The Solvolysis of 5,6-Trimethylene-2-norbornyl *p*-Toluenesulfonates. Evidence for the Formation of Classical Carbonium Ion Intermediates in the Solvolysis

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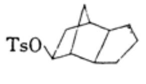
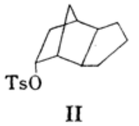
(Received November 27, 1964)

Kinetic studies of the solvolysis of four isomeric 5,6-trimethylene-2-norbornyl *p*-toluenesulfonates (I, II, III and IV) were carried out by Bartlett and Barnes.[2] These authors observed that these isomers obeyed good first-order kinetics in glacial acetic acid, absolute ethanol, and 80% ethanol, and that the first-order rate constants were different with each isomer.



I



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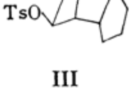
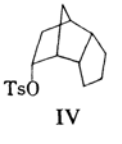
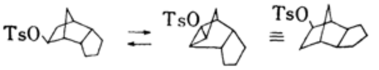


III



IV

These results have been interpreted as indicating that the isomers are not interchanged during solvolysis.[2b,3] However, Winstein and Trifan observed that the rate of the racemization of optically-active *exo*-2-norbornyl *p*-bromobenzenesulfonate exceeds the rate of the formation of *p*-bromobenzenesulfonic acid.[4] This was explained by the mechanism involving internal return. Accordingly, when we consider the solvolyses of I and III, it is conceivable that isomerization between I and III would occur.



(III) (I)

On the other hand, Cristol and his coworkers[3] reported that the addition of methanol to *endo*- and *exo*-5,6-trimethylenenorbornene, in the presence of sulfuric acid, yielded products with different compositions. This seems to suggest that two different precursors exist in these systems.

The purposes of this study were to test the previous work[2] and to clarify the behavior of I and III during solvolysis. We also hoped to examine the propriety of explaining the solvolysis of these systems by the non-classical carbonium ion mechanism which has been proposed by Bartlett and Barnes.[2]

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[1] Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[2] a) R. S. Barnes, Ph. D. Thesis, Harvard University, 1951; b) P. D. Bartlett, Abstracts of Papers, 12th National Organic Chemistry Symposium, June, 1951, p. 1.

[3] S. J. Cristol, W. K. Seifert, D. W. Johnson and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

[4] S. Winstein and D. Trifan, ibid., **74**, 1154 (1952).

Results and Discussion

The Preparation and Characterization of *endo*-5, 6-Trimethylene-*exo*-2-norbornyl *p*-Toluenesulfonate (III).—The *p*-toluenesulfonate III was prepared by the usual method of treating the corresponding alcohol with *p*-toluenesulfonyl chloride in pyridine at 0°C overnight.

Surprisingly enough, the III synthesized by us exhibited a melting point of 76.5—77.0°C instead of 48—49°C or 49—50.5°C, as Bartlett and Barnes[2] or Cristol et al.[3] respectively had reported. The analytical data agreed well with the calculated values, and NMR and infrared spectra also showed that our III should have the assigned structure.[5] A detailed investigation of the melting-points diagram of the mixtures of I and III, as shown in Fig. 1, indicated that an eutectic mixture has a melting point of ca. 50°C.

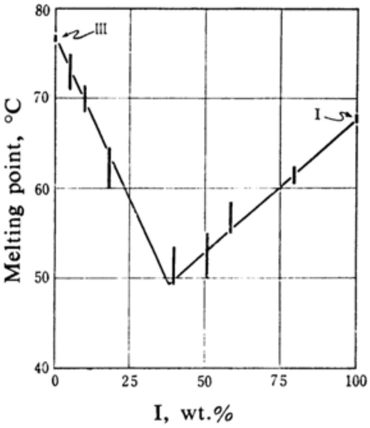


Fig. 1. Melting point diagram for mixtures of I and III.

These results suggested that the III prepared by the authors was pure, while those described in previous articles[2,3] were mixtures of I and III.

