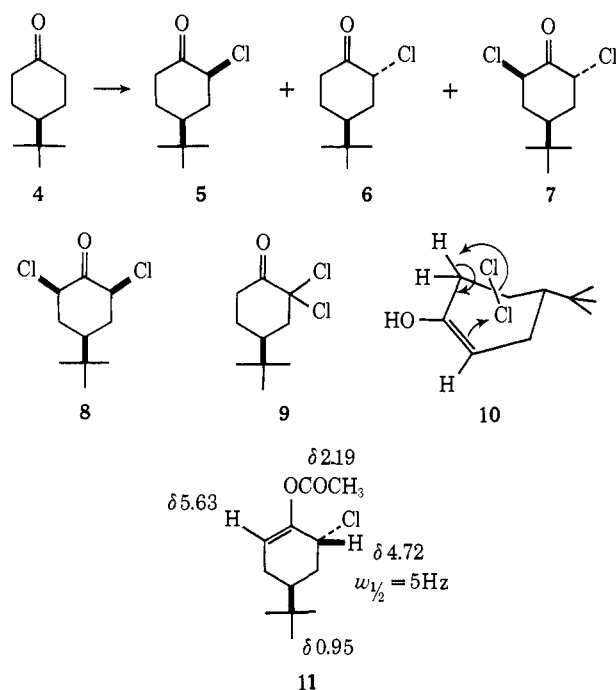


reaction  $1 \rightarrow 2$  to be concerted would require favorable orientation of the available incipient chloride base at the  $\alpha'$ -H instead of nearer the hydroxyl hydrogen, perhaps as in **10** which has analogy in the reaction of singlet oxygen with allylic systems,<sup>9</sup> except that the LUMO of chlorine is  $\sigma_u^*$  whereas the LUMO of singlet oxygen is  $\pi_g^*$ .

Support for such a mechanism was provided by the isolation of a chloroenol derivative when  $Y = \text{Ac}$  (Scheme I). Chlorination of the enol acetate of **4** in carbon tetrachloride at  $5^\circ$  gave, in addition to monochloro ketones **5** and **6**, as much as 30% of *trans*-6-chloro-1-acetoxy-4-*tert*-butylcyclohexene (**11**).<sup>10</sup> Treat-

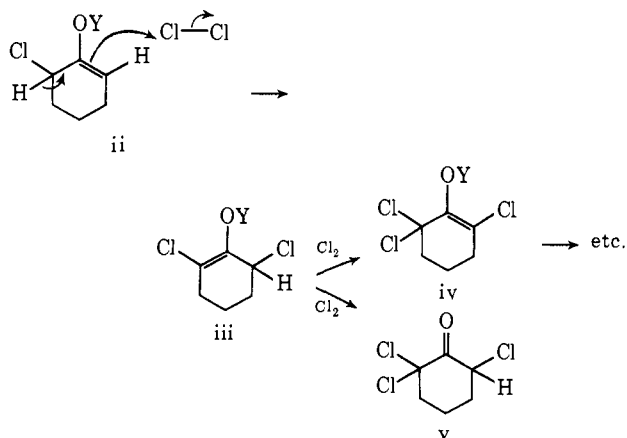


ment of **5** and **6** with  $\text{AcCl-HCl-CCl}_4$  at  $5^\circ$  gave no **11**.

**1** to **2**; **i** would deprotonate from oxygen instead since **5** and **6** do not in fact enolize in the presence of  $\text{HCl-Cl}_2\text{-CCl}_4$  under the conditions used although their carbonyl oxygens are protonated to some extent in this medium.

(9) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(10) The survival of **11** in the presence of some chlorine must be a consequence of the decreased nucleophilic character of the enolic double bond caused by the combined effect of the acetyl and allylic chlorine groups. Similarly, the absence of a continuation of reaction path  $1 \rightarrow 2 \rightarrow 3$  such as  $\text{ii} \rightarrow \text{iii} \rightarrow \text{iv} + \text{v}$  can be due to the greatly decreased reactivity of the dichloro enol **iii** with electrophiles.



The unexpected implication of the mechanism in Scheme I is that, at least in a nonpolar aprotic solvent in which proton removal from the enolic OH during halogenation is not facilitated by the solvent, electrophilic attack on an enol or its derivative with cleavage of an  $\alpha'$ -CH bond to yield the  $\alpha'$ -enol derivative **2** can be closely competitive with cleavage of the OY bond of **1** to form the monosubstituted ketone. It remains to be seen how general the  $\alpha'$ -CH cleavage is.

