Table I. Rate Constants in Solvolyses of **3a** and **4a**[a]

Solvent	Temp, °C	$k \times 10^4$, sec^{-1} 3a	4a	Rate ratio *syn*:*anti*
Acetic acid	139.8		5.37	
	125.0	1.75	1.62	1.08
	99.8	0.217	0.173[b]	1.25
Dioxane-water, 70% v/v	100.0	3.14	2.56	1.23
	70.0	0.302	0.255	1.18
2,2,2-Trifluoroethanol	90.0	0.152	0.0660	2.30
	75.0	0.0338	0.0112	3.01

[a] Rates were determined by potentiometric titration. [ROBs] = 0.02 *M*. Solvents contained 0.021 *M* sodium acetate. [b] Calculated value.

acetic acid and aqueous dioxane, respectively, show that in these solvents assistance of the cyclopropyl ring is absent or of an indistinct order. However, as usually observed,[8] decreasing nucleophilicity of solvent increases assistance. Thus, the solvolysis of **3a** in 2,2,2-trifluoroethanol proceeds three times faster than that of **4a** (75°). This solvent does not attack the cyclopropyl ring, and the brosylates recovered at about the half-lives of **3a** and **4a** did not indicate any structural changes before the *p*-bromobenzenesulfonyloxy group is displaced by the solvent (absence of internal return).[9] Therefore, the factor of 3, though small, clearly demonstrate the existence of participation of the cyclopropyl ring in **3a** (**12**). We call the participation of this type by the name of ∇_5 participation[10] (five-carbon atoms intervene between the reaction site and the ring bonds). The smallness may be due to a nonbonded repulsive interaction of the hydrogens at C-2 and C-4 with the hydrogens at C-10 in the transition state, the factor invoked by Sargent.[1m]

[8] (a) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (b) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, 89, 5902 (1967).

[9] The reactions of both the brosylates in dioxane–water gave only the products of retention. However, the acetolyses and trifluoroethanolyses, respectively, produced a complex mixture.

[10] We thank Professor P. von R. Schleyer for naming this effect.

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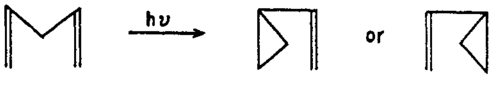
The Photochemistry of Benzo[6.7]bicyclo[3.2.1]octa-2,6-diene

Sir:

A recent study[1] of the photochemical di-π-methane to vinylcyclopropane rearrangement (Chart I) reported

Chart I



a behavior pattern in which bicyclic di-π-methane systems undergo this transformation efficiently from their excited triplet states, while their excited singlets undergo different reactions. Contrastingly, monocyclic and acyclic di-π-methanes seem to convert to vinylcyclopropanes only *via* excited singlet states. Zimmerman noted[1] that rationalizations might be premature. We now report that direct *or* sensitized irradiation[2] of benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (**1**),[3] nominally a bicyclic di-π-methane system, causes facile conversion to benzo[3,4]tricyclo[3.2.1.0^{2,7}]octene (**2**) (Chart II).

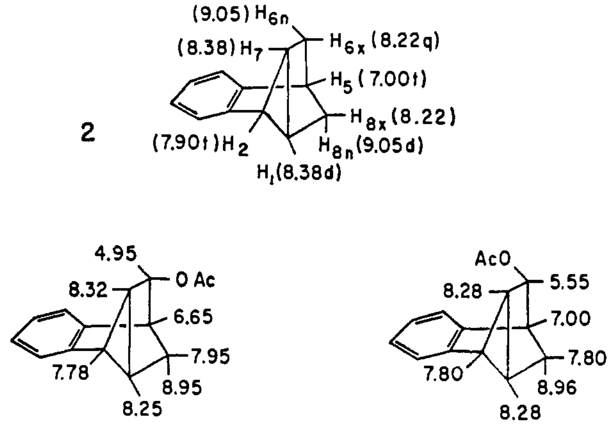
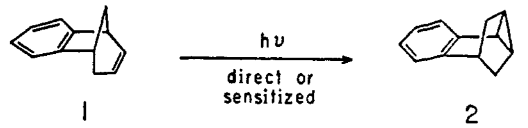


Figure 1. Pmr chemical shifts (τ) for **2** (CDCl$_3$) and 6-hydroxyacetate derivatives (CCl$_4$)[6] at 100 MHz; multiplicities are represented by d (doublet), t (triplet), and q (quartet).

