[2.1.0]pentane which was recrystallized from ethanol to give 31.0 mg of the pure compound, mp 179–180°. Fractions 142–166 contained 172 mg of starting diene whose nmr spectrum showed no deuterium scrambling within experimental error.

The nmr (CCl_4) of the deuterated vinylcyclopropane consisted of τ 8.50 (m, cyclopropyl CH_2, rel area 45), 7.64 (m, cyclopropyl CH, rel area 28), 4.84 (d, J = 10 cps, vinyl, rel area 9.4). The nmr (CCl_4) of the deuterated bicyclo[2.1.0]pentane consisted of τ 7.82 (d, J = 12 cps, rel area 70), 7.40 (d, J = 12 cps, rel area 66), 6.98 (s, rel area 18).

A second identical run gave the following results: vinylcyclopropane, nmr (CCl_4) τ 8.50 (m, cyclopropyl CH_2, rel area 40), 7.64 (m, cyclopropyl CH, rel area 26), 4.84 (d, J = 10 cps, vinyl, rel area 10); bicyclo[2.1.0]pentane, nmr (CCl_4) τ 7.82 (d, J = 12 cps, rel area 50), 7.40 (d, J = 12 cps, rel area 45), 6.98 (s, rel area 12).

Catalytic Reduction of Deuterio-2,2,5,5-tetraphenylbicyclo[2.1.0]-pentane. A sample of deuterio-2,2,5,5-tetraphenylbicyclo[2.1.0]-pentane obtained from photolysis of deuterated 1,1,5,5-tetraphenyl-1,4-pentadiene was catalytically reduced with 10% palladium on charcoal as described above. The nmr (CCl_4) indicated τ 7.57 (s, C-4 and C-5 CH_2, rel area 23) and 6.20 (s, C-2 CH_2, rel area 8.5).

Determination of the Fluorescence Quantum Yield of 1,1,5,5-Tetraphenyl-1,4-pentadiene and 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. An Aminco-Keirs spectrofluorimeter was used to obtain the fluorescence quantum yield for the dienes by three different procedures.

This procedure was used previously by Zimmerman and Baum[10] and involves measuring the fluorescence intensity relative to diphenylethylene (ϕ_f = 0.003[30a]) standard using a mercury lamp for excitation. Solutions were of equal optical density (5.0) at 254 nm, the wavelength of excitation.

Again diphenylethylene was used as a standard but in this case a xenon lamp was used for excitation. This obviates problems resulting from scattering of the mercury 310-nm line which could alter the intensities measured. Solutions of equal optical density (1.85) at the 254-nm wavelength of excitation were again used.

Alternatively, naphthalene (ϕ_f = 0.23[30]) was used as a standard for the fluorescence intensities again using the xenon lamp for excitation. Solutions of equal optical density (1.85) at the 254-nm wavelength of excitation were again used.

The results of these methods are compiled in Table III.

Acknowledgment. Support of this research by National Science Foundation and National Institutes of Health Grant No. GMO7487 is gratefully acknowledged, as is a fellowship to J. P. by the National Research Council of Canada. Additionally, help with an National Institutes of Health Biomedical equipment grant from the Graduate School is acknowledged.

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(30) (a) I. B. Berlman, "Handbook of Fluorescent Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 104. (b) Note also the similar values quoted by J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, p 126.

Kinetic Application of Electron Paramagnetic Resonance Spectroscopy. IX. Preparation and Properties of Di-*tert*-butyliminoxy[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR9. *Received October 3, 1972*

Abstract: Di-*tert*-butyl ketoxime has been prepared by a new and simple procedure. It can be oxidized by a variety of oxidizing agents to a moderately stable free radical, di-*tert*-butyliminoxy (**1**), a blue liquid, fp −21°. Some of the physical and chemical properties of **1** have been determined. It dimerizes slowly and irreversibly at room temperature, $2k_t = 2.1 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$ in benzene at 24°. Di-*tert*-butylnitrimine is formed by reaction of **1** with nitric oxide. Hydrogen is abstracted by **1** from a variety of organic materials including phenols, triethylamine, triethyl phosphite, hydrazine, hydrazobenzene, 1,4-cyclohexadiene, toluene, ethylbenzene, cumene, and hydroxylamines. Kinetic studies have been made on some of these reactions.

Iminoxy[2,3] radicals, RR′C=NO·, derived from the corresponding oximes RR′C=NOH by one-electron oxidation, have received considerable attention since their initial observation by Thomas[4] in 1964. These radicals have, so far, been studied only by epr techniques since most of them dimerize or disproportionate rapidly.[2] A large body of information exists concerning the epr spectra of these radicals,[8-19] though to date none has been isolated and characterized in the pure state.

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(1) Issued as NRCC No. 13147. Part VIII: G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 8784 (1972).

(2) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972).

(3) This name was given by Thomas.[4] Other names given to these radicals include nitroxyl,[5] alkylidene iminoxyl,[6] and alkylidene nitric oxide.[4] In addition, "iminoxy" and "iminoxide" sometimes refer to nitroxides[4,7] or possibly to a general class of radicals.[7]

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

(5) O. L. Chapman and D. C. Heckert, *Chem. Commun.*, 242 (1966).

(6) E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Press, New York, N. Y., 1970.

(7) E. G. Rozantsev and V. P. Ivanov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1416 (1970); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1338 (1970).

(8) B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc., London*, 234 (1964).

(9) (a) H. Lemaire and A. Rassat, *Tetrahedron Lett.*, 2245 (1964); (b) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964).

(10) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965).

(11) (a) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, *B*, 86 (1966); (b) *ibid.*, 722 (1966); (c) *J. Phys. Chem.*, **71**, 14 (1967); (d) *J. Chem. Soc. B*, 981 (1967); (e) *ibid.*, 123 (1968).

(12) (a) J. W. Lown, *ibid.*, 441 (1966); (b) *ibid.*, 644 (1966).

(13) I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **30**, 1950 (1959).

(14) M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); 2276 (1965).

(15) W. M. Fox and M. C. R. Symons, *J. Chem. Soc. A*, 1503 (1966).

(16) L. Burlmacchi and E. Tiezzi, *Gazz. Chim. Ital.*, **99**, 1313 (1969).

(17) B. C. Gilbert and W. M. Gulick, Jr., *J. Phys. Chem.*, **73**, 2448 (1969).

(18) B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, **93**, 3290 (1971).

(19) H. Caldararu, N. Barbulescu, L. Ivan, and V. E. Sabini, *Tetrahedron Lett.*, 3039 (1970), and references therein.

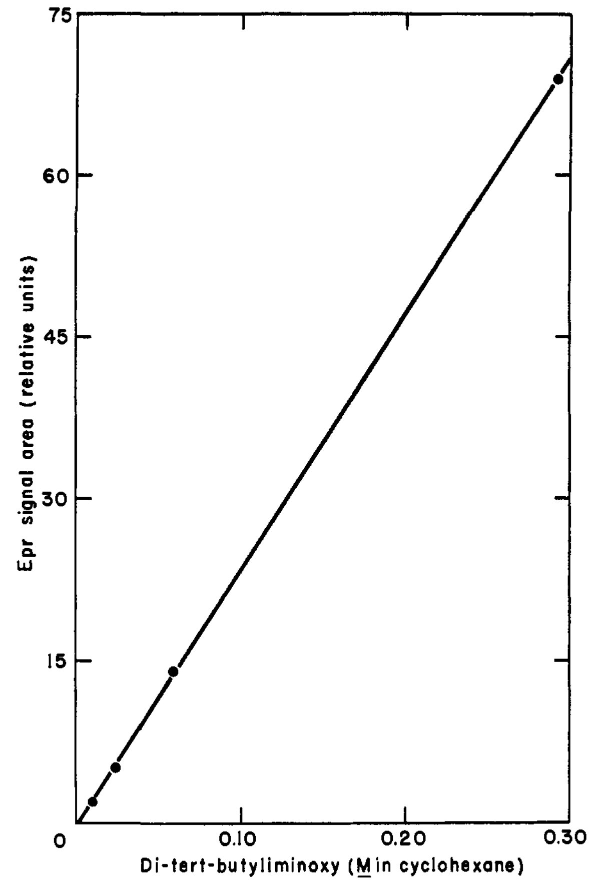
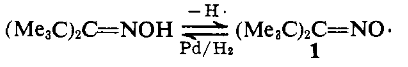


Figure 1. Plot of doubly integrated epr signal intensity *vs.* concentration of di-*tert*-butyliminoxy at 25°.

