tillation and separated into two components by gas chromatography on a silver nitrate–tetraethylene glycol column.[24] The major component showed strong bands at 700 and 3080 cm.$^{-1}$ in the infrared spectrum suggesting that the hydrocarbon contained a *cis*-disubstituted double bond and was therefore *cis*-bicyclo[3.3.0]oct-2-ene.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.86; H, 11.26.

The position of the double bond was confirmed by ozonolysis of a sample (0.20 g.) in 2 ml. of ethyl acetate and 8 ml. of acetic acid at 0° with one molar equivalent of ozone. Hydrogen peroxide (1 ml. of a 30% solution) was added to the cold solution of ozonide, and the mixture was warmed to 45° for 3 days. After addition of platinum black to destroy any remaining hydrogen peroxide, the acetic acid was removed on a rotary concentrator under reduced pressure. The product was shaken with sodium bicarbonate solution and ether. Ether extraction of the acidified bicarbonate layer gave 0.17 g. of acid (53%), which partially solidified. Three recrystallizations from benzene–pentane gave a product with m.p. 90.5–93.0°, which did not depress the melting point of authentic *cis*-2-carboxycyclopentaneacetic acid, m.p. 91.0–93.5°, prepared by nitric acid oxidation of *cis*-bicyclo[3.3.0]octan-2-one.[41] Gas chromatography of the phosphoric acid dehydration product also gave a second hydrocarbon which may have been the expected bicyclo-[3.3.0]oct-1-ene, as indicated by the presence of a peak of medium intensity in the infrared spectrum at 788 cm.$^{-1}$, attributable to a trisubstituted double bond.

Solvolysis of 3-Bromocycloöctene.—3-Bromocycloöctene (17 g.) in 200 ml. of acetic acid, 0.5 molar in sodium acetate was allowed to react at 75° for 100 hr. The reaction mixture was poured into 1 l. of water and 400 ml. of ether, and the ether layer was washed with sodium bicarbonate solution until the aqueous layer was basic. Distillation of the ether extract gave 4.6 g. (47%) of 1,3-cycloöctadiene, b.p. 83° (110 mm.), and 4.0 g. (27%) of 2-cycloöcten-1-yl acetate, b.p. 70° (3.5 mm.). The 1,3-cycloöctadiene was identified by comparison of its infrared spectrum with the spectrum of an authentic sample.[42] Gas chromatography of the diene using a silver nitrate–tetraethylene glycol column[24] showed that there was less than 1% of 1,4-cycloöctadiene or 1,5-cycloöctadiene present. The infrared spectrum of the acetate showed no hydroxyl peak. Conversion of the acetate to the alcohol with lithium aluminum hydride gave 2-cycloöcten-1-ol with an infrared spectrum identical with the spectrum of an authentic sample.[37]

Preparation and Solvolysis of Cycloöctyl Brosylate.—Cycloöctanol (6.23 g.) was allowed to react with *p*-bromobenzenesulfonyl chloride as described for the preparation of 3-cycloöcten-1-yl brosylate. Crystallization from ether and pentane at −10° gave 10.78 g. of crystalline brosylate, m.p. 24.5–25.0°. After a second crystallization the melting point was 25.3–25.7°, but the twice recrystallized material had a greater tendency to decompose, probably because of accumulation of trace amounts of *p*-bromobenzenesulfonic acid which catalyzes further decomposition. Because of the tendency for rapid decomposition at room temperature, the crystalline brosylate (7.78 g.) was solvolyzed immediately without being analyzed. The brosylate was solvolyzed in 50 ml. of acetic acid containing somewhat less than one molar equivalent of sodium acetate. The solvolysis yielded 0.95 g. (39%) of *cis*-cycloöctene, b.p. 105–115° (210 mm.), and 0.38 g. (10%) of cycloöctyl acetate, b.p. 71° (7 mm). The low yields can be attributed partly to the use of a large distillation flask, necessary because of excessive foaming during the distillation. The *cis*-cycloöctene, after being freed from some acetate by gas chromatography on Silicone oil,[24] had an infrared spectrum identical with the spectrum of an authentic sample. The gas chromatogram indicated that 0.07% of *cis*-bicyclo[3.3.0]octane was present. The cycloöctyl acetate was converted to cycloöctanol by lithium aluminum hydride reduction, and the cycloöctanol was identified by its infrared spectrum.

