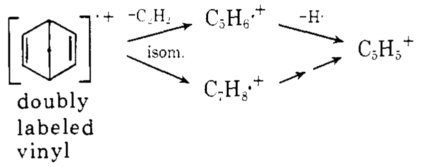
The decomposition of unlabeled norbornadiene has been reported upon by Meyerson[12] and exhibits, in competition with the characteristic C_7H_8 fragmentation, an intense $C_5H_6\cdot^+$ ion ascribed to the electron impact reverse Diels–Alder (EIRDA) process. The splitting of acetylene from norbornadiene-*2,3*-$^{13}C_2$ (70 eV, 160° source temperature) is shown to occur with at most minor scrambling (Table III) and therefore before isomerization. The $C_5H_6\cdot^+$ ion from norbornadiene has substantially the same composition as C_5H_6 formed in the 470° pyrolysis. A significant difference is found between the $C_5H_5^+$ distributions from the norbornadiene and cycloheptatriene. This difference in behavior is attributed in whole or in part to the presence of an additional pathway to $C_5H_5^+$ in the case of norbornadiene, namely through the $C_5H_6\cdot^+$ intermediate.

Table III. High-Resolution Analysis of $C_5H_6\cdot{}^+$ from Norbornadiene-$^{13}C_2$ Mixture[a,b]

Composition	Abundance[b]	Calcd abundance: Scrambling	Calcd abundance: EIRDA
C_5H_6	0.467	0.128	0.518
$^{13}CC_4H_6$	0.139	0.505	0.096
$^{13}C_2C_3H_6$	0.394	0.367	0.386

[a] See footnotes *a–c* and *e* of Table I. [b] Mixture composition 77.2% $^{13}C_2$, 19.3% $^{13}C_1$, 3.5% $^{13}C_0$; independent data for pure norbornadiene-*2*-^{13}C not available.



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Received June 13, 1973

Photochemical Reaction of Oximes with Quinones. A New Method for the Preparation of Iminoxy Radicals

Sir:

There has been considerable interest in the preparation and properties of iminoxy radicals,[1] RR′C=NO·. We have recently found that such radicals are readily produced from oximes using photoexcited quinones as hydrogen abstractors. This method suffers from none of the limitations encountered in previously reported methods for the generation of iminoxy radicals.[1] High concentrations of radical and consequently clean electron paramagnetic resonance spectra can be obtained for all types of radicals, small amounts of oxime are required since radicals are produced in a "static" system, and radicals can be obtained at low temperatures and in rigid media. We describe here the technique used and also propose mechanisms for radical production and decay in these systems.

Experimentally, solutions containing approximately 50 mg of oxime and 20 mg of quinone in 1 ml of dichloromethane or benzene were prepared in 4-mm Pyrex tubing. Good spectra could be obtained without deoxygenation, but solutions were generally degassed by the freeze–thaw technique. Radicals were generated by irradiating the samples with a 150-W Varian EIMAC high-pressure xenon lamp in a Varian rectangular cavity with a 0.25-in. hole in the front plate. Spectra were obtained with a Varian E-3 spectrometer.

Supercooled liquid benzophenone has also been used as both solvent and hydrogen abstractor to generate diaryl- or arylalkyliminoxy radicals. Spectra from dialkyloximes have been observed under these conditions, but the iminoxy signals initially produced are rapidly replaced by the spectra of secondary nitroxide products in these cases. We have also obtained the spectrum of oriented diphenyliminoxy radicals in a benzophenone single crystal by this technique; analysis of the results is in progress.

Since irradiations were carried out at long wavelengths ($\lambda_{ex} > 300$ nm), precluding direct photodecomposition of oxime,[2,3] we presume that iminoxy radicals are produced as the result of hydrogen abstraction by the quinone $^3n\pi^*$ state.[4] It is therefore expected that efficiency of radical production will be independent of temperature as there should be no thermal activation barrier to hydrogen abstraction,[4] in contrast to the case of hydrogen abstraction by photolytically generated *tert*-butoxy radicals.[1] This is indeed what we have observed. For diphenyliminoxy there is a threefold increase in signal intensity for a 35° decrease in temperature. This increase in intensity is caused by a corresponding threefold increase in radical lifetime, from 0.67 sec at +10° to 2.1 sec at −25°, assuming that iminoxy decay is pseudo first order, as shown below.

For benzophenone another mechanism, involving triplet energy ($E_T = 68.5$ kcal/mol)[5] transfer[6] followed by oxime O–H bond rupture, should be considered in addition to hydrogen abstraction by the $^3n\pi^*$ state.[7] However the radical signals obtained in benzene solution using the isoenergetic but nonhydrogen abstracting sensitizers triphenylene ($E_T = 66.6$ kcal/mol)[5] and triphenylamine ($E_T = 70.1$ kcal/mol)[5] are at least two orders of magnitude less intense than those obtained using benzophenone under similar conditions and are probably due to direct light absorption by oxime.[2] This rules out the sensitization process.

