Solvolytic Behavior of the *cis*- and *trans*-1-Tosyloxycyclopentane 3,4-Epoxides. The Absence of Neighboring Epoxy Group Participation[1]

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The epimeric *cis*- and *trans*-1-tosyloxycyclopentane 3,4-epoxides have been synthesized and their solvolytic behavior has been studied in buffered acetic acid. The acetolysis rate of the cis epimer exceeded that of the trans epimer by only a factor of 3.3. Comparison with model compounds showed little, if any, rate acceleration. Analysis of the complex product mixtures has shown that each epimer gave predominantly acetate of inverted configuration. These acetates were unstable to the reaction conditions and underwent rapid opening of the epoxide ring, with a minor amount of 1,3-acetoxyl neighboring group participation in the case of the trans acetate. No indication of neighboring epoxide group participation was found in the solvolysis of the tosylates.

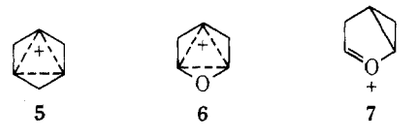
Recently there has been considerable interest in the solvolytic behavior of heterocyclic analogs of cyclopropyl carbinyl systems.[2] The solvolytic behavior of oxiranes[2a-c,g] (**1a**), aziridines[2d-f] (**1b**), and thiiranes[2b,h] (**1c**) has been reported. While these systems resemble the cyclopropyl carbinyl system (**1d**) which has been postulated to give rise to a nonclassical carbonium ion,[3] their behavior is best explained by the intermediacy of heterocyclic bicyclobutonium cations (**2**),[2a,b,d,f,h,i] arising from participation of the unshared pair of electrons on the heteroatom. Only in one of these cases has participation of the carbon–carbon bond of the heterocyclic ring been postulated.[2c]

1a, X = O
b, X = NR
c, X = S
d, X = CH_2

L = leaving group

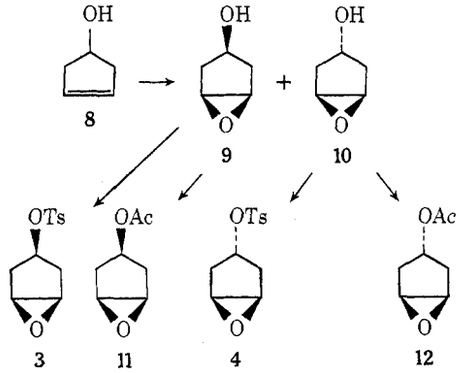
2

We wish to report our studies on *cis*- and *trans*-1-tosyloxycyclopentane 3,4-epoxides (**3** and **4**). These are the oxa analogs of the 3-tosyloxybicyclo[3.1.0]-hexanes studied by Winstein and Sonnenberg[4] and postulated to give rise to the intriguing "trishomocyclopropenyl cation" (**5**). If participation were to occur in the solvolysis of **3** or **4**, it would necessarily involve the 3,4 carbon–carbon bond and could give rise to the nonclassical cation **6**.[5] Direct migration to produce stabilized cation **7** is an additional possibility.



5 **6** **7**

Synthesis and Solvolysis.—The desired *cis*- and *trans*-cyclopentan-1-ol 3,4-epoxides[6] (**9** and **10**) were synthesized by epoxidation of Δ-3-cyclopentenol[7] with *m*-chloroperbenzoic acid. The stereochemistries of **9** and **10** have been established by Darby, Henbest, and McClenaghan[6] by the presence of dilution-independent intramolecular hydrogen bonding (band at 3546 cm^{-1} in the infrared) in **9** which was absent in **10**, and by chemical studies. Reaction of **9** with tosyl chloride and acetyl chloride gave *cis*-1-tosyloxycyclopentane 3,4-epoxide (**3**) and *cis*-1-acetoxycyclopentane 3,4-epoxide (**11**), respectively. Upon reaction with tosyl chloride and acetic anhydride, **10** gave the trans isomers **4** and **12**, respectively.



8 **9** **10** **3** **11** **4** **12**

The rates of solvolysis of compounds **3** and **4** in acetic acid buffered with sodium acetate are given in Table I. Both compounds gave good first-order kinet-

TABLE I

ACETOLYSIS RATES OF 1-TOSYLOXYCYCLOPENTANE 3,4-EPOXIDES

Compd	Temp, °C	Rate, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3	100.0 ± 0.02	(1.81 ± 0.06) × 10^{-4}	20.1	−22.2
	90.0 ± 0.02	(8.19 ± 0.10) × 10^{-5}		
	80.0 ± 0.02	(3.68 ± 0.02) × 10^{-5}		
	(25)[a]	1.55 × 10^{-7}		
4	110.0 ± 0.02	(1.80 ± 0.01) × 10^{-4}	24.8	−11.4
	100.0 ± 0.02	(7.53 ± 0.02) × 10^{-5}		
	90.0 ± 0.02	(2.84 ± 0.04) × 10^{-5}		
	(25)[a]	1.31 × 10^{-8}		

[a] Extrapolated from higher temperatures.