Chart II



Structure **2** is in accord with the mass spectrum (mol wt, 156), 100-MHz pmr spectrum, and chemical reactivity. Pmr assignments for **2** are shown in Figure 1, which includes the *exo*- and *endo*-benzo[3,4]tricyclo-[3.2.1.0^{2,7}]octen-6-ol acetates[5] for comparison. The symmetry in **2** simplifies the spectrum and the analysis. The quartet at τ 8.22 arises from H_{6x} and H_{8x} being split once (J = 11.5 Hz) by their respective geminals, H_{6n} and H_{8n}, and resplit by their common vicinal, H_5 (J = 5.0 Hz). Reciprocal splitting accounts for the H_{6n},H_{8n} doublet at τ 9.05 and the H_5 triplet at τ 7.00. The triplet at τ 7.90 arises from H_2 being split (J = 7.5 Hz) by equivalent neighbors, H_1 and H_7, and reciprocation by H_2 accounts for the H_1,H_7 doublet at τ 8.38.

Aromatic bromination of **2** was found to occur in methylene chloride at −75° without a catalyst to afford a single, crystalline monobromo derivative in 90% yield. Cyclopropylbenzene shows comparable reactivity.[6]

[1] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, 91, 1718 (1969), and references therein. We thank Professor Zimmerman for communicating these results to us prior to publication.

[2] In a typical direct-irradiation experiment, 706 mg of alkene **1** in ether (1100 ml) was irradiated in a quartz vessel under nitrogen for 150 min using a 450-W medium-pressure mercury lamp and a Corex filter (λ >260 mμ). Volatile products consisted of 2.5% unreacted **1**, 94% **2**, and 3.5% of a minor product. Silver nitrate–alumina chromatography gave 532 mg (75% conversion) of >99% pure **2**.[4] A typical sensitized irradiation of 140 mg of **1** in ether (140 ml) with 1.5% v/v acetone for 155 min in the same apparatus afforded 136 mg of volatile material consisting of 8% unreacted **1** and 92% of **2**.

[3] Starting compound **1** was prepared from benzonorbornadiene by a modification of the method used to synthesize bicyclo[3.2.1]oct-2-ene; *cf.* W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, 28, (1963).[4]

[4] Satisfactory elemental analyses were obtained for all new compounds.

[5] H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 89, 3212 (1967).

[6] R. Ya. Levina, P. A. Gembitskii, and E. G. Treshchova, *J. Gen. Chem. USSR*, 33, 364 (1963).

The facility of the unsensitized photochemical transformation 1 → 2 is in marked contrast with the reported reduced rates of the di-π-methane to vinylcyclopropane rearrangements of benzonorbornadiene,[7] tetrafluorobenzobarrelene (3),[8] and various dibenzobarrelenes[9] on direct irradiation, and with the failure of benzobarrelene (4)[10] and 1,4-epoxy-1,4-dihydronaphthalene (5)[11] to undergo such rearrangement on direct irradiation.

These reduced rates might be viewed as a consequence of inefficient singlet to triplet intersystem crossing, as suggested for benzonorbornadiene.[7] Alternatively, if intersystem crossing is efficient in these systems,[12] retardation or total preclusion of the di-π-methane rearrangement may reflect the occurrence of an even more facile competing singlet process. Such a process has been suggested[10,11] to be the photochemically allowed concerted 2 + 2 intramolecular cycloaddition,[13,14] which is facilitated in all of the cited cases by the geometry imposed on [2.2.1] and [2.2.2] bicyclic systems. This intramolecular cycloaddition leads readily to the products observed on direct irradiation of 3, 4, and 5. In many of the cited cases, a light-wasting reversion of the cycloadduct to starting material may occur.[11]

In our system 1, models indicate that geometry is not conducive to a 2 + 2 concerted process, since only one end of the isolated double bond π system can approach the benzene π cloud. However, that end is at least as close as comparable orbitals in benzonorbornadiene or benzobarrelene, and so the excited singlet state of 1 might directly initiate a di-π-methane rearrangement. On the other hand, intersystem crossing and triplet rearrangement could predominate in the absence of an efficient competitive singlet process.

