or an excess of bromine had no effect on the product ratio. In the brominations with excess bromine, the solution was washed with sodium bisulfite followed by water and dried with anhydrous magnesium sulfate prior to concentration of solvent on a Holzman column and glpc analysis.

Carbonations of 2-norbornyllithium were carried out with solid carbon dioxide (crushed Dry Ice) and a solution of the lithium reagent at −70° in pentane according to the following procedures. Since it was shown that the order of addition had no effect on the stereochemical result of this reaction, both methods were used in the carbonations listed above. Solutions of the lithium reagent were added to crushed Dry Ice under pentane and in an argon atmosphere, or crushed Dry Ice was dropped into a stirred solution of the lithium reagent in pentane. The latter method was more inconvenient than the first because bumping occurred occasionally. The solutions were allowed to warm to room temperature, acidified with 2 *N* hydrochloric acid, and treated with boron trifluoride–methanol reagent as discussed above to obtain the methyl ester of 2-norbornanecarboxylic acid for glpc analysis.

Carbomethoxylations of 2-norbornyllithium were carried out with methyl chloroformate and a solution of lithium reagent at −70° in pentane. Since it was again shown that the order of addition of reagents had no effect on the stereochemical result of the reaction, the method of convenience was used in over 90% of the carbomethoxylations; *i.e.*, methyl chloroformate in pentane was added to a stirred solution of the lithium reagent at −70° under argon. The reaction mixture was washed with water to remove any lithium salts, concentrated by distillation of solvent through a Holzman column, and analyzed by glpc.

Bromination with 1,2-dibromoethane of 2-norbornyllithium in pentane at −70° was carried out in the same manner as carbomethoxylation.

Gas chromatographic analyses on the products from norbornyllithium reactions were carried out on an F & M Model 300 chromatograph on a 20-ft QF-1 (5% on Anakrom ABS, 110–120 mesh) 0.25-in., copper column at 75° for 2-norbornyl bromide analyses and at 115° for 2-carbomethoxynorbornane analyses. The temperature was raised to 165° to remove the higher boiling coupling products. Flow rates were varied from 50 to 75 cc/min.

Base-line separations were not obtained for either the esters or the bromides, so that systematic errors due to incorrect assumed peak shapes were evident and probably as high as 20% in unfavorable cases. The errors shown throughout this paper are just average deviations and do not include the systematic errors. It is believed that the qualitative conclusions drawn here are not affected, though the numerical rate constant ratios derived (Table III) can be no more than preliminary approximations.

Acknowledgment. This work was supported in part by the National Science Foundation and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the NSF and to the donors of the Petroleum Research Fund.

π-Electron Participation in the Acetolysis of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate[1]

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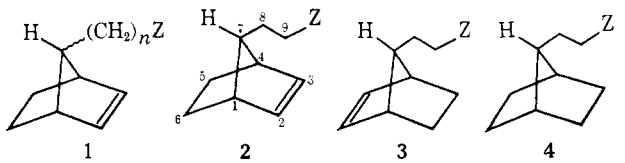
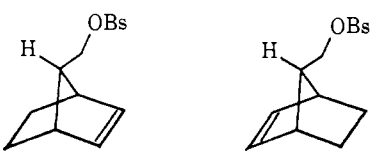
Abstract: The acetolysis of β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate in buffered acetic acid at 25° is ~190,000 times as rapid as that of β-(*anti*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate and is accompanied by a 1,3-type hydrogen shift and extensive ion-pair return. The ultimate products of the acetolysis are tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane, tricyclo[4.2.1.0^{3,7}]non-*exo*-2-yl acetate, and tricyclo[4.3.0.0^{3,7}]non-*exo*-4-yl acetate. When the acetolysis is stopped after 50% reaction, large amounts of returned tricyclo[4.2.1.0^{3,7}]non-*exo*-2-yl *p*-bromobenzenesulfonate can be recovered from the reaction mixture. When the unsaturated brosylate is allowed to stand in unbuffered carbon tetrachloride at 33° it rearranges rapidly to a mixture of tricyclo[4.3.0.0^{3,7}]non-*exo*-4-yl and tricyclo[4.2.1.0^{3,7}]non-*exo*-2-yl *p*-bromobenzenesulfonates which is converted more slowly into the latter brosylate. The rearrangement does not occur in buffered carbon tetrachloride. It is suggested that the facility of the acetolysis compared to that of β-(3-cyclopentenyl)ethyl *p*-bromobenzenesulfonate (~1500 times at 25°) is probably due to the difference in their respective ground-state energies. An explanation is offered to account for the extensive ion-pair return and the nature of the products.

In a continuation of our search for π-electron participation in the solvolysis of some ω-(7-norbornenyl)-alkyl brosylates (**1b**)[2] we have examined the acetolysis of β-(*syn*- and *anti*-7-norbornenyl)ethyl and β-(7-norbornyl)ethyl *p*-bromobenzenesulfonates (**2b**, **3b**, and **4b**, respectively).



1 a, Z = OH; **2** b, Z = OBs; **3** c, Z = OAc; **4**

The β-(7-norbornenyl)ethyl brosylates, **2b** and **3b**, are more suitable for this purpose than the 7-norbornenylmethyl ones, **5** and **6**, examined previously.[2] In addition to possessing a leaving group attached to a primary carbon of "normal" hybridization which is symmetrically disposed with respect to a highly strained



5 **6**

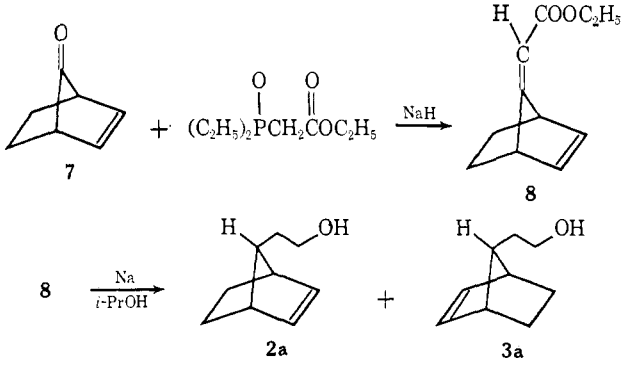
(1) Portions of this work have been presented at (a) the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p 25P, and (b) the 15th Annual Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov 1963; Abstracts, p 79.

(2) R. K. Bly and R. S. Bly, *J. Org. Chem.*, 31, 1577 (1966).

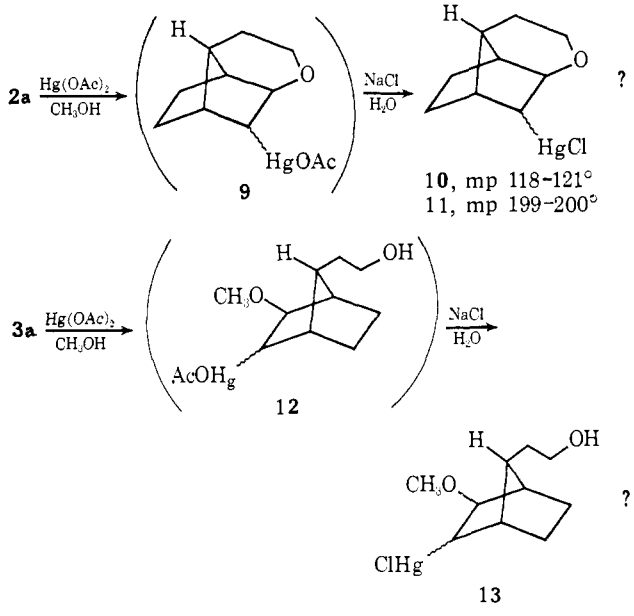
double bond, the *syn*-ethyl derivative, **2**, is geometrically more nearly ideal than the *syn*-methyl, **5**, for maximum π-electron participation.[3] Further, in contrast to the 7-norbornenylmethyl cases, there is no possibility that the β-(7-norbornenyl)ethyl brosylates, **2b** and **3b**, will have their acetolyses complicated by crossover from *syn* to *anti* during the course of the reaction.[2,4]

Results

The synthesis of the requisite alcohols, **2a** and **3a**, was accomplished in the following manner. Norbornen-7-one (**7**)[5] was condensed with triethyl phosphonoacetate according to the procedure of Wadsworth and Emmons[6] to produce ethyl 7-norbornenylideneacetate (**8**) in 73% yield. Reduction of this material with sodium in isopropyl alcohol[7] gave 79% of a 1:3 mixture of the β-(*syn*- and *anti*-7-norbornenyl)ethanols (**2a** and **3a**, respectively) which could be separated by preparative glpc.



Since neither of these alcohols exhibits a π-bonded hydrogen–oxygen stretch in the infrared,[8] their structures were inferred from their relative glpc retention times and from the characteristic appearance of their vinyl hydrogen resonances in the nmr—a clean triplet for **3a**, a perturbed triplet for **2a**.[2] An attempt to confirm these structures chemically by oxymercuration according to the procedure of Henbest and Nicholls[9] gave, in the case of **2a**, an 87% yield of a white crystalline material, mp 118–124°, which could be separated by fractional recrystallization into three parts of a lower melting (118–121°) (**10**) and two parts of a higher melting (199–200°) (**11**) chloromercuri derivative. Neither **10** nor **11** exhibits a hydrogen–oxygen stretch in the infrared. The *anti*-ethanol, **3a**, gave, in poor yield, a viscous, oily chloromercuri derivative **13** which shows a strong hydrogen–oxygen stretch in the infrared at 3450 cm^{-1} and a weak carbonyl stretch at 1735 cm^{-1} (apparently due to undisplaced acetate). Although the structures of these derivatives have not been established with certainty, it seems likely that **10** and **11** are tricyclic ethers (*vide infra*) produced by intramolecular addition of the *syn*-hydroxyl oxygen and mercuric acetate across the double bond while **13** is an addition product of methanolic oxygen and mercuric acetate. The behavior of **3a** is reminiscent of that observed with *anti*-7-norbornenylmethanol under similar conditions.[5] We consider that these results confirm



our structural assignments.

The saturated alcohol, β-(7-norbornyl)ethanol (**4a**), was prepared from **3a** in 96% yield by catalytic hydrogenation.

$$\mathbf{3a} \xrightarrow[\text{Pd–C}]{H_2} \mathbf{4a}$$

Each of the bicyclic ethanols **2a**, **3a**, or **4a** can be converted in the usual manner[2,10] without rearrangement, into the desired brosylate, **2b**, **3b**, or **4b**, respectively.

The solvolysis of **2b** at 25° for 14 hr in anhydrous acetic acid buffered with a slight excess of sodium acetate yields a mixture composed of 22% tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane (**14**) ("deltacyclane"[11]), 42% tricyclo[4.2.1.$0^{3,7}$]non-*exo*-2-yl acetate (**15c**) ("*exo*-2-brendyl" acetate[12]), and 36% tricyclo[4.3.0.$0^{3,7}$]non-*exo*-4-yl acetate (**16c**) ("*exo*-4-brexyl" acetate[12]). These three compounds together constitute more than 99% of the total acetolysis products. When the acetolysis of **2b** was stopped after 1 hr about 23% of the total alkyl brosylate initially supplied as **2b** could be recovered from the reaction mixture as tricyclo[4.2.1.$0^{3,7}$]-non-*exo*-2-yl *p*-bromobenzenesulfonate (**15b**) ("*exo*-2-brendyl" brosylate[12]). After only 8–10 min at 25° both **2b** and **15b** but not tricyclo[4.3.0.$0^{3,7}$]non-*exo*-4-yl *p*-bromobenzenesulfonate (**16b**) ("*exo*-4-brexyl" brosylate[12]) can be detected spectroscopically in the acetolysis mixture. The structures of the products, *e.g.*, **14**, **15b**, **15c**, and **16c**, were established by comparison of their infrared and nmr spectra with those of authentic

(3) We estimate from models that the back side of C_3 in **2** can approach within 2.4 A of the center of the C_2–C_3 double bond without seriously distorting the bond angles at C_1, C_3, C_7, and C_8, while the back side of C_3 in **5** is at least 2.8 A from the center of the double bond in the "undistorted" structure; *cf.* footnote 19 in ref 2.