Rate Measurements.—Sodium acetate (0.0490 mole/liter) in acetic acid was prepared by dissolving anhydrous sodium carbonate in Mallinckrodt glacial acetic acid. The resulting solution therefore contained the half mole of water per mole of sodium acetate formed in the neutralization reaction, but studies in the literature suggest that the water had no important effect on the rates of solvolysis.[43] For convenience our product studies were carried out at higher concentrations than our rate studies, although it is possible that the reaction products may be somewhat dependent upon the concentration of sodium acetate or water. For a rate determination the amount of brosylate or bromide required to make up a 0.0450 molar solution was placed in a 50- or 100-ml. volumetric flask. The 0.0490 molar sodium acetate solution was added from a buret to make a 0.0450 molar solution of brosylate or bromide (slightly less than 50 or 100 ml. was required because of the volume occupied by the brosylate or bromide). The resulting solution was placed in stoppered test-tubes or sealed in ampoules and placed in a bath maintained at a constant temperature ±0.1°. Tubes were removed at intervals and the sodium acetate concentration was determined by titration with 0.0504 molar perchloric acid in acetic acid using bromophenol blue as the indicator. The actual concentrations of bromide or brosylate originally present were determined from the total changes in sodium acetate concentration; these in some cases were several per cent less than expected from the weights of material used. However, first-order plots were linear to more than 80% completion.

---

(41) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 916 (1934).

(42) A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1128 (1950).

(43) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 813 (1948).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. XVIII. Solvolysis of Ditosylates and an Acetoxy Tosylate in the Cycloöctane Series[1,2]

BY ARTHUR C. COPE, SUNG MOON AND PAUL E. PETERSON[3]

RECEIVED SEPTEMBER 2, 1958

The products of solvolysis of *cis*-1,2-cycloöctanediol ditosylate, *trans*-1,2-cycloöctanediol ditosylate, *cis*-1,4-cycloöctanediol ditosylate and *trans*-2-acetoxycycloöctyl tosylate in acetic acid containing sodium acetate and water have been studied. Products formed by transannular hydride shifts were formed from *cis*-1,2- and *trans*-1,2-cycloöctanediol ditosylate, while normal elimination and displacement products were obtained from the solvolysis of *cis*-1,4-cycloöctanediol ditosylate. Solvolysis of *trans*-2-acetoxycycloöctyl tosylate gave products formed both by transannular hydride shifts and by normal elimination and substitution reactions.

Several reactions of medium-sized ring compounds have been reported[2] in which abnormal products are formed by transannular hydride shifts. This paper reports a series of reactions in which substituted cycloöctyl carbonium ions of varying stability are the expected intermediates.

---

(1) Supported in part by a research grant (NSF-G5505) of the National Science Foundation.

(2) Paper XVII, A. C. Cope and P. E. Peterson, THIS JOURNAL, **81**, 1643 (1959).

(3) National Institutes of Health Postdoctoral Fellow, 1956–1958.

TABLE I

PERCENTAGE YIELDS OF PRODUCTS[a] FROM SOLVOLYSIS OF *trans*-1,2-*cis*-1,2- AND *cis*-1,4-CYCLOÖCTANEDIOL DITOSYLATE AND *trans*-2-ACETOXYCYCLOÖCTYL TOSYLATE

Compound	Products XI	XII	XIII	XIV	XV	XVI	XVII	XVIII[c]	XIX[c]	XX	XXI	Total yield
trans-1,2-Cycloöctanediol ditosylate, I	2.9	1.8	2.9	2.1	20	[d]	[d]	40	13			84
cis-1,2-Cycloöctanediol ditosylate, II	9.9	6.8	5.6	11	2.7[b]	15	4	21	21			97
cis-1,4-Cycloöctanediol ditosylate, III	12	1.0	4.2	4.5	3.6	5.3	4.4	42	5			82
trans-2-Acetoxycycloöctyl tosylate, XXII					1.4[b]			37	13	1.3	18	71

[a] Identity of products: XI, bicyclo[3.3.0]oct-2-ene; XII, 1,3-cycloöctadiene; XIII, 1,4-cycloöctadiene; XIV, 1,5-cyclooctadiene; XV, 1,4-epoxycycloöctane; XVI, *endo*-bicyclo[3.3.0]octan-2-ol; XVII, *exo*-bicyclo[3.3.0]octan-2-ol; XVIII, 3-cycloöcten-1-ol; XIX, 4-cycloöcten-1-ol; XX, cycloöctanone; XXI, *cis*-1,2-cycloöctanediol. [b] The presence of this compound was shown by its retention time in gas chromatography. The amount was too small to permit collection to obtain the infrared spectrum. Therefore, this fraction could be the 1,5-isomer or a mixture of the 1,4- and 1,5-isomers. [c] Compounds XVIII and XIX were collected by gas chromatography as a mixture and the composition of the mixture was indicated by its infrared spectrum. [d] Compounds XVI and XVII were formed in a total yield of 1.1% according to their retention time in gas chromatography on Silicone oil.

