Thermal Decomposition of α,α-Diphenyl-N-benzhydrylnitrone. Electron Paramagnetic Resonance Measurements

James S. Vincent[1a] **and Edward J. Grubbs**[1b]

Contribution from the Department of Chemistry, University of California, Davis, Davis, California 95616, and the Department of Chemistry, San Diego State College, San Diego, California 92115. *Received October 12, 1968*

Abstract: Electron paramagnetic resonance (epr) measurements made during the thermal isomerization reaction of α,α-diphenyl-N-benzhydrylnitrone to benzophenone O-benzhydryloxime strongly indicate the presence of the diphenyliminoxy radical as an intermediate. This suggests that the first step in this reaction sequence is a homolytic dissociation at the carbon–nitrogen single bond. Another radical is observed which may be interpreted to be a nitroxide radical which results from an intermediate free-radical addition to the nitrone double bond.

Recent product analysis and kinetic data[2a] have shown that the thermal rearrangement of α,α-diphenyl-N-benzhydrylnitrone (I) to benzophenone O-benzhydryloxime (II) may proceed by a free-radical mechanism rather than a concerted intramolecular mechanism involving a quasi-three-membered-ring transition state as previously postulated.[2b] The disappearance of I in dilute solutions of diethyl Carbitol exhibits first-order kinetics in the temperature range of 130–160°. Analysis of the kinetics over this range of temperatures yields an activation energy of 38.8 ± 0.3 kcal/mol and an activation entropy of 11 eu. The rate of decomposition of the nitrone is insensitive to substitutions in the aromatic rings. The major products from the decomposition of I are II, *sym*-tetraphenylethane, and benzophenone oxime. The last two products are most easily accounted for by assuming that the benzhydryl and diphenyliminoxy radicals are intermediates which yield these products by combination or hydrogen atom abstraction from the solvent. This and the kinetic data suggest that the first step in this reaction sequence may be a homolytic dissociation at the carbon–nitrogen single bond.

Radicals were observed in the course of this reaction by electron paramagnetic resonance (epr), and the spectra strongly support the homolytic mechanism of the thermal rearrangements of these nitrones. The discussion of the epr measurements constitutes the major portion of this paper. Epr spectra are reported for heated solutions of I in diethyl Carbitol and melts of the pure nitrone, I.

Experimental Section

Samples of I (approximately 0.1 *M*) in diethyl Carbitol were sealed off under vacuum after they were thoroughly degassed by a repeated freeze–thaw treatment. The solid nitrone was sealed off in sample tubes under vacuum for the studies of the melt. The samples were kept in dark vessels at liquid nitrogen temperatures prior to the epr experiments. The epr spectra were observed with a Varian Associates V-4500 spectrometer which has a variable-temperature cavity insert.

Experimental Results

The epr spectrum of the radical observed in the diethyl Carbitol solution between the temperatures of 100 and 160°, as shown in Figure 1, consists of three doublets. All six lines are equal in intensity. Each set of doublets is split by 14.3 ± 0.2 G and the doublet splitting is 2.1 ± 0.1 G. The *g* value of this radical is 2.0061 ± 0.0003. The signal decreases in intensity as the temperature increases becoming vanishingly small above 200°. This spectrum is very similar to those of stable nitroxide radicals[3] and suggests an assignment of the spectrum as a coupling with a nitrogen $A_N = 14.3$ G, and a smaller coupling of a single proton $A_H = 2.1$ G.

The epr spectrum of the pure nitrone (I) melt at approximately 180°, as shown in Figure 2, consists of lines identical with those described above in the solution spectrum which are attributed to a nitroxide and two weak lines approximately 2-G wide equally spaced on either side of the nitroxide spectrum. The central nitroxide doublet is broader and more intense than the other doublets. We interpret this total spectrum as being due to a mixture of two radicals, the nitroxide radical and a nitrogen-containing radical which has a larger nitrogen coupling, $A_N = 31.5 \pm 0.3$ G. Both radicals have the same *g* values to within 5 parts in 10^4. The epr spectrum of the diphenyliminoxy radical (generated from benzophenone oxime) has been observed previously[4] and the nitrogen coupling is identical with that of our second radical. This radical observed previously at a lower temperature also has a small coupling with two protons with $A_H = 1.4$ G. Our line width, however, is too large to resolve this splitting. The *g* value we measure is identical with the average *g* value that Miyagawa and Gordy[5] measured for the iminoxy radical of irradiated dimethylglyoxime. The *g* value of di-*t*-butylnitroxide[3] is 2.0065 and is, within experimental accuracy, identical with ours.