(4) J. A. Berson and J. J. Gajewski, *J. Am. Chem. Soc.*, 86, 5020 (1964).

(5) R. K. Bly and R. S. Bly, *J. Org. Chem.*, 28, 3165 (1963).

(6) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, 83, 1733 (1961).

(7) L. Bouveault and G. Blanc, *Bull. Soc. Chim. France*, 31, 1206 (1904).

(8) We thank Dr. Lester P. Kuhn, Ballistics Research Laboratory, Aberdeen Proving Ground, Md., for this determination.

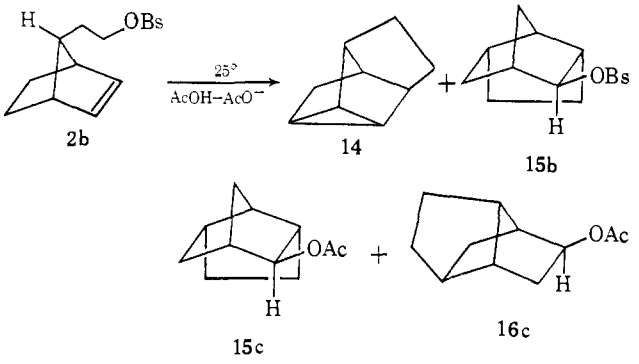
(9) H. B. Henbest and J. B. Nicholls, *J. Chem. Soc.*, 227 (1959).

(10) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).

(11) The name suggested for tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane by Dr. Alex Nickon, Department of Chemistry, Johns Hopkins University, Baltimore, Md., in a private communication to the authors.

(12) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, 87, 1613, 1615 (1965).

samples prepared in a clearly unequivocal manner by Nickon and co-workers.[12]

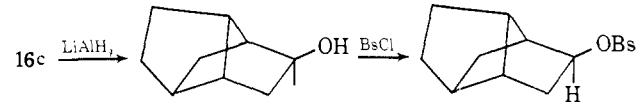


2b 14 15b 15c 16c

The acetolysis of **2b** produces no detectable amount, *i.e.*, less than 0.1%, of the unrearranged ester β-(*syn*-7-norbornenyl)ethyl acetate (**2c**). When an authentic sample of **2c** was added to the acetolysis mixture and analyzed by glpc, it appeared as a new peak, cleanly separated from the other components. When subjected to the acetolysis conditions, *viz.* ~0.2 *M* sodium acetate, it was recovered unchanged after 3 hr at 25°.

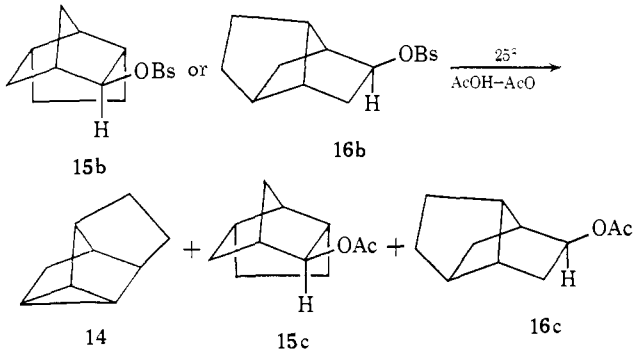
The ratio of brendyl to brexyl acetate, **15c/16c**, remains constant at 1.1–1.2 throughout the course of the acetolysis of **2b** at 25°, and is independent of the nature and amount of added salt (see Table VII in Experimental Section). Each of the volatile products produced in the acetolysis, *i.e.*, **14**, **15c**, and **16c**, is stable in buffered acetic acid at this temperature.

Since it appeared that appreciable amounts of the products obtained in the acetolysis of **2b** must actually arise from the rearranged brosylate(s), we prepared *exo*-4-brexyl *p*-bromobenzenesulfonate (**16b**) as shown below and have examined its acetolysis and that of



16a 16b

exo-2-brendyl *p*-bromobenzenesulfonate (**15b**) separately. At 25° both yield the same products found in the acetolysis of **2b**, *viz.* **14**, **15c**, and **16c**. In each case these three compounds constitute more than 99% of the detectable products. The ratio of brendyl to



15b 16b 14 15c 16c

brexyl acetate, **15c/16c**, produced under these conditions from either **15b** or **16b** is invariant with time and identical (see Table VIII in Experimental Section), *i.e.*, 1.1–1.2, with that found in the acetolysis of the unsaturated brosylate **2b**. When the acetolysis of **15b** was interrupted prior to completion, the starting brosylate was the only one which could be isolated or detected in the reaction mixture. When the acetolysis of **16b** was interrupted after 15 min at 25°, again only *exo*-2-brendyl *p*-bromobenzenesulfonate (**15b**) could be recovered.

In an effort to determine the nature of the intermediates involved, we have followed the solvolysis of β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (**2b**) by nmr. By repetitive scanning of an ~0.18 *M* solution of **2b** in anhydrous acetic acid containing ~0.20 *M* sodium acetate, it is possible to observe the disappearance of the 4-hydrogen singlet at δ 7.74 due to the aromatic hydrogens of an alkyl brosylate, the appearance of the two 2-hydrogen singlets at δ 7.67 and 7.61 due to the aromatic hydrogens of the *p*-bromobenzenesulfonate anion, and the disappearance of the 2-hydrogen triplet centered at δ 5.80 due to the vinyl hydrogens. Unfortunately the complexity of the nmr spectrum in the region from δ 4.50 to 3.85 —resonances of all >C*H*O and C*H*$_2$O hydrogens appear in this region as well as several high-intensity spinning side bands from the solvent itself—and the necessity of working with relatively dilute (for nmr) solutions make it impossible to say with certainty whether any *exo*-4-brexyl *p*-bromobenzenesulfonate (**16b**) is formed during the acetolysis of **2b**, but *exo*-2-brendyl *p*-bromobenzenesulfonate (**15b**) is clearly evident in the acetolysis mixture long after the vinyl hydrogen resonances of **2b** have disappeared.

The rate of acetolysis of **2b** can be followed conveniently by nmr. Since no unsaturated products are produced in the reaction, the over-all rate of disappearance of **2b** can be calculated from integral values of the vinyl hydrogen region of the spectrum (δ 6.0–5.7) at known times. The rate constants, *k*, obtained in this fashion for acetolyses carried out in a controlled-temperature probe of a Varian A-60 nmr spectrometer are recorded in Table I.

$$\mathbf{2b} \xrightarrow[\text{AcOH–AcO}^-]{k} \text{products}$$

In spite of the poor temperature control and bad point-to-point scatter, plots of log [**2b**] *vs.* time gave reasonably good straight lines to about 70% reaction, and the reproducibility between weighted least-squares plots (see Experimental Section) of runs at similar ionic strength ($\mu \sim 0.2$, *viz.* 1–2 and 9–10) is acceptable. The activation parameters, computed from the slope and intercept of a least-squares plot of log (k/T) *vs.* $1/T$ for runs at similar acetate ion concentration (0.197 *M*), are recorded in Table VI, the sodium acetate "*b*" value[13] in Table V.

It is apparent from repetitive nmr scans of solvolyzing **2b** (0.18 *M* **2b** in buffered acetic acid) that this unsaturated brosylate disappears at a faster rate than *p*-bromobenzenesulfonate anion is formed. An attempt to determine the rate at which **2b** rearranges to **16b** and/or **15b**, or dissociates to products, by extending the integral traces to include the aromatic hydrogens of the alkyl brosylates at δ 7.9–7.7 and of the brosylate anion at δ 7.7–7.5 gave values of k_1 and k_2 which fluctuated badly from run to run (Table I). However, fairly consistent values for the *fraction* of **2b** which rear-

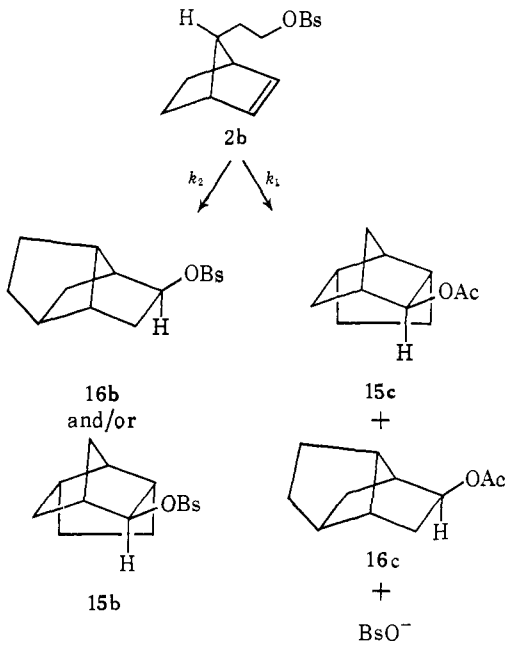
(13) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

Table I. Nmr-Determined First-Order Acetolysis Constants of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (**2b**)

Run	Temp, °C[a]	[**2b**]$_i$, *M*	[NaOAc]$_i$, *M*	μ	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}	10^4k, sec^{-1}	$k_2/(k_1 + k_2)$	n[b]
1	15.8	0.283	0.197[c]	0.188			5.49		8
2		0.198	0.197	0.188			5.72		12
3	23.0	0.183	0.000	0.000			9.48		29
4[d]	23.7	0.176	0.197	0.189	6.1	4.9	11.0	0.45	28
5[d]	24.2	0.173	0.295	0.283	5.6	7.4	13.0	0.57	31
6[d]	24.5	0.174	0.100[c]	0.096	3.3	6.0	9.33	0.65	30
7[d]	24.7	0.193	0.197	0.189	5.8	6.0	11.8	0.51	30
8[d]	29.3	0.186	0.197	0.190	11	8.0	18.8	0.42	20
9	34.5	0.194	0.197	0.189			33.6		11
10		0.294	0.197	0.189			34.0		12

[a] Determined from the chemical shift between the carbon- and oxygen-bound hydrogens of methanol or ethylene glycol. (*Cf.* Publication No. 87-100-110, Varian Associates, pp 29, 32.) We estimate that the temperature within each run is controlled to within ±1°. [b] Number of integral determinations per run. [c] Sufficient to neutralize all the *p*-bromobenzenesulfonic acid produced during the period that the rate was followed kinetically. [d] Total brosylate normalized to 100% at each point.

ranges, $k_2/(k_1 + k_2)$, could be computed from the intercept of a first-order plot of the rate of *p*-bromobenzenesulfonic acid formation, $[(H^+)_\infty - (H^+)]$, during the acetolysis of **2b** at 25°, determined titrimetrically after



99% of the starting brosylate had been rearranged or solvolyzed (see Experimental Section). These data are summarized in Table II, and indicate that upon acetolysis at 25° ($\mu \approx 0.075$) about 40% of the unsaturated brosylate **2b** returns to saturated brosylate(s) which is solvolyzed much more slowly. The fraction returned is apparently independent of the nature and amount of added salts.

Table II. Titrimetric First-Order Acetolysis Constants from β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (**2b**) at 25.00°

Run	[**2b**]$_i$, *M*	[NaOAc]$_i$, *M*	[NaOBs]$_i$, *M*	μ	$k_2/(k_1 + k_2)$	10^5k_3, sec^{-1}[a]
11	0.0178	0.0980	...	0.0939	0.42	2.63
12	0.0236	0.0815	...	0.0781	0.40	2.32
13	0.0209	0.0665	...	0.0617	0.41	2.18
14	0.0218	0.0644	0.0219	0.0827	0.42	2.09
15	0.0228	0.0590	0.0228	0.0784	0.43	1.47
16	0.0235	0.0299	0.0309	0.0583	0.42	1.33
17	0.0241	0.0605	...	0.0795[b]	0.39	2.92

[a] Reproducible to ±0.2 × 10^{-5} sec^{-1}. [b] Contains 0.0225 *M* lithium perchlorate.