It has been reported that a carbonium ion adjacent to a brosylate group is destabilized by the electron-withdrawing power of the brosylate group.[4] Thus, the rates of solvolysis of *cis*- and *trans*-1,2-cyclohexanediol dibrosylate are less than one-thousandth of the rate of cyclohexyl brosylate solvolysis. On the other hand, the rate of *trans*-2-acetoxycyclohexyl tosylate solvolysis is enhanced by a factor of 650 by the neighboring acetoxy group, compared to *cis*-2-acetoxycyclohexyl tosylate.[5]

It was of interest to investigate the reactions of similarly substituted cycloöctyl tosylates. Solvolysis products of *cis*-1,2-, *trans*-1,2- and *cis*-1,4-cycloöctanediol ditosylate and *trans*-2-acetoxycyclooctyl tosylate are reported in this paper.

Preparation and Solvolysis of Tosylates.—The reaction of *cis*-cycloöctene oxide with acetic acid containing sodium acetate is expected to give principally *trans*-1,2-cycloöctanediol monoacetate.[6] The monoacetate thus prepared was separated by chromatography on alumina from *trans*-1,2-cyclooctanediol and *trans*-1,2-cycloöctanediol diacetate. Treatment of purified *trans*-1,2-cycloöctanediol monoacetate with *p*-toluenesulfonyl chloride in pyridine gave crystalline *trans*-2-acetoxycycloöctyl tosylate.

The crystalline cycloöctanediol ditosylates prepared as described previously[7,8] and the crystalline acetoxy tosylate were solvolyzed in acetic acid containing excess sodium acetate and water. The acetates were saponified and the products were separated into several fractions by chromatography on alumina. The fractions were analyzed by gas chromatography and identified by the infrared spectrum of each component collected by gas chromatography. The details are described in the Experimental section and the products of the solvolyses are summarized in Table I.

Ditosylate Solvolysis Products.—The most significant result of the product studies is that in the solvolysis of 1,2-cycloöctanediol ditosylates the products are almost exclusively compounds that must arise from a transannular hydride shift. On the other hand, no hydride shift is necessary to explain the solvolysis products of *cis*-1,4-cycloöctanediol ditosylate, and further considerations (see below) make such a shift seem unlikely. In both cases, however, the products appear to be those formed from the most stable possible carbonium ion intermediate, as discussed below. It seems likely that this principle will be useful in predicting the occurrence of hydride shifts in other reactions of medium-sized ring compounds.

In the following discussion the individual reactions are interpreted in terms of carbonium ion intermediates. It may be pointed out, however, that planar carbonium ion intermediates are inadequate to explain the stereochemical results of this work (for instance *cis*- and *trans*-1,2-cyclooctanediol ditosylate do not give identical products which would arise from a common planar ionic intermediate).

All of the ditosylate solvolysis products presumably arise from an intermediate monotosylate formed by reaction of one of the two tosylate groups. In Fig. 1 these intermediates are depicted as VI, VII, VIII, IX and X, these being the elimination and substitution products that would be formed from the initial carbonium ion or from the ion formed by a 1,5-hydride shift. (A 1,3-shift could lead to the same products.) From the nature of the solvolysis products, 2-acetoxycyclooctyl tosylate (VI) and the allylic tosylate VII may be eliminated with reasonable certainty as intermediates formed from *any* of the ditosylates, I, II or III. Thus the allylic tosylate would probably give 2-cycloöcten-1-ol or 1,3-cycloöctadiene, as does the allylic bromide.[2] Both products are absent or present in small amount only. Also, *trans*-2-acetoxycycloöctyl tosylate, *trans*-VI, gives *cis*-1,2-cycloöctanediol (XXI) on solvolysis (described below). The absence of glycols in the ditosylate solvolysis products provides evidence that *trans*-VI is not an intermediate, but *cis*-VI has not been similarly excluded.

---

(4) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

(5) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

(6) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **81**, 1640 (1959).

(7) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957).