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

(2) (a) H. G. Richey, Jr., and D. V. Kinsman, *Tetrahedron Lett.*, 2505 (1969); (b) H. Morita and S. Oae, *ibid.*, 1347 (1969); (c) D. L. Whalen, *J. Amer. Chem. Soc.*, **92**, 7619 (1970); (d) V. R. Gaertner, *J. Org. Chem.*, **35**, 3952 (1970); (e) V. R. Gaertner, *Tetrahedron Lett.*, 5919 (1968); (f) J. A. Deyrup and C. L. Moyer, *ibid.*, 6179 (1968); (g) J. M. Coxon, R. P. Garland, M. P. Hartshorn, and G. A. Lane, *Chem. Commun.*, 1506 (1968); (h) J. C. Martin and D. J. Anderson, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, Abstract 31-0; (i) R. H. Higgins and N. H. Cromwell, *J. Amer. Chem. Soc.*, **95**, 120 (1973).

(3) See R. Breslow in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 233–294.

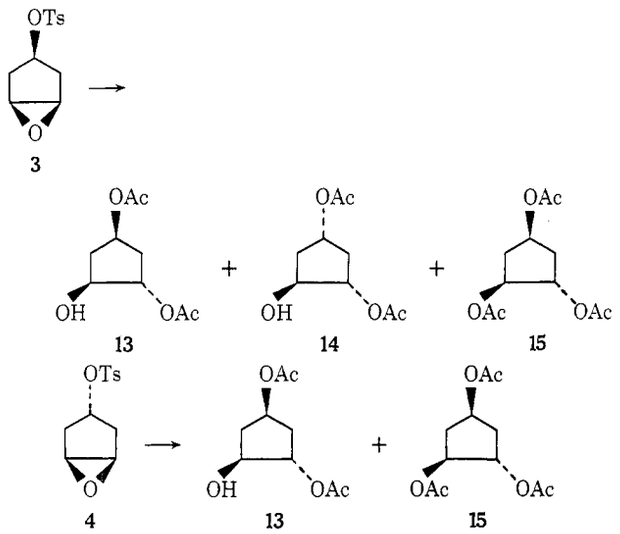
(4) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235, 3244 (1961).

(5) Cation **6** would be destabilized relative to **5** because of the inductive withdrawal of electrons by oxygen. However, resonance donation of the nonbonded electrons on oxygen could provide a stabilizing contribution.

(6) A. C. Darby, H. B. Henbest, and I. McClenaghan, *Chem. Ind. (London)*, 462 (1962).

(7) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960); for a procedure with higher yield see H. M. Hess and H. C. Brown, *ibid.*, **32**, 4138 (1967).

ics through at least two half-lives. The product mixtures obtained from the solvolysis of **3** and **4** were complex. Analysis of the product mixture from **3** by glpc showed 10% of *trans*-2-*cis*-4-diacetoxycyclopentanol (**13**), 24% of *trans*-2-*trans*-4-diacetoxycyclopentanol (**14**), 41% of *trans*-2-*cis*-4-triacetoxycyclopentane (**15**),



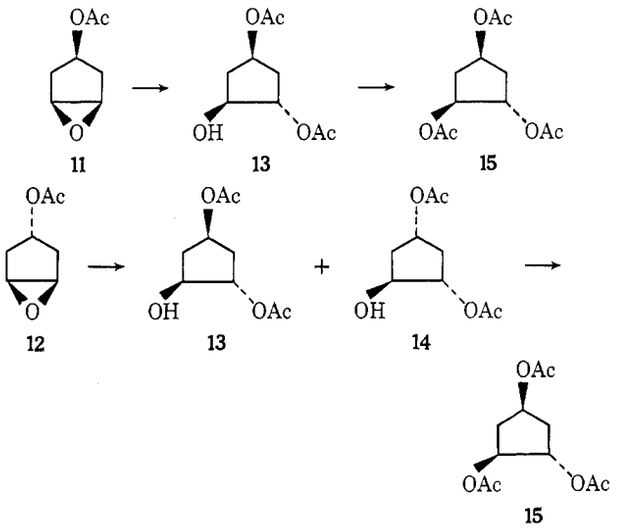
and 25% of seven unidentified components. Analysis of the product mixture from **4** by glpc showed 18% of **13**, 61% of **15**, and 21% of five unidentified components. Although no **14** was detected, amounts of less than *ca.* 5% would not have been resolved from **13**.

