

ing that the mass spectrum of the cyclic dioxolane from IV showed, in addition to the molecular ion at  $m/e$  222, the base peak at  $m/e$  99 which demonstrates the presence of the  $\text{CH}_2\text{CH}_2\text{C}=\text{O}$  unit in the ketone IV.<sup>6</sup>

This efficient cyclization should be a fairly general route to various 7-acylbicyclo[2.2.1]heptanes.

**Acknowledgment.** The support of this work by the National Science Foundation is gratefully acknowledged.

(6) Cf. H. Budzikiewicz, C. Djerassi, and D. H. Williams "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 54.

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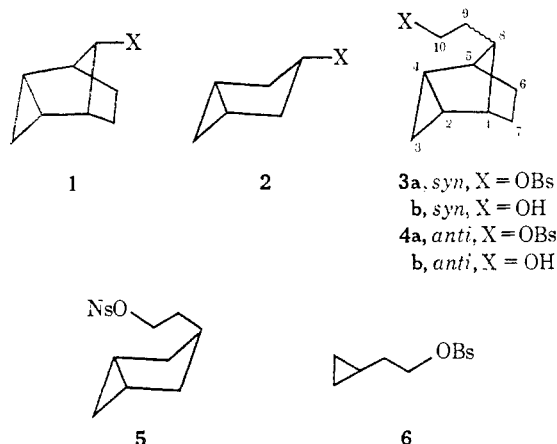
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### Remote Participation of a Cyclopropyl Ring in Solvolysis of $\beta$ -(Tricyclo[3.2.1.0<sup>2,4</sup>]oct-*syn*-8-yl)ethyl *p*-Bromobenzenesulfonate

Sir:

Much attention has been focused on the stereoelectronic effect of a remote cyclopropyl ring on a developing electron-deficient center because of the widely ranging efficiency in assistance.<sup>1</sup> An example of the high efficiency is perhaps our observation that the *endo-anti*-tricyclo[3.2.1.0<sup>2,4</sup>]octan-8-yl derivative **1** solvolyzes 10<sup>6</sup> times faster than a model, *cis*-3-bicyclo[3.1.0]hexyl 2.<sup>1i,k</sup> Another study by us, the solvolysis of  $\beta$ -(*syn*-9-



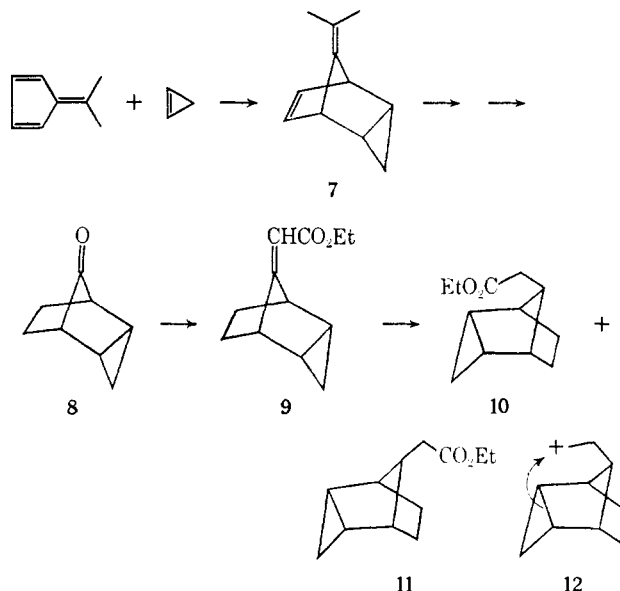
benzonorbornenyl)ethyl brosylate, has provided important evidence for remote aryl participation.<sup>2</sup> As an extension of the related studies, we report here the solvolyses of  $\beta$ -(tricyclo[3.2.1.0<sup>2,4</sup>]oct-*syn*-8-yl)ethyl

(1) For examples, (a) S. Winstein, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5; (b) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965); (c) A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965); (d) M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); (e) R. R. Sauer and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966); (f) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (g) R. R. Sanors, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (h) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (i) C. F. Wilcox and R. G. Jesaitis, *ibid.*, 2567 (1967); (j) H. Tanida, T. Tseji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (k) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, 89, 4954 (1967); (l) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (m) G. D. Sargent, *Tetrahedron Lett.*, 2275 (1968); (n) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968); (o) Y. E. Rhodes and T. Takino, *ibid.*, **90**, 4469 (1968).

(2) R. Muneyuki and H. Tanida, *ibid.*, **90**, 656 (1968).

brosylate (**3a**) and its *anti* isomer (**4a**). While our investigation was in progress, the solvolyses of related systems **5** and **6** were reported and unimportant participation of the cyclopropyl ring was suggested.<sup>1m-o</sup> Nonetheless, the present results indicate definitely participation for a far reaction center.

Introduction of gaseous cyclopropene into a solution of 6,6-dimethylfulvene in *n*-pentane led to the *endo* adduct **7**, bp 194–198°,  $n_D^{23}$  1.5121.<sup>3,4</sup> Catalytic hydrogenation of **7** with 1 equiv of hydrogen followed by ozonolysis afforded the saturated ketone **8** which was identical with that obtained previously from cyclopentadienone diethyl ketal and cyclopropene.<sup>1j</sup> The



