axis of the lone pair of electrons on phosphorus is parallel to the $2p\pi$ orbital axes on carbon.[15] It is now recognized that previous evidence adduced for aromaticity in phosphole derivatives, based on thermochemical[16] and spectroscopic (nmr[4,7] and uv[7]) data, must be referred to the pyramidal (*i.e.*, ground state) rather than planar conformation. Data based on chemical reactivity, which have been offered as evidence against aromaticity,[7,17] bear little relevance to considerations affecting the ground state of the molecule.

The effect of substituents on the barrier to inversion in phospholes and cognate systems is currently under investigation.

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(18) (a) National Aeronautics and Space Administration Fellow, 1969–1970; (b) National Defense Educational Act Fellow, 1969; Public Health Service Predoctoral Fellow, 1969–1970.

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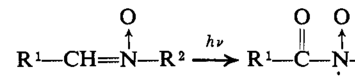
Stable Radicals by Photooxidation of Nitrones

Sir:

The isomerization of nitrones to oxaziranes by exposure to light has been reported.[1,2] We have observed that ultraviolet irradiation of nitrones in solution at room temperature produces long-lived radicals. They arise apparently by a photochemical oxidation of the nitrones. By means of esr measurements these radicals have been identified as N-benzoylnitroxides.



$$R^1{-}CH{=}\overset{\overset{O}{\uparrow}}{N}{-}R^2 \xrightarrow{h\nu} R^1{-}\overset{\overset{O}{\|}}{C}{-}\underset{\cdot}{\overset{\overset{O}{\uparrow}}{N}}{-}R^2$$

Listed in Table I are the nitroxides and their hfsc's. The esr spectrum of N-benzoyl-N-phenylnitroxide (**1**) was reported by Aurich and Baer[3] who prepared this radical by chemical oxidation of N-benzoylphenylhydroxylamine (**5**). The radical has also been obtained by combination of benzoyl radical and nitrosobenzene.[4]

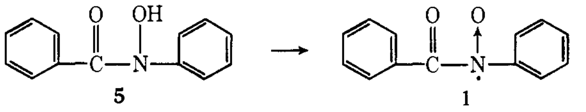


Table I. Splitting Constants of Aroylnitroxides in Benzene[a]

Radical	R^1	R^2	A^N	$A_{o,p}^{H}$ [b]	A_m^{H} [b]
1	C_6H_5	C_6H_5	7.53	1.55	0.70
1	C_6H_5	C_6H_5	7.58[c]	1.55[c]	0.70[c]
2	p-$CH_3OC_6H_5$	C_6H_5	7.78	1.62	0.68
3	C_6H_5	p-$CH_3C_6H_5$	7.53	1.63[d]	0.65
4	C_6H_5	t-C_4H_9	7.92		

[a] A Varian 4500 epr spectrometer was used. Measurements were made at room temperature. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol according to the procedure of E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962). The splittings are given in gauss. [b] The H splittings are from the N-phenyl group. [c] By NiO_2 oxidation of N-benzoyl-N-phenylhydroxylamine in benzene, Aurich and Baer[3] reported A^N 7.55, $A_{o,p}^H$ 1.54, and A_m^H 0.64 G. [d] The *p*-methyl- and *o*-H's are equivalent and give rise to a sextuplet.

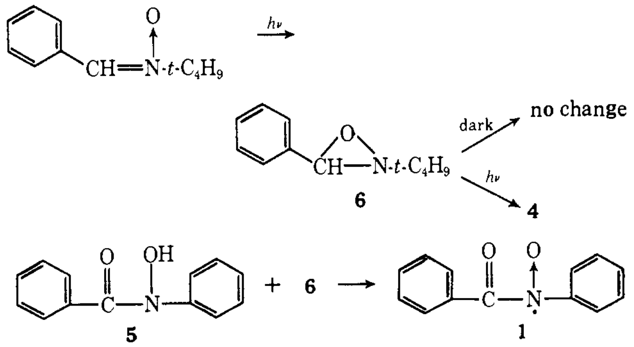
Janzen and Blackburn[5] have apparently formed N-benzoyl-N-*t*-butylnitroxide (**4**) by chemical oxidation of α-phenyl-N-*t*-butylnitrone. A triplet with $A^N = 7.67$ G splitting was attributed to **4**.

The nitrones have also been reported recently as radical traps for short-lived species,[5–8] in which case the short-lived radicals add to the α-carbon atom of the nitrone to give the stable nitroxide radical. The hfsc's of the nitrogen and α-H atoms vary with the added group. The nitrogen hfsc's observed are characteristically larger than those from aroyl nitroxides.

We prepared nitrone solutions approximately 0.05 *M* in benzene and deaerated the solutions with a fine stream of argon bubbles. The solutions were prepared, deaerated, and measured in the dark, and were exposed for 10–30 sec only to the light from a Bausch and Lomb SP 200-W super pressure mercury lamp. No esr signals were detected prior to irradiation. Maximum signal strength was obtained 15–30 min after irradiation and the signals lasted for days. We found that a second deaeration after exposure usually improves the intensity and the resolution of the signal. It is quite likely that oxygen is formed during irradiation of the nitrones, for the liberation of oxygen from N-oxides under irradiation has been observed.[9,10]

Benzoyl nitroxides are also detected when the phenylnitrones are irradiated in methylene chloride, but no esr signals are obtained in ethanol solutions. No esr signal is obtained when the α-hydrogen atom is replaced, *e.g.*, from α-cyano-α-phenyl-N-phenylnitrone when irradiated.