We were unable to observe epr signals from samples of II either in solution or from the pure melt. We were also unsuccessful in observing the epr spectrum of the benzhydryl radical in this same system.

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[1] (a) University of California, Davis, Davis, Calif. 95616. (b) San Diego State College, San Diego, Calif. 92115.

[2] (a) E. J. Grubbs, J. A. Villarreal, J. D. McCullough, Jr., and J. S. Vincent, *J. Amer. Chem. Soc.*, **89**, 2234 (1967); (b) A. C. Cope and A. C. Haven, Jr., *ibid.*, **72**, 4896 (1950).

[3] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966); J. R. Thomas, *J. Amer. Chem. Soc.*, **82**, 5955 (1960); A. K. Hoffman, *ibid.*, **83**, 4671, 4675 (1961).

[4] J. R. Thomas, *ibid.*, **86**, 1446 (1964); B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 86 (1966); M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964).

[5] I. Miyagawa and W. Gordy, *J. Chem. Phys.*, **30**, 1590 (1959).

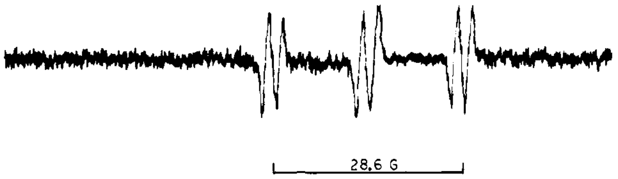


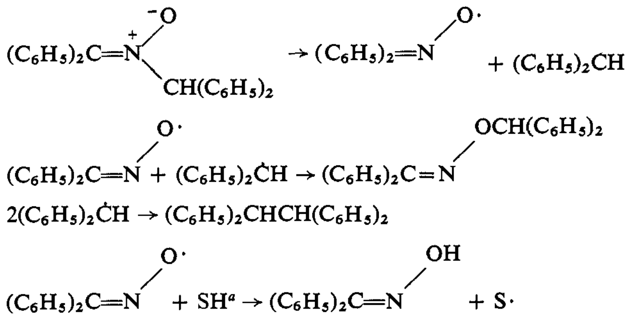
Figure 1. The first derivative of the epr spectrum obtained by heating α,α-diphenyl-N-benzhydrylnitrone above 100° in diethyl Carbitol.

Figure 2. The first derivative of the epr spectrum obtained by heating α,α-diphenyl-N-benzhydrylnitrone above its melting point.

Discussion

1. Iminoxy Radical. The observation of an epr signal with an apparently large nitrogen splitting is most consistent with the homolytic dissociation mechanism proposed for the thermal rearrangement of the nitrone (I) and illustrated below in Scheme I.

Scheme I

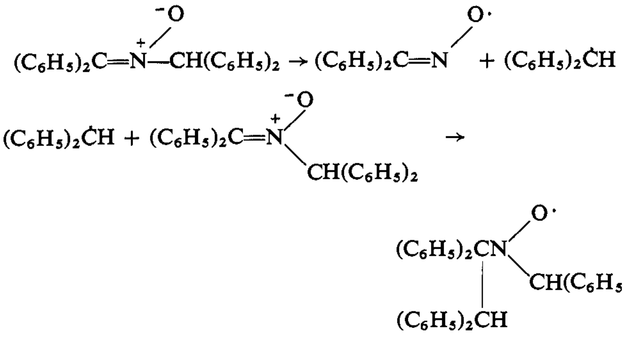


[a]SH represents the solvent, bis(β-ethoxyethyl) ether (diethyl Carbitol)

