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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles and electronic spectra (4 pages). Ordering information is given on any current masthead page.

Photoinitiated Electron-Transfer Reactions. The Radical Cations of Bicyclo[1.1.0]butane Derivatives

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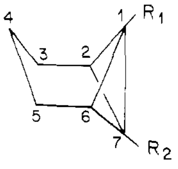
The interaction between photoexcited electron acceptors and several derivatives (**1**) of the bicyclo[1.1.0]butane system have been found to generate strong nuclear spin polarization effects. These results give an insight into the structure of the radical cations of **1** and reveal an unusually rapid isomerization of one of these cations.

The reactions of bicyclo[1.1.0]butane derivatives with excited-singlet electron acceptors have been studied under varied reaction conditions.[1] The structures of the reaction products are compatible with the intermediacy of radical cations, **2**, in which the C1–C7 bond is broken or weakened. Such a structure is readily rationalized on the basis of the bicyclo[1.1.0]butane HOMO, which is bonding principally between the two bridgehead carbons.[2]



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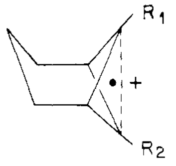

2

a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

In an attempt to obtain further insight into the structures of these radical cations and to assess the involvement of other high-lying bicyclo[1.1.0]butane orbitals, we have applied the CIDNP technique to photoreactions of excited-singlet acceptors such as 1-cyanonaphthalene (1-CN) or triplet acceptors such as chloranil (CA) with bicyclo[1.1.0]butane derivatives. The CIDNP method has proved to be a powerful tool in the elucidation of radical cation structures, especially those derived from strained-ring hydrocarbons.[3]

The irradiation of 1-CN or CA in acetonitrile solutions containing tricyclo[4.1.0.0^{2,7}]heptane (Moore's hydrocarbon, **1a**)[4] resulted in strong nuclear spin polarization for all signals of the strained-ring hydrocarbon (Figure 1). Significantly, the polarization observed for the triplet near 1.5 ppm (H_1, H_7) was opposite to the effects observed for the broad signal at 2.3 ppm (H_2, H_6) and for the multiplet at 1.3 ppm, which represents the protons at C3, C4, and C5. This polarization can be rationalized as being induced by a reaction sequence initiated via electron transfer (eq 1) from **1a** to the photoexcited electron acceptor of spin multiplicity

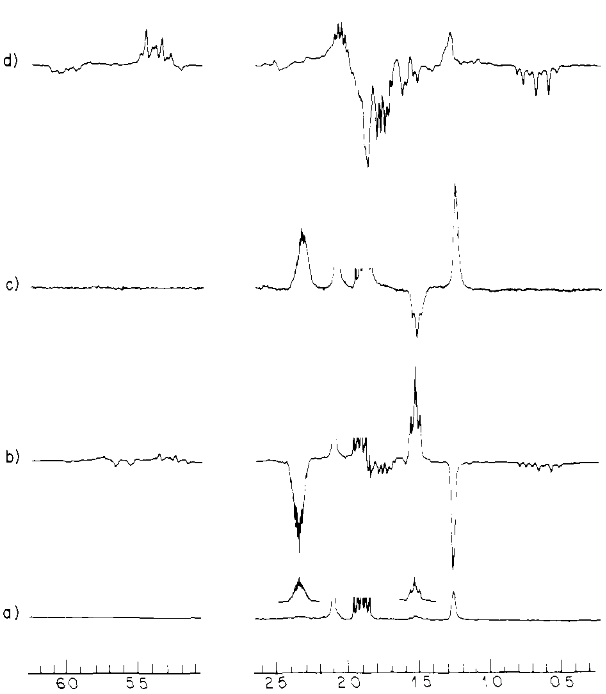

Figure 1. PMR spectra (90 MHz) of (a) an acetonitrile-d_3 solution of 0.02 M tricyclo[4.1.0.0^{2,7}]heptane (**1a**) and 0.02 M chloranil in the dark (insets show detailed spectra for protons at C2 and C6 at ~2.3 ppm and for protons at C1 and C7 at ~1.5 ppm), (b) the same solution during UV irradiation, (c) an acetonitrile-d_3 solution of 0.02 M **1a** and 0.02 M 1-cyanonaphthalene during UV irradiation, and (d) and acetone-d_6 solution of 0.02 M **1a** and 0.02 M chloranil during UV irradiation. A CIDNP spectrum essentially identical with trace d is observed during the irradiation of 0.02 M chloranil in the presence of 0.02 M norcar-2-ene (**6**).

$$^{m}A^{*} + D \rightarrow {}^{m}\overline{A^{-}\cdot D^{+}\cdot} \tag{1}$$

$$^{m}\overline{A^{-}\cdot D^{+}\cdot} \rightleftharpoons {}^{n}\overline{A^{-}\cdot D^{+}\cdot} \tag{2}$$

$$^{1}\overline{A^{-}\cdot D^{+}\cdot} \rightarrow A + D^{\dagger} \tag{3}$$

$$^{3}\overline{A^{-}\cdot D^{+}\cdot} \rightarrow {}^{2}A^{-}\cdot + {}^{2}D^{+}\cdot \tag{4}$$

