Anal. Calcd for $C_6H_7BN_2O_5S$: C, 31.33; H, 3.07; B, 4.70; N, 12.18; S, 13.94. Found: C, 31.07; H, 2.69; B, 4.74; N, 11.89; S, 13.95.

2-Mercapto-4-oxy-5-(oxyboromethyl)-6-iminopyrimidine (7).—A solution of 0.85 g of thiourea, an equimolar quantity of potassium *t*-butoxide, and 3 g of methyl α-cyano-β-dibutoxyborylpropionate in 40 ml of *t*-butyl alcohol was kept at 70° for 2 hr, then neutralized (to pH paper, pH about 7) with glacial acetic acid, and diluted with 40 ml of water. The product crystallized together with some boric acid, evidently tightly held in a chelate since attempted removal as the methyl borate azeotrope did not change the composition: yield 0.57 g (21%), recrystallized from methanol–water; nmr (CD_3SOCD_3) τ 8.46 (s, CCH_2B), 6.16 (s, NH, SH); decomposed at 250° without melting up to 350°; ir (KBr) 3.0 (NH), 6.1–6.5 μ (pyrimidine).[15]

Anal. Calcd for $C_{10}H_{13}B_3N_6O_6S_2$: C, 29.30; H, 3.20; B, 7.92; N, 20.50; S, 15.65. Found: C, 29.29, 29.27; H, 3.79, 3.74; B, 7.95 7.75; N, 19.97, 20.27; S, 15.80, 15.68.

A sample of the pyrimidine **7** without chelated boric acid was obtained on one occasion, but we were unable to purify it to the usual analytical standard. The reaction mixture was treated with acetic acid and then water, as described in the preceding paragraph, and was then extracted with a mixture of 1-butanol and ether. The aqueous phase was concentrated, and the oily residue was treated with acetone and allowed to stand for 1 month in the refrigerator to crystallize it.

Registry No.—**1,** 13251-29-1; iodomethaneboronic acid, 16876-23-6; dibutyl butoxymethaneboronate, 16876-24-7; **2,** 13536-41-9; catechol ester of **3,** 13251-31-5; dimethylaminomethaneboronic acid catechol ester, 16876-27-0; **4,** 16973-90-3; phthalimidomethaneboronic acid, 16876-28-1; catechol ester of S-thioureidomethaneboronic acid, 16876-29-2; dibutyl acetylthiomethaneboronate, 16876-30-5; acetylthiomethaneboronic acid, 16876-31-6; dimethyl (dibutoxyborylmethyl)-malonate, 16876-32-7; **6,** 16876-33-8; diethyl acetamido(catechylborylmethyl)malonate, 16876-34-9; **8,** 16876-35-0; **9,** 16876-36-1; 2-(S-hydroxyboromethyl)thiobarbituric acid, 16876-37-2; oxybis[2-(S-boromethyl)thiobarbituric acid], 16876-38-3; **10,** 16876-39-4; **11,** 16876-40-7; catechol ester of **11,** 16915-93-8; **12,** 16876-41-8; **13,** 16876-42-9; oxybis(2-boromethylthio-4-oxy-6-phenylpyrimidine), 16876-43-0; oxybis(2-boromethylthio-4-oxy-6-propylpyrimidine), 16876-44-1; S-7-bis(dihydroxyborylmethyl)-2-mercapto-6-oxypurine, 16876-45-2; 2-(dihydroxyborylmethylthio)-4-carboxyluracil, 16876-46-3.

The Mechanism of the Prins Reaction. VI. The Solvolysis of Optically Active *trans*-2-Hydroxymethylcyclohexyl Brosylate and Related Arenesulfonates[1]

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The solvolysis of optically active *trans*-2-hydroxymethylcyclohexyl brosylate yields *trans*-2-hydroxymethylcyclohexanol with complete retention of optical activity. This result may be attributed to the intervention of a four-membered oxonium ion intermediate or reaction of the carbonium ion with solvent before any conformational change. The solvolyses of *trans*-2-hydroxymethylcyclopentyl β-naphthalenesulfonate and *threo*-1-hydroxy-2-methyl-3-butyl β-naphthalenesulfonate proceed with elimination, rearrangement, and complete inversion of configuration which indicates that these compounds are not suitable for generating the intermediate responsible for *trans* addition in the Prins reaction. The solvolysis of *cis*-2-hydroxycyclohexylcarbinyl brosylate yields no *trans*-2-hydroxymethylcyclohexanol, a compound which would be expected if four-membered-ring oxonium-ion intermediates were important in these reactions.

One of the most interesting features of the Prins reaction is the highly stereoselective *trans* addition found with simple alicyclic and acylic olefins. The Prins reaction of cyclohexene has been studied most extensively and the major products of the reaction are derivatives of *trans*-2-hydroxymethylcyclohexanol with only traces of the *cis* isomers.[3-5] Similarly, the Prins reactions of *cis*- and *trans*-2-butene appear to yield mainly the products of *trans* addition[6] and we find only a trace of the *cis* addition product in the Prins reaction of *trans*-2-butene.

A case of nonstereospecific addition has been reported by LeBel, Liesemer, and Mehemedbasich who find that the Prins reactions of *cis*- and *trans*-4-octene yield products of both *cis* and *trans* addition.[7] Moreover, the two olefins give different ratios of *trans* to *cis* addition. However, this lack of stereoselectivity may be the result of working in dioxane solution since dioxane is known to alter the stereochemistry of solvolysis reactions.[8] This possibility is also supported by the observation that the Prins reaction with cyclohexene in dioxane solution affords a 20% yield of the *cis* addition product.[9]

Several mechanisms have been proposed to account for the stereoselectivity of the Prins reaction with simple olefins. The mechanism which has been mentioned most frequently involves an intermediate four-membered-ring oxonium ion.[3,7,10,11] The second mechanism involves a three-membered bridged ion similar to the intermediates suggested for other examples of electrophilic additions to double bonds.[5,12,13] It is fair to say that no data have been presented which un-

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(2) Alfred P. Sloan Research Fellow, 1965–1967.

(3) A. T. Blomquist and J. Wolinsky, *J. Amer. Chem. Soc.*, **79**, 6025 (1957).

(4) E. E. Smissman and R. E. Mode, *ibid.*, **79**, 3447 (1957).

(5) L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwarz, *ibid.*, **85**, 47 (1963).

(6) M. Hellin, M. Davidson, D. Lumbroso, P. Giuliani, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 2974 (1964).

(7) N. A. LeBel, R. N. Liesemer, and E. Mehemedbasich, *J. Org. Chem.*, **28**, 615 (1963).

(8) A. Streitwieser, Jr., and S. Andreadas *J. Amer. Chem. Soc.*, **80**, 6553 (1958); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957); H. Weiner and R. Sneen, *ibid.*, **84**, 3599 (1962); **87**, 292 (1965).

