the hydrogen is forced away from the C(19) and C(28) methyl groups toward the O(1) methoxyl group; the O(1)–H(10) contact is 2.10 (6) Å, while the sum of the van der Waals radii is 2.60 Å.[6,12]

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(12) While some of the hydrogen atoms in the difference map were not very well defined, H(10) had a height of 0.4 electron/Å^3 and had a well-resolved peak. Refinement of the thermal parameters of all the hydrogen atoms gave $B\theta$ values ranging from -1.8 (that for H(10)) to $+12.0$ Å^2. While these values are clearly not quantitatively significant, the relatively low $B\theta$ values for H(10) and for many of the other hydrogen atoms involved in close contacts in the *endo* region of the molecule give us confidence in their location.

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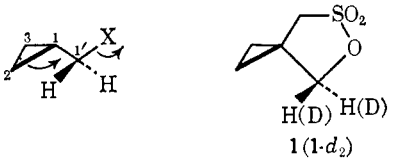
Solvolysis of 1-Hydroxymethylcyclopropanemethanesulfonic Acid Sultone, a Cyclopropylcarbinyl Derivative with an Oriented Leaving Group

Sir:

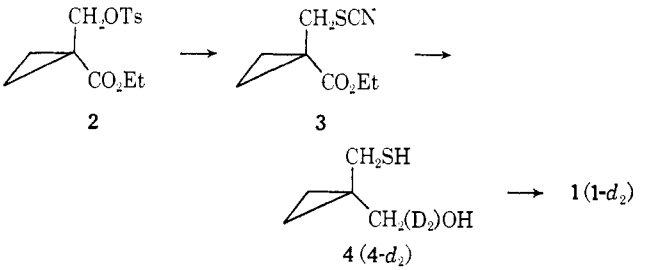
Despite the extensive investigations on the carbonium ion reactions and rearrangements of cyclopropylcarbinyl compounds,[1] it has not been possible to define precisely the character of the solvolytic transition state(s) or the structure of the product-forming intermediate(s).[2] Recent studies have been concerned with structurally rigid precursors of various designs[1b,3] and the mechanism of the cyclopropylcarbinyl to cyclopropylcarbinyl rearrangement.[4,5]

Although the 1,2 bond of the cyclopropane ring clearly participates in rearrangements leading to cyclobutyl and allylcarbinyl products, the 2,3 bond becomes involved in the overall cyclopropylcarbinyl–cyclopropylcarbinyl isomerization process. In order to examine the possibility of direct participation by the 2,3 bond,[6] we have prepared the cyclopropylcarbinyl sultone **1**. In this structure, the sulfonate leaving group is fixed in an orientation which would seem most favorable for involvement of the electron pair of the 2,3 bond in the ionization process. The 1,2 bond is, however, considerably skewed from the apparently optimal geometry for concerted participation. For example, ionization of **1** without bond rotation would give an "in-plane" cyclopropylmethyl cation[7] (or possibly a tricyclonium ion[8]). In order to attain the "bisected"[9] (out of plane[7]) conformation, the 1,1′ bond must rotate through an angle of 90°.[10]



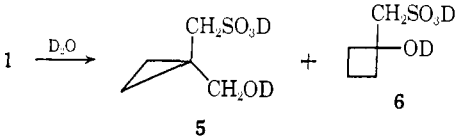
1(1-d_2)

1-Hydroxymethylmethanesulfonic acid sultone (**1**) was synthesized by the route outlined below. The tosylate **2**[12] was converted to the thiocyanate **3** (82%, ν_{max} 2140 cm^{-1})[13] by reaction with sodium thiocyanate in refluxing 90% ethanol. Reduction with lithium aluminum hydride (or deuteride) in ether affords 1-mercaptomethylcyclopropanemethanol (**4** or **4**-d_2) in 73% yield. The sultone **1** or **1**-d_2 is obtained by direct oxidation with 4 equiv of *m*-chloroperbenzoic acid in methylene chloride [yield 56%; mp 36.5–38°; ν_{max} 1340, 1160 cm^{-1}; δ^{CDCl_3} 0.90 and 0.97 (2 m, 4 H), 3.26 (s, 2 H), 4.28 (s, 2 H)].[14]



2 **3** **4** (4-d_2)

Hydrolysis of sultone **1** (*ca.* 1 *M*) in 7:3 v/v acetone-d_6–deuterium oxide at 50° produces a mixture of two sulfonic acids, **5** [40%; δ 0.62 and 0.70 (2 t, J = 1.5 Hz; 4 H), 2.93 (s, 2 H), 3.57 (s, 2 H)] and **6** [60%; δ 1.5–2.5 (m, 6 H), 3.16 (s, 2 H)], which could be isolated as a mixed phenylhydrazine salt (80%; mp 156–163°). The ratio **5**:**6** remains constant throughout the hydrolysis and is unchanged by the presence of an equivalent amount of urea. Hydrolysis in the presence of 1.1–1.2 equiv of sodium hydroxide affords the cyclopropyl product exclusively (phenylhydrazine salt, 66%; mp 147–148°).