(8) A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

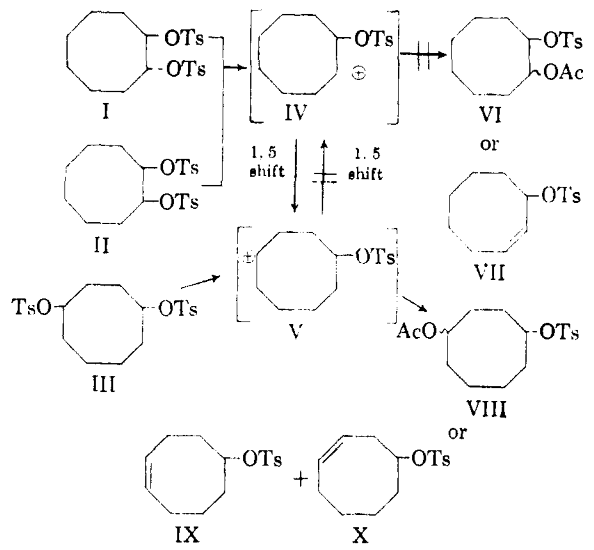
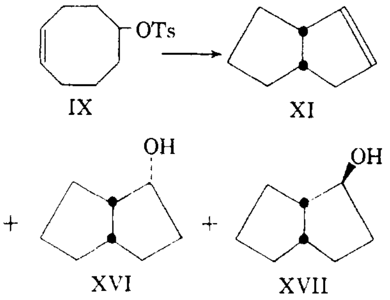


Fig. 1.—Possible intermediates in cycloöctanediol ditosylate solvolyses.

On the other hand, VIII, IX and X are intermediates which can account for the products reported in Table I. Thus, the hydrocarbon XI and the alcohols XVI and XVII are the major products from 4-cycloöcten-1-yl brosylate solvolysis,[2] indicating that the corresponding tosylate IX is an intermediate when these solvolysis products are formed. Only *trans*-1,2-cycloöctanediol ditosylate (I) does not appear to give much IX as an intermediate. In this case *trans*-4-acetoxycycloöctyl tosylate, *trans*-VIII, is a possible intermediate. It has the stereochemistry expected for a substitution product formed by a 1,5-hydride shift, as shown in Fig. 2.



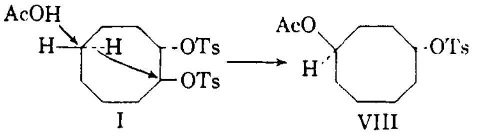


Fig. 2.—Formation of *trans*-4-acetoxycycloöctyl tosylate.

It can give the alcohols XVIII and XIX by elimination but not a bridged alcohol or a hydrocarbon (both of which are present in small amount). Furthermore, its stereochemistry is correct for *intramolecular substitution*, which may occur to the exclusion of substitution by solvent molecules, as shown in Fig. 3. Thus the formation of 20% of 1,4-epoxycycloöctane is explained, and the absence of 1,5-epoxycycloöctane, shown by infrared analysis, provides further evidence for the occurrence of 1,5-shifts (or 1,3-shifts) but not 1,4-shifts of hydride ions in these cycloöctane derivatives. The 1,4-epoxycycloöctane formed from III also could arise from *trans*-VIII.

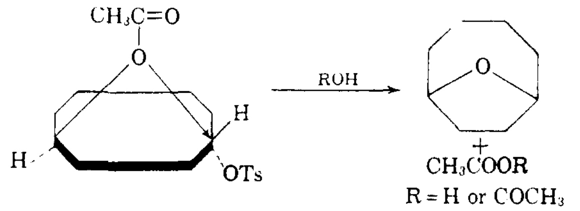


Fig. 3.—Formation of 1,4-epoxycycloöctane.

cis-4-Acetoxycycloöctyl tosylate, *cis*-VIII, can presumably be formed as an intermediate only from the *cis*-ditosylate II. If it is indeed formed, the experimental results show that it does not give a substitution product (glycol) on solvolysis, but probably forms 4-cycloöcten-1-ol, present in unusually large amount from the solvolysis of II.

3-Cycloöcten-1-yl tosylate (X) as an intermediate presumably could give the 3-cycloöcten-1-ol formed in all of the solvolyses, although at lower temperatures bicyclo[5.1.0]octan-2-ol can be isolated from solvolysis of the brosylate.[2]

In the preceding discussion it is shown that the solvolysis products of the various ditosylates can be formed by the routes summarized in Fig. 1. According to this scheme a carbonium ion adjacent to a tosylate group reacts exclusively by a transannular hydride shift, while a carbonium ion across the ring from a tosylate group reacts exclusively by elimination or substitution without a hydride shift. The only product in Table I which may not fit this scheme is 1,3-cycloöctadiene (XII), which could arise from VII (tentatively rejected as an intermediate) by elimination. However, the yield of XII is only 2%, 7% and 1% from I, II and III, respectively. Furthermore, XII may be formed from X at the high temperature of solvolysis, although it is not formed at a lower temperature.[2]