Our study was aided by the development of a convenient synthesis of hindered oximes from a nitrile and an alkyllithium without isolation of intermediates (see Experimental Section). In conjunction with an earlier study,[2] we noted that photolysis of di-*tert*-butyl ketoxime in solutions containing di-*tert*-butyl peroxide gave the epr spectrum due to di-*tert*-butyliminoxy. This radical, which was quite stable in solution, has now been isolated and characterized as a monomeric, though reactive species.[20]

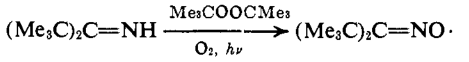
Di-*tert*-butyliminoxy

Characterization. Radical **1** can be obtained by oxidizing di-*tert*-butyl ketoxime with silver oxide,[20] ferricyanide ion, *tert*-butoxy- or *tert*-butylperoxy radicals, or 2,2-diphenyl-1-picrylhydrazyl (DPPH).



$$(Me_3C)_2C{=}NOH \underset{Pd/H_2}{\overset{-H\cdot}{\rightleftharpoons}} \underset{\textbf{1}}{(Me_3C)_2C{=}NO\cdot}$$

Photolysis of di-*tert*-butyl ketimine in the presence of di-*tert*-butyl peroxide and oxygen also gives **1**. The di-*tert*-butyliminyl radical $(Me_3C)_2C{=}N\cdot$ (a_N = 28.9 G, a_H(18 H) = 2.8 G) is observed in the absence of O_2 and is probably an intermediate.



$$(Me_3C)_2C{=}NH \xrightarrow[O_2,\ h\nu]{Me_3COOCMe_3} (Me_3C)_2C{=}NO\cdot$$

Pure radical **1** is a blue liquid that decomposes significantly after several hours at room temperature and detonates when placed in a bath at 100°, though it can be stored indefinitely at −78° at which temperature it is a solid (fp −21°). Catalytic reduction with palladium regenerates the parent oxime. The proof of the monomeric character of **1** follows from (1) the molecular weight in solution, (2) the linearity of plots of the doubly integrated epr signal *vs.* concentration (Figure 1) and of optical density *vs.* concentration (Figure 2), and (3) the increase in the epr signal intensity by a factor of 2.70 on cooling a 0.2 *M* solution of **1** in isopentane from +25 to −150°. This increase is due to the Boltzmann factor and corresponds within experimental error to that shown (2.84) by a 10^{-4} *M* DPPH solution under these conditions.

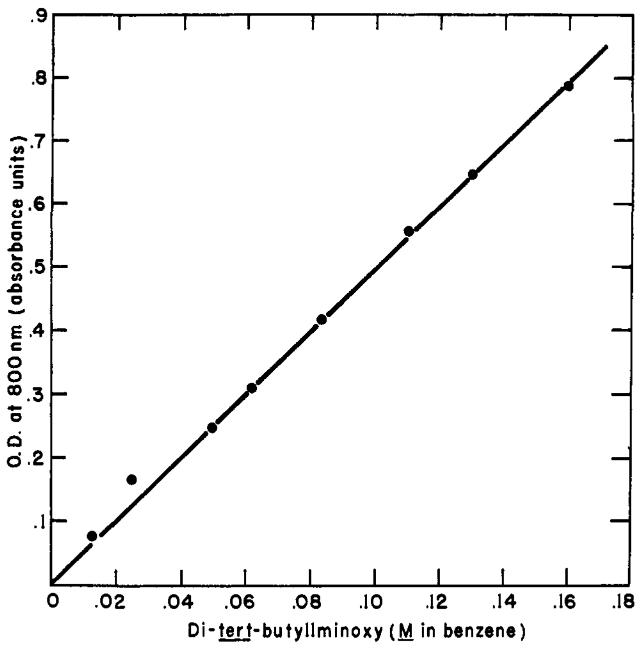


Figure 2. Beer's law plot for di-*tert*-butyliminoxy at 25°.

The absence of reversible dimerization is not really unexpected because any bonding at the N or C in **1** considerably increases crowding in the molecule. There is abundant kinetic evidence for reversible dimers in less substituted iminoxy radicals,[2] however, and it may occur with **1** to an extent we cannot detect.

The blue color of **1** is an inherent property of the radical and is not due to a nitroso impurity. The molar absorbance of the RN=O chromophore in the blue region is about 20,[21] and since the radical shows an extinction coefficient of 4.5, there would have to be about 20% impurity to produce this effect. Such an amount of a nitroso compound would be readily detectable by its infrared absorption at 1560 cm^{-1}. The purified radical does not show such an absorption, though one does appear on standing.

Spectral Properties. The blue color of **1** is due to a weak absorption extending from about 530 nm to beyond 800 nm, ϵ (800 nm) 5.1 in benzene, 5.0 in 95% ethanol, and 4.7 in cyclohexane (Figure 3). The absorption envelope is unusually broad and reminiscent of that of NO_2 which, however, has λ_{max} at about 400 nm.[22] There was no significant change in the absorption

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(20) A preliminary account of this work has appeared: J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 5278 (1971).

(21) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1953, p 98.

(22) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 217.

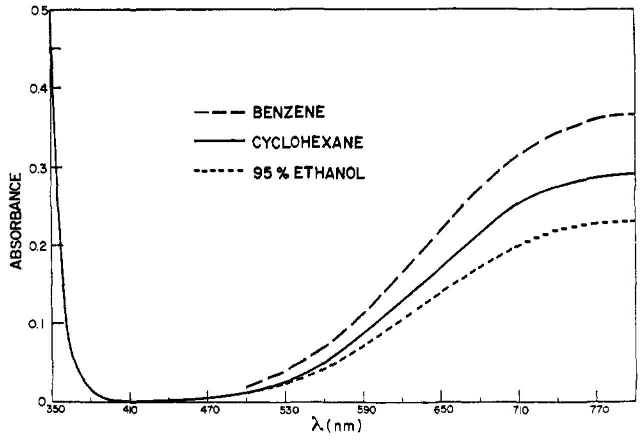


Figure 3. Visible spectrum of di-*tert*-butyliminoxy in benzene (0.72 *M*), cyclohexane (0.61 *M*), and ethanol (0.46 *M*).

maximum with solvents of different polarity (Figure 3). Some samples of **1** appeared to display a maximum at about 700 nm. However, this was shown to be due to the presence of a dimer (**2**, see below) by adding an excess of 1,4-cyclohexadiene. The diene selectively destroyed **1** and left a pale blue solution with λ_{max} 698 nm (typical of a nitroso group) and a normal decrease on either side of the maximum.

The epr spectrum of di-*tert*-butyliminoxy in dilute solutions showed splitting into a triplet due to interaction with the ^{14}N nucleus. In addition, hyperfine splitting of *ca.* 0.4 G could be resolved in a number of solvents (Figure 4), but the relative intensities are not consistent with 18 equivalent protons and the splitting pattern is temperature dependent. It is quite possible that the two *tert*-butyl groups are not rotating freely.[23]

The values of a_N in the epr spectrum of **1** are solvent independent to a surprising degree, changing by less than 0.3 G on proceeding from isopentane to acetic acid (Table I). Neither solvent polarity nor hydrogen bonding ability influence the nitrogen splitting to as great an extent as they do for hindered aliphatic nitroxides such as 2,2,6,6-tetramethylpiperid-4-one-*N*-oxyl[24] and di-*tert*-butyl nitroxide (see Table I). In stronger acids such as sulfuric or trifluoroacetic, the radical was not stable and an epr signal was not obtained.