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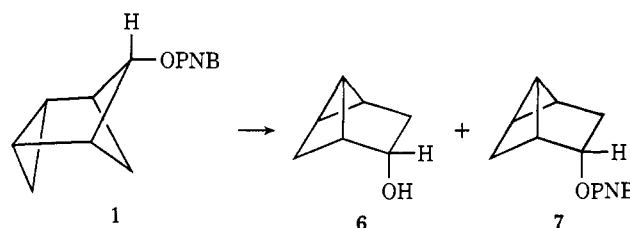
### Solvolysis of Derivatives of *exo*- and *endo*-anti-Tricyclo[3.1.1.0<sup>2,4</sup>]heptan-6-ol<sup>1</sup>

Sir:

The recent report by Masamune and coworkers,<sup>2</sup> on the solvolytic behavior of *exo*-anti-tricyclo[3.1.1.0<sup>2,4</sup>]hept-6-yl *p*-nitrobenzoate (**1**), prompts us to disclose our related studies of **1** and of the epimeric *p*-nitrobenzoate (**2**) and *p*-toluenesulfonate (**3**) of *endo*-anti-tricyclo[3.1.1.0<sup>2,4</sup>]heptan-6-ol (**4**).

The synthesis of the alcohol precursors of **1**, **2**, and **3** has been previously discussed.<sup>3</sup> In a series of 13 steps starting from the known<sup>4</sup> *exo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene, we were able to prepare an 86:14 mixture of **4**:**5** in 4.5% over-all yield. The conversion of **5** into **1** and of **4** into **2** and **3** was readily accomplished.

The solvolysis of **1** gave 61% of **6** and 22% of **7** (*via*



internal return). The structure of **6** was based on spectral comparison with an authentic sample.<sup>5</sup> Lithium aluminum hydride reduction of **7** gave **6**. The acetylation of **3** gave 52% of **8**, 35% of **9**, and 11% of **10** after conversion of the acetates to the corresponding alcohols *via* hydride reduction. The identification of **8** was based on comparison with an authentic sample, while the structural assignment for **9** was made on the basis of spectral evidence and its facile dehydration to **8**. The spectral properties of **10** were consistent with the assigned structure. Furthermore, catalytic reduction of **10** gave *exo*-2-hydroxybicyclo[4.1.0]heptane (**11**) which was identical with an authentic sample.<sup>6</sup>

(1) Paper XXXVII on The Chemistry of Bent Bonds. For the previous paper in the series, see P. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973).

(2) S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Amer. Chem. Soc.*, **94**, 8239 (1972).

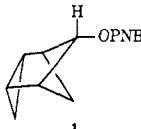
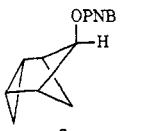
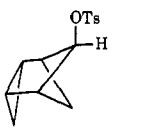
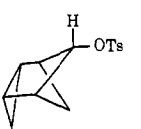
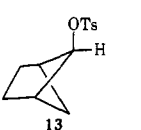
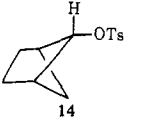
(3) For the initial report of the synthesis of the tricyclo[3.1.1.0<sup>2,4</sup>]heptyl ring system see: P. G. Gassman and X. Creary, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9-14, 1972, Abstracts, ORGN 140.

(4) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

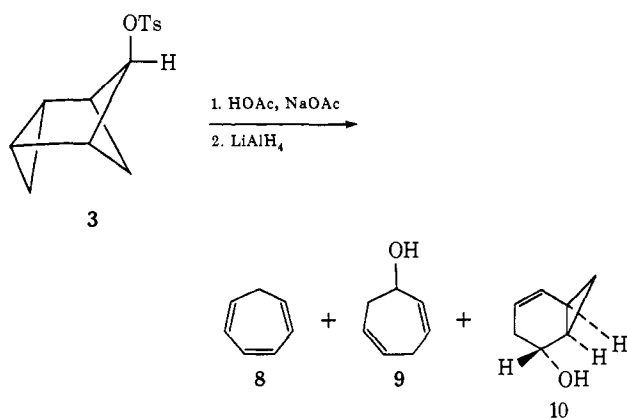
(5) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972). We wish to thank Professor Lustgarten for providing the spectra of authentic **6**.

(6) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **94**, 7748 (1972).