The structure of **15** was suggested by its nmr spectrum, which showed a singlet superimposed on a multiplet at τ 7.85 (relative area of 13) assigned to the nine methyl and four methylene hydrogens, and a broad multiplet at τ 4.60 (relative area of 3) assigned to the hydrogens adjacent to oxygen. The structure was proven by comparison of spectral properties (ir, nmr) and glpc retention time with those of an authentic sample of **15** prepared by reaction of the known[8] *trans*-2,*cis*-4-trihydroxycyclopentane with acetic anhydride.

Although stereoisomers **13** and **14** could be partially resolved by analytical glpc, they could not be separated by preparative glpc and were therefore analyzed as a mixture. Their structures were suggested by the infrared spectrum of the mixture (showing absorptions for both hydroxyl and carbonyl groups) and the nmr spectrum, which showed two singlets superimposed on a broad multiplet at τ 7.86 (relative area of 10) assigned to the six methyl hydrogens and the four methylene hydrogens, a broad peak at τ 6.45 (relative area of 1) assigned to the hydroxyl hydrogen, and a group of broad multiplets at τ 4.5–5.5 (relative area of 3) assigned to the three hydrogens adjacent to oxygen. Upon reaction with acetic anhydride, the mixture produced a single compound which was identified as **15** by comparison with an authentic sample. These data limit the possible structures of the two products to **13**, **14**, and *trans*-3-*cis*-4-diacetoxycyclopentanol. Mechanistic considerations strongly suggested **13** and **14** as the correct structures. Definitive evidence for this assignment and for the individual stereochemistries of the isomers was obtained from the acetic acid mediated cleavage of epoxy acetates **11** and **12** (*vide infra*).

(8) R. Steyn and H. Z. Sable, *Tetrahedron*, **25**, 3579 (1969).

In order to determine if the observed products were arising *via* the intermediacy of epoxy acetates **11** and **12**, the stability of these compounds to the acetolysis conditions was determined. Upon heating at 100° in acetic acid buffered with sodium acetate, the disappearance of **11** with a rate constant[9] of 6×10^{-4} sec^{-1} was observed. Diacetate **13**[10] was formed at the same rate and then disappeared at a slower rate to produce **15**. Epoxy acetate **12** was similarly observed to decompose with a rate constant[9] of 8×10^{-4} sec^{-1} to give a 1:8 mixture of **13** and **14**,[10] which then reacted more slowly to give **15**.



Additional evidence supporting the intermediacy of **11** and **12** in the acetolysis of **3** and **4** was provided by examination of the product composition after reaction for approximately one half-life of the tosylates. The products from acetolysis at 100° of cis tosylate **3** showed the presence of 26% of trans acetate **12** after 30 min.[11] Isolation of the solid product after 60 min gave material whose infrared spectrum was identical with that of authentic cis tosylate **3**. Approximately 2% of **11** could be detected in the acetolysis products of trans tosylate **4** after 60 min at 100°.[11] Only minor amounts of **15** were detected in either case at this stage of reaction.

Discussion

Inversion of configuration in the opening of epoxides by acids to give trans products is a well-documented reaction.[12] Thus, the expected product from the opening of cis epoxide **11** in acetic acid is **13**. This evidence provides confirmation of the general structural assignment and also establishes the stereochemistry of **13**. The expected product from the opening of trans epoxide **12** in acetic acid is **14**.[12] We assigned this structure to the major product observed in the reaction of **12** with acetic acid. The minor product was identical with the major product in the reaction of **11** and thus is **13**. This stereoisomer must arise by inversion at the initial acetate position in addition to opening of the

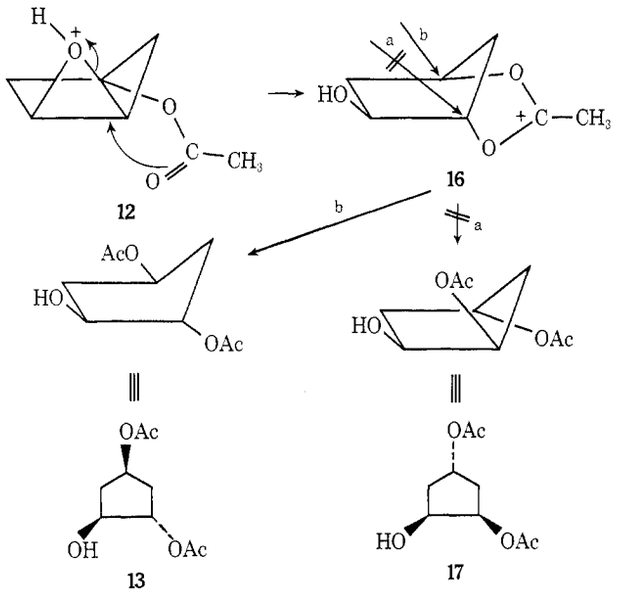
(9) Rates were determined by analysis of aliquots by glpc (see Experimental Section).

