Table I. Measured Residual Quadrupole Splittings of the Nmr Spectra of Deuterium (Δ_D^Q) and of ^{35}Cl (Δ_{Cl}^Q) and the Residual Dipolar Splitting of the Proton Nmr (Δ_{HH}) in the CH_2Cl_2 + CD_2Cl_2 Solvent Molecules of a Magnetically Aligned Concentrated Solution of PBLG

$\Delta_D^Q = \pm(368 \pm 3)$ Hz
$\Delta_{Cl}^Q = \pm(112 \pm 20) \times 10^3$ Hz
$\Delta_{HH} = \pm(107 \pm 2)$ Hz

Eight sets of solutions to eq 1–3 are possible when all combinations of signs are considered. From the magnitudes of the splittings alone it is not possible to select the correct set of S parameters and additional information is necessary. In our case it was obtained from the pmr "powder pattern" [11] and the orientation by an electric field. Either of these observations yields the sign of S_{22}.

Immediately after the cholesterically ordered sample[2a] is placed in the magnetic field, the pmr and dmr spectra replicate those of proton pairs in polycrystalline solids[11] except that the interaction in the liquid crystal is attenuated by 10^3.

We draw the analogy and attribute the intensity at the shoulders of the pmr spectrum to proton pairs aligned parallel to H_0. In the course of alignment the intensity of the pmr and dmr shoulders increases at the expense of that in the center of the pattern, and we interpret this change as a proliferation of proton pairs aligned parallel to H_0. This conclusion provides us with the additional information necessary to establish the signs of eq 1–3. These conditions are, then, (a) $\Sigma S_{ii} = 0$, (b) $S_{22} > 0$, and (c) $S_{22} > S_{11}$.

From eq 3 and restriction b, we obtain $S_{22} = +1.7 \times 10^{-3}$, and from the molecular bond angles the remaining S parameters are calculated by eq 2 and 3 (Table II).

Table II. The S_{ii} Parameters as Calculated from the Data of Table I, Eq 1–3, and Restrictions a–c

Signs of Δ_D^Q, Δ_{Cl}^Q	Nucleus			
	Deuterium		^{35}Cl	
	$\Delta_D^Q(+)$	$\Delta_D^Q(-)$	$\Delta_{Cl}^Q(+)$	$\Delta_{Cl}^Q(-)$
$S_{22} \times 10^3$	+1.7	+1.7	+1.7	+1.7
$S_{11} \times 10^3$	−3.2	+6.6	+6.0	−2.8
$S_{33} \times 10^3$	+1.5	−8.3	−7.7	+1.1

S parameters corresponding to $\Delta_D^Q(+)$ and $\Delta_{Cl}^Q(-)$ are self-consistent, as are those corresponding to $\Delta_D^Q(-)$ and $\Delta_{Cl}^Q(+)$. The former set is chosen to conform with condition c and to be consistent with the molecular geometry.

Using the S parameters derived from the pmr and ^{35}Cl nmr and substituting into eq 1, we calculate $e^2Qq(D)/h$ = 160 kHz, in agreement with the T_1-derived value of 150 kHz.

We emphasize that the unique assignment of the S parameters was possible because the pmr and dmr "powder patterns" reveal the parallel and perpendicular splittings; the time development of the spectra establishes $S_{22} > 0$. Similar use of such observations has been made by others.[12] For mesophases which have short reorientation times the "powder pattern" would not be observable. The sign ambiguity in such cases may be resolved by the application of electric fields which orient the mesophases; the dependence of the spectrum upon the angle between the electric and magnetic fields should suffice to establish the sign of the orientation parameters.

The pmr spectra observed when the samples were subjected to electric fields revealed that electric-field ordering is prompt and always dominates the magnetic ordering for fields of 5 kV cm^{-1}. For periods shorter than 30 min between successive applications of E fields, the ordering influence of H_0 may be neglected. When $\vec{E}$ is parallel to $\vec{H}_0$, the pmr spectra are unperturbed; the dipolar splitting exhibits the angular dependence ($3 \cos^2 \Omega - 1$) when Ω is the angle between $\vec{E}$ and $\vec{H}_0$. We deduce that the pattern of ordering is identical in $\vec{E}$ and in $\vec{H}$ fields.