(9) M. Schwarz, unpublished observation.

(10) L. Bernardi and A. Leone, *Tetrahedron Lett.*, No. 10, 499 (1964).

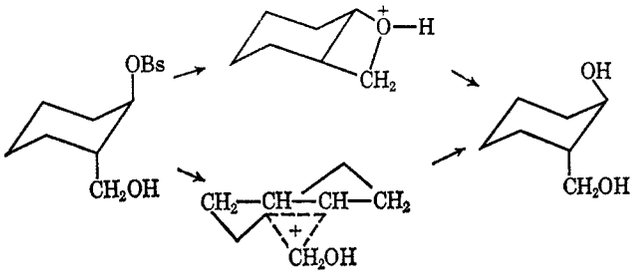
(11) E. Smissman, R. A. Schnettler, and P. S. Portoghese, *J. Org. Chem.*, **30**, 797 (1965).

(12) K. C. Murdock and R. B. Angier, *J. Amer. Chem. Soc.*, **84**, 3758 (1962).

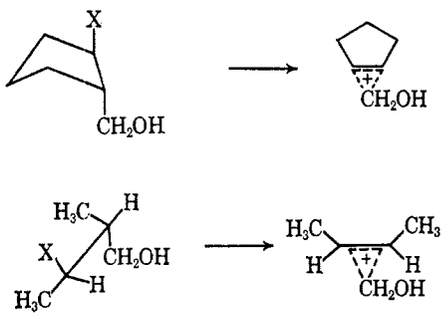
(13) G. Fodor and I. Tomoskozi, *Rev. Chim.* (Bucharest), **7**, 835 (1962).

ambiguously implicate either of these intermediates in the Prins reaction, but the stereospecific formation of two bicyclic alcohol side products in the Prins reaction with cyclohexene cannot be rationalized in terms of four-membered-ring oxonium ions.[14,15]

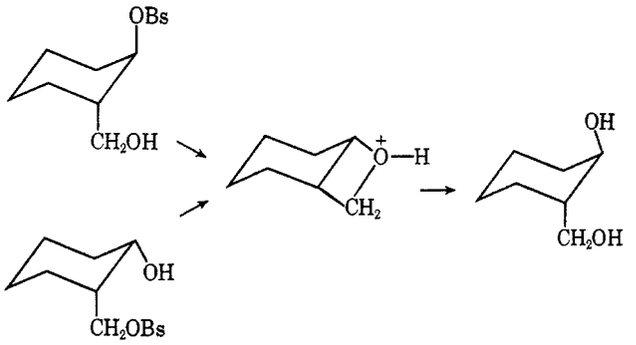
As a general approach to the mechanism of the Prins reaction we have attempted to generate the possible intermediates in solvolysis reactions and discern their intervention from the structures and distribution of the products. This approach was successful in demonstrating that the bicyclic alcohols formed in the Prins reaction of cyclohexene could arise from a common intermediate[15] and further that a mechanism for the Prins reaction in acetic acid involving six-membered acetoxonium ions is quite unlikely.[16] In an earlier study of the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate, an unusually large fraction of retention of configuration was observed.[5] It was suggested that the diol of retained configuration could have been formed from the intermediate responsible for stereoselective *trans* addition in the Prins reaction.[5]



At the time these experiments were initiated it appeared that a distinction between the three-membered bridged ion and the four-membered oxonium ion should be possible since the oxonium ion would be capable of maintaining optical activity but the three-membered cyclic ion would not. This latter conclusion is now suspect. However, more promising compounds for displaying a racemic intermediate are *threo*-2-methyl-1-hydroxy-3-butyl arensulfonates and *trans*-2-hydroxymethylcyclopentyl arenesulfonates.



It was also of interest to examine the product from the solvolysis of *cis*-2-hydroxycyclohexylcarbinyl brosylate. If the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate produces in part a four-membered cyclic oxonium ion which is responsible for the formation of the *trans*-2-hydroxymethylcyclohexanol, then it seems reasonable that *cis*-2-hydroxycyclohexylcarbinyl brosylate should give the same oxonium ion which



would be evidenced by the formation of some *trans*-2-hydroxymethylcyclohexanol.

Some of the above solvolysis reaction were examined in an effort to detect, in simplest terms, the 1,2 migration of a hydroxymethyl group. In an effort to find another system which might show this process we examined the solvolysis of the monotosylate of 2,2-dimethyl-1,3-propanediol. Although this neopentyl system is not one which would be derived by a Prins reaction, it offers the opportunity to measure the migratory aptitude of the hydroxymethyl group compared with that of a methyl group.

Synthesis.—Optically active *trans*-2-hydroxymethylcyclohexanol was obtained from the hydroboration of 1-hydroxymethylcyclohexene with the trialkyldiborane obtained from (−)-α-pinene followed by oxidation with hydrogen peroxide.[17] The absolute configuration of the (−)-*trans*-2-hydroxymethylcyclohexanol obtained in this manner was established as 1*R*:2*S*. A sample of *trans*-2-hydroxycyclohexanecarboxylic acid was partially resolved *via* the brucine salt.[18] The (+)-*trans*-2-hydroxycyclohexanecarboxylic acid, which has been shown to have the 1*S*:2*S* configuration,[18] was esterified with diazomethane and reduced with lithium aluminum hydride to yield (1*S*:2*R*)-(+)-*trans*-2-hydroxymethylcyclohexanol. The optically active *trans*-2-hydroxymethylcyclohexanol was converted into the required brosylate as previously described.[16]

The required arenesulfonate of *threo*-2-methyl-3-hydroxybutanol was prepared by a sequence involving the hydroboration of the benzyl ether of tiglic alcohol with triisopinocampheyldiborane followed by oxidation with hydrogen peroxide to afford *threo*-2-methyl-3-hydroxybutyl benzyl ether. The desired ether was contaminated with approximately 30% isomeric 2-hydroxy-2-methylbutyl benzyl ether from which it was separated by preparative vapor phase chromatography. Although the *threo*-2-methyl-3-hydroxybutyl benzyl ether obtained in this manner was optically active, treatment with β-naphthalenesulfonyl chloride afforded a crystalline naphthalenesulfonate which showed only a trace of optical activity. Hydrogenolysis of this material proceeded with some difficulty to afford the desired hydroxy β-naphthalenesulfonate as an oil.