Table III. Titrimetric First-Order Acetolysis Constants of *exo*-2-Brendyl *p*-Bromobenzenesulfonate (**15b**)

Run	Temp, °C	[ROBs]$_i$, *M*	[NaOAc]$_i$, *M*	μ	10^5k_4, sec^{-1}
18	25.00	0.0243	0.0298	0.0286	1.55[c]
19		0.0230	0.0292	0.0280	1.50[c]
20	40.06	0.0244	0.0303	0.0295	11.8
21		0.0231	0.0297	0.0289	11.6
22	40.04	0.0230	0.0593	0.0577	13.9
23		0.0235	0.0792	0.0771	15.3
24		0.0233	0.0584	0.0785[d]	18.9[d]
25		0.0237	0.0587	0.0784[e]	14.6[e]
26	55.21	0.0227	0.0290	0.0287	69.7
27		0.0225	0.0290	0.0287	62.8

[a] Contains 0.0222 *M* lithium perchlorate. [b] Contains 0.0218 *M* sodium *p*-bromobenzenesulfonate. [c] See Table VI, footnote *f*.

The titrimetric acetolysis rate constant(s) of the rearranged brosylate(s), k_3, may be computed from the slope

16b and/or **15b** $\xrightarrow[\text{AcOH–AcO}^-]{k_3}$ **14**, **15c**, **16c**, and *p*-bromobenzenesulfonic acid

of the same first-order plot of $[(H^+)_\infty - (H^+)]$ formed from **2b** as starting material at times greater than 70 min (see Experimental Section). These data are included in Table II and may be compared with the titrimetric first-order rate constants, k_4, determined in the usual manner for the acetolysis of pure *exo*-2-brendyl *p*-bromobenzenesulfonate (**15b**) (Table III).

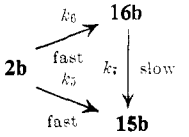
15b $\xrightarrow[\text{AcOH–AcO}^-]{k_4}$ **14**, **15c**, **16c**, and *p*-bromobenzenesulfonic acid

The good linear first-order plots and the excellent agreement between k_3 and k_4 at 25°—when corrected to an initial acetate ion concentration of 0.0298 *M*, $k_3 = 1.63 \times 10^{-5}$ sec^{-1},[14] while measured $k_4 = 1.53 \times 10^{-5}$ sec^{-1} at this concentration (Table III)—indicates that essentially all of the rearranged brosylate present in the acetolysis mixture from **2b** after 70 min at this temperature (*i.e.*, after 99% of the unsaturated brosylate **2b** has disappeared) is the *exo*-2-brendyl, **15b**. Hence either very little returned *exo*-4-brexyl *p*-bromobenzenesulfonate (**16b**) is formed during the acetolysis of **2b**

(14) Computed from the data in Table II using the 25° acetate-"*b*" value in Table V.

under these conditions or the reactivity of **16b** must approach that of the unsaturated brosylate **2b**.

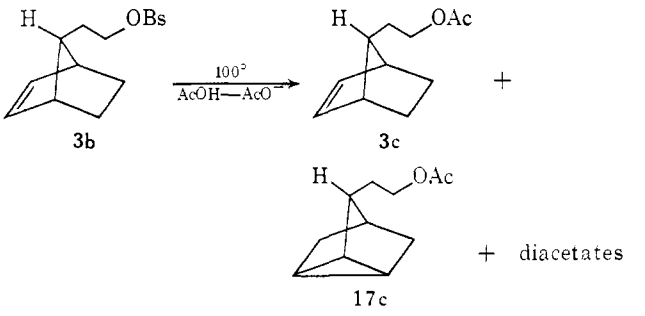
Since we had been unable to detect either kinetically or by product analysis the formation of any *exo*-4-brexyl *p*-bromobenzenesulfonate (**16b**) during the acetolysis of the unsaturated brosylate, **2b**, we examined by nmr the rearrangement of **2b** in the nonnucleophilic solvent, carbon tetrachloride. In the absence of the acetic acid side bands and the interfering resonances of the two tricyclic acetates, **15c** and **16c**, *vide supra*, the formation and disappearance of **16b** is clearly evident. In unbuffered, spectral grade carbon tetrachloride at 33°, the dissolution of **2b** is followed by a 3–8-min induction period after which the triplets at δ 5.80 and 3.91 —due respectively to the vinyl and CH_2O hydrogens of the unsaturated brosylate— are rapidly replaced by a small apparent doublet centered at δ 4.37 and a larger singlet at δ 4.00. The doublet itself is converted more slowly into the singlet. Evaporation of the solvent after the doublet has disappeared yields **15b** uncontaminated with any other alkyl brosylate. Under similar conditions a solution of **16b** rearranges, at a comparable rate, to **15b**. Hence, it appears that in carbon tetrachloride, **2b** rearranges rapidly to a mixture of **15b** and **16b** which in turn is converted more slowly to **15b**, *viz.*



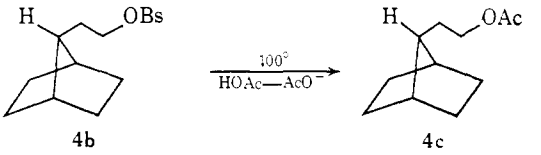
About 2 min after the initial induction period, **16b** constitutes ~35% of the total rearranged brosylate present in the solution, but decreases rapidly thereafter. After 4 hr, its presence can no longer be detected by nmr. An attempt to determine the fraction of **2b** which returns to **16b** was unsuccessful apparently because the rearrangements are not kinetically first order and the ratio $k_6/(k_5 + k_6)$ varies with time. At 33° **2b** is stable for several hours in carbon tetrachloride which contains a small amount of pyridine; thus we believe that both the initial induction period and the kinetic anomalies may be the result of acid catalysis by *p*-bromobenzenesulfonic acid which is formed when **2b** is hydrolyzed by traces of water in the solution.

The rearrangement of the unsaturated brosylate **2b** to the brendyl brosylate **15b** is quite facile even in the absence of added solvent. In fact, **2b** can be converted completely to crystalline **15b** with no apparent decomposition, by heating the former to ~30° (*i.e.*, just above its melting point) for about 2 min, seeding the melt with a small crystal of **15b**, and scratching the mixture with a stirring rod for about 5 min.

The solvolytic reactivity of β-(*anti*-7-norbornenyl)-ethyl and of β-(7-norbornyl)ethyl *p*-bromobenzenesulfonate (**3b** and **4b**, respectively) differs markedly from that of **2b**. Both **3b** and **4b** are essentially unreactive in buffered anhydrous acetic acid at 25°. At 100° after one half-life only **3c** could be detected when the volatile products from the acetolysis of **3b** were analyzed by glpc. A similar analysis after nine half-lives indicates that the reaction mixture contains about 89% **3c**, 2% β-(2-nortricyclyl)ethyl acetate (**17c**), and 9% of at least two diacetates, *viz.*



When heated under solvolytic conditions, pure **3c** is converted slowly to a similar mixture of **17c** and diacetates. Under comparable conditions **4b** yields β-(7-norbornyl)ethyl acetate (**4c**) exclusively.



The acetolyses of both **3b** and **4b** are kinetically first order in alkyl brosylate to greater than 80% reaction. The apparent first-order titrimetric rate constants are recorded in Table IV, the "*b*" values, derived in the usual manner from runs at different initial salt concentrations,[13] are recorded in Table V, and the activation parameters, computed from the slope and intercept on a plot of $\log(k/T)$ *vs.* $1/T$, are given in Table VI.

Table IV. Titrimetric Apparent First-Order Acetolysis Constants of β-(*anti*-7-Norbornenyl)ethyl and β-(7-Norbornyl)ethyl *p*-Bromobenzenesulfonate (**3b** and **4b**, respectively[a])

Run	Compd	Temp, °C	$[ROBs]_i$, *M*	$[NaOAc]_i$, *M*	μ	10^6k, sec^{-1}
28	**3b**	85.1	0.0219	0.0283	0.0290	4.89
29			0.0218	0.0283	0.0290	4.93
30		98.9	0.0216	0.0274	0.0286	18.4
31			0.0215	0.0277	0.0289	18.7
32			0.0216	0.0540	0.0563	25.4
33			0.0216	0.0545	0.0880[b]	26.5[b]
34			0.0216	0.0800	0.0834	32.0
35			0.0216	0.0545	0.0785[c]	26.2[c]
36		99.5	0.0214	0.0299	0.0312	21.4
37		115.0	0.0209	0.0268	0.0284	64.7
38		115.6	0.0214	0.0293	0.0311	69.3
39	**4b**	85.1	0.0217	0.0279	0.0286	4.64
40			0.0217	0.0280	0.0287	4.65
41		98.9	0.0215	0.0275	0.0287	19.8
42			0.0215	0.0275	0.0287	19.8
43			0.0215	0.0275	0.0287	19.9
44			0.0214	0.0273	0.0285	19.4
45			0.0216	0.0544	0.0567	26.4
46			0.0215	0.0811	0.0846	34.8
47			0.0216	0.0543	0.0865[d]	28.4[d]
48			0.0214	0.0547	0.0795[e]	28.7[e]
49		115.0	0.0211	0.0269	0.0285	67.1
50			0.0210	0.0270	0.0286	67.8

[a] Professor J. H. Richards, who has independently synthesized and solvolyzed the tosylates of **3a** and **4a**, reports their titrimetric first-order acetolysis constants at 61.5° as 1.73×10^{-7} and 1.12×10^{-7} sec^{-1}, respectively (private communication from Professor J. H. Richards, Department of Chemistry, California Institute of Technology). The titrimetric acetolysis constants of **3b** and **4b**, extrapolated from our data at higher temperatures, are 4.42×10^{-7} and 4.97×10^{-7} sec^{-1}, respectively. [b] Contains 0.0297 *M* lithium perchlorate. [c] Contains 0.0208 *M* sodium *p*-bromobenzenesulfonate. [d] Contains 0.0287 *M* lithium perchlorate. [e] Contains 0.0215 *M* sodium *p*-bromobenzenesulfonate.

Table V. Dependence of Apparent First-Order Acetolysis Constants upon Added Salts

Compd	Temp, °C	$10^5 k_0$, sec^{-1}	—Values of "b" for added— NaOAc	NaOBs	$LiClO_4$
2b[a]	24.5	83[a]	~3	...	...
15b[b]	25.0	1.20[c]	~12	...	...
15b	40.1	9.51[d]	7.7	3.7	24.3
3b	98.9	1.15	22.4	2.9	2.7
4b	98.9	1.16	25.0	4.7	3.1

[a] Calculated from the nmr-determined data in Table I. [b] Determined from the linear portion of the titrimetric first-order plot of $[(H^+)_\infty - (H^+)]$ formed from **2b** as starting material after eight half-lives. [c] *I.e.*, k_3 at $\mu = 0.0$. [d] *I.e.*, k_4 at $\mu = 0.0$.

than the 7.0–7.2 kcal/mole difference in free energy of activation that these reactivity ratios represent.