5 **6**

The deuterated sultone **1**-d_2 hydrolyzes to 60% **6**-d_2 (not possible to locate the deuterium) and **5**-d_2 with the label in both the carbinyl position (29%) and in the cy-

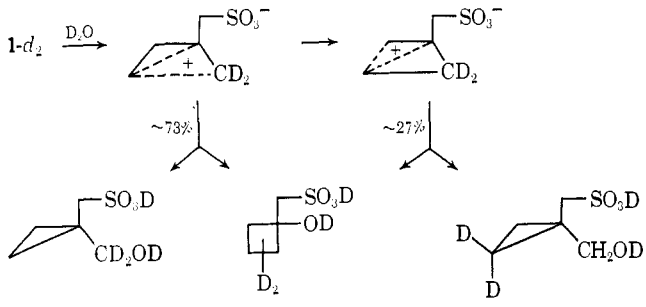
(1) For references to the earlier literature see (a) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); (b) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303, 4311 (1968).
(2) W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).
(3) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).
(4) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968).
(5) C. D. Poulter and S. Winstein, *ibid.*, **91**, 3649, 3650 (1969).
(6) In certain structures, homocyclopropylcarbinyl participation can give rise to very large rate enhancements: H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); R. M. Coates and J. L. Kirkpatrick, *ibid.*, **90**, 4162 (1968); J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).
(7) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
(8) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).
(9) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 150 (1964).
(10) Theoretical calculations[1b,7,11] seem to be in general agreement, predicting that both the in-plane and pyramidal configurations for the cyclopropylmethyl cation should be less stable than the out-of-plane conformation.
(11) C. Trindle and O. Sinanŏglu, *J. Am. Chem. Soc.*, **91**, 4054 (1969); R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).
(12) H. Najer, R. Giudicelli, and J. Sette, *Bull. Soc. Chim. France*, 2118 (1965).
(13) All new compounds gave satisfactory elemental analyses and infrared and nmr spectra consistent with the indicated structures.
(14) This reaction represents a new and especially mild means for preparing sultones. The cyclic sulfinate is evidently an intermediate and is more slowly oxidized to the sulfonate stage. The oxidation of sulfinates to sulfonates under these conditions has recently been reported: R. M. Coates and J. P. Chen, *Tetrahedron Lett.*, 2705 (1969).

clopropane ring (11%), indicating cyclopropylcarbinyl to cyclopropylcarbinyl rearrangement. No internal return to scrambled **1**-d_2 was observed, although 2–3% should have been detectable. Again the product proportions remained constant during hydrolysis and were only slightly affected by the presence of urea.

The rate of hydrolysis of sultone **1** (*ca.* 0.007 *M*) was determined in 70% aqueous acetone by aliquot titration: $k_{50°} = 2.48 \times 10^{-5}$, $k_{70°} = 18.2 \times 10^{-5}$ sec^{-1} ($\Delta H^{\ddagger} = 21.4$ kcal/mol, $\Delta S^{\ddagger} = -14$ eu at 50°). For comparison, the hydrolysis rate of 3-hydroxypropanesulfonic acid sultone (**7**) was measured under the same conditions: $k_{50°} = 1.62 \times 10^{-5}$, $k_{70°} = 9.32 \times 10^{-5}$ sec^{-1} ($\Delta H^{\ddagger} = 18.7$ kcal/mol, $\Delta S^{\ddagger} = -23$ eu at 50°), *i.e.*, $k_1/k_7 = 1.53$ at 50°. Nilsson[15] reports that 2,2-dimethyl-3-hydroxypropanesulfonic acid sultone (**8**) undergoes hydrolysis at a considerably reduced rate ($k_8/k_7 = 0.0035$, 40° in water).[17]

From the kinetic data it appears that the hydrolysis of sultone **1** proceeds with a modest amount of assistance. Although an accurate estimate of the magnitude would be premature, the rate enhancement is evidently well below the usual level. The hydrolysis of cyclopropylcarbinyl tosylate, for example, is some 1550 times faster than ethyl tosylate (90% aqueous acetone, 25°).[19]

The kinetic data, products, and scrambling results can be economically explained in terms of a bicyclobutonium ion intermediate[8] which reacts with water to give **5** and **6** about 2.7 times faster than it rearranges.[20] However, some (16.5%) rearrangement *via* a tricyclonium ion is not excluded by the data. Although there could be an SN2 component in the hydrolysis of **1**, the partial label scrambling in the formation of **5**-d_2 demonstrates that a substantial fraction (41 or 55% depending upon the scrambling mechanism) of the cyclopropyl product **5** results from an SN1 pathway.