The Kinetics of the Solvolyses of I and III in Methanol.—The solvolyses of I and III were followed titrimetrically to approximately 90% completion in methanol at 59.7°C. The plots of $\log a/(a-x)$ vs. the reaction time for the methanolyses of I and III are shown in Fig. 2.

In the case of I, the first-order plot was almost linear to about 53% reaction, but afterwards a slight upward drift was observed.[6] On the other hand, the first-order plot for III showed a considerable downward drift to 44% reaction,[7] and then it became linear, which was nearly parallel to what had been calculated for I between 50 and 90% reaction. These observations suggested that III solvolyzed and isomerized simultaneously in methanol and that isomerization was essentially complete by approximately 44% reaction. This was verified by isolating unsolvolyzed *p*-toluenesulfonate and by observing its melting point and infrared spectrum

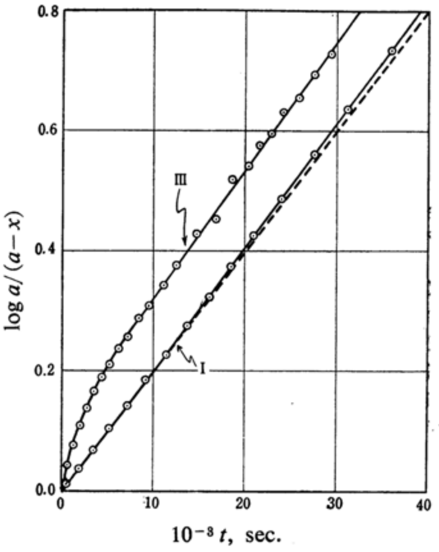
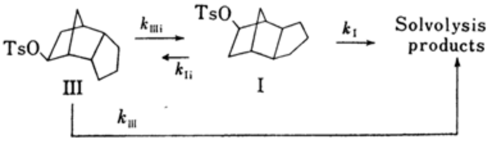


Fig. 2. Solvolysis rates of I and III in absolute methanol at 59.7°C.
$[\text{Tosylate}]_0 = 0.1000$ M

The solvolytic behavior of the isomeric *p*-toluenesulfonates I and III are summarized by the following scheme:



Scheme 1

That the first-order plot for the solvolysis of I showed a slight upward drift after 53% reaction indicates that a small portion of I also isomerized to III.

This behavior is very analogous to the solvolysis of α,α-dimethylallyl chloride, which proceeds with a concurrent intramolecular isomerization to primary chloride γ,γ-dimethylallyl chloride;[8] thus, the same kinetic procedure was used in this work to calculate the

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[5] See "Experimental" section.

[6] Similar trends were observed for the solvolyses in acetic acid and ethanol.

[7] In acetolysis, the first-order plot became linear after about 23% reaction, and in ethanolysis, after about 29% reaction.

[8] W. G. Young, S. Winstein and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951). Similar behavior was found in the solvolysis of bicyclo(2.2.2)octan-2-yl *p*-toluenesulfonate (H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961)) and of *exo*-4-*syn*-8-dichlorodibenzobicyclo(3.2.1)octadiene (S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964)).

specific rate of the solvolysis of III and that of the isomerization of III to I. Table I gives the data for a representative kinetic run for III.

TABLE I. SOLVOLYSIS RATE OF III IN ABSOLUTE METHANOL AT 59.7°C

Time sec.	Tosylate 10^2M	$10^5 k$ sec^{-1} [a)]	$10^5 k_{\mathrm{IIIe}}$ sec^{-1} [b)]
0	10.00	(16.9)[c)]	
240	9.62	15.9	
480	9.27	15.0	
720	8.96	13.7	
960	8.69	12.7	
1200	8.44	11.8	
1440	8.21	11.3	
1680	8.00	10.8	
1920	7.80	10.1	
2160	7.62	9.72	
2400	7.45	9.09	
6000	5.84	5.49	
11040	4.55		4.80
12600	4.20		4.93
14820	3.73		5.05
20400	2.87		4.87
21600	2.66		5.02
22800	2.53		4.94
24300	2.34		4.97
25800	2.21		4.87
29400	1.87		4.84
		Mean :	4.92±0.08

a) Instantaneous first-order rate constant.
b) Values obtained from integrated equation for a first-order reaction, using a starting point after equilibration is attained : t=8400 sec.; [Tosylate]=0.0515 M.
c) Extrapolated value.