The reaction of the ion IV exclusively by a transannular hydride shift is in agreement with the generalization that carbonium ions tend to rearrange when the rearranged carbonium ion is more stable. Approximate rate measurements (reported in the Experimental section) indicate a decrease in rate for *trans*-1,2-cycloöctanediol ditosylate (I) by a factor of 720 at 73.45° and 280 at 89.4° compared to cycloöctyl tosylate; this may be compared with the slow rates of solvolysis of 1,2-cyclohexanediol dibrosylates previously noted.[4] The failure of the ion V to undergo a hydride shift is explained by the fact that a 1,5-shift would give the less stable carbonium ion IV.

***trans*-2-Acetoxycycloöctyl Tosylate Solvolysis Products.**—In the cyclohexane series a neighboring *cis*-acetoxy group slows tosylate solvolysis (compared to cyclohexyl tosylate) by a factor of 2,200 at 99.7°, while a *trans*-acetoxy group participates, resulting in a rate 0.296 times as fast as cyclohexyl tosylate.[5] In order to investigate the possibility that analogous stabilization of the *trans*-2-acetoxycycloöctyl carbonium ion would eliminate the driving force for a transannular hydride shift, solvolysis of *trans*-2-acetoxycycloöctyl tosylate (XXII) was studied. However, approximate measurement of the solvolysis rate immediately showed that it was slowed by a factor of about 62 at 89.4° compared to cycloöctyl tosylate,[9] of the same order of magnitude as the decrease by a factor of 280 observed for the *trans*-ditosylate (compared to cyclooctyl tosylate). Although the rates provided no clear evidence of participation, 18% of *cis*-1,2-cycloöctanediol (XXI) was isolated from solvolysis of XXII. Since the solvolysis was conducted in the presence of 7% of water, this glycol probably arises from hydrolysis of the cyclic acetoxonium ion.[10] Under the conditions of the solvolysis this ion may be partially converted to glycol and partially to transannular elimination products, or alternatively only a portion of the acetoxy tosylate may solvolyze directly to acetoxonium ion, the remainder giving the cycloöctenols XVIII and XIX arising from hydride shifts. In order to confirm the hypothesis that the *cis*-glycol came from hydrolysis of a cyclic acetoxonium ion, *trans*-2-acetoxycyclooctyl tosylate was solvolyzed in dry acetic acid containing acetic anhydride. The infrared spectra of the glycol product and of the ditosylate derivative indicated that a mixture of *cis*- and *trans*-1,2-cycloöctanediol was formed in the solvolysis under anhydrous conditions.

Experimental[11]

***trans*-1,2-Cycloöctanediol Monoacetate.**—*cis*-Cycloöctene oxide (28.0 g.) was added to a solution of 75.0 g. of sodium acetate trihydrate in 140 g. of glacial acetic acid and refluxed for 22 hours. About 100 ml. of acetic acid was removed under reduced pressure (60° at 100 mm.). Water (300 ml.) was added to the residue and the mixture was extracted with three 200-ml. portions of ether. The ether extract was washed with water and dried over magnesium sulfate. Removal of the solvent and distillation gave 19 g. of product (46%, calculated as $C_{10}H_{18}O_3$), b.p. 102° (0.7 mm.), which was chromatographed on 300 g. of acid-washed activity II alumina. Three major fractions were obtained. The first fraction, which was eluted with pentane, was shown to be *trans*-1,2-cycloöctanediol diacetate by comparison of its infrared spectrum with the spectrum of an authentic sample. The latter was prepared from *trans*-1,2-cycloöctanediol[8] and acetic anhydride.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.19; H, 9.11.

The second fraction (8.75 g., $n^{25}\text{D}$ 1.4750) was shown to be *trans*-1,2-cycloöctanediol monoacetate by its infrared spectrum and analysis.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.55; H, 9.67.