A choice between these two pathways is not yet possibile and is under study.[15]

The photochemical behavior of 1 suggests the importance of competitive concerted 2 + 2 cycloaddition in many bicyclic di-π-methane systems by demonstrating the facility of the vinylcyclopropane rearrangement where cycloaddition is not favored.[16]

Acknowledgment. We thank Mr. Gary Elling for the 100-MHz pmr spectrum of 2.

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[7] J. R. Edman, *J. Amer. Chem. Soc.*, 88, 3454 (1966).

[8] J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

[9] E. Ciganek, *J. Amer. Chem. Soc.*, 88, 2882 (1966).

[10] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

[11] G. R. Ziegler, *ibid.*, 91, 446 (1969).

[12] The quantum yield for solution-phase intersystem crossing of the phenyl excited singlet of 1-phenyl-2-butene has been estimated to be at least 0.36: H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968). Intersystem-crossing efficiencies of similar magnitude might be reasonably assumed for the systems in question here.

[13] R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046 (1965).

[14] H. E. Zimmerman, *ibid.*, 88, 1564 (1966).

[15] The *a priori* possibility of forming 2 from 1 *via* a C-8 methylene bridge 1,2 shift has been ruled out by a deuterium labeling study; details will appear in our full paper. Such a shift has been suggested as an alternative to the di-π-methane rearrangement for bicyclo[3.2.1]-octa-2,6-diene: R. R. Sauers and A. Shurpik, *J. Org. Chem.*, 33, 799 (1968).

[16] Very recently triptycene, nominally a bicyclic di-π-methane system, was reported to undergo a photochemical rearrangement on direct irradiation, suggested to proceed through an initial di-π-methane → vinylcyclopropane reaction.[17a,b] In this case, 2 + 2 cycloaddition again may be sufficiently less facile than the same process for the aryl-vinyl–di-π-methane systems discussed above to allow singlet–triplet intersystem crossing to become competitive.

[17] (a) T. D. Walsh, *J. Amer. Chem. Soc.*, 91, 515 (1969); (b) N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, 91, 516 (1969).

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Additions and Corrections

The Excess Free Energy and Related Properties of Solutions Containing Electrolytes [*J. Am. Chem. Soc.*, **90**, 3124 (1968)]. By GEORGE SCATCHARD, Department of Chemistry and Laboratory of Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

In eq 5, the last line should be $(\Sigma_i m_i'/2)^2 \Sigma_j \Sigma_k B_{jk} x_j x_k$.

Equation 8 should be $(G^n/RTW)_4 = \Sigma_i \Sigma_j \Sigma_k \Sigma_l m_i' \cdot m_j' m_k' m_l' f_{ijkl}$.

In the sixth line below, $ka/\sqrt{I} = a'$ should be $\kappa a/\sqrt{I} = a'$.

Equation 11 should be $G^{DH}/RT = WS\Sigma_a{}^+\Sigma_f{}^- m_a' m_f' \cdot (\mathfrak{z}_a + \mathfrak{z}_f) X_{af}/2a_{af}'m'$.

In footnote 17, 289 should be 2898.

In eq 13 "∂" is omitted in the denominator of the second derivative.

In the twelfth line below eq 19, "and 1:2" should be omitted.

On page 3127, the paragraph beginning **Young's rule** should read as follows: Young's rule states that the free energy, the heat, and the volume changes of mixing at constant ionic strength of two 1:1 electrolytes with a common ion af and bf (or af and ag) is independent of the common ion, f (or a). It must hold for G^{DH}/RT and for $(G^n/RT)_2$, and it holds for $(G^n/RT)_3$ if $(2D_{abg} - D_{aag} - D_{bbg}) = (2D_{abf} - D_{aaf} - D_{bbf})$.

I had forgotten that H. E. Wirth, R. E. Lindstrom, and J. N. Johnson [*J. Phys. Chem.*, **67**, 2339 (1963)] had defined Young's rule as the special case in which the changes are zero, which is equivalent to Brønsted's Principle of the Specific Interaction of Ions or our extension of it.[3] They also applied it to mixtures without a common ion for which the earlier treatment is much superior.

On page 3127 in the first paragraph on the cross-square rule the quotation from Young should read "a sufficient but not a necessary condition." The last sentence of that paragraph should be deleted and