The required *trans*-2-hydroxymethylcyclopentyl β-naphthalenesulfonate was prepared by the diborane reduction of the β-naphthalenesulfonate of methyl *trans*-

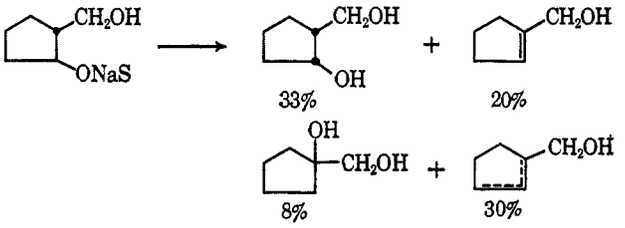
(14) L. J. Dolby, *J. Org. Chem.*, **27**, 2971 (1962).
(15) L. J. Dolby and M. J. Schwarz, *ibid.*, **28**, 1456 (1963).
(16) L. J. Dolby and M. J. Schwarz, *ibid.*, **30**, 3581 (1965).
(17) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 1071 (1964); H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).
(18) J. Sanchez Real and J. Pascual, *An. Real Soc. Espan. Fis. Quim., Ser. B*, **49**, 445 (1953); J. Faixat, A. Fevrer, and J. Pascual, *ibid.*, **57**, 705 (1961); *Chem. Abstr.*, **57**, 5812 (1962).

2-hydroxycyclopentanecarboxylate. The methyl *trans*-2-hydroxycyclopentanecarboxylate was obtained by the sodium borohydride reduction of a mixture of 2-carboethoxycyclopentanone and 2-carbomethoxycyclopentanone which resulted in a mixture of the *cis*- and *trans*-hydroxy esters. The mixed hydroxy esters were separated by fractional distillation into *cis* and *trans* isomers and transesterification with methanol of the *trans*-hydroxy ester mixture afforded pure methyl *trans*-2-hydroxycyclopentanecarboxylate which was converted into the β-naphthalenesulfonate in the usual manner. The remaining arenesulfonate, 3-hydroxyl-2,2-dimethylpropyl tosylate, was prepared by treating the parent diol with a limited amount of *p*-toluenesulfonyl chloride.

Results

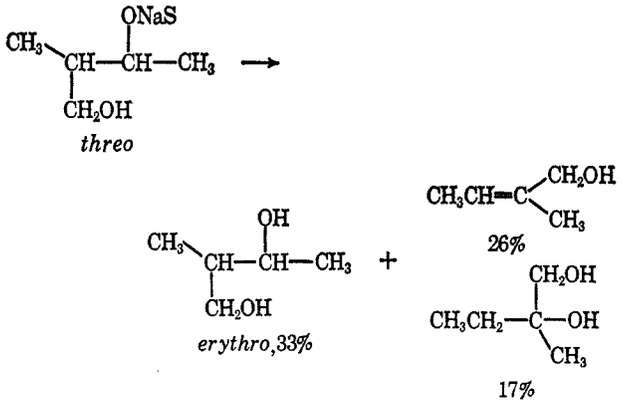
Optically active *trans*-2-hydroxymethylcyclohexyl brosylate was solvolyzed in aqueous acetone containing enough phosphate buffer to maintain the pH at 6 at the end of the reaction. The solvolysis gave 3-hydroxymethylcyclohexene in 60% yield and a mixture of *cis*- and *trans*-2-hydroxymethylcyclohexanols in 30% yield of which 35% was the *trans* isomer. Another component, 1-hydroxymethylcyclohexanol (8%) was identified by comparison with an authentic sample. The unsaturated alcohol and the two 1,3-diols were reported products from the solvolysis in aqueous dioxane and 1-hydroxymethylcyclohexanol is undoubtedly the unidentified compound previously reported.[5] The 1,3-diols were not directly separable by vapor phase chromatography but were collected as a mixture. The mixture of 1,3-diols was converted into the corresponding acetonides which are easily separated by vapor phase chromatography. Since this work was carried out with only partially resolved material, it was not possible to compare the optical activity of the *trans*-2-hydroxymethylcyclohexanol obtained from solvolysis with that of the starting *trans*-2-hydroxymethylcyclohexanol. Accordingly, a sample of the *trans*-2-hydroxymethylcyclohexyl brosylate used in the solvolysis experiment was cleaved with sodium amalgam[19] to regenerate optically active *trans*-2-hydroxymethylcyclohexanol which was converted into the acetonide and compared with the solvolysis product. The acetonides of the optically active *trans*-2-hydroxymethylcyclohexanols have specific rotations much smaller than and opposite in sign to those of the parent diols. Thus it was convenient to measure the rotations of the acetonides in aqueous ethanol which was 0.2 *M* in strong acid and resulted in rapid and quantitative hydrolysis of the acetonides to the parent diol. The specific rotations at four wavelengths of the hydrolyzed acetonides of *trans*-2-hydroxymethylcyclohexanol from the sodium amalgam cleavage and solvolysis of the optically active *trans*-2-hydroxymethylcyclohexyl brosylate were indistinguishable (see Experimental Section). This result establishes that the *trans*-2-hydroxymethylcyclohexanol obtained from the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate is formed without the intervention of a racemic intermediate.

The solvolysis of *trans*-2-hydroxymethylcyclopentyl β-naphthalenesulfonate was carried out as described for *trans*-2-hydroxymethylcyclohexyl brosylate. Four of the ten peaks observed in the vapor phase chromatogram of the products accounted for 91% of the peak area. No *trans*-2-hydroxymethylcyclopentanol was found in the products although it was readily separated from the other products by vapor phase chromatography.



The *cis*-2-hydroxymethylcyclopentanol was identified by comparison with an authentic sample and the other products were identified from their spectral properties. The only significant feature of this result is that the substitution product is formed with complete inversion of configuration as expected in a normal solvolytic process.

The solvolysis of *threo*-2-methyl-1-hydroxy-3-butyl β-naphthalenesulfonate gave products similar to those obtained in the solvolysis of *trans*-2-hydroxymethylcyclopentyl β-naphthalenesulfonate.



The isomeric 1,3-diols were not directly separable by vapor phase chromatography and the 1,3-diol from the solvolysis reaction was collected by vapor phase chromatography and converted into the corresponding cyclopentanone ketal. Analysis of the cyclopentanone ketals which were readily separable by vapor phase chromatography indicated that the product 1,3-diol from the solvolysis reaction was 95% *erythro*-2-methyl-1,3-butanediol and 5% *threo*-diol. Sodium amalgam cleavage of the starting arenesulfonate gave a mixture of diols containing 97% *threo*-diol and 3% *erythro*-diol. Thus the solvolysis proceeds with essentially complete inversion of configuration.

The solvolysis of *cis*-2-hydroxycyclohexylcarbinyl brosylate affords 17% 2-methylcyclohexanone, 76% *cis*-2-hydroxymethylcyclohexanol, and 7% *trans*-1-methyl-1,2-cyclohexanediol identified by comparison with an authentic sample. No *trans*-2-hydroxymethylcyclohexanol was formed.