By extrapolating the instantaneous rate constants to 0% reaction, the first-order rate constant for solvolysis (k_{III}) was estimated to be approximately 16.9×10^{-5} sec^{-1}. The rate constant after equilibration was calculated from the integrated equation ($k_{\mathrm{IIIe}}=(1/t)\ln a/(a-x)$), using a starting point after equilibration had been attained. The estimated value was $(4.92\pm0.08)\times10^{-5}$ sec^{-1}. On the other hand, the first-order rate constant for isomerization (k_{IIIi}) was found to be approximately 37×10^{-5} sec^{-1} by calculating ($k_{\mathrm{III}}+k_{\mathrm{IIIi}}$) (the procedure is shown in Fig. 3).

For the methanolysis of I, the rate constants before 50% (k_{I}) and after 55% reaction (k_{Ie}) were calculated to be $(4.59\pm0.03)\times10^{-5}$ and $(4.81\pm0.04)\times10^{-5}$ sec^{-1} respectively. From these rate constants, the mole fraction of III, F, after equilibration was calculated from Eq. 1[8)] to be 2—3% ;

$$F=(k-k_{\mathrm{I}})/(k_{\mathrm{III}}-k_{\mathrm{I}}) \qquad (1)$$

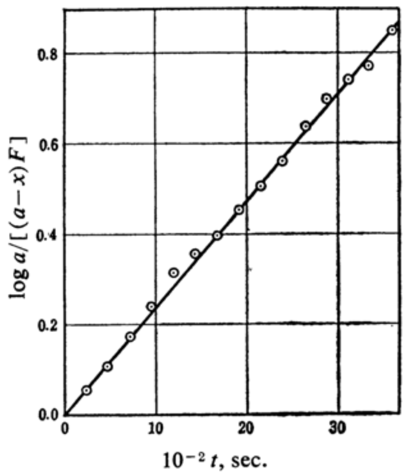


Fig. 3. Calculation of ($k_{\mathrm{III}}+k_{\mathrm{IIIi}}$) for the methanolysis of III at 59.7°C.
$F=(k-k_{\mathrm{I}})/(k_{\mathrm{III}}-k_{\mathrm{I}})$: cf. Ref. 8
$k_{\mathrm{III}}+k_{\mathrm{IIIi}}=54\times10^{-5}$ sec^{-1}

where k is k_{Ie} or k_{IIIe}.

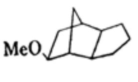
The first-order rate constants of the solvolyses and isomerizations of I and III are summarized in Table II.

TABLE II. SUMMARY OF THE FIRST-ORDER RATE CONSTANTS FOR METHANOLYSES OF I AND III AT 59.7°C

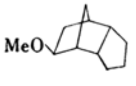
[Tosylate]$_0$=0.1000 M

$10^5 k$, sec^{-1}	Remark
$k_{\mathrm{IIIi}}=37$	Isomerization
$k_{\mathrm{Ii}}=0$	Isomerization
$k_{\mathrm{I}}=4.59\pm0.03$	Solvolysis (Initial rate)
$k_{\mathrm{III}}=16.9$	Solvolysis (Initial rate)
$k_{\mathrm{Ie}}=4.81\pm0.04$	Solvolysis (After equilibration)
$k_{\mathrm{IIIe}}=4.92\pm0.08$	Solvolysis (After equilibration)

The Distributions of Products from Methanolyses of *exo*- and *endo*-5, 6-Trimethylene-*exo*-2-norbornyl *p*-Toluenesulfonates (I and III).— The distributions of products from methanolyses of I and III at an infinite reaction time have been investigated by Cristol et al.[3,9)] by means of the v. p. c. technique; it has thus been revealed that the products are composed of a large portion of V and a small portion of VI, and that no other product is yielded. These authors reported that I and III yielded VI in essentially identical amounts.