The third fraction, which was eluted with 5% methanol–ether, was shown to be *trans*-1,2-cycloöctanediol by comparison of its infrared spectrum with the spectrum of an authentic sample.[8]

***trans*-2-Acetoxycycloöctyl Tosylate.**—*trans*-1,2-Cycloöctanediol monoacetate (7.3 g.) was added dropwise to a solution of 1.5 g. of *p*-toluenesulfonyl chloride in 80 ml. of anhydrous pyridine cooled in an ice-bath, and the mixture was kept at 5° for 22 hours. Excess *p*-toluenesulfonyl chloride was hydrolyzed by adding 10 ml. of water dropwise while the solution was maintained below 5°. The solution was diluted with 150 ml. of water and extracted with three 50-ml. portions of ether. The ether extract was washed with three 30-ml. portions of 6 *N* hydrochloric acid, water and dried over magnesium sulfate. Removal of the solvent and cooling in a refrigerator gave a crude solid product (7.7 g., 57%), m.p. 45.0–48.0°. Recrystallization from pentane–ether gave 5.5 g. of *trans*-2-acetoxycycloöctyl tosylate, m.p. 52.5–53.5°.

Anal. Calcd. for $C_{17}H_{24}O_5S$: C, 59.98; H, 7.11. Found: C, 59.83; H, 7.01.

Solvolysis of *trans*-1,2-Cycloöctanediol Ditosylate.—To a solution prepared by refluxing 12.2 g. of sodium acetate trihydrate, 5 g. of acetic anhydride and 97 g. of glacial acetic acid was added 16.0 g. of *trans*-1,2-cycloöctanediol ditosylate.[7] The mixture was refluxed for 18 hours and then saponified by refluxing with 250 ml. of 40% sodium hydroxide for 3 hours. It was cooled and extracted with three 100-ml. portions of methylene chloride. The extract was washed with water, dried, concentrated and chromatographed on 100 g. of acid-washed alumina, activity II. The column was eluted with pentane, ether and finally with 5% methanol–ether. Three main fractions were obtained. The total yield was 3.68 g. (84%). The first fraction was eluted with pentane from chromatography on alumina and shown by gas chromatography on Silicone oil[12] to contain a hydrocarbon fraction and another fraction with a longer retention time. The hydrocarbon fraction was collected by gas chromatography. Gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane and 3-methyl-3-nitropimelonitrile showed that it contained four components; bicyclo[3.3.0]oct-2-ene (2.9%),[13] 1,3-cycloöctadiene (1.8%), 1,4-cycloöctadiene (2.9%) and 1,5-cycloöctadiene (2.1%). The hydrocarbons were identified by comparison in retention time with authentic samples on gas chromatography and by collection of the individual components from the chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane and comparison of the infrared spectra with the spectra of authentic samples. 1,3-Cycloöctadiene and 1,4-cycloöctadiene were collected from the gas chromatography column as a mixture and identified by comparison of the infrared spectrum of the mixture with the spectra of 1,3-cycloöctadiene[14] and 1,4-cycloöctadiene.[2] The mixture had an ultraviolet maximum at 228 mμ (ϵ 2,465), indicating that the mixture consisted of 45% of 1,3-cycloöctadiene and 55% of 1,4-cycloöctadiene. Gas chromatography on 3-methyl-3-nitropimelonitrile indicated that the mixture contained 38% of 1,3- and 62% of 1,4-cyclooctadiene.

The second fraction obtained by chromatography on alumina showed a single peak on gas chromatography on Silicone oil. Comparison of the gas chromatogram and the infrared spectrum of a sample with the spectrum of an authentic sample showed that it was 1,4-epoxycycloöctane (20%).[15] No bands characteristic of 1,5-epoxycycloöctane were present in the infrared spectrum of this fraction.

The presence of bicyclo[3.3.0]octan-2-ols[16] in 1.1% yield in a third chromatographic fraction was indicated by a gas chromatogram on Silicone oil. The principal alcoholic fraction, obtained in 53% yield, was shown to be a mixture of 75% of 3- and 25% of 4-cycloöcten-1-ol by comparison of its infrared spectrum with the spectra of mixtures of known compositions.[6] The crude phenylurethan obtained from this alcohol fraction had m.p. 93–96°, which was raised to 99.0–100.5° after recrystallization from methanol–water. The infrared spectrum of this derivative was essentially the same as the spectrum of authentic 3-cycloöcten-1-yl phenylurethan.[17]

Solvolysis of *cis*-1,2-Cycloöctanediol Ditosylate.—*cis*-1,2-Cycloöctanediol ditosylate[7] (6.3 g.) was added to a mixture of 4.3 g. of sodium acetate trihydrate and 34 g. of glacial acetic acid. The mixture was refluxed for 21 hours, after which it was hydrolyzed by refluxing with 85 ml. of 40% sodium hydroxide for 4 hours. The products were isolated as described for the *trans*-1,2-cycloöctanediol ditosylate solvolysis except that petroleum ether (b.p. 38–49°) was substituted for pentane in the solvent mixtures used for eluting the chromatography column. The hydrocarbon fraction (isolated by chromatography on alumina) was shown by gas chromatography on three different columns,[12] namely, Silicone oil, 1,2,3-tris-(2-cyanoethoxy)-propane and silver nitrate in tetraethylene glycol to contain bicyclo-

---

[9] H. C. Brown and G. Ham, THIS JOURNAL, **78**, 2735 (1956).