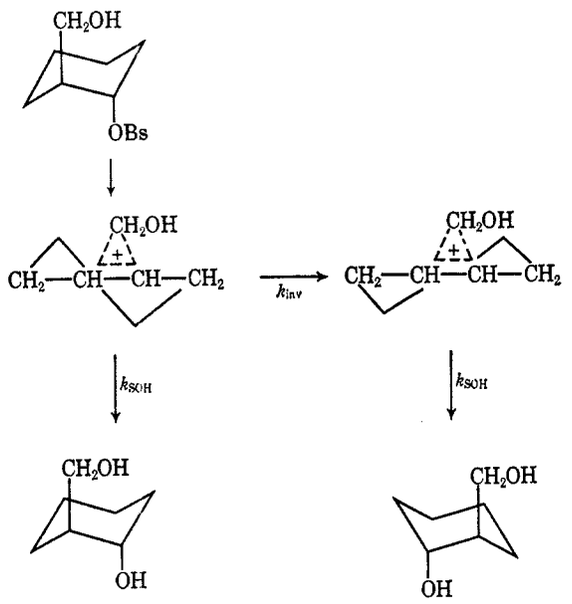
The solvolysis of 2,2-dimethyl-3-hydroxypropyl tosylate in water with an acetate buffer gave only 2-methylbutanal and a small amount of 2,2-dimethyl-1,3-propanediol. When the solvolysis was carried out

(19) P. Levine and J. Compton, *J. Amer. Chem. Soc.*, **57**, 2306 (1935); K. Freudenberg and F. Braums, *Ber.*, **55**, 3233 (1922); C. A. Grob and D. A. Prins, *Helv. Chim. Acta*, **28**, 840 (1945).

using a phosphate buffer at slightly higher pH, the reaction produced several more products. It appears that the solvolysis proceeds almost exclusively by methyl migration. It may be that the primary products of the reaction are mainly unsaturated alcohols which are rearranged to 2-methylbutanal in the more acidic acetate buffer system.

Discussion

The observation that the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate affords the *trans*-diol with complete retention of optical activity may be taken as evidence for a four-membered oxonium-ion intermediate. However, another analysis is possible. Recent investigation by Berson and his collaborators[20] has established that a carbonium ion may be captured by solvent before it undergoes even a subtle conformational change. Thus in the case of *trans*-2-hydroxymethylcyclohexyl brosylate it is not certain that the three-membered bridged intermediate would result in racemization. The initially formed ion must undergo conformational change or capture by solvent would be expected to give the *trans*-diol by *trans*-diaxial opening resulting in optically active *trans*-diol of the same configuration as the starting hydroxy brosylate.



The corresponding bridged intermediates which could be formed from *trans*-2-hydroxymethylcyclopentyl and *threo*-1-hydroxy-2-methyl-3-butyl arenesulfonates would be racemic or present only a small barrier to racemization. However, since these arenesulfonates solvolyze with complete inversion of configuration, it is not possible to draw any further conclusions regarding the intervention of three-membered bridged intermediates in the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate.

The solvolysis of the monotosylate of 2,2-dimethyl-1,3-propanediol also failed to reveal any products resulting from the 1,2 migration of a hydroxymethyl group. In this case, migration of a hydroxymethyl group would have resulted in the formation of unsaturated 3-methylbutanols or 3-methylbutanal which could not be detected among the solvolysis products.

The solvolysis of *cis*-2-hydrocyclohexylcarbinyl brosylate was examined to provide a direct test for the intervention of four-membered oxonium ions in the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate. Both arenesulfonates could give in part the same four-membered cyclic oxonium ion and there should be some overlap in the products of the reaction. In particular, if the *trans*-2-hydroxymethylcyclohexanol obtained from *trans*-2-hydroxymethylcyclohexyl brosylate is properly ascribed to a four-membered cyclic oxonium ion, then the solvolysis of *cis*-2-hydroxycyclohexylcarbinyl brosylate should also afford some *trans*-diol.

In fact, the solvolysis of *cis*-2-hydroxycyclohexylcarbinyl brosylate does not give any of the *trans*-diol and this result weighs heavily against the intervention of four-membered cyclic oxonium ion intermediates in these reactions. It might be argued that *cis*-2-hydroxycyclohexylcarbinyl brosylate and *trans*-2-hydroxylmethylcyclohexyl brosylate give different oxonium ions. Presumably the difference would be in the degree of bonding between the oxygen and the two carbons involved. If this is the case, the four-membered cyclic oxonium ions are grossly different from five- and six-membered cyclic oxonium ions.[21]

Experimental Section[22]

Methyl (+)-*trans*-2-Hydroxycyclohexanecarboxylate.—A sample of (±)-*trans*-2-hydroxycyclohexanecarboxylic acid was partially resolved as described by Real and Pascual[18] to afford (+)-*trans*-2-hydroxycyclohexanecarboxylic acid: mp 104–106°; $[\alpha]_D$ 26.8 (*c* 0.155, chloroform). The acid (11.3 g) was esterified with diazomethane to afford 13.3 g of methyl (+)-*trans*-2-hydroxycyclohexanecarboxylate: bp 90–93° (2.5 mm) [lit.[5] bp 100–103° (6 mm)]; $[\alpha]_D$ 27.0 (*c* 0.426, ethanol).

Lithium Aluminum Hydride Reduction of Methyl (+)-*trans*-2-Hydroxycyclohexanecarboxylate.—The ester obtained above was reduced with lithium aluminum hydride as previously described[5] to afford (+)-*trans*-2-hydroxymethylcyclohexanol: bp 128–130° (2.3 mm) [lit.[5] bp 122–124° (2 mm)]; $[\alpha]_D$ 21.8 (*c* 0.913, ethanol).

(−)-*trans*-2-Hydroxymethylcyclohexanol.—In a dry 5-l. three-necked flask equipped with a thermometer, pressure-equalizing dropping funnel, stirrer, and a condenser was placed 1308 ml of 0.87 *M* diborane (1.13 mol) in tetrahydrofuran. The flask was cooled in a Dry Ice–acetone bath while 462 g (3.4 mol) of α-pinene in 420 ml of tetrahydrofuran was added dropwise during 20 min while purging with dry nitrogen. The reaction mixture was stirred at 0° for 3 hr after which a solution of 63 g (0.56 mol) of 1-hydroxymethylcyclohexene in 135 ml of tetrahydrofuran was slowly added (hydrogen evolution). The resulting solution was stirred at 5° for 10 hr, then treated with water to decompose the residual hydride.