V



VI

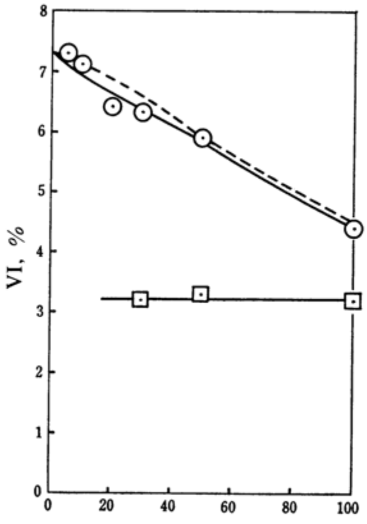
In the present study, the distributions of products from the methanolyses of I and III

TABLE III. PERCENTAGES OF VI IN THE PRODUCTS FROM METHANOLYSES OF I AND III AT 59.7°C

$[\text{Tosylate}]_0=0.1000$ M

Titrimetric conv., %	Tosylate I	Tosylate III
5	—	7.3
10	—	7.1
20	—	6.4
30	3.2	6.3
50	3.3	6.3[a)]
		5.9[a)]
100	3.2	4.4
		4.6[a)]
		4.3[a)]

a) Methanolysis in the presence of 0.101 M NaOMe.



Titrimetric conv., %

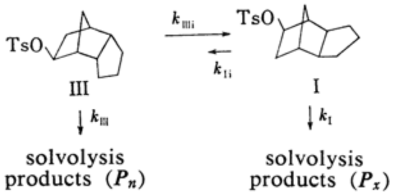
Fig. 4. Percentages of VI in the products from methanolyses of I and III at 59.7°C.
⊙, from III; ⊡, from I;
Dotted line, calculated by Eq. 5

at various percentages of reaction were also determined by the v. p. c. technique. The products were composed of a large portion of V and a small portion of VI; no other product was detected. The results are shown in Table III and Fig. 4.

The distributions of products at an infinite reaction time differed between isomeric *p*-toluenesulfonates I and III; moreover, in the case of III, the percentage of VI in the solvolysis products decreased from 7.3% at 5% reaction to 4.4% at completion (100%). On the other hand, VI in the products from the methanolysis of I was approximately constant (ca. 3.2%) throughout the reaction.

These results show that the distribution of the direct products from III is different than in the case of I. The decrease in the percentage of VI obtained from the methanolysis of III may be attributed to the occurrence of the solvolysis of I which was formed from III through isomerization.

These results were further confirmed by being duplicated with those of isomerization as follows. The solvolytic behavior of III may be described by the following scheme:



Scheme 2

Since it is reasonable to assume k_{Ii} to be negligibly small, the sum (x) of isomerized and solvolyzed III may be obtained by Eq. 2, where a is the initial concentration of III:

$$x=a(1-e^{-(k_{\text{IIIi}}+k_{\text{III}})t}) \tag{2}$$

Then the concentration of P_n is defined by Eq. 3:

$$P_n=a(k_{\text{III}}/(k_{\text{IIIi}}+k_{\text{III}}))(1-e^{-(k_{\text{IIIi}}+k_{\text{III}})t}) \tag{3}$$

By dividing P_n by the titrimetric conversion, it is possible to derive the fraction of product which is produced from III itself, which is given by Eq. 4:

$$P_n/(P_n+P_x)=\frac{(k_{\text{III}}/(k_{\text{IIIi}}+k_{\text{III}}))(1-e^{-(k_{\text{IIIi}}+k_{\text{III}})t})\times 10^2}{\text{Titrimetric conversion (\%) at time } t} \tag{4}$$

When we estimate that the VI values in P_n and P_x are 7.3 and 3.2% respectively, by means of extrapolation in Fig. 4, it is possible to estimate the percentage of VI in the products at any reaction time by Eq. 5:

$$\text{VI in the solvolysis products (\%)}=7.3(P_n/(P_n+P_x))+3.2(1-(P_n/(P_n+P_x))) \tag{5}$$

These values were calculated and are plotted with a dotted line in Fig. 4, a line which is in good agreement with the observed values.