The iminoxy radical is only observed in the most concentrated system studied, the nitrone melt. The signal strength of the radical in the melt is quite weak and requires 25 passes through a signal averager to yield the signal-to-noise ratio exhibited in Figure 2. The benzhydryl radical is presumably too short lived for us to observe under these conditions. The products derived from the solvent following hydrogen abstraction have not been characterized. No epr signals have been observed which may be attributed to solvent radicals. The epr evidence for the validity of Scheme I is the observance of the spectrum which is identical with the iminoxy radical presumed to be one of the intermediates. That the iminoxy radical is not formed from II follows from the absence of any epr signals when samples of II (melt or solution) are heated to temperatures facilitating the nitrone decomposition. This is consistent with our observations that II is quantitatively recovered from solutions in diethyl Carbitol heated at 144° for 48 hr.[2a] These results are also consistent with recently completed experiments which show that pure geometrical isomers of *p*-methylbenzophenone O-benzhydryloxime undergo no detectable configurational isomerization when heated under these same conditions.[6]

2. Nitroxide Radical. Scheme I must be modified significantly to account for the observation of a nitroxide-like radical. This modification may not be the primary course of the reaction because nitroxide radicals are relatively long lived and a comparatively insignificant side reaction may yield readily observable concentrations of the nitroxide radical. We propose in Scheme II a mechanism which yields a likely candidate for this intermediate nitroxide.

Scheme II



III

Radical addition to a double bond as suggested in step two of this scheme has been observed before. Wang and Cohen[7] have described analogous reactions. Iwamura and Inamoto[8] have observed the epr spectrum of the nitroxide resulting from the free-radical addition of $(CH_3)_2CCN$ to the nitrone double bond in $(C_6H_5)CH{=}N(\rightarrow O)\text{-}t\text{-}C_4H_9$. Recently Janzen and Blackburn[9] have observed nitroxide radicals resulting from the reaction of phenyl-*t*-butylnitrone with a variety of radicals.

The nitrogen hyperfine coupling constant of 14.3 G, which we observe, is very similar to that of dibenzyl nitroxide[3] (14.9 G). The doublet splitting of 2.1 G indicates a coupling of only one hydrogen which must be bonded to the α carbon adjacent to the nitroxide nitrogen. No coupling of comparable size has been observed from hydrogens bonded to more distant carbons when the α carbon has been saturated. The hydrogen coupling in III must then arise from the benzhydryl hydrogen. This splitting, however, is much smaller than the proton coupling in dibenzylnitroxide (8.7 G).[3]

Upon the supposition that dibenzhydrylnitroxide would be better radical with which to compare III, we

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(6) E. J. Grubbs and T. S. Dobashi, unpublished results.

(7) C. Wang and S. G. Cohen, *J. Amer. Chem. Soc.*, **82**, 4688 (1960).

(8) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Jap.*, **40**, 702, 703 (1967).

(9) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **90**, 5909 (1968).

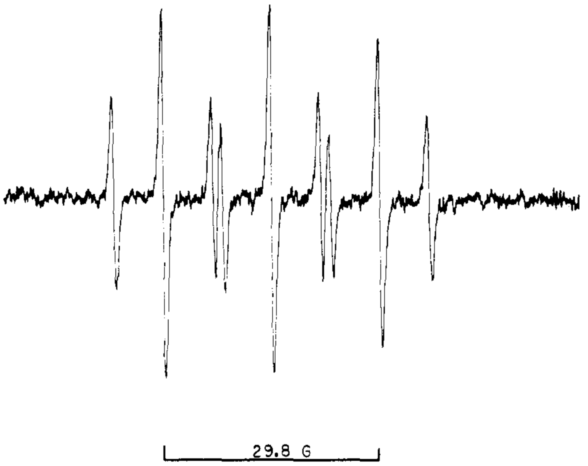


Figure 3. The first derivative of the epr spectrum of bis(diphenylmethyl)nitroxide in methylene chloride at room temperature.

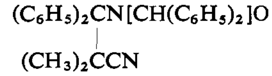
generated[10] the dibenzhydrylnitroxide radical and show its epr spectrum in Figure 3. The nitrogen and hydrogen coupling constants are respectively 14.9 ± 0.1 and 6.8 ± 0.1 G. These constants are very little different from those of dibenzylnitroxide.