The esters[22] produced in the acetolysis of **2b** are derived from an intermediate whose *effective symmetry* within the time scale of the reaction is that of a charge-delocalized, asymmetric ethano-bridged, norbornyl cation.[23] The only esters which we have been able to detect, *viz.* *exo*-2-brendyl *p*-bromobenzenesulfonate and acetate (**15b,c**) and *exo*-4-brexyl acetate (**16c**), could arise from the charge-localized, asymmetric ethano-bridged, norbornyl cations, 2-brendyl (**18**) and 4-brexyl (**19**), respectively. However, since **15c** and **16c** are formed in the same proportion during the kinetically controlled acetolyses of **2b**, **15b**, and **16b**, it appears that the same product-forming intermediate is involved in each case. Our data provide no indication of whether this intermediate owes its effective symmetry to an equilibration of the charge-localized cations **18** and **19** prior to their reaction with nucleophile or to the presence of a single charge-delocalized cation **20**.[23] Whatever its structure, the intermediate resembles a norbornyl cation in its bias for *exo* attack by an external nucleophile.[24]

Table VI. Activation Parameters and Apparent First-Order Acetolysis Constants of the Bi- and Tricyclic Brosylates

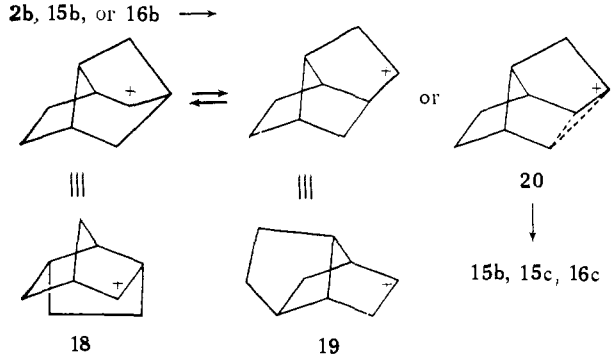
Compd	Method	k, sec^{-1} [a]	ΔH^*, kcal/mole[b]	ΔS^*, eu[b]
2b	Nmr[c]	9.1×10^{-4}	16.3 ± 0.1	-17.0 ± 0.2
15b	Titration[e]	1.56×10^{-5} [f]	23.66 ± 0.04[f]	-1.14 ± 0.15[f]
3b	Titration[e]	4.8×10^{-9} [d]	23.9 ± 0.1	-16.3 ± 0.2
4b	Titration[e]	6.4×10^{-9} [d]	23.0 ± 0.1	-18.8 ± 0.2

[a] At 25° in the presence of 0.03 *M* sodium acetate. [b] Precision estimated as twice the standard deviation. [c] Over-all rate of disappearance of **2b**, *i.e.*, $(k_1 + k_2)$. [d] Extrapolated from the data in Tables I and V. [e] Rate of sodium *p*-bromobenzenesulfonate formation. [f] Nickon, *et al.*, who have measured the acetolysis rate of this compound spectroscopically, report $k = 1.92 \pm 0.03 \times 10^{-5}$ sec^{-1} at 24.9°, $\Delta H^* = 23.1$ kcal/mole, and $\Delta S^* = -2.4$ eu.[26]

Discussion

The *p*-bromobenzenesulfonate of β-(*syn*-7-norbornenyl)ethanol (**2b**) is one of the more reactive primary brosylates. At 25° in acetic acid containing ~0.03 *M* sodium acetate its reactivity is ~1.3 times that of cyclopropylcarbinyl,[15] 110 times that of benzyl,[16] and *only twofold less than the much vaunted secondary brosylate, anti-7-norbornenyl p-bromobenzenesulfonate*.[17]

The acetolysis of **2b** is aided by π-electron delocalization in the transition state. At 25° it is ~190,000 times as rapid as that of the *anti* brosylate,[18] **3b**; ~140,000 times as rapid as β-(7-norbornyl)ethyl *p*-bromobenzenesulfonate (**4b**) (Table VI)! Since these latter two brosylates must be about as reactive as ethyl *p*-bromobenzenesulfonate under these conditions ($k = \sim 5.3 \times 10^{-9}$ sec^{-1})[19] it is clear that the above rate ratios reflect the enhanced reactivity of **2b** rather than the inertness of the model compounds.[20] Furthermore, since the acetolyses of **3b** and **4b** exhibit considerable bimolecular character[21] (*cf.* the "*b*" values for added sodium acetate, Table V), the driving force for unimolecular ionization of **2b** may actually be greater



The acetolysis of **2b** is accompanied by extensive ion-pair return.[25] About 40% of the starting brosylate is

(15) Estimated as three times the acetolysis constant of cyclopropylcarbinyl *p*-toluenesulfonate at this temperature [D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964)].

(16) Estimated as three times the acetolysis constant of benzyl *p*-toluenesulfonate at this temperature [S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951)].

(17) (a) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952); (b) P. Bruck, D. Thompson and S. Winstein, *Chem. Ind.* (London), 590 (1960).

(18) Although we have made no attempt to correct the acetolysis constant of **2b** for "field-induced" retardation by the double bond, our experience with the 7-norbornenylmethyl brosylates (**5** and **6**)[2] suggests that this effect would be quite small in the case of **2b**.

(19) Estimated as three times the acetolysis constant of ethyl *p*-toluenesulfonate at this temperature [S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952)].

(20) See R. C. Fort, Jr., and P. Schleyer, *Chem. Rev.*, **64**, 277 (1964), for a discussion of this point.

(21) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965).

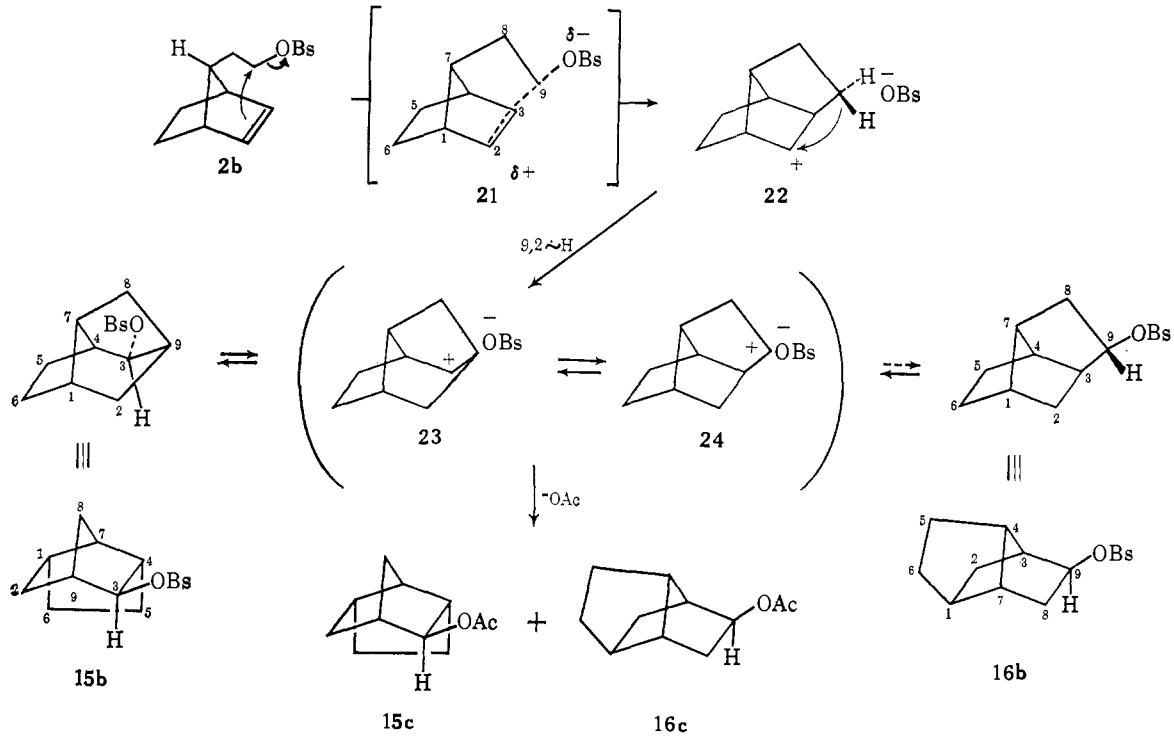
(22) Since many of the ion pairs, in Schemes I, II, and III, could react by hydride abstraction to yield deltacyclane (**14**), we do not know at which stage of the reaction this hydrocarbon is formed.

(23) Let us be *absolutely* clear on this point. We can testify *only* to the effective over-all symmetry of the intermediate, not to the means by which this symmetry is achieved. We have represented the rearranged intermediate in Scheme I as interconverting charge-localized cation anion pairs, *viz.*, **23** and **24**, and in Scheme II as a single charge-delocalized cation anion pair (**32**) purely as a matter of convenience. We cannot distinguish experimentally between these two alternatives.

(24) (a) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965); (b) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(25) See S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109 ff, for a discussion of salt effects and ion pairs in solvolysis reactions.

Scheme I



converted to the less reactive *exo*-2-brendyl *p*-bromobenzenesulfonate (**15b**) (Table II) prior to acetate formation. Since the fraction of solvolyzing **2b** that returns to **15b** is unaffected by added sodium *p*-bromobenzenesulfonate (*cf.* Table II, runs 13–16), it appears that **15b** is formed by ion-pair rather than external-ion return.[25] Since the proportion of **15b** formed in the reaction of **2b** is decreased but slightly by the addition of lithium perchlorate, it is probable that most of the acetates also arise by ion-pair return rather than from a free, solvated cation.[25]

The acetolysis of **2b** may be accompanied by ion-pair return to *exo*-4-brexyl *p*-bromobenzenesulfonate (**16b**) as well. In the poor ionizing solvent carbon tetrachloride, the acid-catalyzed rearrangement of **2b** produces both **15b** and **16b**. Return from the product-forming cation *acetate* ion pair,[23] *vide supra*, under the kinetically controlled conditions of the acetolyses of **2b**, **15b**, and **16b** produces both **15c** and **16c** in nearly equal amounts. Hence it is unlikely that return from a similar cation *brosylate* ion pair[23] would yield **15b** exclusively. Our inability to detect **16b** either titrimetrically or spectroscopically during the acetolysis of **2b** is understandable since the investigations of Nickon and his group reveal that **16b** is sufficiently reactive under these conditions[26] that its steady-state concentration would be quite small even if the remaining 60% of **2b** reacted by this route.[27]

The simplest explanation which will accommodate our experimental observations to date is shown in Scheme I, which suggests the initial formation of a charge-localized, 2-brexyl cation brosylate ion pair (**22**) that rearranges *via* a single 1,3-type hydrogen shift[28] into equilibrating 2-brendyl and 4-brexyl cation brosylate ion pairs, **23** and **24**, respectively.[23] The new cation brosylate ion pairs may then undergo ion-pair return to the corresponding brosylates **16b** and/or **15b** or solvolyze to acetates.

Bartlett and co-workers[29] have recently suggested that the solvolysis of a β-(3-cyclopentenyl)ethyl arenesulfonate occurs with symmetric π-electron delocalization. Bartlett, Bank, Crawford, and Schmid[29a] have observed that the hydrolysis of β-(3-cyclopentenyl)-ethyl *p*-toluenesulfonate (**25d**; R, R′ = H) in 50% ethanol–water (Y = 1.66) at 70° is 5.7 times as rapid as that of β-cyclopentylethyl *p*-toluenesulfonate and that the formolysis of β-(3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**25e**; R, R′ = H) in anhydrous formic acid (Y = 2.05) is about 640 times as rapid at 25.5° as that of the saturated *p*-nitrobenzenesulfonate. Since an *exo*-norbornyl derivative is formed from the β-(3-cyclopentenyl)ethyl arenesulfonate (**25**; R, R′ = H) in each case, they suggest that the solvolyses of these unsaturated compounds are aided by π-electron delocalization in the transition state of the rate-limiting step. Bartlett and Sargent[29b] found that at 60° in buffered acetic acid β-(3-methyl-3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**25e**; R = CH_3, R′ = H) reacts 7.0 times faster than β-(cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**25e**; R, R′ = H) and that the corresponding β-(3,4-dimethyl-3-cyclopentenyl)ethyl ester (**25e**; R, R′ = CH_3) solvolyzes 5.5 times faster than the monomethyl compound. They interpret these roughly similar rate increments to indicate that each methyl group is stabilizing the transition state of the rate-limiting step to about the same extent and

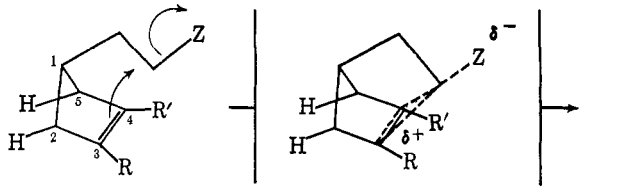
(26) Private communication from Dr. Alex Nickon.