[10] S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948), and references cited therein.

[11] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[12] Reference 2, footnote 24.

[13] All yields of solvolysis products in this paper are based on the weight of tosylate solvolyzed.

[14] A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1128 (1950).

[15] A. C. Cope and B. C. Anderson, *ibid.*, **79**, 3892 (1957).

[16] A. C. Cope, M. Brown and H. E. Petree, *ibid.*, **80**, 2852 (1958).

[17] A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

[3.3.0]oct-2-ene (9.9%), 1,3-cycloöctadiene (6.8%), 1,4-cycloöctadiene (5.6%) and 1,5-cycloöctadiene (11%). The amounts were too small to permit collection of each component, and they were identified by comparison of retention times with authentic samples.

A second fraction from the chromatography on alumina was purified by gas chromatography. Its infrared spectrum indicated that it was *endo*-bicyclo[3.3.0]octan-2-ol containing some of the *exo* isomer (total yield 19%).[16] Gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane and polyethylene glycol indicated the composition to be 75% of the *endo* and 25% of the *exo* isomer. In a repetition of the solvolysis the composition was shown to be 60% *endo* and 40% *exo* isomer.

The presence of epoxycycloöctane (2.7%) was indicated by gas chromatography on Silicone oil.[12]

A third fraction which was eluted with ether in the chromatography on alumina was shown to be a mixture (42%) consisting of 50% of 3- and 50% of 4-cycloöcten-1-ol by comparison of its infrared spectrum with the spectrum of an authentic mixture of known composition.[6]

Solvolysis of *cis*-1,4-Cycloöctanediol Ditosylate.—*cis*-1,4-Cycloöctanediol ditosylate (13 g.)[8] was added to a mixture of 8.8 g. of sodium acetate trihydrate and 34.5 g. of glacial acetic acid. The mixture was heated at 80–90° for 23 hours, after which it was hydrolyzed by refluxing with 85 ml. of 40% sodium hydroxide for 3 hours. The products, 2.909 g. (82%), were isolated as described for the *trans*-1,2-cyclooctanediol ditosylate solvolysis. The hydrocarbon fraction, eluted with pentane from the chromatography on alumina, was isolated in 21.7% yield. It was shown to be a mixture consisting of bicyclo[3.3.0]oct-2-ene (12%), 1,3-cycloöctadiene (1.0%), 1,4-cycloöctadiene (4.2%) and 1,5-cycloöctadiene (4.5%) by gas chromatography on Silicone oil, 1,2,3-tris-(2-cyanoethoxy)-propane and 3-methyl-3-nitropimelonitrile.[12] Bicyclo[3.3.0]oct-2-ene and 1,5-cycloöctadiene were collected separately from the gas chromatography column [1,2,3-tris-(2-cyanoethoxy)-propane] and identified by comparison of the infrared spectra with the spectra of authentic samples.[2] A mixture of 1,3- and 1,4-cycloöctadiene was collected from the gas chromatography column and identified by comparison of its infrared spectrum with the spectra of authentic samples.[2] The ultraviolet spectrum of the mixture had a maximum at 228 mμ (ϵ 830), indicating that the mixture contained 15% of 1,3-cycloöctadiene. The gas chromatogram on 3-methyl-3-nitropimelonitrile[12] indicated the presence of 19% of 1,3-cycloöctadiene in the mixture.

1,4-Epoxycycloöctane (3.6%) was isolated from the second chromatographic fraction on alumina and identified by gas chromatography on Silicone oil and 1,2,3-tris-(2-cyanoethoxy)-propane, and by comparison of its infrared spectrum with the spectrum of an authentic sample.[15] The infrared spectrum of the epoxycycloöctane did not indicate the presence of any 1,5-epoxycycloöctane.