The reaction mixture was treated with 453 g of 30% hydrogen peroxide at 30° while the pH was maintained at 7–9 by the concurrent addition of 3 *M* sodium hydroxide.[23] After stirring for 30 min, the mixture was refluxed overnight. Most of the solvent was removed by distillation and the organic layer was separated and dried over magnesium sulfate. Isopinocampheol and other

(20) J. A. Berson and M. S. Poonian, *J. Amer. Chem. Soc.*, **88**, 170 (1966); J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964); J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964); J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964).

(21) H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *ibid.*, **75**, 4778 (1953); D. S. Noyce and B. N. Bastian, *ibid.*, **82**, 1246 (1960); S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

(22) All melting points and boiling points are uncorrected. Distillations were carried out with a 130-cm modified Podbielniak tantalum spiral column or a 92-cm spinning-band column. Proton magnetic resonance spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as internal standard. Aerograph Models A-90-P and Autoprep A-700 gas chromatographs were used for vapor phase chromatography. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter.

(23) H. C. Brown and K. A. Kelbys, *J. Amer. Chem. Soc.*, **86**, 1791 (1964).

terpenoid material was distilled under reduced pressure to leave a pot residue which showed a postive flame test for boron. Methanol was added to the residue and its was distilled through a 50-cm Vigreux column until boron could not be detected in the distillate. Fractional distillation gave a forerun containing terpenoid materials and 47 g (65%) of (−)-*trans*-2-hydroxymethylcyclohexanol, bp 142–142.5° (13 mm) [lit. bp 122–124° (2 mm)]. The infrared and nmr spectra were identical with those of an authentic sample of *trans*-diol. The rotation of the diol was measured at five wavelengths: $[\alpha]_{578}$ −8.7°, $[\alpha]_{546}$ −10.0, $[\alpha]_{436}$ −17.4°, $[\alpha]_{365}$ −27.2°, and $[\alpha]_{313}$ −40.7° (*c* 0.541, ethanol).

Optically Active *trans*-2-Acetoxymethylcyclohexyl Brosylate.—A sample of (−)-*trans*-2-hydroxymethylcyclohexanol (5.40 g) was converted into the acetate brosylate as previously described.[16] Crystallization of the crude product afforded 7.0 g (43%) of *trans*-2-acetoxymethylcyclohexyl brosylate, mp 79–93°, which showed spectral properties identical with those of an authentic sample of racemic material. The broad melting range is undoubtedly caused by the fact that only partially resolved diol was used.

(−)-*trans*-2-Hydroxymethylcyclohexyl Brosylate.—The optically active *trans*-2-acetoxymethylcyclohexyl brosylate (7.0 g) obtained above was subjected to methanolysis as previously described.[5] Crystallization from ether–petroleum ether (bp 30–60°) yielded 4.52 g of the hydroxy brosylate (72%) in the first crop and a second small crop of much greater otpical activity. These two crops were combined and crystallized again to yield two crops. The first crop (5.06 g) showed mp 63–66°, $[\alpha]_{578}$ −2.25 (*c* 0.71, ethanol), and the second crop (0.5 g) showed mp 55–60°, $[\alpha]_{578}$ −30.9 (*c* 0.90, ethanol). These two crops were dissolved and combined to yield the (−)-*trans*-2-hydroxymethylcyclohexyl brosylate, $[\alpha]_{578}$ −3.07 (*c* 2.70, ethanol), employed in the solvolysis experiment.

***cis*- and *trans*-2-Carbomethoxycyclopentanols.**—A mixture of 2-carbomethoxycyclopentanone and 2-carbethoxycyclopentanone was reduced with sodium borohydride as described by Pascual.[24] The *cis* and *trans* mixed esters were separated using 5 ft × 0.25 in. column packed with 20% Carbowax 20M on firebrick. Fractionation of the crude product from the reduction of 16 g of mixed 2-carboalkoxycyclopentanones afford the following: fraction 1, 7.72 g, bp 92–100° (10 mm), 5.2% *trans;* fraction 2; bp 100–105° (10 mm), 14.5% *trans;* fraction 3, 8.34 g, bp 105–106° (10 mm), 48% *trans;* fraction 4, 4.90 g, bp 72–74° (0.35 mm), 95% *trans;* and pot residue, 9.0 g. A sample of *trans* rich hydroxy esters was transesterified with methanol–perchloric acid and separated by preparative vapor phase chromatography to afford pure *trans*-2-carbomethoxycyclopentanol, n^{25}D 1.4582 (lit.[25] n^{25}D 1.4569), and some *cis*-2-carbomethoxycyclopentanol. The 3,5-dinitrobenzoate of *cis*-2-carbomethoxycyclopentanol was prepared and melted at 98.5–99.5° [lit.[26] mp 103–103.5°].

***cis*-2-Hydroxymethylcyclopentanol** was prepared by lithium aluminum hydride reduction of the mixed ethyl and methyl esters of *cis*-2-hydroxycyclopentanecarboxylic acid. The material distilled at 123–125° (10 mm) [lit.[26] bp 160–165° (30 mm)] and melted at 31–33° after crystallization from ether.

Anal. Calcd for $C_6H_{12}O_2$: C, 62.00; H, 10.47. Found: C, 61.64; H, 10.36.

***trans*-2-Carbomethoxycyclopentyl β-Naphthalenesulfonate.**—A stirred solution of 10 g of *trans*-2-carbomethoxycyclopentanol in dry pyridine (100 ml) was cooled to 0° and treated with 28 g of β-naphthalenesulfonyl chloride. The reaction mixture was stirred overnight at room temperature and processed in the usual manner. The crude product was crystallized from ether to afford 12.0 g (52%) of *trans*-2-carbomethoxycyclopentyl β-naphthalenesulfonate, mp 69–79°, unchanged on further crystallizations.

Anal. Calcd for $C_{17}H_{18}SO_5$: C, 61.06; H, 5.39. Found: C, 60.87; H, 5.30.

***trans*-2-Hydroxymethylcyclopentyl β-Naphthalenesulfonate.**—In a three-necked flask fitted with a dropping funnel, condenser, and drying tube was placed 8.5 g of *trans*-2-carbomethoxycyclopentyl β-naphthalenesulfonate in dry tetrahydrofuran (40 ml). The reaction vessel was cooled in an ice bath and 125 ml of diborane (1 *M*) in tetrahydrofuran was added. The reaction mixture was refluxed for 2 hr and hydrolyzed with water followed by 15 ml of 6 *N* hydrochloric acid. Most of the solvent was evaporated, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and dried over magnesium sulfate. The crude product obtained in nearly quantitative yield was crystallized at low temperature from carbon tetrachloride, but the material melted upon warming to room temperature.

***trans*-2-Acetoxymethylcyclopentyl β-naphthalenesulfonate** was prepared by acetylating some of the material obtained above with acetyl chloride and pyridine. The material crystallized from ether–hexane and showed mp 85.5–86.5°.