* signifies an excited state and † signifies nuclear spin polarization

m (m = 1 for 1-CN, m = 3 for CA). The resulting cation radical–anion radical pairs begin random diffusion as well as intersystem crossing. The latter process (eq 2) may be either slightly accelerated or somewhat retarded due to the involvement of different nuclear spin states in the radical cations. Depending on the prevailing electron spin multiplicity at the time of a secondary encounter, the pairs may recombine, usually from the singlet state (eq 3), or diffuse apart (eq 4).

On the basis of this mechanism and on the assumption that the bicyclo[1.1.0]butane radical cation has a lower g factor than either of the acceptor anions (CA$^{-}\cdot$ g = 2.0051; 1-CN$^{-}\cdot$ g = 2.0031), the polarization of the regenerated starting material can be used to assign the hyperfine coupling (hfc) pattern of the cation radical. The results observed during the photoreaction with 1-CN (Figure 1c) indicate negative hfc's for H_1 and H_7 and positive hfc's for H_2, H_6, and also $H_{3,3'}$ and $H_{5,5'}$ of the intermediate. This pattern supports a radical cation with a broken (or weakened) C1–C7 bond, in full agreement with the structure assigned on the basis of the reaction products.[1]

Surprisingly, an entirely different result is obtained during the photoreaction of CA with **1a** under only slightly different reaction

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[1] (a) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977–4979. (b) Gassman, P. G., Olson, K. D. *Ibid.* **1982**, *104*, 3740–3742.

[2] (a) Pomerantz, M.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1966**, *88*, 3970–3972. (b) Whitman, D. R.; Chiang, J. F. *Ibid.* **1972**, *94*, 1126–1129. (c) Haddon, R. C. *Tetrahedron Lett.* **1974**, 2797–2800. (d) Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5783–5797. (e) Gassman, P. G.; Greenlee, M. L.; Dixon, D. A.; Richtsmeier, S.; Gougoutas, J. Z. *Ibid.* **1983**, *105*, 5865–5874.

[3] (a) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027–1035. (b) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 115–117. (c) Roth, H. D.; Schilling, M. L. M.; Wamser, C. C., unpublished results. (d) Roth, H. D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1983**, 5815–5818.

[4] Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019–2020.

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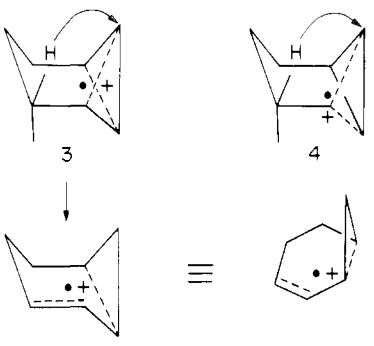
conditions, i.e., with acetone-d_6 as solvent. Under these reaction conditions, very little polarization is generated for the reactant hydrocarbon, but strong CIDNP effects are observed for a bicyclic isomer, norcar-2-ene (**6**). Significantly, these effects (Figure 1d) are identical with those generated in the reaction of **6** with CA. Obviously, a rapid rearrangement, either of the reactant in the dark, or of a radical cation immediately after its generation, is occurring. Although Moore's hydrocarbon is known to suffer rapid acid-catalyzed rearrangement to **6**,[4] this conversion cannot explain the current results. Simple NMR experiments indicate that **1a** does not rearrange at sufficiently fast rates under the reaction conditions. Accordingly, there is little doubt that the rearrangement of **1a** is a consequence of the photoreaction with CA.

The observed results are most readily explained by invoking a different radical cation, such as **3** or **4**, an efficient 1,3-hydrogen migration, which would convert this intermediate to the radical cation **5**, and geminate electron return, which would generate the isomeric hydrocarbon **6**.



3 4

5

The involvement of a different radical cation under only slightly different conditions requires a relatively delicate balance between the two radical cations; such a situation is not without precedent. For example, we have found evidence that two different cations are derived from hexamethyl(Dewar benzene)[3b] and likewise, from methylenebicyclo[2.2.0]hexene.[3c] Similarly, two types of radical cations are derived from cyclopropane and several examples are known for each structure type.[3a,5] These provide an even closer analogue to the proposed balance between **2** and **3** or **4**.

The mono- and dimethyl derivatives of Moore's hydrocarbon, **1b** and **1c**, respectively, also give rise to CIDNP effects upon reaction with photoexcited CA. These spectra are dominated by strong emission singlets representing the methyl groups. In addition, the broad resonance of the single C7 proton of **1b** appears in enhanced absorption, whereas the remaining signals of **1b** and **1c** show emission. These results can be interpreted on the basis of the same mechanistic scheme discussed for the reaction of the parent compound with 1-CN*.

