the oximes of acetophenone and phenacyl alcohol was oxidized by lead tetraacetate or was irradiated in the presence of di-tert-butyl peroxide in various solvents. In chloroform, the spectrum observed showed partially resolved splitting (0.05 mT) from three nuclei of $I = {}^3/_2$, which is typical of iminoxy radicals with the group CCl$_3$ syn to the N–O bond (cf. ref 5): it is accordingly assigned to the species 1 derived from the radical ·CCl$_3$.

When a mixture of the nitrile N-oxide and di-tert-butyl peroxide or tert-butyl perbenzoate in benzene, chloroform, or diethyl ether containing a small amount of an aldehyde was irradiated, radicals derived from oxidation of the aldehyde were observed. The spec-

(3) B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. B, 86 (1966).
(4) R. Huisgen and W. Mack, Tetrahedron Lett., 583 (1961).
(5) R. O. C. Norman and B. C. Gilbert, J. Phys. Chem., 71, 14 (1967).

Table I. Esr Characteristics of Iminoxy Radicals from Nitrile N-Oxides

Radical[a]	a^N, mT	a^H, mT	g
Ph–C=N–O· / Ph	3.15	0.135 (2 H)	2.0059
Ph–C=N–O· / CH₃	3.16	0.135 (5 H)	2.0055
Ph–C=NO·[b] / HOCH₂	3.02	c	2.0057
Ph–C=N–O· / Cl₃C	3.27	d	2.0048
Ar–C=N–O· / CH₃CO	3.16	0.130 (2 H)[e] 0.075 (3 H)[f]	2.0048
Ar–C=N–O· / CH₃CO	2.94	0.038 (5 H)[g]	2.0051
Ar–C=N–O· / PhCO	3.27	0.130 (2 H)[h] 0.055 (2 H)	2.0045
Ar–C=N–O· / PhCO	2.96	0.038 (2 H)[i]	2.0051
Ar–C=N–O· / Me₃C	3.15	0.135 (2 H)	2.0057
Ar–C=N–O· / Me₃C	3.07	0.090 (9 H)	2.0057

[a] Ar = p-ClC₆H₄. [b] Stereochemistry not determined. [c] Proton hyperfine splittings were not resolved; the line width was unusually large (0.17 mT). [d] a^{Cl}(3Cl) = 0.05 mT. [e] Attributed to the ortho protons; cf. ref 3 and 5. [f] Attributed to the methyl protons; cf. ref 5. [g] $a^{CH_3} = a^{o-H}$; cf. ref 5. [h] The larger and smaller proton splittings are attributed, respectively, to the ortho protons in Ar and Ph; cf. ref 5. [i] Attributed to the ortho protons in Ar by analogy with the data for **2** (R = CH₃).

trum from acetaldehyde showed the presence of **2** (R = CH₃) and its geometrical isomer; an identical spectrum was obtained by treating benzyl methyl ketone with nitrogen dioxide,[6] although in this case the signals

Ar CCl₃   Ar COR   Ar CMe₃
 \ /   \ /   \ /
  C   C   C
  ‖   ‖   ‖
  N   N   N
  \   \   \
   O·   O·   O·

1   **2**   **3**
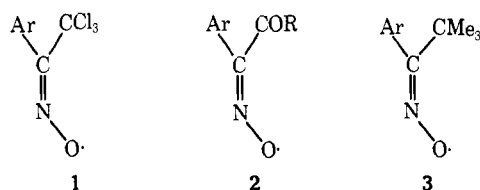
Ar = Ph or p-ClC₆H₄

were less well resolved. Likewise, benzaldehyde gave the radical **2** (R = Ph) and its geometrical isomer[3] (Figure 1). With trimethylacetaldehyde, the spectrum showed the presence of **3** and its isomer (previously observed during the oxidation of pivalophenone oxime[7]), from which we infer that the radical Me₃CCO· from the aldehyde decarbonylates readily.

The long-range electron–nucleus interactions such as those involving the methyl protons in **2** (R = CH₃), the ortho protons in the benzoyl fragment in **2** (R = Ph), and the *tert*-butyl protons in **3** are characteristic of iminoxy radicals.[3,5,7] Thus, the esr spectra of many iminoxy radicals from nitrile N-oxides (particularly

(6) W. M. Fox, J. McRae, and M. C. R. Symons, *J. Chem. Soc. A*, 1773 (1967).

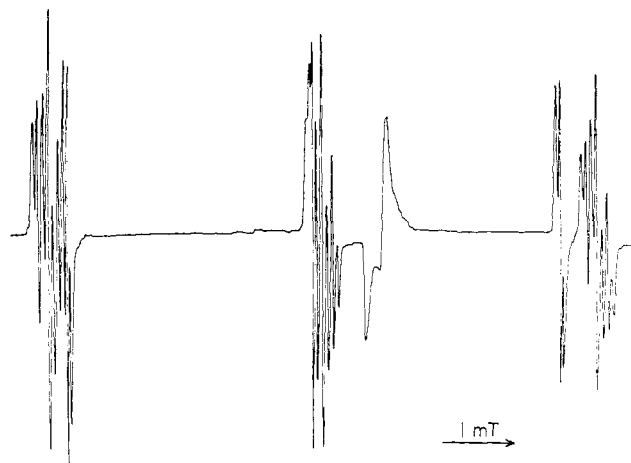(7) B. C. Gilbert and R. O. C. Norman, *ibid., B*, 123 (1968).

Figure 1. Esr spectrum of the radical **2** (Ar = p-ClC₆H₄, R = Ph) and its geometrical isomer; the asymmetric resonance is from irradiated quartz.

those with acyl fragments) can give direct information about the structure of the addend (which is rarely true for nitrone adducts or for acyl adducts of nitroso compounds). Spectral complication which results from the occurrence of geometrical isomerism might prove a disadvantage if more than one radical is trapped; however, nitrogen splittings vary sufficiently for separate resonances to be resolved in most cases and, in addition, the observation of two isomers from a given adduct can provide extra evidence for the nature of the trapped species. It is notable that, in the nitrile oxide reaction, spin adducts from alkoxy radicals (*e.g.*, *tert*-BuO· from di-*tert*-butyl peroxide) are not detected, in contrast with the use of nitrones and nitroso compounds.

Since nitrile N-oxides are readily prepared, we believe that they constitute a useful addition to the types of spin trap available. In addition, the spectra of the iminoxy radicals we have obtained have narrower line widths (*e.g.*, for the radicals in Figure 1, 0.030 mT) than those of the same radicals obtained by the oxidation of oximes with, for example, lead tetraacetate; consequently, very small splittings can be resolved, and this should enable further information to be gained about long-range effects in these radicals and the factors on which they depend. Finally, our esr observations support the suggestion[8] that iminoxy radicals are intermediates in some radical-catalyzed reactions of nitrile N-oxides which lead to oximes.

(8) T. Caronna, A. Quilico, and F. Minisci, *Tetrahedron Lett.*, 3633 (1970).

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The Facile Photochemical or Oxygen Initiated Free-Radical Chain Reactions of Trialkylboranes with Organic Disulfides. Convenient New Synthesis of Organic Sulfides *via* Hydroboration

Sir:

Trialkylboranes readily participate in free-radical chain reactions with organic disulfides. The reactions