(10) See Discussion for assignment of structures to these products.

(11) The half-life of **3** at 100° is *ca.* 1 hr. The half-life of **4** at 100° is *ca.* 2.5 hr.

(12) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); see especially pp 757–762.

epoxide ring with inversion. A possible mechanism for the formation of this product involves neighboring group participation.[13] Thus 1,3-acetoxyl participation[14-18] in the opening of **12** would give acetoxonium ion **16**. Nucleophilic attack on **16** could occur *via* path a to give *cis*-2,*trans*-4-diacetoxycyclopentanol (**17**) or

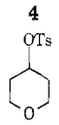


via path b to give **13**. The failure to observe **17** in the product mixture implies steric hindrance to path a attack in **16** by the hydroxyl group. The product ratio shows that intramolecular participation is only one eighth as fast as direct solvent displacement in this system.[19]

Reaction rates greater than expected and unusual product compositions (rearrangements, retention of configuration, etc.) are usually taken as evidence of neighboring group participation in solvolysis reactions.[20] Considering the question of rates first, it is difficult to find a good model for this system. Table II lists rela-

TABLE II

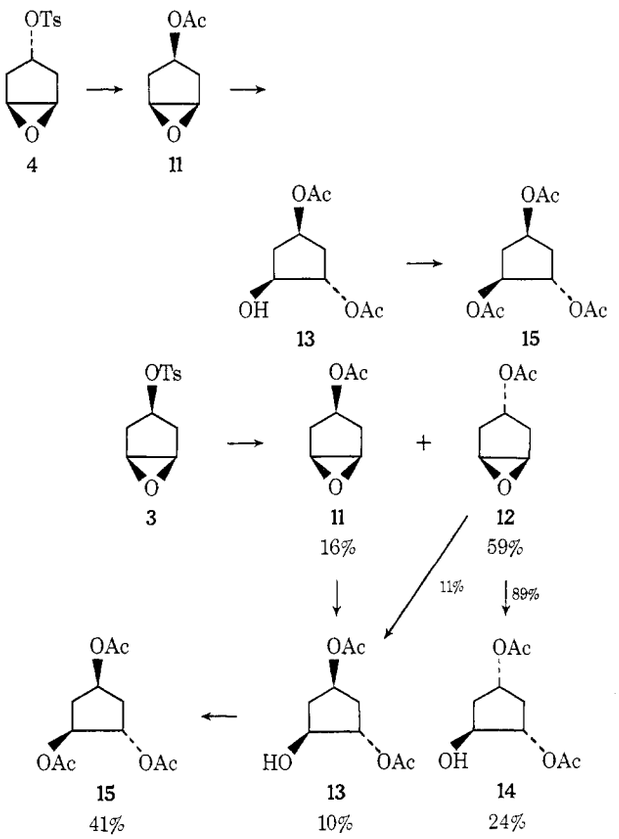
ACETOLYSIS RATES AT 84.8°

Compd	Rate, sec^{-1}	Relative rates
3	5.6×10^{-5} [a]	15
4	1.7×10^{-5} [a]	4.6
		
18	3.7×10^{-6} [b]	1

[a] Extrapolated from other temperatures. [b] See ref 21.

tive relative rates for **3**, **4**, and 4-tosyloxytetrahydropyran (**18**).[21] It is seen that the solvolysis rate of **3** is enhanced over that of **18** by a factor of 15. However, this rate difference may not be meaningful since bridging carbons 2 and 6 in **18** should also increase the amount of strain relieved upon ionization and thus increase the solvolysis rate of **3** and **4** relative to **18**. For example, cyclopentyl tosylate undergoes acetolysis some 20 times faster than cyclohexyl tosylate at 50°.[4] If the solvolysis rate of trans tosylate **4** is used as a model for that of **3**, a modest rate acceleration of 3.3 at 84.8°[22] is seen.[23] It must be concluded, therefore, that rate acceleration in **3** due to neighboring group participation is small, if present at all.