The Mechanism of the Solvolyses of *exo*- and *endo*-5, 6-Trimethylene-2-norbornyl *p*-Toluenesulfonates (I and III).—The results of the distributions of products suggest that the intermediates are classical carbonium ions. A reasonable reaction mechanism would be as follows:

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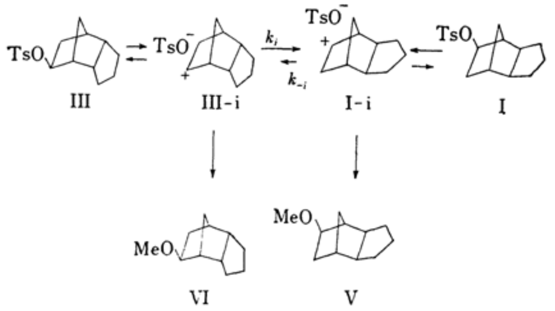
9) The melting point of III used by these authous was 49—50.5°C.

TABLE IV. FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSES OF FOUR ISOMERIC *p*-TOLUENESULFONATES

p-Toluene-sulfonate	Solvent	Temp. °C	k 10^5 sec^{-1}	$\Delta H^{\ddagger}$ kcal./mol.	$\Delta S^{\ddagger}$ e. u.	Relative rates for methanolysis at 74.8°C		
I	AcOH	74.8	21.9					
		50.1	1.11	26.3	0.0			
	MeOH	74.8	25.3			1.00	10.4	40.6
		59.7	4.59					
		50.1	1.35	25.8	−1.1			
	EtOH	99.5	45.1					
		74.8	3.65	25.5	−5.7			
II	AcOH	99.5	30.9					
		74.8	2.32	26.3	−4.4			
	MeOH	99.5	30.8					
		74.8	2.44	25.8	−5.9	0.0965	1.00	3.92
	EtOH	99.5	8.46					
		74.8	0.694	25.4	−9.4			
III	MeOH	59.7	16.9[a]					
		39.8	1.30[a]	26.0	−2.2			
		(74.8)	(97.3)[b]			3.84	39.9	156
IV	AcOH	99.5	12.1					
		74.8	0.803	27.6	−2.8			
	MeOH	99.5	8.63					
		74.8	0.623	26.7	−5.8	0.0246	0.255	1.00
	EtOH	124.8	24.6					
		99.5	2.19	27.5	−6.7			

a) Initial rate. b) Extrapolated from the values at other temperatures.



Scheme 3

VII

The fact that the isomerization of III to I is much faster than the reverse may be explained by assuming that III-i isomerizes to I-i faster than the reverse; i. e., $k_i \gg k_{-i}$. This is supported by the fact that *exo*-trimethylenenorbornanes are more stable than their *endo*-counterparts to the extent of 2—3 kcal./mol.[10] A common non-classical carbonium ion VII cannot account for the quite different distribution observed in the products from I and III. In addition, it appears difficult to account for the very large amount of V in the product (97% V, 3% VI) on the basis of a highly selective opening of the non-classical ion, VII. On the other hand, the marked difference in the stabilities of the two classical ions (or ion-pairs), III-i and I-i, provides a simple, plausible explanation for the observed distribution.

The Solvolysis Rates of Four Isomeric 5, 6-Trimethylene-2-norbornyl *p*-Toluenesulfonates (I, II, III and IV).—Although the kinetics of the solvolysis of these four isomers had been extensively studied by Bartlett and Barnes,[2] it seemed necessary to investigate them again, this time using the *p*-toluenesulfonates prepared by us. The results are summarized in Table IV. The solvolyses of II and IV obeyed good first-order kinetics, no trend of isomerization being observed.