In contrast to the second-order decay previously reported for aryl-substituted iminoxy radicals,[1] we have observed clean first-order decay in our systems (Figure 1). This decay presumably occurs by radical addition to quinone. This assumption is supported by the pronounced effect of quinone structure on the lifetime of the iminoxy radical, as well as by the appearance of nitroxide radicals concurrent with iminoxy

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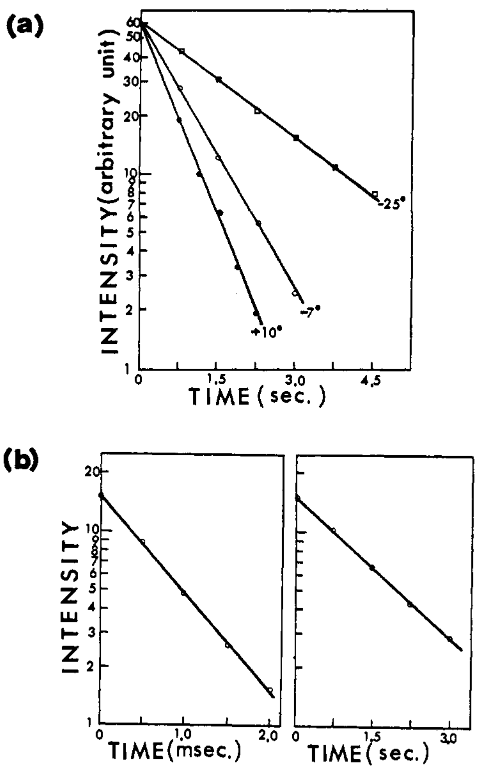

Figure 1. First-order decay plots of iminoxy radicals, log (intensity) *vs.* time: (a) diphenyliminoxy generated by chloranil in dichloromethane at −25, −7, and +10°; (b) 2,4,6-trimethylphenyliminoxy in dichloromethane, generated by duroquinone (left) and chloranil (right).

decay. Thus the lifetime of 2,4,6-trimethylphenyliminoxy is only 0.86 msec when generated from the corresponding oxime with duroquinone, compared with 1.3 sec when generated with chloranil. This is consistent with the relatively high activation energy found for radical decay with chloranil, *e.g.*, +4.6 kcal/mol for diphenyliminoxy.

Nitroxide formation during diphenyliminoxy decay is particularly informative, as a reversible equilibrium between iminoxy and nitroxide radicals is observed

$$\mathrm{quinone} + (C_6H_5)_2C{=}NO\cdot \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} \mathrm{nitroxide}$$

With benzoquinone the nitroxide spectrum is complex (Figure 2), but can be assigned to splitting arising from three nonequivalent protons which presumably originated with the quinone superimposed on the characteristic ^{14}N triplet. This interpretation is supported by the observation of a simple sharp three line nitroxide spectrum when chloranil is substituted for benzoquinone.

Radical production from benzaldoximes is complicated by the facile abstraction of the aldehydic as well as the hydroxyl proton by photoexcited quinones. Thus a clean spectrum can be obtained from the sterically hindered 2,4,6-trimethylbenzaldoxime using benzoquinone but not from benzaldoxime unless sterically hindered quinones such as chloranil or duroquinone are used. These steric effects also influence radical stability, as shown by the enhanced lifetimes, ~1.3 sec, of the hindered 2,4,6-trimethylphenyl- and 2,6-dichlorophenyliminoxy radicals generated with chloranil compared with the 1.2 msec lifetime of the *p*-nitrophenyliminoxy radical prepared under the same conditions. This lifetime enhancement implicates aldehydic proton abstraction as an additional pathway for aldoxime iminoxy radical decay.

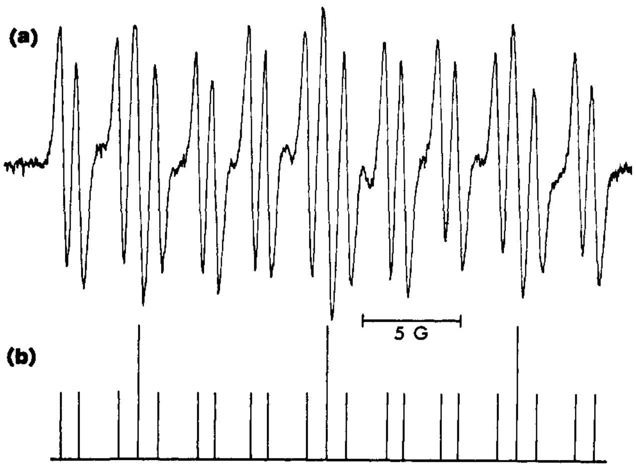

Figure 2. (a) Epr spectrum of nitroxide resulting from decay of diphenyliminoxy with benzoquinone; (b) reconstructed spectrum using $a_N = 9.70$, $a_{H_1} = 3.75$, $a_{H_2} = 3.00$, and $a_{H_3} = 0.95$ G.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. One of us (N. O.) was supported as a National Science Foundation Centers of Excellence postdoctoral fellow.

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Interpretation of the Pseudocontact Model for Nuclear Magnetic Resonance Shift Reagents. V. Collinearity in the Structural Elucidation of Nitriles

Sir:

The transformation of Hinckley's[1] widely applicable method of lanthanide-induced shifts (LIS) into an instrument for making distinctions among structures with statistical criteria of reliability[2,3] was recently applied to the structure assignment of the four diastereoisomeric nitriles **1**–**4**, as reported by Doering and Birladeanu.[4] We report here an important and useful extension to the application of this method—the assumption of collinearity of lanthanide with the nitrile bond and the consequent improvements in confidence levels for structure assignment.

Minimum values of $R^{2,3}$ were obtained for all 16 binary combinations of the four structural possibilities with the four sets of experimental relative slopes (obtained by least-squares treatment of the Eu(fod)$_3$ LIS data with six or more dopings), with the assumed N-Eu distance ranging from 2.0 to 3.5 Å and the C-N-Eu

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