We propose the scheme presented below to explain the identified solvolysis products of **3** and **4**. Upon acetolysis, trans tosylate **4** produces 79% of cis acetate **11** and only a small amount, if any, of trans acetate **12** in addition to 21% of unidentified products. Acetate **11** completely decomposes to produce **13** during the course of the reaction so that **13** and its esterification product **15** are the only isolable products. In the case



of cis tosylate **3**, both cis and trans acetates **11** and **12** are initially produced in the amounts of 16 and 59%, respectively. Both acetates decompose completely during the course of the reaction, **11** giving only **13** and **12** giving **13** and **14** in a 1:8 ratio. This results in a

(13) For an example of neighboring carbonyl participation in epoxide opening, see H. O. House, *J. Org. Chem.*, **21**, 1306 (1966); also see ref 12, p 763.

(14) L. J. Dolby, C. N. Lieske, D. R. Rosencrantz, and M. J. Schwartz, *J. Amer. Chem. Soc.*, **85**, 47 (1963).

(15) L. J. Dolby and M. J. Schwartz, *J. Org. Chem.*, **30**, 3581 (1965).

(16) R. J. Ouellette and R. D. Robins, *Tetrahedron Lett.*, 397 (1968).

(17) P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

(18) O. Kovacs, G. Schneider, and L. K. Lang, *Proc. Chem. Soc.*, 374 (1963).

(19) See ref 15 for evidence that 1,3-acetoxyl participation is less favorable than 1,2-acetoxyl participation.

(20) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

(21) D. S. Tarbell and J. R. Hazen, *J. Amer. Chem. Soc.*, **91**, 7657 (1969).

(22) This acceleration increases to a factor of 12 at 25°.

(23) It might be argued that the rate of **4** is accelerated by direct participation of the oxygen nonbonded electrons. Such participation is highly unlikely due to the large amount of strain that would be incorporated during such participation and the rarity of R_2O-4 participation.[21,24,25] In addition product studies discount this possibility (*vide infra*).

(24) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958); L. A. Paquette and M. K. Scott, *J. Amer. Chem. Soc.*, **94**, 6751 (1972).

(25) For examples of proposed R_2O-4 participation see P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968), and L. A. Paquette and M. K. Scott, *J. Amer. Chem. Soc.*, **94**, 6760 (1972).

3:7 ratio of **13** to **14**, both of which undergo slow conversion to **15**.[26]

It can be seen that both **3** and **4** give predominantly acetolysis products resulting from inversion of configuration. Inversion is incompatible with neighboring group participation, but it is not unusual in the absence of participation. For example, the unrearranged ester from acetolysis of cyclohexyl tosylate is entirely of inverted configuration.[27] These observations and the absence of significant rate acceleration force the conclusion that neighboring group participation is not an important pathway in the acetolysis of **3** and **4**.

Although *cis*-3-tosyloxybicyclo[3.1.0]hexane has been postulated to undergo solvolysis *via* the "trishomocyclopropenyl cation" (**5**), the driving force for the proposed participation is not large, as evidenced by the only modest enhancement of the solvolysis rate.[4,28] In the oxa analog, **3**, the inductive withdrawal of electrons from the carbon–carbon σ bond by oxygen overwhelms the weak driving force for neighboring group participation in the solvolysis reaction. This system provides another example of the inefficacy of resonance donating but inductive withdrawing substituents in stabilizing the transition states leading to σ delocalized cations.[30]

Experimental Section[31]

cis- and *trans*-**Cyclopentan-1-ol 3,4-Epoxides (9 and 10)**.—The epoxides **9** and **10** were prepared by a modification of the procedure of Darby, Henbest, and McClenaghan.[6] A solution of 18.0 g (0.215 mol) of Δ^3-cyclopentenol[7] in 20 ml of tetrahydrofuran was added to an ice-cooled solution of 43.5 g (0.215 mol) of 85% *m*-chloroperbenzoic acid in 100 ml of tetrahydrofuran at such a rate that the temperature remained below 20°. After standing overnight at 5°, the solution was diluted with 1.5 l. of water and 5 g of sodium bisulfite was added followed by 30 g of sodium bicarbonate. The aqueous solution was continuously extracted with ether and the ether solution was dried over anhydrous magnesium sulfate. Distillation through a 6 in. Vigreux column at 62 mm gave the following fractions: fraction 1, bp 30–45°, forerun; fraction 2, 4.2 g, bp 87–91°, pure **9**; fraction 3, 2.2 g, bp 94–99°, pure **9**; fraction 4, 0.5 g, bp 100–126°, mixture containing predominantly **9** and some **10**; fraction 5, 1.4 g, bp 127–134°, mixture containing 70% **10** and 30% **9**. Fractions were analyzed by glpc (6 ft × 0.125 in., 3% SE-52 on 80/100 Chromosorb W at 80°). The yield of cis epoxy alcohol **9** was 35% and of trans epoxy alcohol **10** was 5%. An additional 2.1 g (10%) of product mixture was obtained from two additional continuous extractions of the aqueous solution. Distillation fractions containing **10** from several runs were combined and chromatographed on silica gel using 25% ether in hexane as eluent. The fractions containing **10**, which eluted after **9**, were combined and distilled to give pure trans alcohol **10**, bp 132–133° (67 mm).

