The benzvalene dipole moment is unusually large compared to those normally found in monocyclic and bicyclic hydrocarbons. For example, the moment is 0.13 D in cyclobutene,[12] 0.19 D in cyclopentene,[13] 0.26 D in bicyclo[2.1.0]pentane,[14] and 0.40 D in bicyclo[2.1.0]pent-2-ene.[15] The saturated molecule bicyclobutane has, however, a quite large value, 0.68 D.[16] It is interesting to note that the sum of the moments of cyclobutene and bicyclobutane is quite similar to that of benzvalene. This is reasonable when it is recognized that the benzvalene moment may be considered to consist of the vector sum of parallel group moments of cyclobutene and bicyclobutane fragments. Since the unsaturated portion of the cyclobutene fragment is surely the negative end, we may conclude from this simple analysis that the negative ends of both bicyclobutane and benzvalene lie below the bridgehead bond. This conclusion is in accord with the theoretical analyses of Gierke, *et al.*,[17] and Schulman and Fisanick.[18]

With the present data we cannot make an unambiguous structural determination. However, the observed rotational constants are in good agreement with a C_{2v} structure consisting of a bicyclobutane fragment (R_{CC} = 1.50 Å, dihedral angle = 110°,[19] R_{34} = 1.31 Å, R_{23} = 1.55 Å, and typical hydrogen atom parameters). More definitive structural information must await studies of isotopically substituted species. This work is currently underway and will be reported at a later time.

Acknowledgments. This work was supported in part by NSF Grant GP-15127 and KU Grant 3939. Computation time was provided by the University of Kansas Computation Center.

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(12) H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **42**, 3728 (1965).

(13) S. S. Butcher and C. C. Costain, *J. Mol. Spectrosc.*, **15**, 40 (1965).

(14) R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972). The dipole moment data in Table V are off slightly due to inadvertent use of incorrect conversion factors. Numbers in the column headed "Obs" should be multiplied by 0.896 and those in the "Calc" column by 0.893. The correct value of μ_c should be 0.255 which rounds to 0.26 ± 0.01.

(15) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, and W. H. Flygare, *J. Amer. Chem. Soc.*, **92**, 5250 (1970).

(16) M. D. Harmony and K. W. Cox, *ibid.*, **88**, 5049 (1966).

(17) T. D. Gierke, R. C. Benson, and W. H. Flygare, *ibid.*, **94**, 339 (1972).

(18) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6653 (1970).

(19) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969). The dihedral angle needed to fit the benzvalene data is smaller than that for bicyclobutane (122°). This is a reasonable result, but it may be an artifact of the other structural assumptions. Verification must await the complete structural results.

Richard D. Suenram, Marlin D. Harmony*
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

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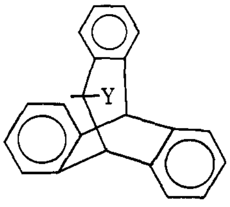
Photochemical Transformations. VII. Carbenium Ion Nature of Photosensitized Hydrolysis of 2-Bromohomotriptycene[1]

Sir:

Photoinduced solvolyses, competing with homolytic reactions, of substituted benzyl chlorides, acetates, and ethers in aqueous dioxane or aqueous ethanol were first reported by Zimmerman and his students.[2] More recently, similar competitions with benzyl and substituted benzyldialkylsulfonium salts,[3] in water, alcohols, and acetonitrile, and with analogous ammonium salts,[4] in alcohols and acetonitrile, have been demonstrated. Although direct irradiation was utilized in these cases, absence of photosensitization and systematic quenching[5] experiments do not permit determination of the multiplicity of reaction intermediates.

All three groups have given reasonable arguments for their assumption that the photosolvolysis reactions involve carbenium[6] ion intermediates, although their data do not exclude direct displacement mechanisms. Addition–elimination mechanisms have been proposed for displacement reactions in aromatic systems[7] and in the photosolvolysis of aryl benzoates,[8] consistent with "normal" ground-state mechanisms; again direct displacement mechanisms are conceivable, and, in the second case, acylium ion intermediates are also possible.