Table I. Epr Parameters for Di-*tert*-butyliminoxy and Two Hindered Aliphatic Nitroxides

Radical	Solvent	a_N, G	g
$(Me_3C)_2C{=}NO\cdot$	Isopentane	31.31	2.00525
	Benzene	31.32	2.00522
	Abs. EtOH	31.3	
	$HCON(CH_3)_2$	31.4	
	CH_3COOH	31.55	2.00503
$(Me_3C)_2NO\cdot$	Benzene	15.44	2.00604
	CH_3COOH	16.46	2.00574
2,2,6,6-Tetra-methylpiperid-4-one-*N*-oxyl	Benzene^a	14.5	2.0062
	Water^a	16	2.0055

^{a} Data from A. Rassat, *Mol. Spectrosc., Proc. Conf., 4th,* 145 (1968), and ref 24a.

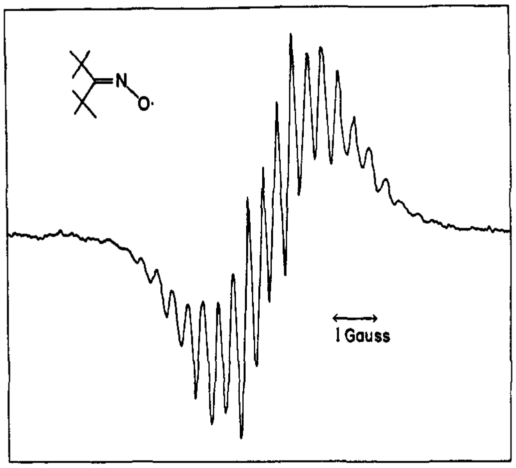
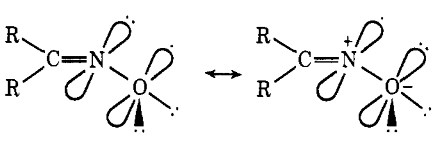
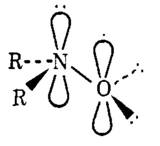


Figure 4. Epr spectrum of highest field multiplet of **1** showing incompletely resolved proton splitting (*o*-dichlorobenzene, 25°).

The lack of solvent effect on both the epr and the visible spectrum can be rationalized by noting that the nitrogen atom in an iminoxy radical is (to a first approximation) sp^2 hybridized (**3** and **4**). It is therefore less polarizable and less basic than the sp^3 hybridized nitrogen in nitroxides (**5**). The orbital energies and electron distribution in iminoxy radicals will therefore be less affected by a change of solvent polarity than they will for nitroxide radicals. Calculations[14,15] indicate that in iminoxy radicals the unpaired electron is approximately equally distributed between the nitrogen and oxygen; *i.e.*, the radicals are best represented by the canonical structures **3** and **4**.



3 **4**



5

The ir spectrum of freshly prepared **1** (Figure 5) shows intense absorption at 1610 cm^{-1}, due either to C=N or N=O stretching vibrations. A peak at 1650 cm^{-1} in di-*tert*-butyl ketoxime (C=N) does not appear in the spectrum of the radical. Probably the force constants for both the C–N and N–O bands change on proceeding from oxime to radical and it is possible that the band at 1610 cm^{-1} results from overlap of the two.[25] Peaks at 2960, 1480, 1390, and 1366 cm^{-1} in the radical are also present in the spectrum of di-*tert*-butyl ketone and are assigned to C–H vibrations.

The mass spectrum of **1** was identical with that of the parent oxime. In our experience, hydroxylamines and nitroxides also often show this behavior.

Decomposition. At −20° an initially pure sample of **1** slowly developed several new peaks in its ir spectrum at the expense of the strong 1610-cm^{-1} band. After 9 weeks the sample had partly solidified and was only weakly paramagnetic, though it remained blue. Low-temperature crystallization from isopentane afforded dimer **2** as an unstable, diamagnetic blue solid. Although a correct combustion analysis for **2** was not obtained, the spectral evidence, the molecular weight, and analogy with a similar compound formed from

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(23) The epr spectrum of the *tert*-butylisopropyliminoxy radical in benzene at 8° indicates that neither alkyl group is rotating.

(24) (a) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.,* 3273 (1965); (b) Y. Y. Lim and R. S. Drago, *J. Amer. Chem. Soc.,* **93,** 891 (1971).

(25) The ir spectrum of *tert*-butyl-1-adamantyliminoxy shows a single peak at 1605 cm^{-1}.

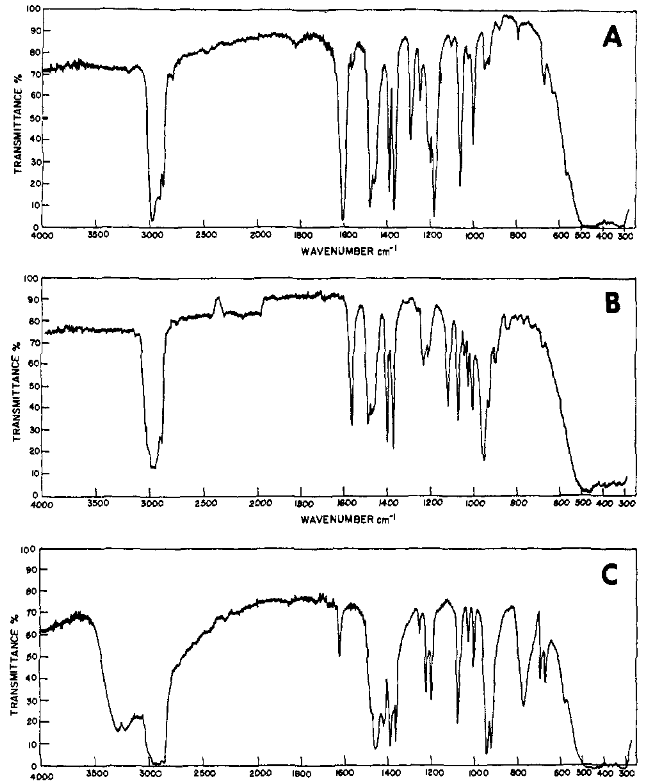
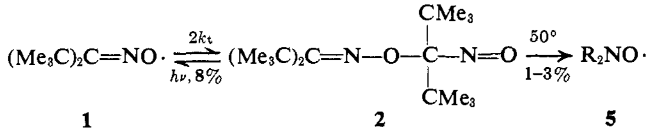


Figure 5. Infrared spectra: A, di-*tert*-butyl ketoxime (hydrocarbon mull); B, di-*tert*-butyliminoxy (neat); C, dimer **2** (hydrocarbon mull).

diisopropyliminoxy[2] favor the structure shown. Measurement of the rate of decay of **1** at 24° (neat and in benzene) showed that this process is initially second order in **1** (see Figure 6). The rate constant, $2k_t$, for dimerization in benzene at this temperature is $(2.1 \pm 0.1) \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$.

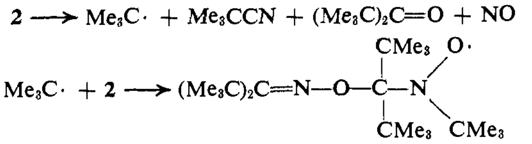


$$(Me_3C)_2C{=}NO\cdot \underset{h\nu,\,8\%}{\overset{2k_t}{\rightleftharpoons}} (Me_3C)_2C{=}N{-}O{-}\underset{CMe_3}{\overset{CMe_3}{C}}{-}N{=}O \xrightarrow[1-3\%]{50^\circ} R_2NO\cdot$$

1 **2** **5**

When an air-free solution of **2** in benzene (0.006 *M*) was heated to 50°, **1** did not reappear but a new stable radical with triplet splitting of 15.46 ± 0.05 G and a *g* value of 2.00606 was generated in 1–3% yield.[26] The corresponding values for di-*tert*-butyl nitroxide were measured as 15.44 ± 0.06 and 2.00604. Formation of the nitroxide was inhibited by dissolved oxygen and by added **1**. This result suggests that one decomposition pathway for **2** involves fragmentation to give radicals that are trapped by the nitroso group in undecomposed **2**[28] or by nitric oxide. A Beckmann fragmentation of **2**

$$\mathbf{2} \longrightarrow Me_3C\cdot + Me_3CCN + (Me_3C)_2C{=}O + NO$$



$$Me_3C\cdot + \mathbf{2} \longrightarrow (Me_3C)_2C{=}N{-}O{-}\underset{CMe_3}{\overset{CMe_3}{C}}{-}N\overset{O\cdot}{\underset{CMe_3}{}}$$

$$Me_3C\cdot + NO \longrightarrow Me_3CNO \xrightarrow{Me_3C\cdot} (Me_3C)_2NO\cdot$$