Table I. Rates of Solvolysis of Derivatives of the Bicyclo[2.1.1]hexyl Ring System

Compound	Solvent <sup>a</sup>	Temp ( $\pm 0.03^\circ\text{C}$ )	$k$ , $\text{sec}^{-1}$	$k_{\text{rel}}$
 1	$\alpha$	105.0	$(1.67 \pm 0.02) \times 10^{-5}$	
	$\alpha$	120.0	$(7.30 \pm 0.07) \times 10^{-6}$	
	$\alpha$	135.0	$(2.75 \pm 0.01) \times 10^{-4}$	
	$\alpha$	25.0 <sup>b</sup>	$6.31 \times 10^{-10}$	
	$\beta$	25.0 <sup>b,c</sup>	$7.79 \times 10^{-11}$	
 2	$\alpha$	150.0	$(8.67 \pm 0.01) \times 10^{-6}$	
	$\alpha$	160.2	$(1.83 \pm 0.01) \times 10^{-5}$	
	$\alpha$	170.0	$(3.75 \pm 0.01) \times 10^{-5}$	
	$\alpha$	25.0 <sup>b</sup>	$1.15 \times 10^{-11}$	
 3	$\gamma$	16.7	$(7.70 \pm 0.02) \times 10^{-5}$	$1.0 \times 10^7$
	$\gamma$	25.0	$(2.27 \pm 0.01) \times 10^{-4}$	
	$\gamma$	33.8	$(6.82 \pm 0.01) \times 10^{-4}$	
 12	$\gamma$	25.0 <sup>d</sup>	$1.25 \times 10^{-2}$	$5.6 \times 10^8$
 13	$\gamma$	25.0 <sup>e</sup>	$2.64 \times 10^{-3}$	$1.2 \times 10^8$
 14	$\gamma$	25.0 <sup>b,e</sup>	$2.24 \times 10^{-11}$	1

<sup>a</sup>  $\alpha = 30:70$  v/v  $\text{H}_2\text{O}:\text{acetone}$ ,  $\beta = 40:60$   $\text{H}_2\text{O}:\text{dioxane}$ ,  $\gamma = \text{acetic acid buffered with } 0.1 \text{ M sodium acetate}$ . <sup>b</sup> Extrapolated rate. <sup>c</sup> See ref 2. <sup>d</sup> Extrapolated rate calculated using the assumption that  $k_3/k_2 = k_{12}/k_1$ . <sup>e</sup> See ref 8.



The rates of solvolysis of **1**, **2**, **3**, and certain related bicyclic esters (for comparison purposes) are listed in Table I.<sup>7</sup> As can be noted from the table, **3** and **12** (**1** and **2**) differ by only a factor of  $1.8 \times 10^{-2}$ , while the corresponding esters without the cyclopropane ring (**13** and **14**) differ<sup>8</sup> by  $1.2 \times 10^8$ . The over-all change in relative rates resulting from addition of the cyclopropyl rings amounted to  $6.7 \times 10^9$ .

(7) The rates listed for **1** are based on measured infinity titers and are corrected for internal return. All rates measured in this study gave excellent pseudo-first-order plots. In the case of **1**, this had to be corrected for internal return.

(8) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970).

The large difference in rates noted for the comparison of **3** and **12** with **14** indicates that both **3** and **12** (or **2** and **1**) are solvolyzing with considerable neighboring group participation. Since it appears that **14** may also solvolyze with neighboring group participation,<sup>9</sup> the extent of rate acceleration in **3** and **12** will be dependent on the amount of anchimeric assistance occurring in the acetolysis of **14**. Since an exact value for the rate acceleration involved in the solvolysis of **14** is not readily available, we have chosen to compare **12** with **16**. It is currently thought that the solvolysis of **16** does not involve any participation of the cyclopropane ring other than a small rate-retarding inductive effect. Solvolysis of **16**, with a  $\text{C}_1\text{-C}_5\text{-C}_6$  bond angle of  $97^\circ$ ,<sup>10</sup> occurs at an extrapolated rate<sup>11</sup> (for the corresponding tosylate) of  $2.4 \times 10^{-15} \text{ sec}^{-1}$ . However, **12**, with the much smaller  $\text{C}_1\text{-C}_5\text{-C}_4$  angle<sup>12</sup> of  $82^\circ$ , solvolyzes at  $1.25 \times 10^{-2} \text{ sec}^{-1}$ . It is important to note that **12**, with a bond angle at the incipient carbonium ion center approximately  $15^\circ$  smaller than that of **16**, solvolyzes ca.