Anal. Calcd for $C_{18}H_{20}SO_5$: C, 62.06; H, 5.70. Found: C, 62.28; H, 5.93.

***erythro*-2-Methyl-1,3-butanediol.**—In a stainless steel bomb was placed 70 g of paraformaldehyde and a solution of 87 g of concentrated sulfuric acid and 206 ml of water. The sealed bomb was heated at 80° for 1 hr and then cooled in a Dry Ice–acetone bath. *trans*-2-Butene (88 g) was added and the sealed bomb was heated for 2 hr at 80–130° with rocking. The cooled bomb was opened and the reaction mixture was neutralized with aqueous sodium hydroxide after which it was continuously extracted with ether. Preparative vapor phase chromatography on a 10 ft × 3/8 in. column packed with 10% cyanoethoxypropane on firebrick afforded *cis*-4,5-dimethyl-1,3-dioxane, which showed the same spectral properties noted previously.[5]

A 2.0-g sample of *cis*-4,5-dimethyl-1,3-dioxane was refluxed for 7 days with methanolic sulfuric acid (0.1 *N*). The sulfuric acid was neutralized with sodium bicarbonate and the mixture was filtered and concentrated. The residue was purified by vapor phase chromatography on a 10 ft × 0.25 in. column packed with cyanoethyl sucrose in Chromosorb G to afford *erythro*-2-methyl-1,3-butanediol. The nmr spectrum of the material obtained in this manner exhibited four signals ascribed to the two methyl groups (τ 8.77, 8.87, 9.07, and 9.18).

Anal. Calcd for $C_5H_{12}O_2$: C, 57.76; H, 11.54. Found: C, 57.51, H, 11.43.

Cyclopentanone Ketal of *erythro*-2-Methyl-1,3-butanediol.—A sample of the diol obtained above was heated with a 2 *M* excess of cyclopentanone at 80° overnight. Dry benzene was added and the water–benzene azeotrope was distilled through the Podbielniak column. The residue was subjected to glpc on a 20 ft × 0.25 in. column packed with silicone XF 1150 on Chromosorb P. The material contained 96% of the *cis* ketal (from the *erythro*-diol) and 4% of its epimer. The nmr spectrum of the *cis* ketal showed two signals at τ 8.92 and 9.01 (6 H) ascribed to the two methyl groups and a multiplet at τ 8.3 ascribed to the cyclopentane protons.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.65; H, 10.67. Found: C, 70.55; H, 10.54.

Tiglic alcohol was prepared by the reduction of tiglaldehyde using aluminum hydride prepared *in situ* as described by Jorgenson.[27] Tiglic alcohol, bp 133–139° (lit.[28] bp 133–140°), was obtained in 74% yield.

***threo*-2-Methyl-1,3-butanediol.**—Hydroboration–oxidation of tiglic alcohol was carried out in the conventional manner.[29] The crude product was processed as described for (−)-*trans*-2-hydroxymethylcyclohexanol. Distillation afforded slightly impure diol, bp 95–114° (18 mm), in 76% yield. Vapor phase chromatography on a 5 ft × 0.25 in. column packed with 20% Carbowax 20M showed an impurity (5%) with the same retention time as 2-methyl-1,2-butanediol. The nmr spectrum of the pure *threo*-2-methyl-1,3-butanediol showed peaks at τ 8.82, 8.92, 9.13, and 9.25 attributed to the two methyl groups. Mixtures of the *erythro*- and *threo*-diols show eight peaks in the region τ 8.8–9.3.

Anal. Calcd for $C_5H_{12}O_2$: C, 57.76; H, 11.54. Found: C, 57.68; H, 11.83.

The cyclopentanone ketal of *threo*-2-methyl-1,3-butanediol was prepared as described for the *erythro* isomer. The nmr spectrum showed a doublet (3 H) at τ 8.93, J = 7 cps, and a doublet (3 H) at τ 9.02, J = 7 cps, ascribed to the two methyl groups. The cyclopentane protons appeared as a multiplet at τ 8.3.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.65; H, 10.67. Found: C, 70.59; H, 10.65.

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Tiglyl Benzyl Ether.—To a stirred mixture of 16 g of sodium hydride and 590 ml of dry N,N-dimethylformamide was added 52.5 g of tiglic alcohol. Benzyl chloride (130 g) was slowly added to the resulting suspension and the mixture was stirred for 36 hr. The mixture was hydrolyzed with water and the crude product was isolated by extraction with hexane. Fractional distillation afforded 46 g of pure tiglyl benzyl ether, bp 126–128° (21 mm).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.20; H, 9.23.

(−)-*threo*-2-Methyl-3-hydroxybutyl Benzyl Ether.—Tiglyl benzyl ether (46 g) was subjected to hydroboration–oxidation as described for the preparation of (−)-*trans*-2-hydroxymethylcyclohexanol. The crude product was fractionally distilled to yield a forerun of terpene material and the following fractions: fraction 1, 7.5 g, bp 100–105° (3 mm); fraction 2, 19 g, bp 105–114° (3 mm); fraction 3, 24 g, bp 114–140° (1.5 mm). The first two fractions were separated by preparative glpc on a 10 ft × 3/8 in. column packed with 5% Carbowax 20M on Chromosorb G. A total of 11 g (22%) of (−)-*threo*-3-hydroxy-2-methylbutyl benzyl ether, $[\alpha]_{578}$ 5.16 (*c* 3.94, CCl_4), was obtained along with 5 g (10%) of 2-hydroxy-2-methylbutyl benzyl ether. The nmr spectrum of the *threo*-3-hydroxy-2-methylbutyl benzyl ether showed normal absorption for the benzyloxy group and four sharp signals (6 H) at τ 9.23, 9.12, 8.98, and 8.89 ascribed to the two methyl groups.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.29; H, 9.35. Found: C, 74.16; H, 9.13.

The nmr spectrum of the 2-hydroxy-2-methyl-1-butyl benzyl ether showed normal benzyloxy absorption, a triplet (3 H) at τ 9.15 (J = 7 cps), and a singlet (3 H) at τ 8.92 ascribed to the two methyl groups.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.29; H, 9.35. Found: C, 74.13; H, 9.18.

2-Methyl-1,2-butanediol.—A mixture of 1.2 g of the 2-hydroxy-2-methyl-1-butyl benzyl ether and 0.4 g of 30% palladium on carbon in 40 ml of ethanol was hydrogenated at room temperature. The theoretical amount of hydrogen was absorbed overnight to furnish a quantitative yield of the diol which was purified by vapor phase chromatography using a 5 ft × 0.25 in. column pcked with 20% Carbowax 20M on firebrick. The nmr spectrum showed a singlet at τ 8.92 (3 H) and a triplet τ 9.10 (J = 7 cps) (3 H), attributed to the two methyl groups. The bis(*p*-nitrobenzoate) derivative melted at 106–107° (lit.[30] mp 107–109°).