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(11) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

(12) K. D. Lawson and T. J. Flautt, *J. Am. Chem. Soc.*, **89**, 5489 (1967).

(13) On leave from the Hebrew University, Jerusalem, Israel.

(14) National Research Council of Canada NATO Postdoctoral Fellow.

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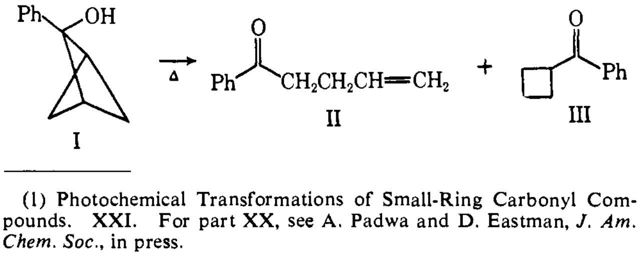
Thermal Reorganization of Phenylbicyclo[1.1.1]pentanol[1]

Sir:

Recent studies on the Norrish type II photoelimination suggests that the abstraction of the γ hydrogen is reversible and can occur from either the excited singlet or triplet state.[2] The lines of evidence implicating the reversibility of the hydrogen-transfer step are based on kinetic data[3,4] and are reinforced by stereochemical[5,6] and deuterium isotope effects.[7,8] We felt that it should be possible to gain further insight into the nature of the reverse hydrogen-transfer step by generating the 1,4 diradical by a nonphotochemical route. The present study reports on the ground-state generation of such a species and shows the behavior of the diradical to be the same as is observed in the Norrish type II process.

Thermal decomposition of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane[9] (I) in the gas phase (20 mg in a 100-ml carefully neutralized tube sealed at −78° at 0.05 mm) at 135° afforded a mixture of 1-phenyl-4-penten-1-one (II; 65%) and cyclobutyl phenyl ketone (III; 35%).



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(1) Photochemical Transformations of Small-Ring Carbonyl Compounds. XXI. For part XX, see A. Padwa and D. Eastman, *J. Am. Chem. Soc.*, in press.

(2) P. J. Wagner and G. S. Hammond, *ibid.*, 88, 1245 (1966).

(3) P. J. Wagner, *ibid.*, 89, 5898 (1967); *Tetrahedron Letters*, 1753 (1967).

(4) J. A. Barltrop and J. D. Coyle, *ibid.*, 3235 (1968).

(5) K. H. Schulte-Elte and G. Ohloff, *ibid.*, 1143 (1964).

(6) J. Orban, K. Schaffner, and O. Jeger, *J. Am. Chem. Soc.*, **85**, 3033 (1963).

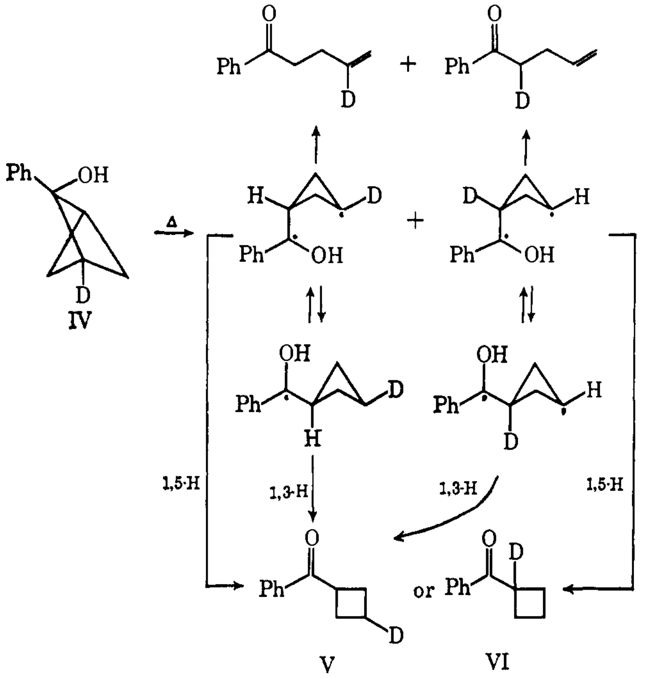
(7) R. D. Coulson and N. C. Yang, *ibid.*, 88, 4511 (1966).