(27) It is also clear that the acetolysis of 2b produces no 2-brexyl *p*-bromobenzenesulfonate[12] since the latter is sufficiently unreactive under these conditions[26] that its presence in the reaction mixture would have been apparent.

(28) Such shifts are well documented in norbornyl ions and ion pairs; *cf.* (a) J. A. Berson in "Molecular Rearrangements," Vol. I, P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 139 ff; (b) J. A. Berson and P. W. Grubb, *J. Am. Chem. Soc.*, **87**, 4016 (1965); (c) B. M. Benjamin and C. S. Collins, *ibid.*, **88**, 1556 (1966).

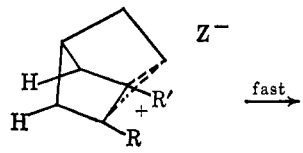
(29) (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Am. Chem. Soc.*, **87**, 1288 (1965); (b) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

suggest that the π-electron delocalization must, therefore, be symmetric with respect to C_3 and C_4 in the transition state **26**. Finally, they reason that the solvolysis of a *symmetric starting material* which proceeds *via* a *symmetric transition state*[30] should yield a *symmetric intermediate* and propose that the ionization of a β-(3-cyclopentenyl)ethyl arenesulfonate occurs essentially as shown below.



25 **26**

b, Z=OBs; d, Z=OTs;



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e, Z=ONs

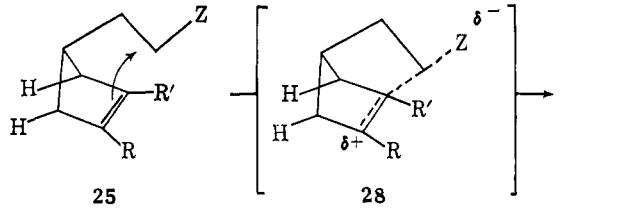
Since the β-(*syn*-7-norbornenyl)ethyl (**2**) and the β-(3-cyclopentenyl)ethyl (**25**; R, R′ = H) systems are quite similar it is likely that their ionizations will follow a similar course and the acetolysis of **2b** might thus be better represented as shown in Scheme II. Here the initial ionization is presumed to occur with symmetric π-electron participation in the transition state **30** to yield a symmetric π-electron-delocalized,[30] symmetric ethano-bridged, norbornyl cation brosylate ion pair **31**, which is converted by a single 1,3-type hydrogen shift[28] into a charge-delocalized, asymmetric ethano-bridged, norbornyl cation brosylate ion pair **32**.[23] In the same manner as its kinetic and stereochemical equivalent, the equilibrating ion pair **23** and **24** of Scheme I,[23] this new ion pair may either return to the brosylates **16b** and/or **15b** or solvolyze to the corresponding acetates **15c** and **16c**.

A comparison of our data with that of Bartlett and co-workers emphasizes the important role that the ground state may play in determining the extent of π-electron participation during solvolysis. We estimate from the data of Bartlett, *et al.*,[29] that the reactivity of **2b** in acetic acid buffered with 0.03 *M* sodium acetate at 25° would exceed that of **25b** (R, R′ = H) by about 1500 times.[31] Since the two acetolyses have similar entropies of activation, this rate factor must reflect a difference of nearly 4.3 kcal/mole in their respective activation enthalpies, a value considerably smaller than the 7.3 kcal/mole difference in the heats of hydrogenation in acetic acid at 25° of norbornene (33.13 kcal/mole)[32] and cyclopentene (25.67 kcal/mole).[32] Therefore it is likely that the enhanced reactivity of **2b** with respect to **25b** (R, R′ = H) reflects the increased nucleophilicity of the more highly strained norbornene double bond rather than a greater stability of **30** with respect to **26** (R, R′ = H).[33]

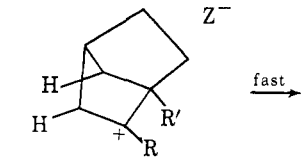
Our data appear to exclude the possibility that the acetolysis of **2b** is accompanied by a C_5 or C_6 hydrogen shift. If such a shift were to occur from either **22** or **31** it would produce an ion pair(s) (**33** or **35**) with a greater net-charge separation—a process which Lee and Lam have shown to be unfavorable in the related β-(3-cyclopentenyl)ethyl case[34]— and the anion of the new ion pair(s) would then have to diffuse rapidly, without dissociating, to the opposite side of the cation before returning to *exo*-4-brexyl and/or *exo*-2-brendyl *p*-bromobenzenesulfonate, as shown below.[35] We can conceive of no obvious path by which such diffusion could occur in a structured, intimate ion pair,[36]

(30) A referee has suggested that the large rate enhancement which we have observed in the acetolysis of **2b** and attributed in part to the increased ground-state energy of the starting material brings "into serious question the basis for the argument used by Bartlett and Sargent" and is "clearly inconsistent with the thesis that the rate enhancement observed in the cyclopentenylethyl system requires the resonance stabilization of a bridged norbornyl cation to be explicable." His point is probably well taken since Bartlett and Sargent apparently did not consider the effect of methyl substitution on the ground-state energies of the starting material **25**. We doubt, however, that the inclusion of such effects would seriously alter Bartlett and Sargent's argument.

It is clear from steric and bond-energy considerations that, apart from their effect on the developing positive charge, successive methyl substitutions on the double bond of a β-(3-cyclopentenyl)ethyl derivative should stabilize the starting material **25** with respect to their less olefin-like solvolytic transition states **26** or **28** and cause a progressive *decrease* in reactivity. Only if appreciable positive charge is developed in the transition state at the site of the methyl substitution(s) could the transition state be stabilized with respect to the ground state. The first methyl substitution (R = CH_3) should result in a rate enhancement whether the transition state is symmetric or asymmetric, but the second methyl substitution (R′ = CH_3) should increase the solvolytic rate



25 **28**



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for this reason only if appreciable charge is developed in the transition state at both olefinic carbons. If the transition states are asymmetric (**28**) the first methyl substitution (R = CH_3) would decrease by a factor of two the number of ways in which solvolyzing **25** (R = CH_3, R' = H) could reach the transition state. The second methyl substitution (R' = CH_3) would then double the number of paths to the disubstituted asymmetric transition state (**28**; R, R′ = CH_3), but could in this manner enhance the rate by only a factor of two. Thus, although the introduction of statistic and ground-state considerations make it appear unlikely that the first and second methyl substitutions would enhance the solvolytic rate of a β-(3-cyclopentenyl)ethyl derivative to the same extent even if the transition state were perfectly symmetric, it is apparently necessary to postulate some delocalization of charge to both olefinic carbons to account for the 5.5 times rate enhancement which the second methyl substitution causes.

(31) We estimate from the data of Bartlett, *et al.*,[29a] on the tosylate, that the first-order acetolysis constant of β-(3-cyclopentenyl)ethyl *p*-bromobenzenesulfonate in the presence of 0.03 *M* sodium acetate would be $\sim 6 \times 10^{-6}$ sec^{-1} at 25°.

(32) (a) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, 79, 4116 (1957); (b) R. B. Turner, in "Theoretical Organic Chemistry," Abstracts of Papers from the Kekulé Symposium, London, Sept 1958, Butterworth and Co., London, 1959, p 67 ff.

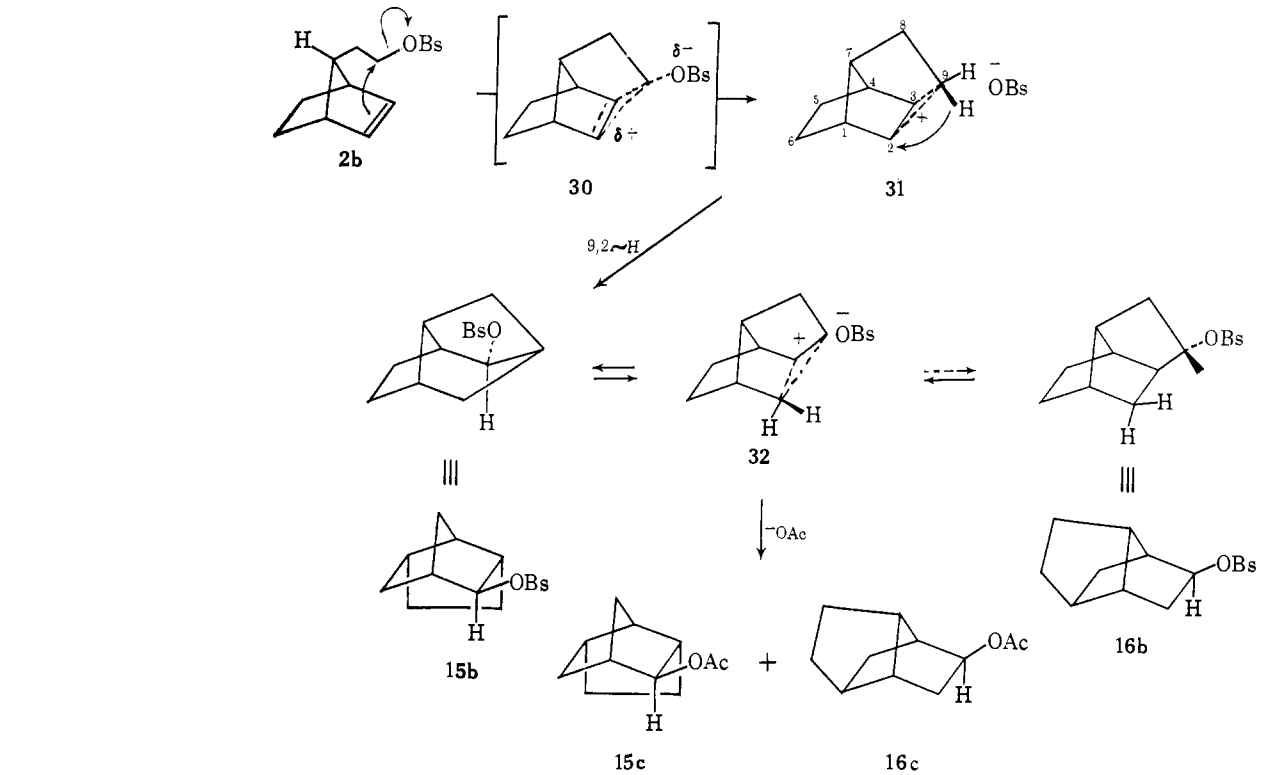
(33) See S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, 81, 4399 (1959), for a discussion of such ground-state effects.