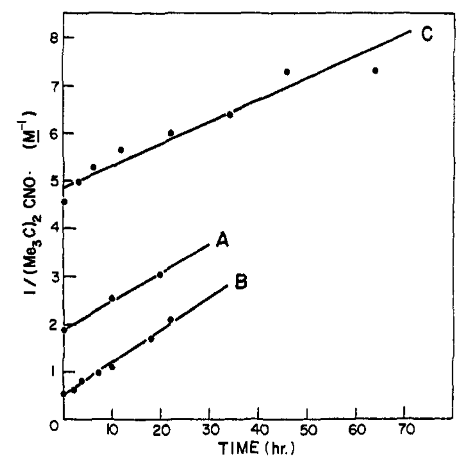


Figure 6. Dimerization of di-*tert*-butyliminoxy at 24 ± 2°: (A), (initial concn) 5.27 *M* (neat); (B) 1.98 *M* in benzene; (C) 0.216 *M* in benzene. A and B, decay followed by epr; C, decay by spectroscopy at 800 nm in a 0.1-cm quartz cell (solution degassed and sealed off). The axes for line A are expanded times 10.

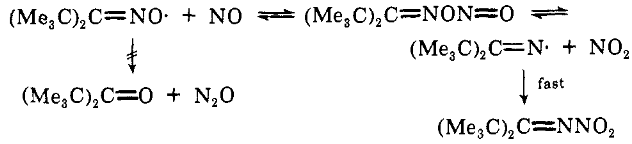
should give rise to *tert*-butyl radicals. However, we were not able to generate any stable radical by photolyzing a mixture of **2** and 2,2′-azoisobutane.

Photolysis of **2** (2×10^{-3} *M* in benzene) in the epr cavity with λ >313 nm did regenerate **1** in a maximum yield of about 8% in benzene. However, the signal due to **1** was not stable. It disappeared quickly even in the dark, and was replaced by a simple triplet identical with that observed in the thermal decomposition of **2**. The iminoxy radical, **1**, decomposes irreversibly under these conditions, and no new stable paramagnetic species are formed when benzene solutions of **1** are irradiated. Attempts to trap the *tert*-butyl radical by irradiating dilute **1** at −80° in oxygen saturated isopentane or $CFCl_3$ were not successful.

Samples of **1** kept at room temperature for a week gave di-*tert*-butyl ketone (42%), di-*tert*-butylnitrimine (20%), pivalonitrile (4%), and several other compounds that were not identified. In dilute solution, **1** is rather stable. Its epr spectrum can be easily recorded at 150° in degassed hexadecane.

Reaction with Nitric Oxide. A sample of **1** exposed to oxygen-free nitric oxide decomposed over a period of 1 hr to give a colorless low-melting solid. The weight gain indicated that 0.92 equiv of NO had reacted. The nmr spectrum of the product displayed two sharp 1:1 singlets at δ 1.34 and 1.40, and five minor peaks. Strong bands at 1600, 1550, and 1310 cm⁻¹ were assigned to C=N, and to asymmetrical and symmetrical stretching modes of a nitro group, respectively.[29] A weak band at λ 272 nm (ε 460) in the uv spectrum is similar to one that has been observed for nitrimines.[29] A reasonable pathway to account for the oxygen migration is shown in Scheme I. A similar sequence

Scheme I



$$\begin{array}{lcl} (Me_3C)_2C{=}NO\cdot + NO \rightleftharpoons (Me_3C)_2C{=}NON{=}O & \rightleftharpoons & \\ \quad\downarrow & & (Me_3C)_2C{=}N\cdot + NO_2 \\ (Me_3C)_2C{=}O + N_2O & & \quad\downarrow\text{fast} \\ & & (Me_3C)_2C{=}NNO_2 \end{array}$$

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[26] The formation of nitroxide radicals during the oxidation of oximes has been noted by many workers.[2,8,9,11a,12,16,27]

[27] P. Smith and W. M. Fox, *Can. J. Chem.*, **47**, 2227 (1969); A. Caragheogheopol, H. Caldararu, T. Constantinescu, and V. Em. Sahini, *Tetrahedron Lett.*, 4161 (1967); *J. Amer. Chem. Soc.*, **93**, 6766 (1971).

[28] E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

[29] J. P. Freeman, *J. Org. Chem.*, **26**, 4190 (1961).

was proposed by Horner, *et al.*,[30] and by Chapman and Heckert[5] to explain the formation of nitrimines from diazomethane derivatives and nitric oxide. The intermediacy of NO_2 is consistent with the succession of colors observed in the reaction (green to yellow-brown to colorless), though we were not able to detect NO_2 by mass spectrometry of the gas above reacting mixtures. Nitrous oxide was also not detected, though it is often found as a product on oxidizing oximes[2] and (we felt) might arise here along with di-*tert*-butyl ketone.

We were gratified to find that the nitrimine was identical to one of the minor products present in the mixture from thermally decomposed **1**. This supports our proposed pathway for decomposition of **2**; the nitric oxide formed from the unstable dimer is intercepted in this case by undimerized iminoxy radical.

Reactions with Some Other Reagents. At room temperature, solutions that were $\sim 5 \times 10^{-3}$ *M* in di-*tert*-butyliminoxy and in the free radicals DPPH, 2,2,6,6-tetramethylpiperidine-*N*-oxyl, or nortropane-*N*-oxyl showed only stable superimposed spectra of the two species.

Radical **1** was insoluble in aqueous concentrated HCl and NaOH. It did not react with methyl iodide but liberated iodine from moist potassium iodide–starch paper. Bromine vapor reacted with neat **1** to give a diamagnetic, unstable, red solid. Methanolic ceric ammonium nitrate (0.2 *M*) was decolorized within a few minutes by addition of neat **1**. This fact is interesting because ceric ion is frequently used to prepare iminoxy radicals from oximes. A reaction between Ce^{IV} and $Me_2C{=}NO\cdot$ has been previously suggested[2] on kinetic grounds. In the present case, since there is no α hydrogen, the initial step may be the loss of an electron from **1** to give an alkylidene nitronium ion.

Di-*tert*-butyliminoxy was decolorized within a few minutes by neat samples or concentrated solutions of phenol, 2,4,6-tri-*tert*-butylphenol, triethylamine, triethyl phosphite, and triethylphosphine. We have not investigated these reactions other than to show (tlc and pmr) that di-*tert*-butyl ketoxime was a product in most cases, and that the reaction with triethyl phosphite did not give a product with phosphorus in a different valence state (by ^{31}P nmr). No reaction occurred with triphenylphosphine. With aliphatic amines (but not with pyridine), **1** gave green solutions apparently as a result of molecular complex formation. The visible spectrum of **1** in the presence of various amounts of triethylenediamine is shown in Figure 7. This amine, unlike triethylamine, reacts slowly, if at all, with **1** and the green color could be discharged by extracting the solution with water.

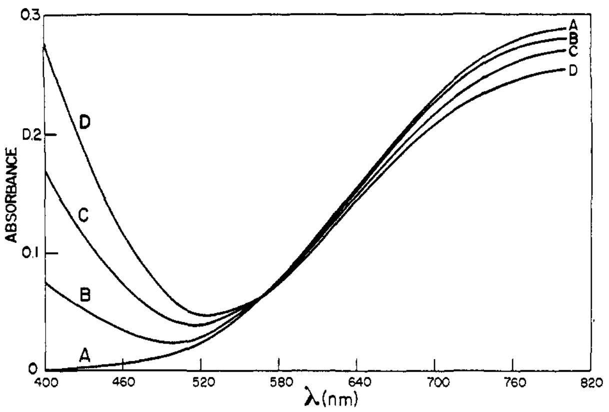


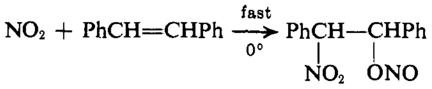
Figure 7. Visible spectrum of 0.56 *M* di-*tert*-butyliminoxy in benzene (1-mm cell): (A) alone; (B, C, and D) in the presence of triethylenediamine at concentrations of 0.35, 0.86, and *ca.* 1.7 *M* (saturated), respectively.