(8) A. Padwa and R. Gruber, *ibid.*, **90**, 4456 (1968).

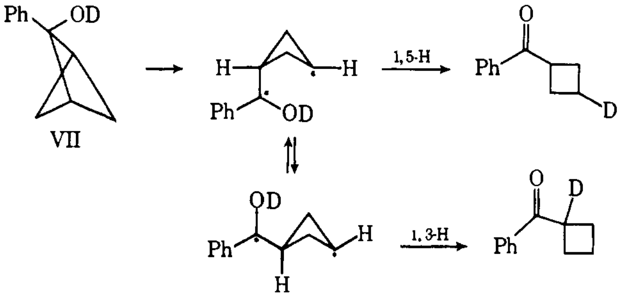
(9) A. Padwa and E. Alexander, *ibid.*, **89**, 6376 (1967).

The reaction followed first-order kinetics, and rate constants were determined from three runs each at three different temperatures constant to $\pm 0.1°$, 135 ($k = 3.3 \times 10^{-6}$ sec^{-1}), 182 ($k = 5.4 \times 10^{-4}$ sec^{-1}), and 208° ($k = 3.0 \times 10^{-3}$ sec^{-1}). An Arrhenius plot gives $E_a = 37.6 \pm 0.5$ kcal/mol and $\log A = 13.36$ at 182°, from which values of $\Delta H^{\ddagger} = 36.6$ kcal/mol and $\Delta S^{\ddagger} = -0.23$ eu can be calculated. Extrapolation of the data to 305° indicated that I rearranged 4.8×10^{3} times more rapidly than the parent bicyclo[1.1.1]pentane.[10]

While the formation of II can be accounted for by a thermal cleavage of the bridgehead C–C bond and subsequent ring opening of the diradical, the mechanistic origin of cyclobutyl phenyl ketone is less clear. It would arise either by ring inversion[11] of the diradical followed by a 1,3-H shift, or much more simply by a 1,5-H transfer. Analogies for the latter route have already been cited, and there are a number of reports in the literature that provide reasonable precedents for the former path.[13,14] Decisive information concerning this mechanistic question was gleaned from the thermal rearrangement of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane-1-*d* (IV). The synthesis of this compound, containing 98% deuterium at the bridgehead carbon as determined by nmr and mass spectroscopy, was carried out by irradiating cyclobutyl phenyl ketone-1-*d*.[9] Formation of cyclobutyl phenyl ketone *via* the 1,3-H transfer route should only lead to V, while a 1,5-H transfer sequence would be expected to give equivalent amounts of V and VI (neglecting small kinetic isotope effects). The products, isolated by vpc, were analyzed for their total deuterium content, and the fraction of the deuterium atoms attached to the carbon adjacent to the carbonyl was then determined by washing out these atoms with protonic solvents, rechromatographing by vpc, and analyzing the resultant products for the remaining deuterium. Analysis of the mixture obtained from the thermolysis of IV indicated that both products (II and III) retained only 50% of the deuterium, thus providing strong support for the 1,5-H transfer mechanism.



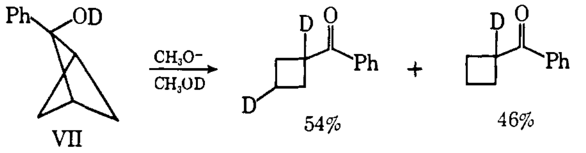
Surprisingly, the route to give cyclobutyl phenyl ketone on pyrolysis of the deuterated alcohol VII did not proceed exclusively by means of a 1,5-H transfer. This conclusion derives from examination of the distribution of deuterium in the product after proton exchange.



For this case, 60% of the cyclobutyl phenyl ketone contained deuterium and the remaining 40% was devoid of deuterium. Control experiments demonstrated that no exchange of starting alcohol occurred under the reaction conditions employed.

Since only 60% of the deuterium appeared on the cyclobutyl ring,[15] the 1,3-H transfer route must have occurred. An attractive explanation to account for the difference noted between the two systems might be based on the existence of a deuterium isotope effect. Substitution of deuterium for hydrogen on the alcohol portion of the the molecule may sufficiently retard the 1,5-H transfer to allow for competitive ring inversion and the occurrence of a 1,3-H shift. It is noteworthy that the rate of rearrangement of VII is essentially the same as I and IV but the product composition has been slightly altered (80% II, 20% III). This observation is fully compatible with the dual mechanistic sequence proposed.