The β-naphthalenesulfonate of *threo*-2-methyl-3-hydroxybutyl benzyl ether was obtained from the corresponding alcohol by the action of β-naphthalenesulfonyl chloride in pyridine. The arensulfonate was obtained in 49% yield as plates, mp 36.5–38.5°, on crystallization from ether–hexane. The crystalline material showed only very slight optical activity.

Anal. Calcd for $C_{22}H_{24}SO_4$: C, 68.72; H, 6.29. Found: C, 68.78; H, 6.48.

***threo*-1-Hydroxy-2-methyl-3-butyl β-Naphthalenesulfonate.**—A mixture of 5.5 g of the β-naphthalenesulfonate of *threo*-2-methyl-3-hydroxybutyl benzyl ether, 15 drops of 2% palladium chloride in 2 *N* hydrochloric acid, and 0.74 g of 30% palladium on carbon in ethyl acetate (70 ml) was hydrogenated at room temperature. After 5 hr the theoretical amount of hydrogen had been absorbed. The spectra of the crude product indicated that some of the material had been acetylated after hydrogenolysis and the entire crude product was subjected to methanolysis as previously described.[5] The product from the methanolysis reaction showed the anticipated spectra properties but it was not obtained in crystalline form.

2-Methyl-2-hydroxymethylpropyl Tosylate.—A solution of 2,2-dimethyl-1,3-propanediol in 3 ml of pyridine was cooled to 0° and a solution of 1.22 g of *p*-toluenesulfonyl chloride in pyridine (4 ml) was added with stirring. The mixture was stored at room temperature for 1.75 hr and processed in the usual manner. The crude product was chromatographed over silica gel with chloroform to give 400 mg (16%) of the ditosylate, mp 117–118° (lit.[31] mp 116–120°) after crystallization from chloroform–petroleum ether (bp 30–60°). Continued elution with chloroform afforded the monotosylate, 810 mg (50%), which could not be crystallized.

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.81; H, 6.97. Found: C, 55.74; H, 7.00.

Solvolysis of (−)-*trans*-2-Hydroxymethylcyclohexyl Brosylate.—A solution of 4.0 g of the hydroxy brosylate, 80 ml of acetone, and 100 ml of 1.26 *M* phosphate buffer (pH 6.8) was heated under reflux for 30 hr and processed as previously described.[5] The product mixture contained 60% 3-hydroxymethylcyclohexene, 30% *cis*- and *trans*-2-hydroxymethyl cyclohexanols, 8% 1-hydroxymethylcyclohexanol identified by comparison with an authentic sample prepared previously,[16] and 2% unidentified products. The mixture of *cis*- and *trans*-2-hydroxymethylcyclohexanols (0.163 g, 11%) was collected and converted into the corresponding acetonides which were separated as previously described.[16] Because the rotation of the optically active acetonides are much smaller and opposite in sigh to those of the corresponding diols, the acetonide was hydrolyzed *in situ* using 80% ethanol–water 0.2 *M* in *p*-toluenesulfonic acid. This solvent caused rapid and complete hydrolysis of the acetonide. The rotation of the diol was measured at five wavelengths: $[\alpha]^{22}_{578}$ −6.85°, $[\alpha]^{22}_{546}$ −7.77°, $[\alpha]^{22}_{436}$ −12.6°, $[\alpha]^{22}_{365}$ −19.2° (*c* 2.51).

Sodium Amalgam Cleavage of (−)-*trans*-2-Hydroxymethylcyclohexyl Brosylate.—A solution of 0.45 g of the hydroxy brosylate in 30 ml of dry methanol was stirred overnight with 13 g of 4% sodium amalgam.[32] The resulting mixture was made slightly acidic with anhydrous hydrogen chloride and then basified to pH with anhydrous potassium carbonate. The mixture was filtered and the solid was extracted with hot ether and combined with the filtrate. Evaporation of the organic extracts and vapor phase chromatography afforded 0.083 g (50%) of (−)-*trans*-2-hydroxymethylcyclohexanol which was converted into the acetonide. The rotation of the diol resulting from the *in situ* hydrolysis of the acetonide was measured at four wavelengths: $[\alpha]^{22}_{578}$ −6.89°, $[\alpha]^{22}_{546}$ −7.84°, $[\alpha]^{22}_{436}$ −13.2°, $[\alpha]^{22}_{365}$ −20.1° (*c* 4.61).

Solvolysis of *threo*-1-Hydroxy-2-methyl-3-butyl β-Naphthalenesulfonate.—A solution of 2.0 g of the arenesulfonate, 60 ml of acetone, 66 ml of 1.26 *M* phosphate buffer (pH 6.8), and 50 ml of water was refluxed for 60 hr. The acetone was distilled under a fractionating column and the aqueous residue was continuously extracted with ether. Vapor phase chromatography of the product on 10 ft × 0.25 in. column packed with 5% cyanoethylsucrose on Chromosorb G showed six products. The following products were isolated and identified (the yields correspond to the percentage of the peak area): tiglic–angelic alcohol mixture (26%), 2-methyl-2-hydroxybutanol (17%), 2-methyl-3-hydroxybutanol. The 1,3-diol mixture (119 mg) isolated by glpc was dissolved in benzene and cyclopentanone after which some of the benzene was distilled to yield the cyclopentanone ketal. The ketal was subjected to glpc on a 20 ft × 0.25 in. column packed with 10% silicone XF 1150 on Chromosorb P and found to contain 95% of ketal derived from the *erythro*-diol and 5% of its diastereomer. A sample of the arenesulfonate was cleaved with sodium amalgam and the diol obtained was converted into the cyclopentanone ketal which was found to contain 97% ketal derived from the *threo*-diol and 3% isomeric ketal.

Solvolysis of *trans*-2-Hydroxymethylcyclopentyl β-Naphthalenesulfonate.—A solution of 4 g of the arenesulfonate, 100 ml of acetone, 120 ml of 1.26 *M* phosphate buffer (pH 6.8), and 60 ml of water was heated under reflux for 55 hr. The reaction mixture was processed as described for the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate. Vapor phase chromatography on a 5 ft × 0.25 in. column packed with 20% Carbowax 20M on firebrick at 200° indicated the presence of ten components, but the mixture did not contain any *trans*-2-hydroxymethylcyclopentanol. *cis*-2-Hydroxymethylcyclopentanol compressed 33% of the material and three other components were tentatively identified. The first eluted component (30%) appeared to be 2- or 3-hydroxymethylcyclopentene: nmr, multiplet at τ 4.35 (2 H), vinyl protons; doublet at τ 6.60 (2 H), J = 6 cps, carbinyl protons. The second component (20%) appeared to be 1-hydroxymethylcyclopentene: nmr, multiplet at τ 4.48 (1 H), vinyl proton; singlet at τ 5.95 (2 H), carbinyl protons. The third component (8%) appeared to be 1-hydroxymethylcyclopentanol: nmr, singlet at τ 6.49 (2 H) carbinyl protons; broad singlet at τ 8.34 (8 H).