cis-**1-Tosyloxycyclopentane 3,4-Epoxide (3)**.—To an ice-cold solution of 3.0 g (0.030 mol) of **9** in 30 ml of pyridine was added 9.5 g (0.05 mol) of *p*-toluenesulfonyl chloride. After standing overnight at 5°, the solution was diluted with 500 ml of water and extracted with three 150-ml portions of chloroform. The combined extracts were washed twice with dilute aqueous hydrochloric acid, then with aqueous sodium bicarbonate, and finally with water and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to leave 7.7 g of oil which crystallized on standing. Two recrystallizations from hexane–methylene chloride gave 5.0 g (66%) of **3**, mp 87.5–89°.

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55; S, 12.61. Found: C, 56.66; H, 5.48; S, 12.54.

trans-**1-Tosyloxycyclopentane 3,4-Epoxide (4)**.—The trans tosylate **4** was prepared from **10** in the manner described for **3** in 61% yield, mp 66.5–67.5.

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55; S, 12.61. Found: C, 56.61; H, 5.48; S, 12.60.

cis-**1-Acetoxycyclopentane 3,4-Epoxide (11)**.—To an ice-cold solution of 0.50 g (5.0 mmol) of **9** in 15 ml of pyridine was added 0.8 g (10 mmol) of acetyl chloride. After standing overnight at 5°, the solution was diluted with 250 ml of water and extracted with three 50-ml portions of chloroform. The combined extracts were washed twice with dilute aqueous hydrochloric acid, then with aqueous sodium bicarbonate, and finally with water, then dried over anhydrous magnesium sulfate. Distillation gave 0.51 g (72%) of **11**, bp 122–125° (29 mm). Preparative glpc (5 ft × 0.25 in., 15% Carbowax 20M on 60/80 Chromosorb W, at 148°) followed by distillation gave an analytical sample, mp 30–31°.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.14; H, 6.93.

trans-**1-Acetoxycyclopentane 3,4-Epoxide (12)**.—The trans acetate **12** was prepared from **10** by the procedure described for the preparation of **11** with the exception that acetic anhydride was used in place of acetyl chloride. This procedure gave a 79% yield of **12**, bp 107–108° (31 mm). Preparative glpc (same column as for **11**) at 135° followed by distillation gave an analytical sample, mp 44–45°.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.16; H, 7.06.

trans-**2,*cis*-4-Triacetoxycyclopentane (15)**.—*trans*-2,*cis*-4-Trihydroxycyclopentane was prepared by the procedure of Steyn and Sable[8] and carried on directly to the triacetate.

A solution of 2.02 g (20.2 mmol) of **9** in 50 ml of 0.05 *N* aqueous sulfuric acid was heated in a boiling water bath for 1.5 hr. Two grams of barium carbonate were added and the solution was filtered through Celite. The water was removed by distillation to leave yellow oily triol.

Acetyl chloride (5 g, 0.064 mol) was added dropwise to an ice-cold solution of the triol in 25 ml of pyridine. After standing overnight at 5°, the solution was diluted with 250 ml of water and extracted with ether. The extracts were washed twice with dilute aqueous hydrochloric acid, then with aqueous sodium bicarbonate, and finally with water, then dried over anhydrous magnesium sulfate. Distillation gave 1.96 g (40% from **9**) of **15**, bp 112–114° (0.4 mm).

Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 53.76; H, 6.54.

Kinetics. Reagents.—Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride and sodium acetate in glacial acetic acid for 24 hr and subsequent fractional distillation in a dry atmosphere. Standard sodium acetate in acetic acid (*ca.* 0.1 *M*) was prepared by the careful addition of anhydrous acetic acid to a solution of anhydrous sodium carbonate in acetic anhydride, such that *ca.* 1% acetic anhydride remained after the water of neutralization was removed, followed by refluxing in a dry atmosphere for 5 hr[32] (calculated to be 1.325 g of anhydrous sodium carbonate and 3.78 g of acetic anhydride diluted to 250 ml with anhydrous acetic acid). Standard perchloric acid in acetic acid (*ca.* 0.02 *M*) used in titrating acetolysis aliquots was prepared by the careful addition of 70% perchloric acid to a solution of anhydrous acetic acid and acetic anhydride, such that 1% acetic anhydride remained after the water was removed (calculated to be 2.8756 g of 70% perchloric acid and 14.920 g of acetic anhydride diluted to 1 l. with anhydrous acetic acid),

(26) In this analysis it is assumed that **13** and **14** are converted to **15** at similar rates.