Rather surprisingly, **1** (0.1 *M*) was stable in styrene (2 hr, 25°) and in vinyl acetate (20 min, 60°; ≤10% decomposition after 3 days, 25°). Iminoxy radicals are formally ylides of nitrogen dioxide and nitrogen dioxide reacts extremely rapidly with olefins even at 0° to give addition products by a free-radical pathway.[31] Again we must assume that steric factors make formation of the intermediate adduct or coupling of a second molecule to this adduct an energetically unfavorable process.

$$(Me_3C)_2C{=}NO\cdot + PhCH{=}CH_2 \longrightarrow \text{no reaction}$$

$$(Me_3C)_2C{=}NO\cdot + CH_2{=}CHCOOCH_3 \longrightarrow \text{no reaction}$$

Cf.



$$NO_2 + PhCH{=}CHPh \xrightarrow[0°]{\text{fast}} \underset{NO_2}{PhCH}{-}\underset{ONO}{CHPh}$$

The epr spectrum of a solution of **1** (10^{-4} *M*) in benzene containing 0.05 *M* nitrosobenzene changed over a period of 2 hr from a triplet of **1** to a new triplet with $a_N = 12.6$ G that was stable for hours. We cannot distinguish between several possible structures for this radical.

Hydrogen Abstraction by 1. In benzene solution at room temperature **1** was rapidly reduced to the oxime by hydrazine and by hydrazobenzene. The latter reaction was quantitative and has yielded a value of *ca.* 81 kcal/mol for the O–H bond strength in di-*tert*-butyl ketoxime.[32] Radical **1** also reacted rapidly and exothermically at room temperature with 1,4-cyclohexadiene (for which the carbon–hydrogen bond dissociation energy, *D*(R–H), is 71 kcal/mol[33]) to give stoichiometric amounts of oxime and benzene.

The abstraction of hydrogen from benzylic hydrocarbons occurs at much lower rates (Table II).

$$(Me_3C)_2C{=}NO\cdot + RH \xrightarrow{k_{abs}} (Me_3C)_2C{=}NOH + R\cdot$$

$$(Me_3C)_2C{=}NO\cdot + R\cdot \xrightarrow{\text{fast}} (Me_3C)_2C{=}NOR$$

From the reaction of cumene and **1** between 80 and 120° (Figures 8 and 9) the following Arrhenius equation was derived.

$$k_{abs} = 10^{6.3}\exp(-16{,}800 \text{ cal mol}^{-1}/RT)\ M^{-1}\text{ sec}^{-1}$$

Substitution of deuterium into the α position of cumene resulted in a greatly decreased reactivity. At 120° the measured isotope effect, k_H/k_D, was 14.4 ± 1.8. This isotope effect is exceptionally large for a hydrogen abstraction, probably because of a combination of factors. In the first place, the reaction is only ~2 kcal/mol exothermic and the presumed symmetry of

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(30) L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961).

(31) See, *e.g.*, H. Shechter, J. J. Gardikes, and A. A. Pagano, *J. Amer. Chem. Soc.*, **81**, 5420 (1959), and reference therein.

(32) L. R. Mahoney, K. U. Ingold, and G. D. Mendenhall, unpublished work.

(33) From the data summarized by S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

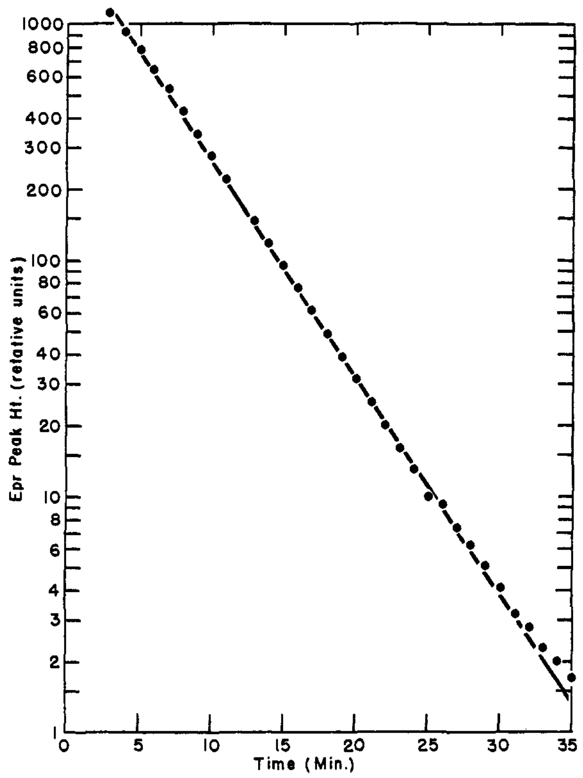

Figure 8. Pseudo-first-order decay of di-*tert*-butyliminoxy (initially 0.026 *M*) in neat cumene at 100 ± 1° followed by epr.

Table II. Rate Constants for H Abstraction by Di-*tert*-butyliminoxy

Radical 1 initial concn	Solvent	Temp, °C	$t_{1/2}$, min	$10^4 \times 2k_{abs}$, M^{-1} sec^{-1}
0.08	Toluene	120	9.3	1.4
0.026	Toluene	120	8.3	1.6
0.08	Ethylbenzene	120	1.6	8.8
0.026	Ethylbenzene	120	1.4	10
0.08	Cumene	78	10	1.76
0.08	Cumene	80	9.0	1.94
0.04	Cumene[a]	97	6.2	5.6
0.026	Cumene	100	3.2	5.45
0.26	Cumene	100	3.6	4.85
0.08	Cumene	100.5	2.5	7.0
0.08	Cumene	100.5	3.0	5.8
0.08	Cumene	116	1.1	16
0.08	Cumene	120	0.7	25
0.08	Cumene	120	0.83	21
0.026	Cumene-α-*d*	119	12	1.5
0.08	Cumene-α-*d*	120	10	1.8

[a] In 1:1 by volume *tert*-butylbenzene–cumene.

the transition state should maximize k_H/k_D.[34,35] Secondly, there must be considerable steric hindrance to the reaction and this can increase isotope effects in hydrogen atom transfers.[36] Finally, it seems certain that hydrogen tunneling[37] is significant which, if true, would help to account for the very low preexponential factor for this reaction.

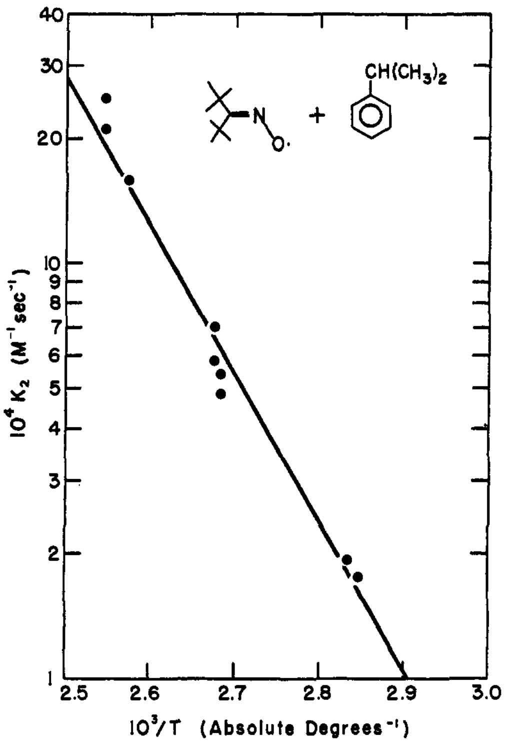

Figure 9. Arrhenius plot of the reaction between cumene and di-*tert*-butyliminoxy.