Wittig reaction of **8** with carbethoxymethylenetriphenylphosphorane under forced conditions<sup>5</sup> afforded **9**, bp 86–88° (1 mm),  $n_D^{23}$  1.5070, which was converted into a 6:4 mixture of the *syn* ester **10** and the *anti* ester **11** by catalytic hydrogenation. By preparative vpc separation, **10**, bp 90° (1 mm),  $n_D^{24}$  1.4790, and **11**, bp 91–92° (1 mm),  $n_D^{24}$  1.4796, were obtained in the pure states. These two isomers were transformed by  $\text{LiAlH}_4$  reduction into the corresponding alcohols **3b** and **4b**. Assignments of the *anti* and *syn* configuration are determined by the fact that the C-9 methylene protons in **3b** (centered at  $\tau$  8.06) are markedly deshielded compared to those in **4b** (centered at  $\tau$  8.62). The measurements were performed by decoupling of the C-10 methylene protons (for **3b**,  $\tau$  6.38, triplet,  $J$  = 6.7 Hz; for **4b**,  $\tau$  6.51, triplet,  $J$  = 7.0 Hz).<sup>6</sup> The brosylates **3a**,  $n_D^{26}$  1.5605, and **4a**,  $n_D^{26}$  1.5629, were obtained by the usual manner and solvolyzed in 70% aqueous dioxane, acetic acid, and 2,2,2-trifluoroethanol.

The first-order rate constants are set forth in Table I. The acetolysis rate of **4a** is nearly the same as the "unassisted" rate observed for primary brosylates<sup>7</sup> in buffered acetic acid, indicating the unimportance of an inductive effect due to the cyclopropyl in **4a**. The rate ratios of **3a** and **4a** by the factors of 1.08–1.23 in

(3) This is the first example of cycladdition of cyclopropene to a fulvene system.

(4) Satisfactory analyses were obtained for all compounds described.

(5) G. Fodor and I. Tomoskozi, *Tetrahedron Lett.*, 579 (1961).

(6) Varian Model HA-100 in  $\text{CCl}_4$ .

(7) Some examples of the rate are found in ref 2.

Table I. Rate Constants in Solvolyses of 3a and 4a<sup>a</sup>

Solvent	Temp, °C	$k \times 10^4, \text{sec}^{-1}$ 3a	4a	Rate ratio <i>syn:anti</i>
Acetic acid	139.8		5.37	
	125.0	1.75	1.62	1.08
	99.8	0.217	0.173 <sup>b</sup>	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-Trifluoro- ethanol	90.0	0.152	0.0660	2.30
	75.0	0.0338	0.0112	3.01

<sup>a</sup> Rates were determined by potentiometric titration. [ROBs] = 0.02 M. Solvents contained 0.021 M sodium acetate. <sup>b</sup> 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,<sup>8</sup> 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).<sup>9</sup> 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  $\nabla_5$  participation<sup>10</sup> (five-carbon atoms intervene between the reaction site and the ring bonds). The smallness may be due to a non-bonded 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.<sup>1m</sup>

(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<sup>1</sup> of the photochemical di- $\pi$ -methane to vinylcyclopropane rearrangement (Chart I) reported

Chart I



a behavior pattern in which bicyclic di- $\pi$ -methane systems undergo this transformation efficiently from their excited triplet states, while their excited singlets undergo different reactions. Contrastingly, monocyclic and acyclic di- $\pi$ -methanes seem to convert to vinylcyclo-

(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.

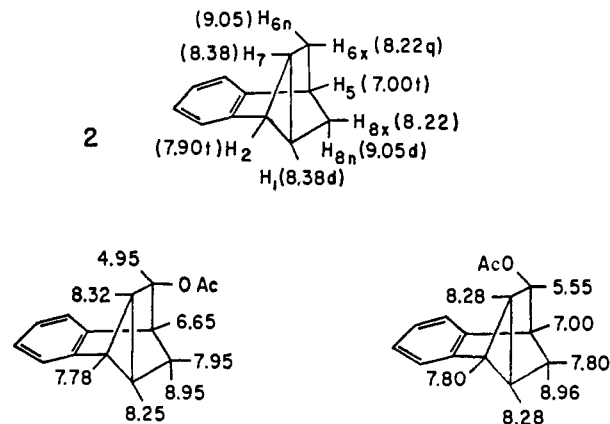
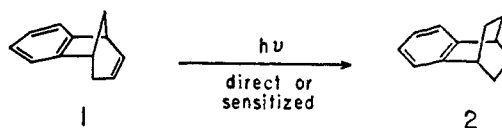


Figure 1. Pmr chemical shifts ( $\tau$ ) for 2 ( $\text{CDCl}_3$ ) and 6-hydroxyacetate derivatives ( $\text{CCl}_4$ )<sup>5</sup> at 100 MHz; multiplicities are represented by d (doublet), t (triplet), and q (quartet).

propanes only *via* excited singlet states. Zimmerman noted<sup>1</sup> that rationalizations might be premature. We now report that direct *or* sensitized irradiation<sup>2</sup> of benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (1),<sup>3</sup> nominally a bicyclic di- $\pi$ -methane system, causes facile conversion to benzo[3,4]tricyclo[3.2.1.0<sup>2,7</sup>]octene (2) (Chart II).

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<sup>2,7</sup>]octen-6-ol acetates<sup>5</sup> for comparison. The symmetry in 2 simplifies the spectrum and the analysis. The quartet at  $\tau$  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  $\tau$  9.05 and the  $H_5$  triplet at  $\tau$  7.00. The triplet at  $\tau$  7.90 arises from  $H_2$  being split ( $J = 7.5$  Hz) by equivalent neighbors,  $H_1$  and  $H_7$ , and reciproprocation by  $H_2$  accounts for the  $H_1, H_7$  doublet at  $\tau$  8.38.

Aromatic bromination of 2 was found to occur in methylene chloride at  $-75^\circ$  without a catalyst to afford a single, crystalline monobromo derivative in 90% yield. Cyclopropylbenzene shows comparable reactivity.<sup>6</sup>

(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 Correx filter ( $\lambda > 260 \text{ m}\mu$ ). 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.<sup>4</sup> 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 benzenorbornadiene 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).<sup>4</sup>

(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).