In the last column of Table IV, the relative rates of the methanolysis of the four isomers at 74.8°C are given. A comparison of the rate ratio of 10.4 for I to II with that of 156 for III to IV suggests that the trimethylene group in III assists ionization, while that in IV retards it. This is also verified by the finding that $k_{\mathrm{III}}/k_{\mathrm{I}}$ is 3.84, while $k_{\mathrm{IV}}/k_{\mathrm{II}}$ is only 0.255. Apparently the retarding effect by the trimethylene group in IV should be attributed to a steric hindrance toward the leaving TsO-group.[11]

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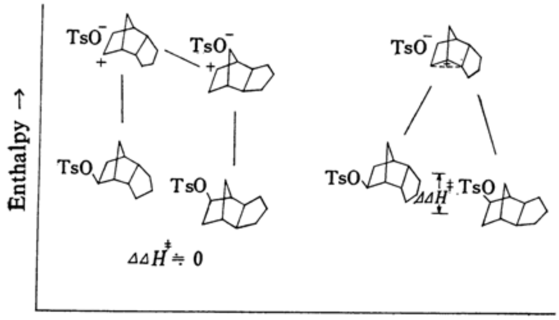
[10] L. Kaplan, H. Kwart and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960), footnote 15.

[11] A similar interpretation has been made for the solvolysis of the *endo*-2-norbornyl system, in which the steric hindrance by the hydrogen atoms at the 5- and 6-carbons toward the leaving group was considered. H. C. Brown, F. J. Chloupek and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

With respect to the activation enthalpy $\Delta H^{\neq}$, I has about the same value as III. This fact supports the theory that the intermediate is different with each isomer; that is, if the intermediate is common to two isomers, some higher $\Delta H^{\neq}$ for I may be expected. As the schemes show, the approximately identical values of $\Delta H^{\neq}$ for I and III can be explained only by assuming two classical carbonium ions. It has also been reported that anchimeric assistance is but slight in the case of I.[12]

Scheme 4. Classical ions

Scheme 5. Non-classical ions



The Distributions of Products from Methanolyses of *endo*- and *exo*-5,6-Trimethylene-*endo*-2-norbornyl *p*-Toluenesulfonates (II and IV).— The finding that the solvolyses of II and IV obeyed good first-order kinetics shows that these *p*-toluenesulfonates do not isomerize to any other isomers, which is in accord with the solvolysis of *endo*-2-norbornyl *p*-bromobenzenesulfonate, in which no internal return was observed.[13] Accordingly, the products of the solvolysis of II and IV at completion (100%) give exactly the distribution of products from II and IV respectively.

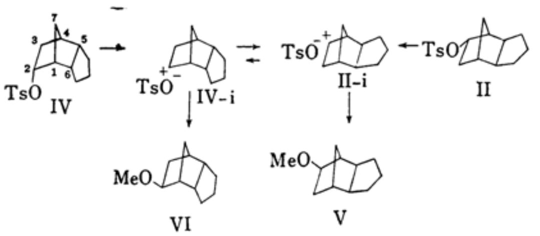
TABLE V. PERCENTAGES OF VI IN THE PRODUCTS FROM METHANOLYSES OF FOUR ISOMERIC *p*-TOLUENESULFONATES

[Tosylate]$_0$=0.1000 M

	p-Toluenesulfonates			
	I	II	III	IV
Reaction temp., °C	59.7	74.8	59.7	74.8
% Reaction	100	100	0[a]	100
VI in products, %	3.2	1.6	7.3[a]	23.4

a) Extrapolated to 0% reaction in Fig. 4.

The results are shown in Table V, where they are compared with those from I and III. In all cases, the products were composed of V and VI. The finding that IV yielded 23% of VI may be explained by the mechanism by which the reaction proceeds through ion pairs with classical structures. The finding that the percentage of VI from IV was greater than that from III may be explained by assuming that the C_1-C_6 bond migration is hindered by the departing TsO^- and also that the attack by the solvent molecule from the *exo*-direction is more favored for IV-i than for III-i.