Our own ideas regarding the plausibility of intermediacy of carbenium ions in photoinduced rearrangements[9] led us to systems where rearrangements and solvolyses compete and to an interest in solvolysis of benzyl halides.[10] Ground-state solvolyses of 2-tribenzobicyclo[3.2.2]nonatrienyl bromide (bromohomotriptycene, **1**-Br) have been previously investigated.[11]



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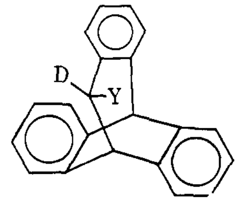

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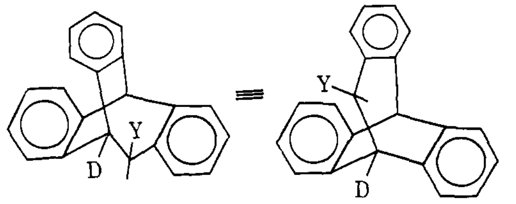

3

The cationic intermediate(s) led to complete scrambling of C-1 and C-2, as noted by deuterium labeling, *i.e.*, **2**-Br gives a 50% mixture of **2**-OCH_3 and **3**-OCH_3 upon methanolysis and **2**-OAc and **3**-OAc on acetolysis. On the other hand the analogous radical intermediate resists rearrangement, **2**-D giving pure **2**-Br under Wohl–Ziegler conditions.[11]

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(1) Paper VI: S. J. Cristol, G. A. Lee, and A. L. Noreen, *Tetrahedron Lett.*, 4175 (1971).

(2) (a) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); (b) H. E. Zimmerman and S. Somasakhara, *ibid.*, **85**, 922 (1963).

(3) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970).

(4) M. A. Ratcliff and J. Kochi, *ibid.*, **36**, 3112 (1971).

(5) Ratliff and Kochi used oxygen to try to trap free radicals in the photolysis of dibenzyldimethylammonium chloride in ethanol. Their report that this did not affect the product ratio suggests that both the radical and ionic processes involved singlet states.

(6) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(7) (a) E. Havinga and M. L. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); (b) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969).

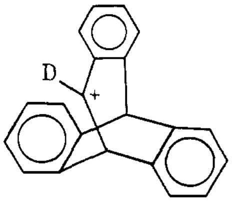
(8) J. G. Pacifici, J. S. Zannucci, G. R. Lappin, J. C. Ownby, and C. A. Kelly, *Mol. Photochem.*, **3**, 175 (1971).

(9) (a) S. J. Cristol, G. O. Mayo, and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 214 (1969); (b) S. J. Cristol and G. A. Lee, *ibid.*, **91**, 7554 (1969).

(10) G. C. Schloemer, Ph.D. Thesis, University of Colorado, 1972.

(11) S. J. Cristol and D. K. Pennelle, *J. Org. Chem.*, **35**, 2357 (1970).

When 2-Br was irradiated in 95% aqueous acetone (degassed) with a 450-W Hanovia lamp for 9 hr at room temperature in the presence of sodium carbonate, the product mixture (pmr analysis) showed 37% hydrolysis with equal amounts of **2**-OH and **3**-OH and with partial scrambling in the bromide (**2**-Br:**3**-Br = 3:1). A similar experiment (no Na_2CO_3) for 20 hr at 5° gave 50% alcohol (equal quantities of **2**-OH and **3**-OH, analyzed by mass spectral analysis of ketone derived from the alcohol mixture by oxidation[12]) and the recovered bromide was a 2:1 mixture of **2**-Br and **3**-Br (pmr analysis). **1**-Br and **2**-Br were stable to solvolysis and to rearrangement in acetone in the dark for 48 hr at room temperature, and solvolyzed only to the extent of 17% in 90% acetone in 68 hr. Thus, the reactions described above are photoinduced,[13] and clearly proceed *via* cationic intermediates,[14] *viz.*, **4** and **5** or their undeuterated analog, or the corresponding nonclassical ion. The partial deuterium scrambling in the bromide, contrasted with the complete scrambling in the product alcohol, is consistent only with this viewpoint, and also introduces the interesting question of the nature of the return process. We intend to investigate the question of ion-pair intermediates and/or external return in photosolvolysis.