The reduced rate enhancement in the hydrolysis of **1** indicates that 2,3 participation probably contributes at most a small factor to the high solvolytic reactivity of cyclopropylcarbinyl derivatives and that the magnitude of the kinetic acceleration depends markedly upon the orientation of the leaving group.[3] This conclusion is in line with the theoretical calculations concerning the relative instability of the in-plane cyclopropylmethyl cation.[1b,7,11]

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(21) National Science Foundation Undergraduate Research Participant, summer, 1969.

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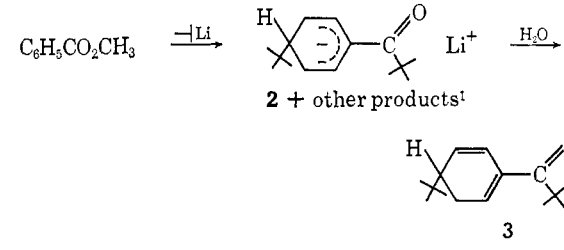
Electrocyclic Addition of a Cyclohexadienylic Anion to a Diene. Route to Polycyclic Compounds

Sir:

One of the consistent products of reaction of methyl benzoate with *t*-butyllithium (eq 1) was a compound, **1**, which can be formally represented as a dimer of two pivaloyl-*t*-butylcyclohexadienes.[1] *A priori* one can imagine a large number of electrocyclic reactions of the neutral dienes that would result in dimer formation or Michael addition of an anion **2** to a diene. None of these structures is, however, consistent with the spectroscopic and chemical data obtained for the material. The diene dimer **1** could be isolated only under specific



(1)

conditions. A solution of 85 ml of *t*-butyllithium, 2 *M* in pentane, was added to 10 g of methyl benzoate in 35 ml of isooctane at such a rate that the mixture refluxed gently. The mixture was brought to 95° and 10 ml of water was added over 10 min. After cooling, an additional 30 ml of water was added and compound **1** immediately precipitated, 0.6 g (mp 244–244.5) from this hydrolysate. Heating the mixture of products (dienones, carbinols, and aromatic ketones) from the above reaction had no effect on the yield of **1**, nor did varying the reaction temperature. On the other hand, the yield of **2** increased markedly with the temperature of the hydrolysis reaction, ~0% at −10–0°, 1% at 35°, and 5% at 100°. Evidently, compound **1** is only formed during the hydrolysis reaction.

Infrared (2980 s, 1650 s, 1640 s, 1608 w, 1272 m, 1142 s, 764 cm^{-1}) and ultraviolet (234 mμ (ε 1400)) spectra indicate the presence of a conjugated ketone chromophore.[2] The nmr spectrum shows four different *t*-butyl resonances at τ 8.78, 8.83, 9.20, 9.26, and two

(15) T. Nilsson, Ph.D. Dissertation, University of Lund, 1946, quoted by Bordwell, Osborne, and Chapman.[16]
(16) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *J. Am. Chem. Soc.*, **81**, 2698 (1959).
(17) The low rate of solvolysis of **8** is apparently not entirely a result of steric hindrance since the relative rate of neopentyl benzenesulfonate in water at 40° is 0.10 compared to propyl benzenesulfonate as 1.0.[16,18] Bordwell, *et al.*, have suggested that the increased barrier to rotation about the 2,3 bond in the heterolytic ring opening of substituted sultones is an important factor in determining the hydrolysis rate.[16]
(18) P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955).
(19) D. D. Roberts, *J. Org. Chem.*, 30, 23 (1965).
(20) A mechanism involving distinct cyclopropylcarbinyl (*e.g.*, the "bisected" conformation) and cyclobutyl (or C_s bicyclobutonium[1b]) intermediates interconverting through a bicyclobutonium-like transition state will satisfy the results described here equally well. At present we prefer the equilibrating bicyclobutonium ions since this scheme will accommodate as well the apparent stereochemical integrity maintained in the cyclopropylcarbinyl rearrangements.[4]

(1) G. Fraenkel and E. Pecchold, *Tetrahedron Letters*, in press. The main products are pivalophenone and di-*t*-butylbenzyl alcohol.
(2) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).