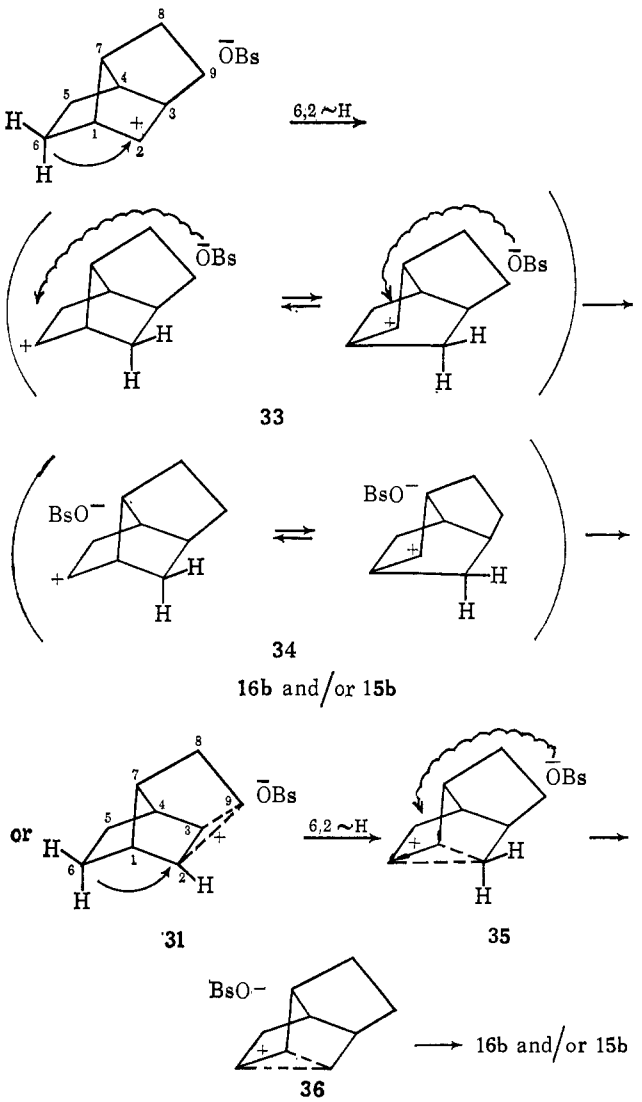
(34) C. C. Lee and L. M. K. Lam, *ibid.*, 88, 2834 (1966), and footnote 11 cited therein.

(35) See Chart I in ref 29a and the Ph.D. dissertation of G. D. Sargent, Harvard University, 1963, p 138, for discussion of a similar point in the β-(3-cyclopentenyl)ethyl case.

(36) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, 80, 169 (1958).

Scheme II





nor of a reason why it could compete so effectively with diffusion or attack by acetate ion in a more loosely associated solvent-separated ion pair.

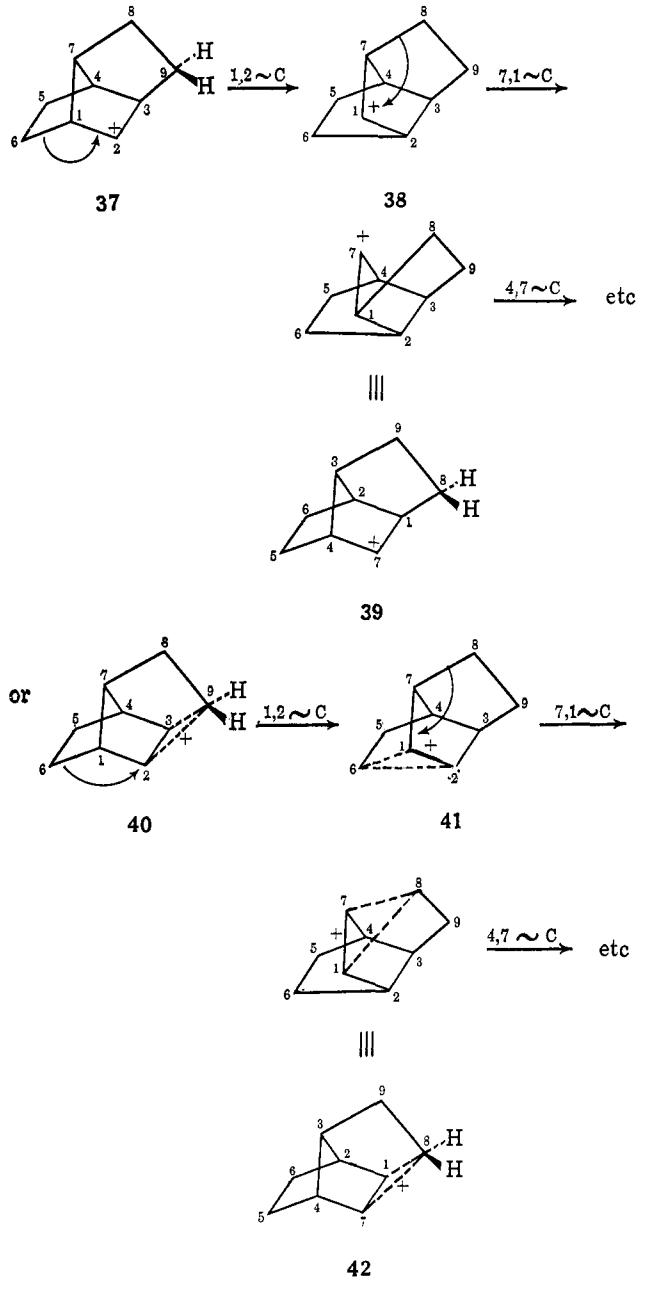
Although we discount the possibility that the 9,2 hydrogen shift of Scheme I or II is accompanied by a C_5 or C_6 hydrogen shift, it may be that some 8,7 hydrogen shift occurs instead. It is characteristic of a cation such as **37** or **40** that it may be converted in either case by successive 1,2 carbon shifts into new cations which differ from the former only in the relative positions of their atomic nuclei,[1a,12] *e.g.*, Scheme III. Since a C_9 hydrogen in **37** or **40** is equivalent, respectively, to a C_8 hydrogen in **39** or **42**, either could migrate if one or more such 1,2-type carbon shifts accompany the acetolysis of **2b** (Scheme III). Since 20-carbon shifts in a forward direction will suffice to return all the atomic nuclei of **37** or **40** to their original positions,[1a] the initially formed ion pair in Scheme I or II may *appear* degenerate if a 1,2-type carbon shift is sufficiently more facile in this system than a 1,3-type hydrogen shift. *Under such circumstances the effective symmetry of this ion pair within the time scale of its reaction* would be C_{5h}—rather than C_1 in the case of **22** or C_s in the case of **31**— and the extent of C_8 and C_9 hydrogen migration would be identical. Although the symmetry of the initial ion pair may, in principle, be distinguished by the use of labeled **2b**, we cannot determine on the basis of our present data whether the cationic portion of the initial ion pair is charge localized (Scheme I) or charge delocalized (Scheme II), or whether the 1,3-type hydrogen shift is preceded by a 1,2-type (Wagner–Meerwein) rearrangement as shown in Scheme III.

Experimental Section[37]

The Preparation of Ethyl 7-Norbornenylideneacetate (8). A solution of 22.4 g (0.100 mole) of triethyl phosphonoacetate (Aldrich

(37) Melting and boiling points are uncorrected. Microanalyses

Scheme III



37 38 39 40 41 42

Chemical Co., Inc.) in 20 ml of anhydrous diethylene glycol dimethyl ether (diglyme) was added dropwise to a slurry of 2.4 g (0.10 mole) of sodium hydride (*i.e.*, 4.8 g of a 50% suspension in mineral oil, Metal Hydrides, Inc.) in 100 ml of the same solvent.[6] The mixture was maintained below 20° during the addition and then stirred at room temperature until the evolution of hydrogen had ceased (∼30 min). While the temperature of the reaction mixture was maintained below 30°, 10.3 g (0.0945 mole) of norbornen-7-one (**7**) in 10 ml of diglyme was slowly added with stirring.[6] The mixture was stirred at room temperature for 10 min after the addition had been completed, poured onto chopped ice, and diluted with water to a total volume of 750 ml. This aqueous mixture was extracted with six 100-ml portions of ether, and the combined extract was dried over anhydrous magnesium sulfate. The ether was removed at atmospheric pressure and the residue distilled to yield 12.3 g (72.3%) of product, bp 72–74° (1.5 mm). Glpc analysis on the 8-ft Carbowax column[37] at 150° showed the product to be pure. The infrared spectrum (CCl_4) shows characteristic peaks at 3070, 1575, 732 (CH=CH, *cis*), 1690, and 1720 cm^{-1} (C=O); the nmr spectrum (CCl_4) has signals at δ 6.18 (quintet, 2 =C*H*), 5.06 (singlet, 1 >C=C*H*CO), 4.09 (a 1:2:2:1 quartet, J = 6.2 cps, 2 OCH_2CH_3), 3.00 (broad singlet, 2 >C*H*, bridgehead), 1.24 (triplet, J = 6.2 cps, 3 CH_3) superimposed on a multiplet at δ 1.9–0.9 (4 *H*).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.84; H, 8.23.

The Preparation of β-(*syn*- and *anti*-7-Norbornenyl)ethanols (2a and 3a). A solution of 23 g (0.13 mole) of ethyl 7-norbornenylideneacetate (**8**) in 200 ml of anhydrous isopropyl alcohol was heated to 65°. To the hot solution was added gradually, with rapid stirring, 18 g of finely cut sodium at a rate sufficient to maintain the temperature at 80°.[7] The reaction was sufficiently exothermic that only occasional heating was necessary. After the addition had been completed, the reaction mixture was heated under reflux until all of the sodium had dissolved. The solution, while still hot, was poured over 500 ml of chopped ice. The mixture was extracted with five 200-ml portions of pentane. The combined pentane extract was washed with three 100-ml portions of water and dried over anhydrous sodium sulfate, and the pentane was removed by distillation at atmospheric pressure. Distillation of the residue in a short-path still yielded 14 g (70%) of product, bp 75–78° (2 mm). Gas chromatographic analysis of the distillate on the 7-ft Ucon column[37] at 140° or on the 8-ft Carbowax column[37] at 160° showed two peaks whose relative retention times and areas () were Ucon, 1.00 (25%) and 1.18 (75%); Carbowax, 1.00 (25%) and 1.31 (75%). The two components were separated by collection from the 20-ft preparative Carbowax column at 190°.

The *first peak* showed infrared absorptions (film) at 3320 (O–H, bonded), 3060, 1635, and 760 cm^{-1} (CH=CH, *cis*); the high-dilution spectrum (CCl_4) shows a nonhydrogen-bonded O–H stretching frequency at 3638 cm^{-1}.[8] The nmr spectrum (CCl_4) shows signals at δ 5.84 (perturbed triplet, J = 2 cps, 2 =C*H*), ∼3.8 (singlet, concentration dependent, 1 O*H*), 3.38 (triplet, J = 6 cps, 2 CH_2O), 2.64 (broad singlet, 2 >C*H*, bridgehead), and 1.8–0.8 (complex multiplet, 7 *H*).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.37; H, 10.27.

On the basis of its relative retention time and the perturbed triplet at δ 5.84,[5,38,39] we conclude that this material is β-(*syn*-7-norbornenyl)ethanol (**2a**).

The *second peak* showed infrared absorptions (film) at 3320 (O–H, bonded), 3045, 1600, and 700 cm^{-1} (CH=CH, *cis*); the high-dilution spectrum (CCl_4) shows a nonhydrogen-bonded O–H stretching frequency at 3638 cm^{-1}.[8] The nmr spectrum (CCl_4) shows signals at δ 6.04 (triplet, J = 2 cps, 2 =C*H*), ∼3.8 (singlet, concentration dependent, 1 O*H*), 3.45 (triplet, J = 6.5 cps, 2 CH_2O), 2.64 (broad singlet, 2 >C*H*, bridgehead), and 2.2–0.7 (complex multiplet, 7 *H*).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.18.

On the basis of its relative retention time and the clean triplet at δ 6.04,[2,38] we conclude that this material is β-(*anti*-7-norbornenyl)-ethanol (**3a**).