Experimental[14]

Materials.—Four isomeric 5,6-trimethylene-2-norborneols (VIII, IX, X and XI) were prepared by the methods described in early articles. *exo*-5,6-Trimethylene-*exo*-2-norborneol (VIII) was prepared by adding water to *endo*-dicyclopentadiene in the presence of sulfuric acid,[15] followed by hydrogenation in the presence of platinum(IV) oxide in ethanol at room temperature; m. p. 51.5—53.5°C (reported,[3] 53—54°C).

exo-5,6-Trimethylene-*endo*-2-norborneol (IX) was prepared by the oxidation of VIII to ketone with Chromium(VI) oxide in acetic acid, b. p. 105—106°C/12 mmHg (reported,[2a] 113.5—116.5°C/19 mmHg), n_D^{20} 1.5024[16] (reported,[2a] n_D^{24} 1.5152), followed by reduction with lithium aluminum hydride, b. p. 113—114°C/11.5 mmHg (reported,[2a] 129°C/24 mmHg), n_D^{20} 1.5136, *p*-nitrobenzoate, m. p. 107.5—108.5°C (reported,[2b] 108—109°C). *endo*-5,6-Trimethylene-*exo*-2-norborneol (X) was prepared by the method described by Cristol et al.,[17] via the reaction of NBS with *exo*-5,6-trimethylenenorbornene derived from VIII, m. p. 80.0—80.8°C (reported,[17] 80.5—81.5°C), *p*-nitrobenzoate, m. p. 128—128.5°C (reported, 123—124°C,[2b] 129.5°C[17]). *endo*-5,6-Trimethylene-*endo*-2-norborneol (XI) was prepared by the oxidation of X to ketone with chromium trioxide in acetic acid, followed by reduction with lithium aluminum hydride; m. p. 113.5—115.0°C (reported, 89—90°C,[2a] 120—121°C[18]). The alcohols VIII, IX and X were proved not to be contaminated with other isomeric alcohols on v. p. c. analyses. Analyses were carried out with a Perkin-Elmer vapor phase fractometer, model 154-D, on a 1/4″×2 m. (4 m. in the case of X)

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[12] P. von R. Schleyer, ibid., **86**, 1856 (1964).

[13] S. Winstein and D. Trifan, ibid., **74**, 1147 (1952).

[14] All melting points were observed in capillary tubse by heating them in a sulfuric acid bath and were then corrected.

[15] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

[16] In repeated oxidation experiments, the authors observed a n_D^{21} value of 1.5018.

[17] S. J. Cristol, W. K. Seifert and S. B. Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).

[18] Although Bruson and Riener did not confirm the structure, the compound they synthesized was probably XI. See Ref. 14.

stainless steel column packed with "R" Ucon oil LB-550-X. The alcohols showed the following retention times under the respective corresponding conditions; VIII, 81.2 min.; X, 92.0 min. at 150°C with a helium flow of 72 cc./min.; and IX, 79.9 min. at 190°C with a helium flow of 40 cc./min. The analysis of XI has not been carried out.

Four isomeric *p*-toluenesulfonates (I, II, III and IV) were prepared by treating the above alcohols with *p*-toluenesulfonyl chloride in pyridine at 0°C overnight. All the *p*-toluenesulfonates, with the exception of II, were recrystallized three times from *n*-hexane: m. p.: I, 67.5—67.8°C (reported, 60—61°C,[2] 65.3—67.5°C[3]); II, liq. (reported,[2] liq.); III, 76.5—77.0°C (reported, 48—49°C,[2] 49—50.5 °C[3]); IV, 54.0—55.0°C (reported,[2] 59.5—60°C). Anal. for III, calcd. for $C_{17}H_{22}O_3S$; C, 66.63; H, 7.24; S, 10.46; solvolysis equiv., 306.42; molecular weight, 306.42. Found; C, 67.11; H, 7.71; S, 10.29; solvolysis equiv., 301; molecular weight, 310 (determined by vapor pressure osmometer model 301 A, Mechrolab Inc.). II was used without any purification.

Methanol and ethanol were dried by refluxing them over the corresponding magnesium alkoxide for 10 hr. and then distilled carefully. Anhydrous acetic acid was prepated by refluxing reagent-grade acetic acid with the calculated amount of acetic anhydride for 10 hr. and by subsequent distillation. They were stored under an argon atmosphere.