(27) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972); J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972).

(28) The intermediacy of the "trishomocyclopropenyl cation" has been questioned[29] because of the observation that 1,5-diphenyl substitution does not lead to an enhanced solvolysis rate. However, it has recently been demonstrated by Wilcox and Banks[30] that phenyl substituents are unable to stabilize the transition states leading to σ delocalized ions.

(29) E. J. Corey and H. Uda, *J. Amer. Chem. Soc.*, **85**, 1788 (1963).

(30) C. F. Wilcox, Jr., and H. D. Banks, *J. Amer. Chem. Soc.*, **94**, 8231, 8232 (1972).

(31) Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian Model EM-360 or Varian Model DP-60 spectrometer. Gas–liquid partition chromatographic work was performed with a Hewlett-Packard Model 5750 research chromatograph and an Aerograph Model A-700 preparative chromatograph. Elemental analyses were obtained from Spang Microanalytical Laboratory, Ann Arbor, Mich.

(32) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

followed by standing at room temperature for 12 hr. The molarity of the standard perchloric acid in acetic acid was determined by titrating an aliquot *vs.* potassium acid phthalate (primary standard) in anhydrous acetic acid using Bromophenol Blue as the indicator.

Procedure.—The kinetic procedure followed was essentially that of Winstein and coworkers.[33] All rates were determined in duplicate using infinity titers.[34]

Acetolysis Product Analysis of *cis*-1-Tosyloxycyclopentane 3,4-Epoxide (3).—A solution of 1.002 g (3.94 mmol) of **3** in 50 ml of 0.09413 *M* sodium acetate in acetic acid was heated to 100° for 11 hr (*ca.* 10 half-lives). The solution was diluted with 500 ml of water and neutralized by the careful addition of 150 g of sodium bicarbonate. The solution was ether extracted and the extracts were dried over anhydrous magnesium sulfate. The solvent was removed by distillation. Analysis of the residue by glpc (6 ft × 0.125 in., 10% silicone gum rubber UC-W 982 on 80/100 Porapak S, temperature-programmed run, 100–156° and 10 ft × 0.125 in., 20% Carbowax 20M on 80/100 Chromosorb P at 180°) showed a complex mixture of products containing 41% of **15**, 10% of **13**, 24% of **14**, and 25% of seven unidentified compounds. Preparative glpc (5 ft × 0.25 in., 15% Carbowax 20M on 60/80 Chromosorb W at 166°) allowed isolation of pure **15** and a mixture of **13** and **14**. The triacetate **15** was identified by comparison of its nmr spectrum, infrared spectrum, and glpc retention times on three different columns (the two columns listed above and 5 ft × 0.125 in., 10% butanediol succinate on 80/100 Chromosorb P at 173°) with those of an authentic sample.

The diacetate alcohols **13** and **14** were identified by the infrared (hydroxyl and carbonyl) and nmr spectra of the mixture and conversion of the mixture to **15** by treatment with acetic anhydride as described below.

To an ice-cold solution of 39 mg (0.2 mmol) of the **13** and **14** mixture in 5 ml of pyridine was added 0.3 g (2.9 mmol) of acetic anhydride. After standing overnight at 5°, the solution was diluted with 100 ml of water and ether extracted. The extracts were washed twice with dilute hydrochloric acid, then with sodium bicarbonate, and finally with water, then dried over anhydrous magnesium sulfate. The solvent was removed by distillation. The residue showed only one component with retention time identical with that of **15** on three different glpc columns (columns and conditions as above). Preparative glpc (as above) gave a pure sample which had an infrared spectrum identical with that of authentic **15**. The relative stereochemistries were established by comparison with the decomposition products of **11** and **12** by glpc (three different columns described above).

Samples which had not been solvolyzed to completion were also analyzed for products. Two-milliliter aliquots of a solution of 0.0949 g (0.374 mmol) of **3** in 10 ml of 0.09413 *N* sodium acetate in acetic acid were sealed in tubes and placed in a bath at 100.0°. Duplicate tubes were withdrawn after 30 and 60 min (half-life is 1 hr at 100°). The contents were diluted with 40 ml of water, neutralized with 5 g of sodium bicarbonate, and ether extracted. Analysis by glpc (UCW column described above, temperature-programmed run, 100–155°) showed the presence of **12** (26% after 30 min, 7% after 60 min). Cis acetate **11** may have been present in small amounts. The triacetate **15** was not observed in the 30-min run and was present only in 1% in the 60-min run. The identity of **12** was established by comparison of glpc retention times on three different columns (UCW column and conditions described above; Carbowax 20M column, described above, at 129°; 6 ft × 0.125 in., 3% OV-17 on 100/120 Chromosorb W at 96°.