The Preparation of β-(7-Norbornyl)ethanol (4a). A solution containing 3.68 g (2.67 mole) of β-*anti*-7-norbornenyl)ethanol (**3a**) in 50 ml of ethyl alcohol was hydrogenated at room temperature and atmospheric pressure using 10% palladium on charcoal as catalyst. The product was distilled in a short-path still to give 3.57 g (96%) of product, bp 73–75° (1.2 mm). The infrared spectrum shows a bonded O–H stretching frequency at 3320 cm^{-1} and no peaks in the double-bond regions; the nmr spectrum (CCl_4) has signals at δ 3.55 (perturbed triplet, J = 6.1 cps, 2 CH_2O), ∼3.5 (singlet, concentration dependent, 1 O*H*), 1.93 (broad singlet, 2 >C*H* bridgehead), and 1.8–0.9 (complex multiplet, 11 *H*).

were performed by either Bernhardt Mikroanalitisches Laboratorium, Mülheim, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nmr spectra on a Varian A-60 spectrometer equipped with a variable-temperature probe and using tetramethylsilane (δ 0.00) and/or chloroform (δ 7.31) as internal standards. Gas chromatographic analyses were carried out in an F & M Model 500 chromatograph equipped with a hot-wire detector using either an 8 ft × 0.25 in. coiled copper tube packed with 20% Carbowax 20M on 60–80 mesh Chromosorb W or a 7 ft × 0.25 in. column packed with 20% water-insoluble Ucon on 60–80 mesh Chromosorb P or in a Model 500 equipped with a Model 1609 flame ionization detector using a 300 ft × 0.02 in. stainless steel capillary coated with water-insoluble Ucon. Preparative gas chromatography was performed in an Aerograph Autoprep Model 700-A using a 20 ft × 3/8 in. aluminum column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb W.

(38) E. J. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

(39) *syn*-7-Norbornenylmethanol also does not exhibit a π-bonded O–H stretching frequency in the infrared; *cf.* footnote 26 in ref 2.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.85; H, 11.38.

The Chloromercuration of β-(*syn*-7-Norbornenyl)ethanol.[9] A solution of 38 mg (0.36 mmole) of **2a** and 88 mg (0.36 mmole) of mercuric acetate in 0.2 ml of methanol was allowed to stand at room temperature for 15 min. A solution of 20 mg (0.36 mmole) of sodium chloride in 0.1 ml of water was added. The resulting precipitate was filtered, washed with water, and dried under vacuum, yield 89 mg (87%), mp 118–124° (gives a cloudy melt). Two recrystallizations from benzene gave a product with a melting point of 199–200° (**11**). A second product (**10**), mp 118–121°, was obtained by evaporation of the benzene mother liquors.

The infrared spectrum (KBr) of the higher melting product (**11**) has strong characteristic peaks at 2950, 2925, 2860, 1081, 1056, 1048, 1031, 978, 928, 882, and 824 cm^{-1}; the nmr spectrum ($CDCl_3$) has signals at δ 4.33 (singlet, 1 >C*H*O), 3.68 (triplet, 2 CH_2O), and 3.4–0.8 (complex multiplet, 10 *H*).

Anal. Calcd for $C_9H_{13}ClHgO$: C, 28.96; H, 3.51; O, 4.29; Hg, 53.74. Found: C, 29.22; H, 3.42; O, 4.47; Hg, 53.49.

The infrared spectrum of the lower melting material (**10**) has characteristic strong absorptions at 2955, 2927, 2870, 1060, 1048, 928, 818, and 731 cm^{-1}; the nmr spectrum ($CDCl_3$) shows signals at δ 4.02 (doublet, J = 6 cps, 1 >C*H*O), 3.67 (broad, poorly resolved, 2 CH_2O), and 3.3–0.8 (complex multiplet, 10 *H*).

Anal. Calcd for $C_9H_{13}ClHgO$: C, 28.96; H, 3.51; O, 4.26; Hg, 53.74. Found: C, 29.00; H, 3.44; O, 4.41; Hg, 53.67.

It can be estimated from the relative areas of the singlet at δ 4.33 and the doublet at δ 4.04 in the nmr spectrum of the crude product mixture that the two products **10** and **11** are present in the ratio of 1:2.

The Chloromercuration of β-(*anti*-7-Norbornenyl)ethanol.[9] A 25-mg sample of the alcohol **3a** was treated with mercuric acetate and with sodium chloride in the manner described for the *syn* isomer **2a**. No crystalline chloromercuri derivative formed when the sodium chloride was added. Instead, a viscous, oily layer gradually separated on the walls of the reaction flask. The solvent was decanted, and the oil was triturated with two 1-ml portions of ether. The ether was decanted, and the residue was dried under vacuum. The infrared spectrum ($CHCl_3$) of this material shows no evidence of unsaturation but has peaks at 3450 (O–H, bonded) and 1735 cm^{-1} (ester C=O).

β-(*syn*-7-Norbornenyl)ethyl Acetate (2c). A mixture of 100 mg (0.72 mmole) of alcohol **2a**, 1 ml of acetic anhydride, and 1 ml of pyridine was allowed to stand at room temperature for 25 hr. The solution was poured into about 10 ml of ice–water, and extracted with three 5-ml portions of pentane, and the combined extract was washed with saturated sodium chloride. The pentane was removed at atmospheric pressure, and the residue was distilled in a short-path still at an oil-bath temperature of ~100° (1.5 mm) to give 81 mg (62%) of the acetate **2c**. The infrared spectrum of the product (CCl_4) shows absorptions at 3060, 1630, 708 (CH=CH, *cis*), 1745 (C=O), 1235, and 1030 cm^{-1} (CO–O); the nmr spectrum (CCl_4) has peaks at δ 5.88 (triplet, J = 2 cps, 2 =C*H*), 3.91 (triplet, J = 6.5 cps, 2 CH_2O), 2.69 (broad singlet, 2 >C*H*, bridgehead), 1.97 (singlet, 3 CH_3CO), and 1.9–0.8 (complex multiplet, 7 *H*).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.14; H, 9.07.

β-(*anti*-7-Norbornenyl)ethyl Acetate (3c). A mixture of 0.999 g (7.24 mmoles) of β-(*anti*-7-norbornenyl)ethanol (**3a**), 1.30 g of acetic anhydride, and 1.34 g of pyridine was heated under reflux for 3 hr. The solution was cooled in an ice bath and the pH adjusted to about 5 with dilute hydrochloric acid. The solution was extracted with three 25-ml portions of chloroform, and the combined extracts were dried over magnesium sulfate. The solvent was removed under atmospheric pressure, and the residue was distilled to give 0.818 g (62.8%) of the acetate **3c**, bp 82° (1.5 mm); characteristic infrared absorptions (film) are at 3055, 1580, 737, 701 (CH=CH, *cis*), 1747 (C=O), 1238, and 1036 cm^{-1} (CO–O); nmr absorptions are at δ 6.02 (triplet, J = 2 cps, 2 =C*H*), 3.94 (triplet, J = 6.2 cps, 2 CH_2O), 7.43 (broad singlet, 2 >C*H*, bridgehead), and 1.98 (singlet, 3 CH_3CO) superimposed on a complex multiplet at 1.8–0.7 (7 *H*).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.36; H, 8.72.

β-(7-Norbornyl)ethyl Acetate (4c). This compound was prepared in the manner described for the acetate **3c** using 0.180 g (1.28 mmoles) of β-(7-norbornyl)ethanol (**4a**), 0.653 g (6.39 mmoles) of acetic anhydride, and 0.675 g (8.54 mmoles) of pyridine. The product was isolated by glpc on the 8-ft Carbowax column giving 0.129 g (56%) of the acetate **4c**. The infrared spectrum (film) shows no evidence of unsaturation and has characteristic peaks at 2948 (CH_3), 1745 (C=O), 1240, and 1038 cm^{-1} (CO–O). Nmr peaks (CCl_4) are at δ 4.02 (perturbed triplet, J = 6.5 cps, 2 CH_2O), 2.00 (singlet, 3 CH_3CO) superimposed on a complex multiplet at 2.1–1.0 (13 *H*).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.25; H, 9.84.

β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (2b).[10] A 310-mg (2.25 mmoles) sample of β-(*syn*-7-norbornenyl)ethanol (**2a**) was dissolved in 5 ml of anhydrous pyridine, the solution cooled to −10°, 650 mg (2.55 mmoles) of *p*-bromobenzenesulfonyl chloride was added in one portion, and the mixture was swirled to effect solution. The reaction mixture was maintained at −20° for 4 hr and then poured over 25 ml of cracked ice. The product was filtered with suction, washed with ice–water, and dried under high vacuum at 0°. The dried product was *immediately* dissolved in about 50 ml of pentane and warmed briefly with a small amount of activated charcoal. The solution was filtered, cooled in an ice bath, and concentrated under aspirator pressure until the product crystallized. The crystals were separated by decantation, quickly washed with a small volume of chilled pentane, and dried under vacuum at 0° to yield 332 mg of the brosylate **2b**, mp 29–31°; a second crop, mp 28–30°, was obtained upon further concentration of the pentane solution to give an over-all yield of 422 mg (52.4%) of **2b**. Infrared absorptions (CCl_4) are at 3065, 718 (CH=CH, *cis*), 1186, 1173 (SO_2O), and 611 cm^{-1} (CBr); and nmr peaks (CCl_4) are at δ 7.79 (singlet, 4 =C*H*, aromatic), 5.79 (perturbed triplet, J = 2 cps, 2 =C*H*), 3.91 (perturbed triplet, J = 6.2 cps, 2 CH_2O), 2.59 (broad singlet, 2 >C*H*, bridgehead), and 1.9–0.7 (complex multiplet, 7 *H*).

This material was used for the acetolysis rate and product determinations without further purification. It can be stored at −20° for several months without decomposition. However, at room temperature it is very unstable and rapidly rearranges to *exo*-2-brendyl brosylate (**15b**). This transformation was affected quantitatively by the following procedure.

Freshly prepared β-(*syn*-7-norbornenyl)ethyl brosylate (**2b**) was kept in a water bath at 30–35° until it had melted (about 2 min); the molten material was seeded with a crystal of **15b** and stirred at room temperature with a glass rod until it had crystallized completely (about 5 min). The crude, off-white product melted at 81–91° dec; its nmr spectrum indicated that it consisted of about 3% starting brosylate **2b** and 97% *exo*-2-brendyl brosylate (**15b**). The infrared spectrum agreed with that of authentic **15b**.[12,26] Recrystallization from hexane with a small amount of activated charcoal gave white crystalline **15b** which melted at 88–91°.

β-(*anti*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (3b).[10] A solution of 0.87 g (6.3 mmoles) of β-(*anti*-7-norbornenyl)ethanol (**3a**) in 10 ml of anhydrous pyridine was cooled to −10° in an ice–salt bath, and 1.75 g (6.89 mmoles) of *p*-bromobenzenesulfonyl chloride was added in three portions. The mixture was swirled at this temperature for 10 min and then allowed to stand at −20° for 3 hr. The solution was poured into ice–water and the crystalline precipitate was separated by filtration. The product was recrystallized from pentane to give 1.68 g (75%) of the brosylate **3b**, mp 42–43.5°; infrared absorptions (KBr) at 3090, 3056, 1288 (SO_2O), 740 (CH=CH, *cis*), and 610 cm^{-1} (CBr); nmr peaks (CCl_4) at δ 7.69 (singlet, 4 =C*H*, aromatic), 5.98 (triplet, J = 2 cps, 2 =C*H*), 3.97 (perturbed triplet, J = 6.2 cps, 2 CH_2O), 2.48 (broad singlet, 2 >C*H*, bridgehead), and 1.8–0.7 (complex multiplet, 7 *H*).

Anal. Calcd for $C_{15}H_{17}BrO_3S$: C, 50.42; H, 4.80; Br, 22.37; O, 13.44. Found: C, 50.61; H, 4.56; Br, 22.30; O, 13.37.

This material was used for the acetolysis rate and product studies without further purification.