α-Phenyl-N-*t*-butyloxazirane (**6**), which is a stable compound at room temperature,[11] when irradiated in benzene gives the same triplet with $A^N = 7.92$ G as the



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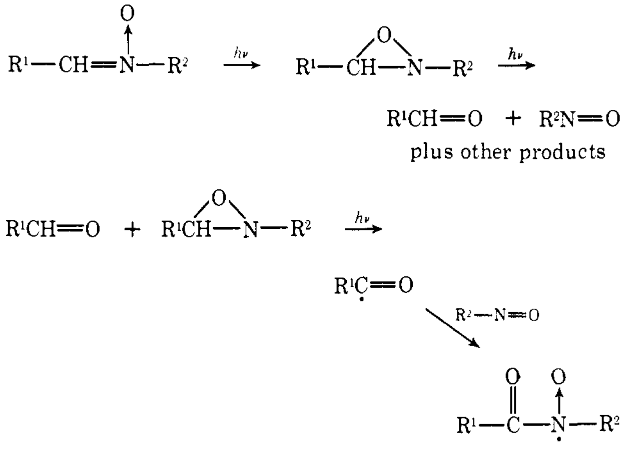
isomeric nitrone. No signal is detected prior to irradiation. In the dark, **6** converts a benzene solution of N-benzoyl-N-phenylhydroxylamine (**5**) to the benzoylnitroxide (**1**). Although this demonstrates further the oxidizing properties of the oxazirane structure, the observation that a benzene solution of **6** does not give **4** in the dark demonstrates that the conversion of oxazirane to benzoylnitroxide is light dependent.

After a brief irradiation of the nitrones in solution we observe that the radical signal continues to grow in intensity when kept in the dark, which would indicate a thermal or chain reaction. Amides are considered to be secondary thermal products arising from the irradiation of nitrones,[12,13] and to explore the possibility that the amide might be a precursor to the nitroxide radicals, we irradiated N-phenylbenzamide in benzene. No esr signal was detected. To simulate conditions where oxazirane might be present, **6** was added to the benzanilide solution. Irradiation did give rise to a signal, but the splittings were not characteristic for **1**.

Apparently an excited form of the oxaziranes is involved initially in the formation of the observed nitroxide radicals. After conversion of the nitrones to oxaziranes by light, photooxidation could lead to the production of benzoylhydroxylamines, such as **5**. The subsequent conversion to the nitroxide radicals could take place in the dark, by the action of residual oxazirane, as shown earlier.

Another scheme might involve fragmentation and recombination as shown below.



The formation of aldehydes and nitroso compounds from the irradiation of nitrones has been reported.[12,14,15] Combination of benzoyl radicals with nitroso compounds has been used to prepare benzoyl nitroxides.[4]

Extended irradiation of the nitrone solutions leads to changes in the esr signals, and in some cases the signals are destroyed. The reaction mechanism which leads to aroylnitroxides is being studied.

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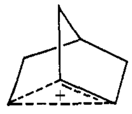
Gas-Phase Stabilities of Bicyclic Cations

Sir:

The long-standing controversy regarding nonclassical carbonium ions in norbornyl systems has focused upon whether the ion I, possessing a three-center bond, is



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best represented as a transition state between two rapidly equilibrating classical ions or as an intermediate lower in energy than either classical ion.[1,2] An important aspect of the controversy is the intrinsic question of stabilities of ions as a function of their geometry. Spectroscopic,[3] kinetic,[1,4] and stereochemical[5] data related to this problem have been obtained only in solution where solvent effects may and probably do play a significant role. We wish to report the relative stabilities of sets of protonated bicyclic olefins and ketones, free of solvation effects, which establish the presence of σ (nonclassical) delocalization in the norbornyl cation.

Limits on heats of formation in the gas phase can be established by observing and identifying ion–molecule reactions.[6] For example, if reactions 1 and 2 are observed, they must be exothermic with respect to the

$$M + AH^+ \longrightarrow MH^+ + A \tag{1}$$

$$B + MH^+ \longrightarrow BH^+ + M \tag{2}$$

state of the reactants. Therefore, $\Delta H_f(AH^+ - A) > \Delta H_f(MH^+ - M) > \Delta H_f(BH^+ - B)$. If M is the compound being studied and A and B are reagents for which $\Delta H_f(AH^+ - A)$ and $\Delta H_f(BH^+ - B)$ are known, then limits on $\Delta H_f(MH^+ - M)$ can be set. Using ion cyclotron resonance techniques[7,8] and available data in the literature, we have studied the gas-phase stabilities of bicyclic cations. The results are summarized in Table I.

The relative stabilities of bicyclic cations can be evaluated by comparing differences in the heats of formation of an ion and its saturated hydrocarbon (Table I, lines 5 and 6). The bicyclo[2.2.1]heptyl cation compared to its saturated system is approximately 6 kcal/mol more stable than the bicyclo[2.2.2]octyl cation compared to its hydrocarbon. Changes in angle strain, nonbonded interactions, torsional strain, and bond deformation which includes σ delocalization in going from the hydrocarbon to the ion in the two bicyclic systems account for this difference. A greater increase in angle strain in the bicyclo[2.2.1]heptyl system and comparable changes in nonbonded interactions and torsional strain in the two bicyclic systems would be expected.[1] This would predict greater stability for

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