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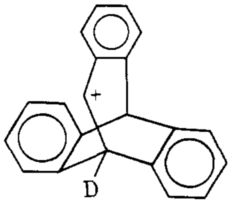

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It seems to be generally assumed that photosolvolysis occurs from electronically excited states,[2] but our results[10] with triplet sensitizers which can deliver only 70–80 kcal/mol of triplet energy suggest that this is impossible in our examples, unless the triplet energy of a carbenium ion is less than about 50 kcal/mol. We presently prefer the idea that the intermediate immediately preceding the carbenium ion is a vibrationally excited ground state.[9a] Hopefully we will have more precise data in hand in the near future, as well as information on differences, if any, between direct and photosensitized reactions, in this and other systems.

Acknowledgment. The authors are indebted to the National Science Foundation for support of this work.

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[12] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[13] Work with similar systems[10] has shown that these solvolyses are photosensitized by triplet photosensitizers, and show the typical quenching phenomena for "triplet" reactions.

[14] A small amount of homotriptycene is also produced from **1**-Br, presumably *via* radical intermediates.

Stanley J. Cristol,* George C. Schloemer
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

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The Homoallyl Cation

Sir:

The rapid interconversion of cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives in solution has come under constant and thorough experimental scrutiny since its discovery several decades ago.[1–3] Although carbocation intermediates were long ago implicated in the mechanism, and although the chemical evidence for them is now overwhelming, it has not been until fairly recently that direct spectroscopic (structural) measurements have been performed.[4] High-resolution proton and carbon-13 magnetic resonance spectroscopy have now provided important information about the symmetry of possible intermediate ions. Such methods, however, cannot yield specific structural data, nor in practice are they normally able to detect several isomeric forms connected by only low-energy barriers.

In this communication we describe the predictions of simple molecular orbital theory on the possible existence of homoallyl-like carbocations, and their relation to the cyclopropylcarbinyl system. Future studies will both further explore the $C_4H_7^+$ potential surface (to include forms of the cyclobutyl cation not considered here), and more deeply probe into the energetics of interaction of carbocationic centers with areas of high electron density.

We employ single determinant *ab initio* molecular orbital theory throughout, utilizing the STO-3G[5] and 4-31G[6] Gaussian basis sets. The STO-3G minimal basis has been shown to be especially suitable for the calculation of molecular equilibrium geometries; it is relatively inexpensive and has on numerous occasions proven its reliability.[7] It is for this purpose that it is employed here. The extended 4-31G functions are more costly to use and only a limited number of calculations have been performed in order to firmly establish the relative energies at selected points on the STO-3G potential surface. All computations have been carried out using the GAUSSIAN 70 series of programs.[8]

It must be cautioned at the outset that the theoretical calculations described herein, as well as those of others,[3] apply rigorously only to isolated molecules. No attempt has been made to account for solvation effects,

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[1] The first report of interconversion between cyclobutyl and cyclopropylcarbinyl derivatives in solution appears to be N. J. Demjanov, *Ber.*, **40**, 4393, 4961 (1907). Involvement of homoallyl derivatives was noted some 20 years later, P. Bruylants and A. Dewael, *Bull. Cl. Sci. Acad. Roy. Belg.*, **14**, 140 (1928); *Chem. Zentralbl.*, **99**, 2708 (1928).

[2] Reviews published in the last decade include R. Breslow in "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, pp 233–294; B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964); G. D. Sargent, *ibid.*, **20**, 301 (1966); M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III in "Carbonium Ions," Vol. III, Interscience, New York, N. Y., 1972. We thank Professor Wiberg (Yale) for a copy of this latter manuscript before publication.

[3] Applications of semiempirical molecular orbital methods to the $C_4H_7^+$ potential surface include: C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 4045 (1969); N. S. Issacs, *Tetaahedron*, 3555 (1969); K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 3133 (1970). No studies at the *ab initio* level have been reported.

[4] G. A. Olah, C. J. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972), and references cited therein.

[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[6] R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

[7] See, for example: W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971); W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971).

[8] GAUSSIAN 70, a series of programs designed to perform *ab initio* molecular orbital calculations on organic molecules; W. J. Hehre, W. A. Lathan, and J. A. Pople, to be submitted to Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.