Acetolysis Product Analysis of *trans*-1-Tosyloxycyclopentane 3,4-Epoxide (4).—A solution of 0.764 g (3.00 mmol) of **4** and 0.4 g of sodium acetate in 40 ml of anhydrous acetic acid was heated to 100° for 25.5 hr (10 half-lives). The solution was diluted with 500 ml of water and neutralized with 100 g of sodium bicarbonate. The solution was ether extracted and the combined extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed by distillation. Analysis of the residue by glpc (as for the products from **3**) showed a mixture of products containing 61% of **15**, 18% of **13**, and 21% of five unidentified compounds. The diastereomeric **14** may have been present in less than 5%. Preparative glpc (conditions as above) allowed isolation of pure **15** and **13**. The triacetate **15** was identified by comparison of its infrared spectrum and glpc retention times with those of an authentic sample (*vide supra*). The diacetate alcohol **13** was identified by comparison of its infrared spectrum and glpc retention times on three different columns (*vide supra*) with those of the mixture of **13** and **14** obtained from acetolysis of **3**. The stereochemistry was established by comparison with the decomposition products of **11** and **12** (three different columns as described above).

Samples which had not been solvolyzed to completion were also analyzed for products as described above for **3**. Reaction times were 60 and 120 min (half-life is 2.56 hr at 100°). Analysis as above showed *ca.* 2% of **11** present in the 60-min runs. No **15** was found in the 60-min run and *ca.* 2% was found in the 120-min run. The cis acetate **11** was identified by comparison of glpc retention times on two of the columns (UCW and Carbowax columns, conditions described above).

Decomposition of *cis*-1-Acetoxycyclopentane 3,4-Epoxide (11) in Acetic Acid.—A solution of 24.94 mg (0.176 mmol) of **11** was diluted to 10.0 ml with 0.09413 *N* sodium acetate in acetic acid. Aliquots (1.2 ml) of this solution were sealed in solvolysis tubes and placed in a constant-temperature bath at 100.0°. The tubes were withdrawn at timed intervals (0, 10, 30, 60, 120, 180, 300, 420 min) and quenched in ice water. Aliquots (1.0 ml) from each tube were added to 20 ml of water. The solutions were neutralized with 2.5 g of sodium bicarbonate. To this solution was added 1.0 ml of a solution of 0.02804 g of naphthalene diluted to 10.0 ml with tetrahydrofuran. The solutions were then ether extracted. Analysis by glpc (UCW column described above, temperature-programmed run, 100–156°) showed that **11** decomposed with a rate constant of 6×10^{-5} sec^{-1} and **13** appeared initially at approximately the same rate and then reacted further to produce **15** at a slower rate. Identity of **13** was established by comparison of its glpc retention times with those of the solvolysis products of **3** and **4** on three different columns (as described above). Stereochemistry was established by assuming trans opening of the epoxide ring (see Discussion).

Decomposition of *trans*-1-Acetoxycyclopentane 3,4-Epoxide (12) in Acetic Acid.—The decomposition of trans acetate **12** was analyzed as described for **11**. It was found that **12** decomposed with a rate constant of 8×10^{-4} sec^{-1} at 100.0° and an 89:11 mixture of **14** and **13**, respectively, appeared initially at approximately the same rate, then reacted further to produce **15** at a slower rate. Product identities were established as described above.

Acetolysis of *cis*-1-Tosyloxycyclopentane 3,4-Epoxide (3) for One Half-Life.—A solution of 0.500 g (1.97 mmol) of **3** and 0.26 g (3.2 mmol) of sodium acetate in 20 ml of anhydrous acetic acid was heated to 100.0° for 1 hr (half-life is 1.06 hr). The solution was diluted with 500 ml of water and neutralized with 50 g of sodium bicarbonate. The solution was ether extracted and the combined extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* to leave 0.398 g of an oily mixture of tosylate and solvolysis products. Crystallization from ether–hexane gave 0.122 g (49% of theoretical) solid tosylate. The infrared spectrum of this material was identical with that of **3**.

Registry No.—**3**, 42142-25-6; **4**, 42142-26-7; **9**, 25494-14-8; **10**, 25494-15-9; **11**, 34310-94-6; **12**, 25494-20-6; **15**, 42142-31-4; Δ^3-cyclopentenol, 14320-38-8; *trans*-2,*cis*-4-trihydroxycyclopentane, 42142-32-5.

(33) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948).

(34) The amount of acid produced as measured titrimetrically in each kinetic run was in excellent agreement with the theoretical amount (average difference of less than 2%).