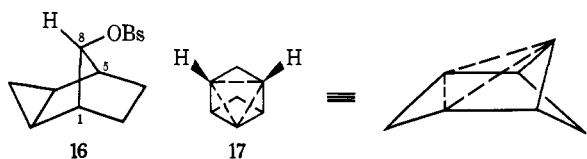
(9) The solvolysis of **14** occurs  $5 \times 10^3$  faster than that of 7-norbornyl tosylate (**15**) even though the bond angle at the incipient cationic center should be smaller in **14** than in **15**.<sup>8</sup>

(10) A. C. MacDonald and J. Trotter, *Acta Crystallogr.*, **18**, 243 (1965).

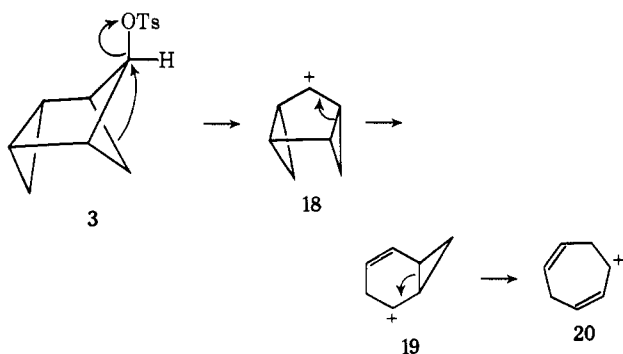
(11) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(12) This angle has been measured for the corresponding *p*-bromobenzoate.<sup>2</sup>

$5 \times 10^{12}$  times faster. This suggests that the appropriately situated cyclopropyl group can provide anchimeric assistance in the form of a rate acceleration much greater than  $10^{13}$ . Presumably, this is due to the formation of an ion represented by 17.<sup>13</sup>



Comparison of the rates of solvolysis of 3 and 13 indicates that the cyclopropyl group of 3 shows only a slight rate-retarding inductive effect. Both the rate and products obtained from 3 indicate that the major influence is the rearrangement of the four-membered ring, presumably to yield 18, followed by opening of 18 to give 19, and partial opening of 19 to give 20. The



intermediacy of 19 would account for the formation of 10, while 20 would serve as a precursor of 8 and 9.

**Acknowledgment.** We are indebted to the National Science Foundation for a grant in partial support of this study.

(13) For a detailed discussion of this ion, generated from a different precursor see ref 5.

(14) Goodyear Research Fellow, 1971-1972.

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## The 8,8-Dimethylcyclooctatrienyl Anion

Sir:

A great deal of progress has been made in recent years in the study of homoconjugation, and, in particular, in the preparation of homoaromatic species.<sup>1</sup> In contrast, only a few potentially antihomoaromatic species (all of which are carbocations) have been prepared.<sup>2</sup> We now report the preparation and direct observation of the title anion, a potentially antihomoaromatic  $8\pi$ -electron analog of the homotropylium cation.<sup>3</sup>

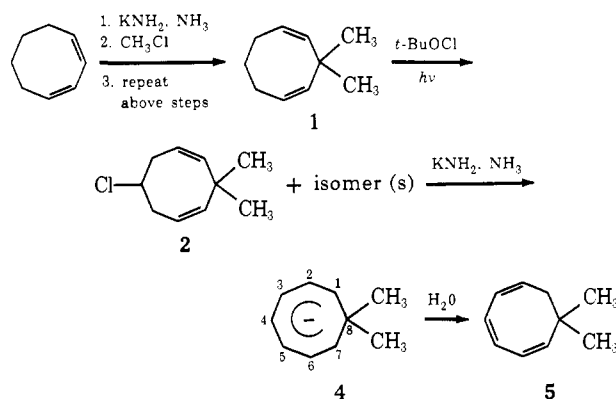
(1) Reviews: (a) S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967); (b) S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969); (c) P. R. Story and B. C. Clark, Jr., in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, p 1007.

(2) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, 91, 7785 (1969), and references cited therein.

(3) (a) J. L. v. Rosenberg, Jr., J. E. Mahler, and R. Pettit, *ibid.*, 84, 2842 (1962); (b) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references cited.