Given this mechanism, the results indicate that, in the radical cations derived from **1b** and **1c**, the methyl groups and the single proton on C1 and C7 are attached to centers of positive spin density. This identifies the radical cations as species in which the the C1–C7 bond is broken or weakened, that is as in **2b** and **2c**. The results obtained in acetonitrile-d_3 and acetone-d_6 are quite similar. Obviously the introduction of one or two methyl groups has suppressed the propensity for rearrangement, which is so pronounced for the reaction of **1a** with CA in acetone.

The divergent results observed for the reaction of **1a** with CA in two different solvents suggest the involvement of two different high-energy occupied MO's. We are continuing our studies in an effort to identify factors influencing the relative energies of these occupied MO's and to elucidate the nature of the rearrangement.

Acknowledgment. We thank the National Science Foundation for a grant to P.G.G., which partially supported this investigation.

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(5) (a) Roth, H. D., Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956–7958; (b) *Ibid.* **1983**, *105*, 6805–6808.

Trapping of a Stable Complex in the Reaction between C(^{3}P) and Trimethylamine

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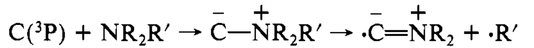
We recently reported a combined theoretical and experimental study of the reaction between C(^{1}D) and ammonia which indicated that an initial complex between these two species was not an energy minimum but rapidly cleaved an N–H bond to generate products.[1] We now report calculations and experiments which indicate that the triplet complex between C(^{3}P) and amines is an intermediate that can be trapped in some cases.

Ab initio calculations at the UMP3/6-31G** level[2] indicate that complex **1a** is an energy minimum that lies 20.1 kcal/mol lower in energy than C(^{3}P) + NH$_3$. The lowest energy reaction for **1a** is calculated to be the cleavage in eq 1 (ΔH = 30.4 kcal/mol).



$$\mathrm{C(^3P) + NR_2R' \rightarrow \overset{-}{C}\text{—}\overset{+}{N}R_2R' \rightarrow \cdot\overset{-}{C}\text{=}\overset{+}{N}R_2 + \cdot R'} \qquad (1)$$

1a, R = R′ = H
1b, R = CH$_3$; R′ = H
1c, R = R′ = CH$_3$

If **1** has the ylid structure shown in eq 1, it is expected that the addition of methyl groups as in **1b** and **1c** will stabilize the positive charge on nitrogen and increase the stability of **1b** and **1c** relative to **1a**. Not surprisingly, the calculations indicate this to be true. Although the number of atoms in **1b** and **1c** preclude UMP3/6-31G** calculations, we have approximated [UMP3/6-31G*] calculations for **1b** by combining 6-31G* and UMP3/6-31G calculations.[3] This approximation leads to the conclusion that **1b** is 24.7 kcal/mol more stable than methylamine and C(^{3}P) and has a barrier of 22.3 kcal/mol to the methyl cleavage shown in eq 1. The energy of **1c** was calculated at the UMP2/6-31G level and indicates that **1c** is 30.9 kcal/mol more stable than trimethylamine and C(^{3}P) with a barrier to methyl cleavage of 30.5 kcal/mol.[4] In order to compare the relative stabilities of **1a–c**, the energy of each species relative to that of reactants and the barrier to cleavage of R′ was calculated at the UMP2/6-31G level. The results of these calculations, shown in Table I, indicate that these amine adducts of C(^{3}P) lie in relatively deep energy wells and are potentially trappable.

Since these complexes are calculated to be triplets and C(^{3}P) itself has been observed to react rapidly with oxygen to generate carbon monoxide, trapping with oxygen was attempted. In these studies carbon atoms were generated in a carbon arc under high dynamic vacuum and cocondensed with substrate at 77 K.[5,6] After

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(1) McPherson, D. W.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 6493.

(2) (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "GAUSSIAN80" QCPE 406, Indiana University. The version used here has been developed in other laboratories to run on an IBM machine. (b) The correlation treatment follows that presented by: Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1. (c) All geometries were optimized at the 3-21G level. (d) Geometries of NH$_3$, CHNH$_2$, and CH$_3$NH$_2$ at the 3-21G level were taken from: Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University: Pittsburgh, 1981. (e) For basis set description, see: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. For UMP3 treatment, see: Pople, J. A.; Brinkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(3) (a) Additivity has been demonstrated to be accurate to within 1–4 kcal/mol of the full calculation. We would like to suggest that calculations that use additivity enclose the appropriate basis set in brackets.[3b,c] (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. (c) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

(4) The true barrier is likely to be 5–15 kcal/mol lower as inclusion of the point energy correction and additional correlation should preferntially stabilize the transition state.

(5) The carbon atom reactor is based on that described by: Skell, P. S.; Wescott, L., Jr.; Goldstein, J.-P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

0002-7863/84/1506-2712$01.50/0