The relative rate constants (per benzylic hydrogen) for hydrogen abstraction by **1** from (neat) toluene [*D*(R–H) = 85 kcal/mol[33]], ethylbenzene [*D*(R–H) = 82], and cumene [*D*(R–H) = 79] are 1:10:46 at 120°. Comparison is made in Table III with analogous data for some other commonly used radicals and atoms. It is quite clear that there is no correlation between the

Table III. Relative Reactivities of Benzylic C–H Bonds toward Some Radicals, X·

$$X\cdot + RH \xrightarrow{k_{abs}} XH + R\cdot$$

X· (temp, solvent)	Relative reactivities[a] Toluene	Ethylbenzene	Cumene	*D*(X–H), kcal/mol	Toluene k_{abs}, M^{-1} sec^{-1} at 120°[b]
Cl$_3$C·[c] (40°, CCl$_4$)	(1)	50	260	96	80[d]
Br·[e] (80°, CCl$_4$)	(1)	24	50	87	~10^6 [f]
(Me$_3$C)$_2$C=NO· (120°, RH)	(1)	10	46	81	7.5 × 10^{-5}
Me$_3$COO·[g] (30°, RH)	(1)	8.3	13	88	4[h]
Me·[i] (110°, RH)	(1)	4.2	13	104	2 × 10^3 [j]

[a] Per benzylic hydrogen. [b] Per molecule, not per H. [c] G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963). [d] Calculated from data of K. Schwetlick and S. Helm, *Tetrahedron*, **22**, 793 (1963). [e] Bromination with *N*-bromosuccinimide: C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963). [f] Gas phase value at 100°: H. R. Anderson, M. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953); see also S. W. Benson and J. H. Buss, *ibid.*, **28**, 301 (1958). [g] From ref 33. [h] Extrapolated value. [i] W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972). [j] Gas-phase value calculated from data of M. Cher, C. S. Hollingsworth, and F. Sicilio, *J. Phys. Chem.*, **70**, 877 (1966).

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(34) W. A. Pryor and K. G. Kneipp, *J. Amer. Chem. Soc.*, **93**, 5584 (1971), and references cited therein.

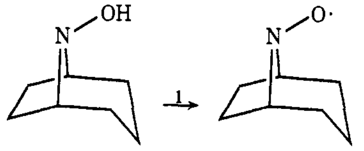
(35) It should perhaps be added that iminoxy radicals are multident and could, in principle, accept the H at carbon or nitrogen as well as at oxygen.

(36) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962); E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, **89**, 2322 (1967).

(37) See, *e.g.*, E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).

relative reactivities of these hydrocarbons and the thermochemistry of the reactions or their absolute rate constants.

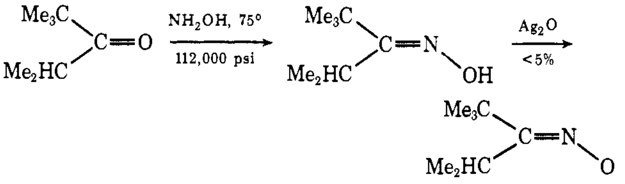
A solution of **1** (*ca.* 10^{-3} *M*) in isopentane was treated with excess solid 8-hydroxy-8-azabicyclo[3.2.1]-octane (**6**). The iminoxy triplet was replaced completely by a new triplet of about equal intensity, with a_N = 19.6 G and a_{2H} = 5.3 G, identical with that of authentic nortropane-*N*-oxyl (**7**).[38] This reaction is



6 **7**

easily rationalized if the O–H bond strength in **6** is as low as that found for 2,2,6,6-tetramethyl-4-piperidone-*N*-oxyl (*viz.*, 72 kcal/mole).[32]

***tert*-Butylisopropyliminoxy.** *tert*-Butyl isopropyl ketoxime was synthesized by the high-pressure method of Jones, *et al.*[39] However, treatment with silver oxide according to the procedure for **1** led only to small (<5%) conversion to the iminoxy radical **8**. The



$$\begin{matrix}Me_3C \\ Me_2HC\end{matrix}\!\!>C{=}O \xrightarrow[112{,}000\ \text{psi}]{NH_2OH,\ 75°} \begin{matrix}Me_3C \\ Me_2HC\end{matrix}\!\!>C{=}N\backslash OH \xrightarrow[<5\%]{Ag_2O} \begin{matrix}Me_3C \\ Me_2HC\end{matrix}\!\!>C{=}N\backslash O$$

8

spectrum so obtained was stable for many hours. The same radical could be obtained by photolysis of the oxime in benzene solution containing di-*tert*-butyl peroxide. At 8° a solution prepared in this manner showed splitting by all but two methyl groups: a_N = 30.35 G, a_H = 5.45 G (1 H), a_H = 1.0 G (6 H), a_H = 0.2 G (3 H), and g = 2.0057 (Figure 10). The smallest coupling results in a quartet which is assigned to a methyl in the *tert*-butyl group. Between 8 and 75° the only change in the spectrum is loss of this 0.2-G splitting.

From the large methine coupling (5.4 G) we conclude that the C–H bond lies close to the plane defined by the radical-containing orbital.[40] There are four conformations in which this arrangement is possible, since the oxygen can be syn or anti and the methine C–H can be oriented two ways. A Briegleb model of the radical indicates a good "fit" is achieved as shown in Figure 10 and also with the isopropyl group rotated through 180° The butyl group rotates somewhat more easily than the propyl.

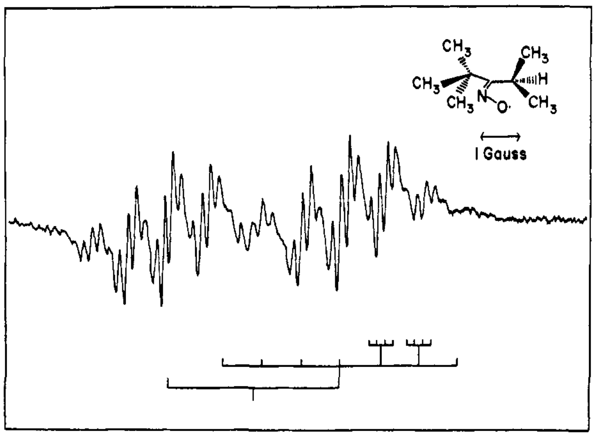
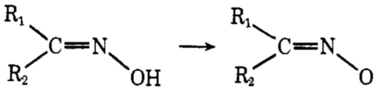


Figure 10. Highest field multiplet of *tert*-butylisopropyliminoxy (benzene, 8°).

In benzene at 25° the decay of **8**, prepared in an initial concentration of 0.005 *M*, was found to be second order with a rate constant of 0.03 M^{-1} sec^{-1} (di-*tert*-butyl peroxide) and 0.08 M^{-1} sec^{-1} (silver oxide).

Origin of the Stability of 1. The transformation of an oxime to an iminoxy radical will be accompanied by some reorientation of the groups around the C=N axis. The radical may be stabilized (relative to its



$$\begin{matrix}R_1 \\ R_2\end{matrix}\!\!>C{=}N\backslash OH \longrightarrow \begin{matrix}R_1 \\ R_2\end{matrix}\!\!>C{=}N\backslash O$$

parent) by (1) the loss of R_2–H interaction, (2) a decrease in the R_2–O interaction (*i.e.*, an increase in the CNO angle), (3) a decrease in the R_1–R_2 interaction (*i.e.*, an increase in the R_1CR_2 angle), and (4) delocalization of the free electron onto nitrogen and its interaction with the alkyl groups (hyperconjugation or spin polarization). Of these factors (1) appears to be less important than (2) or (3) from model studies. The CNO iminoxy angle has been calculated[15] to be about 140°, whereas in crystalline acetoxime[42] it is 111°. That the oxygen is easily displaced is also consistent with the facile interconversion of syn and anti iminoxy radicals[4,8] (in contrast to oximes). There is no direct evidence concerning the third and fourth factors, though it is probably relevant to (2) and (3) that the CCN angles in crystalline acetoxime differ by nearly 20°.[42]

The kinetic stability of **1** is of course due to these factors operating in reverse. To the extent that (2), (3), and (4) are relevant, the addition of a hydrogen atom or any larger group (*e.g.*, as in dimerization) to **1** will have energetic consequences greater than those steric effects directly associated with the entering group.

Dimerization is a reaction particularly influenced by these factors because both monomer halves are affected on coupling. This is apparent in the hundred millionfold difference of second-order rate constants for decay of **1** and of methyl-*tert*-butyliminoxy.[2] There does not appear to be any correlation between the logarithm of these decay rates and Taft's steric substituent constants.[43]

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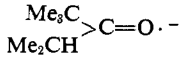
[38] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, in press.