The interpretation of the epr spectrum of the nitroxide radical depends upon whether the radical is indeed III or some other species. It is not readily apparent how a nitroxide-like species would arise save by a mechanism outlined in Scheme II. If the radical species is III, it is also very likely that the benzhydryl group does not rotate freely about the NC bond because of the extreme crowding of the phenyl groups about the nitroxide moiety. Models of III demonstrate that this steric problem is severe and indicate that the only way the compound can be formed is with the C–H bond of the benzhydryl group nearly parallel to the CN(O)C plane and antiparallel to the NO bond. The hyperfine interaction,[11] of β hydrogens is quite dependent upon the angle that the C–H bond makes with the π orbital containing the unpaired electron. In this case the unpaired electron partially resides in the nitrogen p orbital perpendicular to the CN(O)C plane. The β hydrogen hyperfine interaction,[11] A_H may be approximated by

$$A_H = (B \cos^2 \theta)\rho_n^\pi$$

where ρ_n^π is the spin density in the nitrogen p_z orbital, θ is the angle between the nitrogen p_z orbital axis and the C–H bond, both projected on a plane perpendicular to the C–N bond. B is a function of the exchange integrals between the appropriate nitrogen, carbon, and hydrogen atomic orbitals and is thus essentially a constant among radicals of similar electronic structure. The benzhydryl group in the nitroxide, III, should have a very high barrier to rotation and using the calculations of Stone and Maki[12] it is possible to estimate the equilibrium angle of the C–H bond. We may approximate the motion of the benzhydryl group as very small harmonic torsions about an angle θ in a deep potential well. Using the classical approximation we find that if we assume dibenzhydrylnitroxide freely rotates then the equilibrium angle, θ, for the C–H bond in III is approximately 70°. The C–H bond then lies about 20° out of the CN(O)C plane. This configuration is not unreasonable.

Additional evidence for the validity of the assignment of III is the work of Iwamura and Inamoto[8] and Janzen and Blackburn.[9] These authors observe nitroxide radicals from the reaction of various radicals adding to $C_6H_5CH{=}N({\rightarrow}O)\ C(CH_3)_3$. The β-hydrogen coupling constant for most of the nitroxides is approximately 2–3 G. The nitrogen coupling constants are about 14 G which indicates that the spin density on the NO portion is approximately the same as in III, dibenzylnitroxide, and dibenzhydrylnitroxide but that the moiety containing the C–H bond is not freely rotating and that the C–H bond is close to the CN(O)C plane. We have also seen a similar radical by heating a mixture of α,α′-azobisisobutyronitrile (AIBN) and I in degassed diethyl Carbitol. The nitrogen coupling is the same (14.3 ± 0.2 G) as III but the proton coupling is slightly larger (2.4 ± 0.2 G) than III. This slight increase in coupling constant is consistent with the change in the spatial configuration of the new nitroxide.



$$\begin{array}{l}(C_6H_5)_2CN[CH(C_6H_5)_2]O\cdot \\ \quad\ \ | \\ (CH_3)_2CCN\end{array}$$

An attempt to generate III from I and azobisdiphenylmethane in diethyl Carbitol at temperatures from 70 to 140° met with no success. This, however, is not surprising since it is difficult to avoid extensive cage recombination of the geminate benzhydryl radicals prior to diffusion. For example Cohen[13] isolated 90% *sym*-tetraphenylethane even when this azo compound was decomposed in a reasonably good hydrogen atom-donating solvent such as decalin.

Conclusion

Epr measurements on the thermal decomposition products of α,α-diphenyl-N-benzhydrylnitrone indicate that one of the intermediates is an iminoxy radical, presumably diphenyliminoxy, and a nitroxide radical. The nitroxide radical is formed by radical addition to the nitrone double bond. The occurrence of radicals further indicates that an initial homolytic dissociation plays at least a partial role in the isomerization reaction of α,α-diphenyl-N-benzhydrylnitrone to benzophenone O-benzhydryloxime.

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(10) Dibenzhydrylamine, synthesized according to G. W. H. Cheeseman, *J. Chem. Soc.*, 115 (1957), by Mr. Richard Gilbert, was oxidized with benzoyl peroxide in methylene chloride.

(11) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960).

(12) E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962).

(13) J. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 2457 (1955).