The saturated alcohol fraction was separated from the unsaturated alcohol fraction by the silver nitrate extraction method described in ref. 2. The saturated alcohol was shown to be bicyclo[3.3.0]octan-2-ol (9.7%) by comparison of the gas chromatogram and infrared spectrum with an authentic sample.[16] The infrared spectrum of the bicyclic alcohol indicated it to be principally the *endo* isomer containing some of the *exo* isomer. Gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane indicated that the bicyclic alcohol consisted of 55% *endo* and 45% *exo* isomer. In another similar solvolysis, the bicyclic alcohol fraction was shown to contain 80% of the *endo* and 20% of the *exo* isomer by gas chromatography on polyethylene glycol[12] at 110°. It gave a phenylurethan which melted at 77–81° after recrystallization from methanol-water. This phenylurethan did not depress the melting point of an authentic sample of the phenylurethan of *endo*-bicyclo[3.3.0]octan-2-ol,[16] but depressed the m.p. of the *exo* derivative.

The unsaturated alcohol separated by the silver nitrate extraction method showed a single peak on gas chromatography on 1,2,3-tris-(2-cyanoethoxy)-propane. The unsaturated alcohol fraction (47%) was shown to be a mixture of 90% of 3- and 10% of 4-cycloöcten-1-ol by comparison of the infrared spectrum with the spectrum of an authentic mixture.[6] The unsaturated alcohol fraction gave a phenylurethan, m.p. 92–94°, which was raised to m.p. 98.5–99.5° by recrystallization from methanol-water. The infrared spectrum of the phenylurethan was practically identical with the spectrum of authentic 3-cycloöcten-1-yl phenylurethan.[17]

Solvolysis of *trans*-2-Acetoxycycloöctyl Tosylate.—*trans*-2-Acetoxycycloöctyl tosylate (4.99 g.) was added to a solution of 4.5 g. of sodium acetate trihydrate in 17.5 g. of glacial acetic acid, which had been heated to dissolve the sodium acetate. The solution was heated at 90 ± 3° for 15 hours. The mixture was cooled in an ice-bath, diluted with 200 ml. of water and extracted with three 100-ml. portions of ether. The ether extract was washed with water, sodium bicarbonate solution and water, and dried over sodium sulfate. Removal of the ether at atmospheric pressure gave 2.88 g. of crude product. Gas chromatography showed that no hydrocarbon was present. The crude product was saponified by refluxing with 10 ml. of 20% sodium hydroxide and 5 ml. of methanol for 2 hours, after which the mixture was diluted with 20 ml. of water and extracted with three 40-ml. portions of ether. The ether layer was washed with water and dried over sodium sulfate; the residual liquid after removal of the solvent amounted to 1.032 g. The water washing of the ether layer was further extracted with three 40-ml. portions of methylene chloride. After washing with water, drying over magnesium sulfate and removal of the solvent, the methylene chloride extract gave 0.2 g. of additional material bringing the yield to 71%. The products were chromatographed on alumina as described for the *trans*-1,2-cycloöctanediol ditosylate solvolysis.

Cycloöctanone (1.3%) was isolated from the first chromatography fraction on alumina as its 2,4-dinitrophenylhydrazone, m.p. 173.0–174.0°. It was identified by mixed melting point with an authentic sample and comparison of its infrared spectrum with the spectrum of authentic cycloöctanone 2,4-dinitrophenylhydrazone.

Gas chromatography on Silicone oil indicated the presence of 1,4- or 1,5-epoxycycloöctane or a mixture of the two.

The unsaturated alcohol fraction isolated from chromatography on alumina was shown to be a mixture consisting of 75% of 3- and 25% of 4-cycloöcten-1-ol by comparison of its infrared spectrum with the spectrum of an authentic mixture.[6]

A glycol fraction isolated from the chromatography on alumina was shown to be *cis*-1,2-cycloöctanediol by comparison of its infrared spectrum with the spectrum of an authentic sample.[8] A mixed melting point with an authentic sample showed no depression.

Repetition of the solvolysis of the acetoxy tosylate in dry acetic acid instead of wet acetic acid gave a glycol fraction which yielded a mixture of ditosylates, m.p. 89–96° after recrystallization from ether. The infrared spectrum of the mixture showed that it was composed of *cis*- and *trans*-1,2-cycloöctanediol ditosylate.

Rate Measurements.—The rates of solvolysis were determined as described in ref. 2, except that only a few points were taken. The first-order rate constants for solvolysis of *trans*-1,2-cycloöctanediol ditosylate in acetic acid containing sodium acetate and water was 9.9×10^{-6} at 73.45° and 7.4×10^{-5} at 89.4°. The rate constant for *trans*-2-acetoxycycloöctyl tosylate was 3.4×10^{-4} at 89.4°.

CAMBRIDGE, MASS.