The (potassium) cyclooctatrienyl anion cannot be observed in liquid ammonia since it is apparently thermodynamically unstable and rapidly disproportionates to 1,3,5-cyclooctatriene and the cyclooctatetraene dianion.<sup>4</sup> This problem is eliminated in the case of the 8,8-dimethylcyclooctatrienyl anion, the synthesis of which is given in Scheme I. The key step

Scheme I



is the direct introduction of geminate methyl groups onto 1,3-cyclooctadiene by the methylation of cyclooctadienyl anions in a strongly basic medium. This reaction, in which 3-methyl-1,4-cyclooctadiene is an intermediate, is made possible by the fact that cyclooctadienyl anions are preferentially alkylated at C<sub>3</sub> rather than C<sub>1</sub>,<sup>5</sup> and it occurs in 12-17% overall isolated yield.

Diene 1<sup>6</sup> could be chlorinated with *tert*-butyl hypochlorite in 18% isolated yield (at low conversion) to afford a product mixture consisting predominantly of two monochlorides in a 55:45 ratio which could be separated by glpc only with difficulty. The major component was readily identified as 7-chloro-3,3-dimethyl-1,4-cyclooctadiene (2),<sup>7</sup> whereas the complex nmr spectrum of the minor isomer appears to be consistent with the structure of 6-chloro-3,3-dimethyl-1,4-cyclooctadiene (3).<sup>8</sup>

Treatment of a mixture of chlorides 2 and 3 with potassium amide in liquid ammonia produced a dark-red solution of anion 4 whose nmr spectrum (obtained at  $-55^\circ$  with trimethylamine as internal standard) cleanly displayed a doublet of doublets at  $\delta_{\text{TMS}} 5.43$  (H<sub>2</sub> and H<sub>6</sub>,  $J_{12} = 12.4$  Hz,  $J_{23} = 9.0$  Hz), a triplet at 5.21 (H<sub>4</sub>,  $J_{34} = 11.0$  Hz), an asymmetric doublet at 4.58 (H<sub>1</sub> and H<sub>7</sub>,  $J_{12} = 12.4$  Hz), a doublet of doublets at 3.56 (H<sub>3</sub> and H<sub>5</sub>,  $J_{23} = 9.0$  Hz,  $J_{34} = 11.0$  Hz), and a sharp singlet at 1.41 (methyl protons) which remained sharp down to  $-77^\circ$  in ammonia-*d*<sub>3</sub>.<sup>9</sup> The nmr spectrum of the cesium salt of 4 was very similar to that of

(4) H. Kloosterziel and E. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, 88, 1373 (1969).

(5) F. L. Wiseman, Jr., Ph.D. Thesis, University of Maryland, 1970.

(6) Nmr (CCl<sub>4</sub>):  $\delta$  4.64 (d, H<sub>2</sub> and H<sub>4</sub>,  $J = 11.5$  Hz), 5.10 (t of d, H<sub>1</sub> and H<sub>5</sub>,  $J_{1,2} = 8.2$  Hz), 2.23 (t of d, 4 H, H<sub>6</sub> and H<sub>8</sub>,  $J_{6,7} = 6.7$  Hz) 1.48-1.12 (m, 2 H, H<sub>3</sub>), and 1.08 (s, 6 H, methyl); uv (hexane) end absorption ( $\epsilon_{220 \text{ nm}}$  106).

(7) Nmr (CCl<sub>4</sub>): AB system at  $\delta$  5.67 (d, H<sub>2</sub> and H<sub>4</sub>,  $J_{12} = 11.8$  Hz) and 5.67 (t of d, H<sub>1</sub> and H<sub>5</sub>,  $J_{1,2} = 8.6$  Hz,  $J_{1,5} = 7.4$  Hz), t of t at 3.97 (H<sub>7</sub>,  $J_{6,7} = 6.5$  Hz,  $J_{6,7} = 5.3$  Hz), two d of d at 2.66 and 2.63 (H<sub>6a</sub> and H<sub>6b</sub> and H<sub>8b</sub>), respectively, and two s at 1.14 and 1.11 (methyl).

(8) Nmr (CCl<sub>4</sub>): multiplets at  $\delta$  4.7-5.8 (5 H) and 1.3-3.0 (4 H) and a six-proton singlet at 1.13. A mixture of 2 and 3 gave a correct analysis for C<sub>10</sub>H<sub>15</sub>Cl.

(9) I. Melczynski, *Angew. Chem.*, 74, 32 (1962). We thank Dr. John Morrison for assistance with this preparation.