The Mixed Melting Points of I with III.—About 50-mg. portions of mixtures of I and III were prepared. The melting points were observed in capillary tubes by heating these portions in a sulfuric acid bath.

Infrared Spectra Measurements.—The infrared spectra of the *p*-toluenesulfonates (I, II, III and IV), corresponding alcohols (VIII, IX, X and XI), corresponding methyl ethers and tetrahydro-*endo*-dicyclopentadiene were taken in 0.1 M carbon disulfide; it was thus revealed that the compounds posessing an *endo*-trimethylene group exhibited a characteristic peak at 1250 cm^{-1}.

NMR Spectra Measurements.[19]—Proton NMR spectra of I, III and tetrahydro-*endo*-dicyclopentadiene were run at 20±2°C on a Japan Electron Optics Lab., model JNM-C-60, high-resolution spectrometer at 60 Mc. in carbon tetrachloride solutions, using tetramethylsilane as an internal standard. The spectra of III and tetrahydro-*endo*-dicyclopentadiene exhibited characteristic peaks between $\tau=8.7$ and 8.3, whereas I exhibited a broad peak between $\tau=9.5$ and 8.8 which was not observed in either III or tetrahydro-*endo*-dicyclopentadiene. The complete analysis of the NMR spectra has not been carried out.

Kinetic Measurements. — The sealed ampoule technique was emloyed. Methanolysis and ethanolysis were followed by titrating produced *p*-toluenesulfonic acid with standard sodium ethylate in ethanol, using bromocresol purple as an indicator. Acetolysis was followed by titrating with standard sodium acetate in acetic acid, using crystal violet as an indicator. Several infinity titers showed the purities of the *p*-toluenesulfonates to be; I, 99.2%; II, 96.2%; III, 99.0%; IV, 99.2%.

The Isolation of the Unsolvolyzed *p*-Toluenesulfonate in the Methanolysis of III.—A solution of 733 mg. (2.5 mmol.) of III in 25 ml. of absolute methanol was heated in an ampoule at 59.7°C in a constant temperature bath. After 184 min. (55% reaction), the reaction mixture was cooled at 0°C and poured into 100 ml. of ice-water. Unsolvolyzed *p*-toluenesulfonate, separated as fine crystals, was isolated by filtration and washed with two 5-ml. portions of water and dried in a vacuum desiccator. The yield was 198 mg. (60% of theor.); m. p. 66—67°C. The infrared spectrum (0.1 M in carbon disulfide) agreed exactly with that of an authentic sample (I) in the 650—4000 cm^{-1} range.

The Analysis of the Products from the Methanolyses of Four Isomeric *p*-Toluenesulfonates (I, II, III and IV).—A solution (50 ml.) of the *p*-toluenesulfonates in anhydrous methanol (0.1000 M) was divided into several portions (5—25 ml.), placed in ampoules, and heated in a constant temperature bath. The reaction was stopped by cooling at various percentages of reaction, and the reaction mixture was poured into ice-water and extracted with two 5-ml. portions of *n*-pentane. The pentane extracts were combined, washed with a 10% sodium carbonate solution and water, and dried over sodium sulfate. After concentration to about half volume, the pentane solution was cooled to −50°C in order to crystallize the unsolvolyzed *p*-toluenesulfonate. After the solution had stood overnight at that temperature, the pentane layer was decanted and concentrated to about 0.5 ml. The v. p. c. analyses of the products, methyl ethers, were carried out with a Perkin-Elmer vapor phase fractometer, model 154-D, on a 1/4″×4 m. stainless steel column packed with "R" Ucon oil LB-550-X at 190°C and with a helium flow of 40 cc./min. The ethers V and VI showed retention times of 37.2 and 40.1 min. respectively. The percentage compositions of a mixture were determined by measuring the peak areas of the chromatogram by the triangularization method. Analytical data were reproducible to about ±0.3%.

The authors wish to thank Professor Herbert C. Brown for his many helpful suggestions, Dr. Kunio Okamoto for his valuable discussions, and Mr. Hiroshi Wakida for his measurements of the solvolysis rates.

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[19] We are indebted to Mr. Kato for measuring the spectra.