[39] W. H. Jones, E. W. Tristram, and W. F. Benning, *ibid.*, **81**, 2151 (1959).

[40] The ketyl radical anion



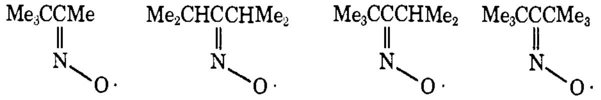
$$\begin{matrix}Me_3C \\ Me_2CH\end{matrix}\!\!>C{=}O\cdot^{-}$$

displays an unusually *small* methine coupling constant (2.38 G) because the free electron is in an orbital orthogonal to the molecular plane.[41] This suggests that the alkyl groups in this radical are in a conformation similar to that in **8**. This is consistent with the conclusion (from molecular models) that alkyl–alkyl interactions are more important than alkyl–oxygen or alkyl–nitrogen interactions in these radicals.

[41] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960).

[42] T. K. Bierlein and E. C. Lingafelter, *Acta Crystallogr.*, **4**, 450 (1951).

[43] R. W. Taft, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956.



$Me_3CC(=NO\cdot)Me$ — 2000; $Me_2CHC(=NO\cdot)CHMe_2$ — 190; $Me_3CC(=NO\cdot)CHMe_2$ — 0.05; $Me_3CC(=NO\cdot)CMe_3$ — 0.000021

$2k_t$ ($M^{-1}sec^{-1}$)

Intramolecular repulsive interactions should be less in *tert*-butyl isopropyl ketoxime than in di-*tert*-butyl ketoxime. The O–H bond strength is therefore expected to be greater in the former (**8**-H) than in the latter (**1**-H). This may explain our qualitative observation that *tert*-butyl isopropyl ketoxime (and other, even less hindered oximes[44]) are oxidized more slowly by silver oxide than di-*tert*-butyl ketoxime. Support for a stronger O–H bond in *tert*-butyl isopropyl ketoxime than in **1**-H is provided by a preliminary value of 300 in benzene at 24° for the equilibrium constant [**8**-H][**1**]/[**8**][**1**-H].

Conclusion

Di-*tert*-butyliminoxy does not have the shelf life possessed by many di-*tert*-alkyl nitroxides, but the radical is stable enough in dilute solution to make possible extensive kinetic studies. The air stability of **1** and ease of preparation are features not shared by many stable radicals, and the high O–H bond strength (81 kcal) confers on it a wider range of reactivity than observed for stable nitroxides. We have not explored the use of **1** or **1**-H as radical-counting agents,[28] though the fact that high concentrations of di-*tert*-butyl ketoxime can be prepared entirely free from **1** is an advantage not shown by dialkylhydroxylamines. Equilibrium studies between **1** and other R·/RH pairs may furnish useful information on the thermodynamic stabilities of free radicals. Biological applications of hindered iminoxy radicals should not be thwarted by the dimerization reaction (which is very slow even at moderate dilution), but may be subject to interference by reaction with certain functional groups, *e.g.*, amines. Again, reactions of the latter type may themselves prove useful because of their selective nature.

Experimental Section

Preparation of Ketoximes. In our preliminary work,[20] di-*tert*-butyl ketoxime was prepared by the high-pressure method of Jones and Tristram.[45] This method is not suitable for large quantities of material. Hartzler[46] has shown recently that hindered imines undergo nucleophilic attack readily, however, and we developed the following procedure on this basis.

Di-*tert*-butyl Ketoxime (1-H). A solution of 1.25 *M* *tert*-butyllithium in *n*-pentane, 40 ml (Foote Mineral Co.), was placed in a flask under a nitrogen atmosphere, and 4.1 g (50 mmol) of pivalonitrile was added dropwise from an addition funnel. This mixture was stirred magnetically during this time. After the mixture stood for 1 hr at 25°, there was added successively 5 ml of absolute ethanol, 3 ml of acetic acid and 3.5 g of hydroxylamine hydrochloride. An additional 65 ml of absolute ethanol was used to transfer the mixture to a flask with a condenser attached, and the mixture was refluxed 5 hr. About 25 ml of water was added, and the mixture was cooled in ice. The colorless crystals were filtered off, sucked partly dry, and sublimed under *ca.* 1 mm pressure. The yield was 3.3 g (46%), sublimes 158° (lit.[45] mp 157.5–158.5°).

***tert*-Butyl Isopropyl ketoxime (8-H).** This compound was prepared by the high-pressure method.[45]

A mixture of pentamethylacetone (2.7 g, Chemsamco), hydroxylamine hydrochloride (2.2 g), and sodium acetate trihydrate (5.4 g) was thoroughly ground in a mortar. The paste was thinned with absolute ethanol, filtered, and diluted to 25 ml. Half this solution was placed in a 15-ml Teflon cup that was then filled with absolute ethanol and placed in a high-pressure apparatus. The mixture was heated to 50° under 112,000 psi for 17 hr. After releasing the pressure and cooling the sample several hours at −20°, the crystalline product was filtered, washed with 95% ethanol, and sucked dry, 1.40 g (84%). Sublimation gave a white powder: sublimed 139° (lit.[45] mp 140–141°); nmr δ 1.12 (singlet, 9 H), 1.32 (doublet, 6 H, J = 7 Hz), 2.61 (septet, 1 H, J = 7 Hz).

Preparation of Iminoxy Radicals and Dimer. Di-*tert*-butyliminoxy (1). Di-*tert*-butyl ketoxime (0.3 g in 30 ml of benzene) was stirred or shaken 90 min with 0.7 g of silver oxide (Fisher) to give a blue solution that was filtered and concentrated at 25°. The resulting oil (0.22 g, 74%) was distilled twice *in vacuo* by the bulb-to-bulb technique with the receiver in liquid nitrogen: fp −21°; $n^{21}D$ 1.4452; $d^{22°}$ 0.824; mass spectrum (50 eV) *m/e* (rel intensity) 214 ± 1 (2 (probably C_4H_9 capture, 213)), 171 (1 (CH_3 capture)), 157 (5 (H capture)), 142 (7.5), 115 (26), 100 (11), 84 (22), 68 (65), 67 (22), 57 (100). *Anal.* Calcd for $C_9H_{18}NO$: C, 69.18; H, 11.61; N, 8.97, mol wt, 156.24. Found: C, 68.96; H, 11.77; N, 9.15; mol wt 160 (vapor pressure osmometry in benzene at 37°).

Epr spectroscopic parameters (Table I) were obtained on a Varian E-9 epr spectrometer with automatic provision for measuring the frequency and magnetic field.

***tert*-Butylisopropyliminoxy (8).** Treatment of the parent oxime **8**-H with silver oxide in benzene as described above gave a colorless solution containing 0.0016 *M* (2.2%) radical by comparison with a standard DPPH solution.

Di-*tert*-butyliminoxy Dimer (2). An old, partly crystalline sample of **1** was crystallized several times from isopentane at −78°. The blue crystals were dried *in vacuo* at 0°: mp 48–53°; nmr (benzene, 10°) four singlets in ratio 1:2:1 at δ 1.10, 1.23, and 1.32, respectively; λ_{max} (benzene) 698 nm (ε 9.5). *Anal.* Found: C, 69.02; H, 8.80; N, 11.85; and C, 66.56; H, 11.80; N, 12.14; mol wt (vapor pressure osmometer), 307. For comparison, the analogous compound from diisopropyliminoxy has λ_{max} 703 nm (ε 11).[2]

Reactions of Di-*tert*-butyliminoxy (1). Catalytic Reduction. A sample of **1** (0.103 g) was dissolved in benzene (1 ml) and ethyl acetate (1.5 ml) containing 0.02 g of 5% Pd/C (Engelhard Industries). The mixture was stirred magnetically for 3 days under a slight positive H_2 pressure. Filtration and concentration of the filtrate gave a white crystalline solid, 0.0909 g (89%). This was identified as di-*tert*-butyl ketoxime (**1**-H) by comparison of its ir and nmr spectra with those of an authentic sample.