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Solvolysis of *cis*-2-Hydroxycyclohexylcarbinyl Brosylate.—A solution of 3.52 g of the hydroxy brosylate, prepared as previously described, 100 ml of acetone, 83 ml of 1.26 *M* phosphate buffer (pH 6.8), and 60 ml of water was refluxed for 151 hr. The reaction mixture was processed in the usual manner and glpc on a 5 ft × 0.25 in. column packed with 20% Carbowax 20M on firebrick gave three products (in order of elution): 2-methylcyclohexanone (17%) identified by comparison with an authentic sample, *cis*-2-hydroxymethyl cyclohexanol (76%), and *trans*-2-hydroxy-1-methylcyclohexanol (7%) identified by comparison with an authentic sample, mp 78–80° (lit.[33] mp 85°), prepared as previously described.[33] A component of shorter retention time than 2-methylcyclohexanone was found to be formed from acetone when exposed to the reaction solvent in the absence of the hydroxy brosylate.

Solvolysis of 2-Methyl-2-hydroxymethylpropyl Tosylate.—A mixture of 1.95 g of the tosylate and 50 ml of 0.4 *M* acetate buffer (pH 4) was heated in a sealed tube at 115° for 72 hr. The mixture was continuously extracted with ether and the ether was distilled under a factionating column. The residue was found to contain 95% 2-methylbutanal and 5% 2,2-dimethyl-1,3-propanediol by glpc using a 5 ft × 0.25 in. column packed with 5% SE 30 on Chromosorb W at 120°. An alliquot of the reaction mixture was treated with 2,4-dinitrophenylhydrazine solution to afford 2-methylbutanal 2,4-dinitrophenylhydrazone, mp 125–126° (lit.[34] mp 120°). The yield corresponded to 32% based on starting arenesulfonate. Another experiment afforded 2-methylbutanal 2,4-dinitrophenylhydrazone in 36% yield. A weighed sample of pure 2-methylbutanal gave the 2,3-dinitrophenylhydrazone in 36% yield.

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Registry No.—(−)-*trans*-2-hydroxymethylcyclohexyl brosylate, 16897-79-3; *cis*-2-hydroxymethylcyclopentanol, 1883-85-8; *trans*-2-carbomethoxycyclopentyl β-naphthalenesulfonate, 16897-81-7; *trans*-2-acetoxymethylcyclopentyl β-naphthalenesulfonate, 16897-82-8; *erythro*-2-methyl-1,3-butanediol, 16897-83-9; cyclopentanone ketal of *erythro*-2-methyl-1,3-butanediol, 16897-84-0; *threo*-2-methyl-1,3-butanediol, 16897-85-1; cyclopentanone ketal of *threo*-2-methyl-1,3-butanediol, 16897-86-2; tiglyl benzyl ether, 16897-87-3; (−)-*threo*-methyl-3-hydroxybutyl benzyl ether, 16897-88-4; 2-hydroxy-2-methyl-1-butyl benzyl ether, 16897-89-5; β-naphthalenesulfonate of *threo*-2-methyl-3-hydroxybutyl benzyl ether, 16897-90-8.

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Synthesis of γ- and δ-Chloroalkanesulfonamides *via* the Photorearrangement of N-Chlorosulfonamides

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The photorearrangement of N-*t*-butyl- and N-methyl-N-chloroalkanesulfonamide in benzene and in acid solution was studied with the object of preparing γ- and δ-chloroalkanesulfonamides, intermediates for sultam synthesis. In benzene, γ- and δ-chloroalkanesulfonamides were formed almost exclusively from N-*t*-butyl derivatives, while, in the reaction of N-methyl-N-chlorobutanesulfonamide, β-chlorobutanesulfonamide was apparently formed in addition to γ- and δ-chlorobutanesulfonamides. In acid solution (H_2SO_4–AcOH), on the other hand, the rate of formation of γ-chloro derivatives increased and that of β-chloro derivatives decreased owing to the relatively higher reactivity of the protonated sulfonamide radical for intramolecular hydrogen abstraction. The isolation of each rearranged product from the reactions was undertaken and N-*t*-butyl-γ-chlorobutanesulfonamide N-*t*-butyl-δ-chloropentanesulfonamide, and N-*t*-butyl-γ-chloropentanesulfonamide were obtained pure.

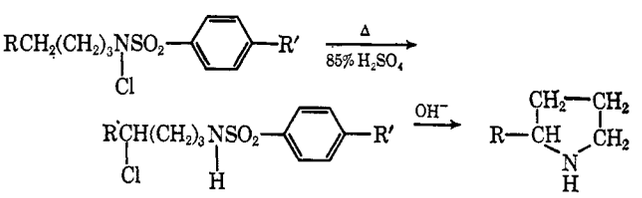
In studies on the free-radical rearrangement of N-halo compounds, the synthesis of pyrrolidine derivatives from N-haloamines (Hofmann–Löffler reaction[1]) and γ-lactone formation from N-haloamides[2–5] and N-haloimides[6] have been reported.

Although N-alkyl-N-chloroarylsulfonamides are reported to rearrange to N-δ-chloroalkyl derivatives[7] under similar reaction conditions as the Hofmann–Löffler reaction (Scheme I), the analogous rearrangement of N-alkyl-N-chloroalkanesulfonamides has not yet been reported.

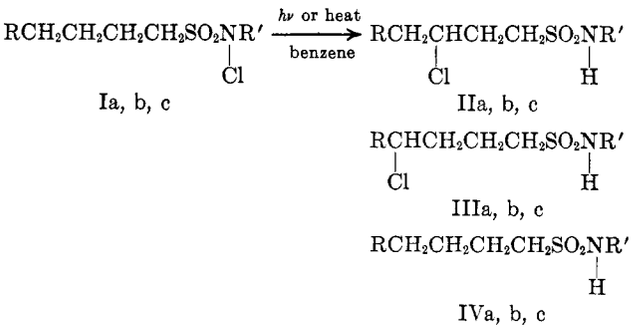
In a previous paper,[8] the authors reported that N-alkyl-N-chloroalkanesulfonamides readily rearrange to the corresponding chloroalkanesulfonamides under the influence of photoirradiation or heat (Scheme II).

The purpose of the present study was to investigate

SCHEME I



SCHEME II



a, R = H; R′ = *t*-C_4H_9
b, R = H; R′ = CH_3
c, R = CH_3; R′ = *t*-C_4H_9

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