It should also be pointed out that similar results were obtained with the base-catalyzed rearrangement of VII. When the reaction was carried out with sodium methoxide in CH_3OD, the only product formed was cyclobutyl phenyl ketone. Here, 54% of the ketone contained deuterium on both the α- and 3-carbon atoms; the remaining 46% contained deuterium on only the α position. This result indicates that 1,3-proton transfer can successfully complete with protonation of the ring carbanion. Undoubtedly the stability of the enolate anion provides the driving force for the 1,3-proton shift.



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[10] K. B. Wiberg and D. S. Connor, *J. Am. Chem. Soc.*, 88, 4437 (1966).

[11] The cyclobutyl ring is quite flexible and exhibits a dynamic ring-bending equilibrium which has been termed "pseudorotation" and allows for the conformational equilibration of monosubstituted cyclobutanes.[12] A similar ring inversion might be anticipated for the diradical produced by thermal ring opening of I.

[12] J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).

[13] M. J. Jorgenson and T. J. Clark, *ibid.*, **90**, 2189 (1968).

[14] R. Kh. Freidlina, *Advan. Free Radical Chem.*, 1, 211 (1965).

[15] This was also verified by nmr analysis of the product mixture prior to exchange with protonic solvents.

Research is continuing on the ground-state chemistry of the bicyclo[1.1.1]pentanol system, and a detailed investigation of the acid-catalyzed transformations of this bicyclic ring system will be reported at a later date.

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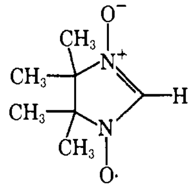
Studies of Stable Free Radicals. III. A 1,3-Dioxy-2-imidazolidone Zwitterion and Its Stable Nitronyl Nitroxide Radical Anion

Sir:

In a previous communication the highly stable nitronyl nitroxide free radical **1** was described.[1] Deuterium exchange at position 2 in **1** was found to occur by both a base-catalyzed and a pH-independent process. The most likely pH-independent exchange mechanism is electrophilic substitution with deuterium oxide as the electrophile. This suggested the possibility that the nitronyl nitroxide **1** may undergo chemically more interesting substitution reactions directly on the radical π system. We present here results of our studies of electrophilic and nucleophilic substitution of the nitronyl nitroxide radical.