Decomposition. A sample of **1** was allowed to stand at 25° in the dark for 1 week. During this time the blue color faded to pale yellow. Part of the sample was dissolved in $CDCl_3$, and the spectrum was recorded. In addition to a small amount of benzene, the following signals (all singlets) were recorded.

δ	Rel ht	δ	Rel ht
1.16	1.3	1.34	5.2
1.22	3.5	1.37	2.5
1.24	15.5	1.40	3.7
1.33	4.0	1.54	1.0

Compounds assigned to these signals include di-*tert*-butyl ketone (δ 1.245, 42%), di-*tert*-butylnitrimine (1.34, 1.40, 20%), and pivalonitrile (1.37, 4%). The identity of the ketone was confirmed by ir and tandem glc–mass spectral comparison of the mixture with an authentic sample. The nitrimine could be isolated in small amounts by fractional bulb-to-bulb distillation of the mixture, and its identity follows from nmr and ir comparison with the product from **1** and nitric oxide.

Absent from the mixture were di-*tert*-butyl ketoxime (δ 1.25, 1.41), *tert*-butylnitrile oxide dimer[2] (δ 1.47, 1.49), hexamethylethane (δ 0.87), and the dimer **2**.

Reaction with Nitric Oxide. This reaction was carried out in the apparatus shown in Figure 11. The sample tube was weighed accurately before and after adding a sample of pure **1** (0.05360 g). The flask was attached to the center portion of the apparatus and degassed at −196°. The stopcocks were closed under vacuum, and argon and then nitric oxide (Matheson) were added through the attachment shown at left. The sample was exposed to NO by opening the stopcocks and rotating the apparatus occasionally to

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[44] Though in these cases, increased intermolecular hydrogen bonding of the oximes will tend to retard oxidation.

[45] W. H. Jones and E. W. Tristram, U. S. Patent 3,256, 331 (1966); W. H. Jones, E. W. Tristram, and W. F. Benning, *J. Amer. Chem. Soc.*, **81**, 2151 (1959).

[46] H. D. Hartzler, *ibid.*, **93**, 4527 (1971).

expose fresh surfaces of the oil. After 1 hr the sample tube was frozen and degassed. After warming, the sample tube was removed and a gain of 0.00945 g was noted (theoretically 1 equiv = 0.01029 g): nmr spectrum (CDCl$_3$) singlets at δ 1.34 and 1.40; very small signals at 1.16, 1.17, 1.24, 1.51, 1.57 (sum <10% of major signals); ir (neat) major ν_{max} at 2950, 1600, 1550, 1480, 1310, 1065, 995, and 895 cm^{-1}. A sample crystallized from aqueous ethanol was analyzed.

Anal. Calcd for $C_9H_{18}N_2O_2$: C, 58.03; H, 9.74; N, 15.04; mol wt, 186.25. Found: C, 58.12; H, 9.86; N, 14.96; mol wt, 195 (vapor pressure osmometry, benzene, 37°); λ_{max} (cyclohexane) 270 nm (ϵ 460).

Reaction with 1,4-Cyclohexadiene. A mixture of 0.05940 g of **1**, 0.437 g of CDCl$_3$, and 0.06255 g of 1,4-cyclohexadiene (Columbia, distilled from triphenylphosphine and MgSO$_4$) decolorized rapidly with evolution of heat. Glc comparison (2 m × 0.25 in. SE-30 column at 60°, FGM Model 700 instrument) of the peak areas of benzene and cyclohexadiene indicated the yield of benzene was 90.3 ± 0.5%. The nmr spectrum of the solution showed resonances at δ 1.22, 1.40 (di-*tert*-butyl ketoxime), 2.62, 5.64 (1,4-cyclohexadiene), and 7.3 (benzene, yield calculated to be 90.3 ± 1.6%). Two small peaks also appeared at δ 1.29 and 1.32, each about 10% of the height of the oxime signals. Evaporation of the reaction solution gave a colorless, crystalline residue of di-*tert*-butyl ketoxime, 0.05360 g (90.4%), identified by comparison of ir and mass spectrum with those of an authentic sample.

Reaction with Cumene, Ethylbenzene, and Toluene. The epr kinetic studies were done on a Varian E-3 epr spectrometer equipped with a signal integrator. The general experimental procedure has been described in previous papers in this series.[1]

Mixtures of **1** in the alkyl aromatic hydrocarbon, triphenylphosphine (to destroy any hydroperoxides present in the solvent), and magnesium sulfate were degassed three times and distilled *in vacuo* into the epr tube. After admitting argon, the tubes were sealed and placed in the preheated cavity of the instrument. The decay of **1** in cumene, ethylbenzene, and toluene was pseudo first order for 5-11 half-lives. Small initial deviations (Figure 6) were ascribed to line-broadening effects at high concentrations. At very small concentrations (~10^{-5} *M*) of **1** the rate frequently decreased. This was probably due to regeneration of **1** from the oxime and radicals formed by slow decomposition of products or some adventitious material. Second-order rate constants were obtained by dividing by the concentration of hydrocarbon in pure solvent. This requires a knowledge of the density at the temperature involved. For toluene the density at 100° was calculated as 0.792 from a published formula.[47] The density of cumene at 100° was measured as 0.791 and the densities of ethylbenzene and cumene-α-*d* were assumed to be 0.79. The errors arising from use of these densities at 80 and 120° are small.

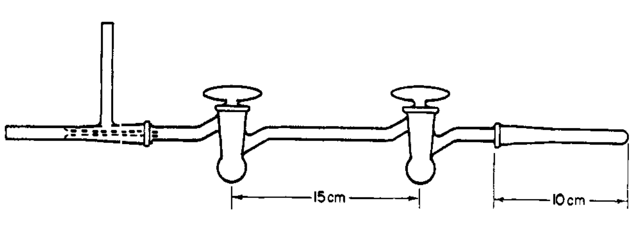

Figure 11.

The samples of **1** in styrene and in vinyl acetate were prepared in the same way as the alkylbenzene samples, except that magnesium sulfate was omitted.

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(47) "International Critical Tables," Vol. 3, 1st ed, McGraw-Hill, New York, N. Y., 1928, p 29.

Some Unusual Stereochemistry in a Transamination Reaction

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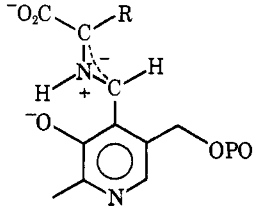
Abstract: In contrast to all potassium *tert*-butoxide catalyzed methylene–azomethine rearrangements previously studied in *tert*-butyl alcohol, the interconversion of *N*-(α-methyl-4-methoxybenzylidene)-α-phenylethylamine (I) and *N*-(α-methylbenzylidene)-α-(4-methoxyphenyl)ethylamine (II) has been found to occur with a very low degree of stereospecificity. Several explanations are offered and the intermediacy of a twisted carbanion is suggested.

The study of base-catalyzed isomerization of methylene–azomethine systems has provided some interesting stereochemical analogies to the enzymatic reactions by which amino acids are reversibly produced from the corresponding keto acids. The mechanism of the enzymatic reaction involves a proton shift in an imine formed by condensation of the requisite keto acid with enzyme bound pyridoxamine phosphate which in turn arises from pyridoxal phosphate cofactor. The incisive studies of Dunathan, Snell, and their coworkers[1] have shown that the stereochemistry of such transaminase catalyzed reactions is explicable in terms of suprafacial transfer in a system of the geometry displayed in 1. This geometry is presumably specified by some combination of steric effects, electrostatic interactions of charged sites, and geometry of the surrounding protein. The suprafacial stereochemistry must be dictated by an immobilization of the substrate–cofactor compound relative to the proton vehicle on the enzyme surface.



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(1) (a) H. C. Dunathan, *Vitam. Horm.* (*New York*), **28**, 399 (1970); (b) H. C. Dunathan, L. Davis, P. G. Kury, and M. Kaplan, *Biochemistry*, 7, 4532 (1968); (c) J. E. Ayling, H. C. Dunathan, and E. E. Snell, *ibid.*, 7, 4537 (1968); (d) H. Wada and E. E. Snell, *J. Biol. Chem.*, **237**, 133 (1962).