When a carbon tetrachloride solution of the nitronyl nitroxide **1** containing a little pyridine was treated with iodine, there was isolated a deep purple radical, **2**, R = I, which displayed a simple five-line esr pattern characteristic of the nitronyl nitroxide grouping [$a_N^{C_6H_6} = 7.3$ G, *m/e* 283 (M); λ_{max}^{EtOH} 326 mμ (ϵ 14,000), 550 (1240), 585 (1060)].[2] Identical treatment of **1** with bromine led to the corresponding bromo radical **2**, R = Br [*m/e* 235 and 237 (M); λ_{max}^{EtOH} 320 mμ (ϵ 15,600), 540 (1240), 565 (1160)][2] which, unlike the iodo derivative, had an esr spectrum of five quartets resulting from weak coupling with bromine ($a_N^{C_6H_6} = 7.3$ G, $a_{Br}^{C_6H_6}$ incompletely resolved; $a_N^{C_6H_{14}} = 7.15$, $a_{Br}^{C_6H_{14}} = 1.4$ G). Failure to observe coupling with iodine in **2**, R = I, despite the large iodine nuclear magnetic moment may be due to rapid quadrupole relaxation of the iodine nucleus. Hyperfine coupling with bromine and iodine is rare in organic free radicals and has not previously been observed in π radicals. However, coupling in several haloiminoxyl σ-type radicals has recently been reported.[3] The spectra of **2**, R = Br, like that of the iminoxyl radicals, display the pronounced viscosity dependence expected from the effect of nuclear-quadruople relaxation.[3b]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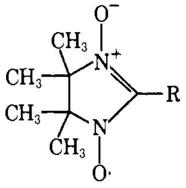
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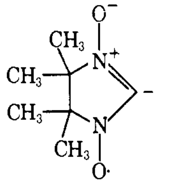
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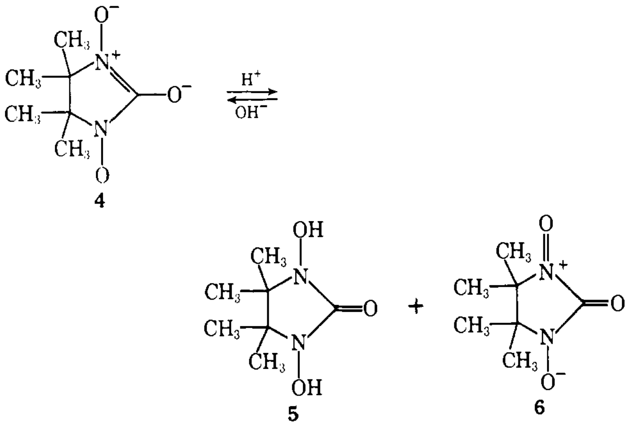
Alternative and more efficient preparations of **2**, R = Br and I, were possible by treatment of bicarbonate solutions of **1** with cyanogen bromide or iodide, respectively (>80% yields). Although **2**, R = Cl, was not formed using cyanogen chloride, direct chlorination of **1** gave 75% of this very hydrolytically unstable radical [*m/e* 191 and 193 (M); λ_{max}^{EtOH} 315 mμ (ϵ 19,300), 536 (1350), 562 (1340)].[2] This compound displayed the usual five-line esr pattern ($a_N^{C_6H_6} = 7.25$ G) in which the unobserved coupling with chlorine may be of the same order of magnitude as unresolved coupling with the α-methyl protons ($\sim$0.2 G).[1]

Susceptibility of the nitronyl nitroxide ring to nucleophilic attack was demonstrated by heating the halides with sodium cyanide in dimethylformamide. Thus **2**, R = Br, gave a 38% yield of the blue nitrile **2**, R = CN [$a_N^{C_6H_6} = 6.94$ G; ν_{max}^{KBr} 2240 cm^{-1} (CN); *m/e* 182 (M)],[2] which displayed the usual five-line esr spectrum with no observable coupling with the nitrile nitrogen.[4] Unexpectedly, attempts to prepare the nitrile in methanol as solvent led quantitatively to the imino ester **2**, R = $C(=NH)OCH_3$ [$a_N^{C_6H_6} = 7.17$ G (five lines);[4] $\nu_{max}^{CHCl_3}$ 1635 (C=N), 3260 cm^{-1} (NH); *m/e* 214 (M)].[2] This product was also formed when the nitrile **2**, R = CN, was treated with methanolic sodium carbonate. Hence the normal base-catalyzed equilibrium of nitriles with imino esters[5] is strongly shifted toward the imino ester because of the strong electron-withdrawing effect of the nitronyl nitroxide grouping.[1]

Nucleophilic displacement on the halo radicals was also possible with hydroxide ion. On warming **2**, R = I, with aqueous sodium hydroxide the solution became intensely blue. Extraction with chloroform yielded small amounts of the starting iodide and **1**, which is presumably formed by nucleophilic displacement on iodine with expulsion of the relatively stable anion **3**.[1] The major product was a water-soluble blue radical anion, **4** [$\lambda_{max}^{H_2O}$ 251 mμ (ϵ 4200), 650 (5000)], which displayed the largest nitronyl nitroxide nitrogen coupling yet observed ($a_N^{H_2O} = 8.75$, $a_H^{H_2O} = 0.21$ G). Although no attempt to isolate this compound has been made, in alkaline solutions it was extraordinarily stable toward heat, light, and oxygen. On



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[1] D. G. B. Boocock, R. Darcy, and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 5945 (1968).

[2] Satisfactory elemental analyses were obtained.

[3] (a) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965); (b) B. C. Gilbert and R. O. C. Norman, *ibid.*, *C*, 981 (1967); 123 (1968).

[4] Lack of coupling with the side-chain nitrogen is consistent with MO calculations suggesting that the free electron is in an antisymmetric orbital with a node at C_2.

[5] F. C. Schaeffer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).