β-(7-Norbornyl)ethyl *p*-Bromobenzenesulfonate (4b).[10] This material was prepared in a manner analogous to that employed for the preparation of **3b** using 0.830 g (5.92 mmoles) of *p*-bromobenzenesulfonyl chloride and 8 ml of pyridine. The product was recrystallized from pentane to give 1.85 g (87%) of the brosylate **4b**, mp 39–40°; infrared absorptions (KBr) at 1270 (SO_2O), 602 cm^{-1} (CBr); nmr peaks (CCl_4) at δ 7.69 (singlet, 4 =C*H*, aromatic), 4.00 (perturbed triplet, J = 6.1 cps, 2 CH_2O), 1.89 (broad singlet, 2 >C*H*, bridgehead), and 1.8–0.9 (complex multiplet, 11 *H*).

Anal. Calcd for $C_{15}H_{19}BrO_3S$: C, 50.14; H, 5.33; Br, 22.24; O, 13.30. Found: C, 50.40; H, 5.01; Br, 22.18; O, 13.32.

This material was used for the acetolysis rate and product studies without further purification.

The Acetolysis of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (2b). The procedure described here for the isolation of the

acetolysis products of **2b** was used in all subsequent brosylate acetolyses.

A solution (10 ml) containing 75 mg (0.21 mmole) of **2b** in anhydrous acetic acid,[40] 0.03 *M* in sodium acetate, was allowed to react at 25° for 14 hr. The solution was then diluted to 75 ml with ice–water and extracted with six 10-ml portions of pentane. The pentane extracts were combined, washed once with 15 ml of saturated sodium chloride solution, once with 25 ml of saturated sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solution was concentrated to ~0.5 ml by slow distillation of the pentane through a 10 × 0.5 cm wire-spiral-packed column. The concentrate, when analyzed by glpc on the 8-ft Carbowax column at 130°, showed in addition to the solvent three components whose relative retention times and areas () were 1.0 (22%), 12.5 (42%), and 13.5 (36%).[41] Samples of each of these materials were collected for spectral examination.

The *first component* had infrared and nmr spectra identical with those of authentic deltacyclane (**14**) prepared in a different manner by Nickon and co-workers.[12,26]

The *second component* had infrared and nmr spectra identical with those of *exo*-2-brendyl acetate (**15c**) prepared independently by Nickon and co-workers.[12,26]

The *third component* had infrared and nmr spectra identical with those of authentic *exo*-4-brexyl acetate (**16c**) prepared by Nickon and co-workers in an independent manner.[12,26]

A second sample containing 150 mg (0.42 mmole) of **2b** in 10 ml of anhydrous acetic acid,[40] 0.1 *M* in sodium acetate, was allowed to stand at 25° for 1 hr. The solution was poured into ice–water, and the precipitate was separated by filtration to give 35 mg (23%) of a crystalline brosylate, mp 81–91°. After recrystallization from hexane this material melted at 89–92°; the nmr spectrum (CCl_4) has signals at δ 7.70, 7.72 (4 =C*H*, aromatic), 4.00 (singlet, 1 >C*H*O), 2.5–0.4 (complex multiplet, 12 *H*). The infrared and nmr spectra are identical with those of an authentic sample of **15b** prepared independently by Nickon and co-workers.[12,26]

Another sample containing 70 mg (0.19 mmole) of **2b** in 4 ml of anhydrous acetic acid,[40] 0.1 *M* in sodium acetate, was allowed to stand at room temperature for 8 min. The products were extracted as before, and the pentane solution was concentrated to ~0.5 ml and cooled in a Dry Ice–acetone bath. The supernatant solution was drawn off, and the oily precipitate was dried under high vacuum. The nmr spectrum of this material showed that it consisted of unreacted **2b** and **15b** in a ratio of 3:1 and a small amount of acetates. The mother liquor, after removal of the pentane, was shown by infrared analysis to contain the hydrocarbon **14**, the acetates **15c** and **16c** (in approximately equal amounts), and some unreacted **2b**.

In order to determine whether the composition of the acetolysis products of **2b** is dependent upon the nature and amount of added salts, we solvolyzed this brosylate at different concentrations of sodium acetate or in the presence of added lithium perchlorate. Portions of the acetolysis solutions were withdrawn after various reaction times and analyzed by glpc in the previously described manner.

The samples which were worked up before all of the unsaturated brosylate had reacted showed different product compositions when the analysis was performed on the 300-ft capillary Ucon column[37] and when it was performed on the 8-ft packed Carbowax column.[37] For example, after a sample of **2b** was allowed to react for 8 min, analysis on the Carbowax column showed the ratio of **15c** to **16c** to be ~3:1 while analysis on the capillary Ucon column showed this ratio to be 1.6:1. The higher **15c**/**16c** ratio was accompanied by a relatively larger proportion of the hydrocarbon **14** and the appearance of a broad, badly tailing peak, presumably due to acetic acid. Both **15c** and **16c** could be collected from the Carbowax column and reinjected on either the Carbowax or the Ucon column without apparent isomerization or decomposition. It therefore appears that unreacted **2b** must decompose in the injection port or immediately upon absorption to give *p*-bromobenzenesulfonic acid which further catalyzes either the isomerization of **16c** to **15c** or, more likely, the preferential decomposition of **16c** into acetic acid and hydrocarbon. If the solutions were mixed with a small amount of pyridine prior to injection, the ratio of products was independent of the type of column used. The proportions of the volatile products found after **2b** had undergone acetolysis under various conditions are tabulated in Table VII.

Table VII. Volatile Products from the Acetolysis of *β*-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (**2b**) at 25°

Time, min	[NaOAc], *M*	[$LiClO_4$], *M*	%[a] **14**[b]	**15c**	**16c**	Ratio **15c**/**16c**
8	0.1	...	40	32	28	1.14
	0.1	0.1	29	37	34	1.09
	0.2	...	50	26	24	1.08
60	0.1	...	21	42	37	1.12
	0.1	0.1	12	46	42	1.10
	0.2	...	19	42	39	1.09
840	0.03	...	22	42	36	1.17

[a] See ref 41. [b] Must be considered approximate because the high volatility of **14** renders some loss inevitable and because entrained ROBs produces hydrocarbon(s) when pyrolyzed in the heated injection port of the gas chromatograph.

Stability of the Acetolysis Products of 2b in the Solvolysis Medium. Small samples of the hydrocarbon **14** and the acetates **15c** and **16c** were dissolved in anhydrous acetic acid[40] containing 0.1 *M* sodium acetate and allowed to stand at 25° for 72 hr. The solutions were extracted with pentane and analyzed by glpc on the 8-ft Carbowax column as before. All were found to be unchanged, indicating that no isomerization or addition of acetic acid takes place under the acetolysis conditions. When a sample of **2c** was treated in a similar manner for 2 hr it also was recovered unchanged.

***exo*-4-Brexanol (16a).** To a suspension of 16 mg (0.42 mmole) of lithium aluminum hydride in 2 ml of anhydrous ether was added dropwise a solution of 110 mg (0.80 mmole) of the acetate **16c** (isolated from the acetolysis products of **2b** by glpc on the 20-ft preparative Carbowax column) in 3 ml of ether. The mixture was stirred at room temperature for 3 hr and then decomposed by adding a drop of water and a drop of 15% sodium hydroxide. The inorganic salts were removed by filtration and washed with ether. The filtrate and washings were dried over anhydrous sodium sulfate, and the ether was removed by distillation at atmospheric pressure. Sublimation of the residue at 90° (15 mm) gave 83 mg (99%) of crystalline product, mp 52–55°. The spectra of this material are identical with those of authentic **16a** prepared in an unequivocal manner by Nickon and co-workers.[12,26]

***exo*-4-Brexyl Brosylate (16b).**[10] This compound was prepared by the procedure described for the brosylate **3b** using 72 mg (0.52 mmole) of the alcohol **16a** and 144 mg (0.56 mmole) of *p*-bromobenzenesulfonyl chloride in 0.5 ml of pyridine. The reaction was allowed to proceed for 12 hr. The product was recrystallized from pentane to give 67 mg (36%) of *exo*-4-brexyl brosylate (**16b**); mp 42–46°; characteristic infrared peaks (KBr) are at 3090, 2940, 2860, 1575, 1475, 1390, 1182, 1091, 1067, 1021, 1009, 949, 925, 912, 890, 865, 820, 810, 771, 740, 611, 576, 518, and 412 cm^{-1}; nmr peaks (CCl_4) are at δ 7.70 (4 =C*H*, aromatic), 4.37 (doublet, J = 5.5 cps, 1 >C*H*O), and 2.4–0.5 (complex multiplet, 12 *H*). These spectra are distinctly different from those of the known *exo*-2-brendyl *p*-bromobenzenesulfonate.[12,26]

When allowed to stand at room temperature the brosylate **16b** rearranges to **15b**. This transformation, as indicated by nmr analysis of partially rearranged material, proceeds to about 50% within 5 hr. At −20° **16b** is stable for several weeks.

The Acetolysis of *exo*-2-Brendyl and *exo*-4-Brexyl *p*-Bromobenzenesulfonates (15b and 16b). Solutions containing 60 mg (0.17 mmole) of each of the brosylates in 4 ml of anhydrous acetic acid[40] buffered with sodium acetate were allowed to react at 25°. Samples were withdrawn at various times, and the products were extracted in the manner described for **2b**.

The unreacted brosylates were recovered by cooling the concentrated pentane solutions to −20°, and were characterized by infrared analysis. In the case of *exo*-2-brendyl brosylate (**15b**), only the starting material was obtained from the incompletely reacted samples. Only *exo*-2-brendyl brosylate (**15b**) was recovered when *exo*-4-brexyl brosylate (**16b**) was allowed to react for 15 min.

The composition of the volatile product mixtures was determined by glpc analysis of the pentane mother liquors on the 8-ft Carbowax column. The results are summarized in Table VIII.

The Acetolysis of *β*-(*anti*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (3b). A 0.02 *M* solution of **3b** (10 ml) in anhydrous acetic acid,[40] 0.03 *M* in sodium acetate, was heated at 100° for 80 hr (*ca.* nine half-lives). The products were isolated in the manner described for **2b** and analyzed by glpc on the 8-ft Carbowax column at 150°. Four components were found whose relative retention

(40) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, 30, 10 (1965).

(41) No attempt has been made to correct these peak areas for differences in the thermal conductivities of the components.

Table VIII. Volatile Products from the Acetolysis of *exo*-2-Brendyl and *exo*-4-Brexyl *p*-Bromobenzenesulfonates (**15b** and **16b**) at 25°[a]

ROBs	Time, min	% [b] 14b[c]	% [b] 15b	% [b] 16b	Ratio 15b/16b
15b	60	23	41	36	1.14
	180	18	44	38	1.16
	1800	19	43	39	1.10
	8640[d]	5	50	45	1.11
16b	15	14	45	41	1.10
	180	10	47	43	1.10
	240	12	47	41	1.09
	1560	9	48	43	1.12

[a] Contains 0.1 *M* sodium acetate unless otherwise specified. [b] See ref 41. [c] Table VII, footnote *b*. [d] Contains 0.03 *M* sodium acetate.

times and areas () were 1.0 (89.5%), 1.3 (2%), 4.4 (2.5%), and 4.9 (6%).[41]

The *first component* was identical in all respects with β-(*anti*-7-norbornenyl)ethyl acetate (**3c**).

The second component had the following spectral properties: infrared absorptions (CCl_4) at 3070 (CH, nortricyclyl), 1750 (C=O), 1235, and 1040 (CO–O) cm^{-1}; nmr peaks at δ 4.01 (triplet, J = 6.5 cps, 2 CH_2O), 1.98 (singlet, 3 CH_3CO), and 1.9–0.8 (complex multiplet, 11 *H*). Neither the infrared nor the nmr spectrum shows any evidence for a double bond. This material is identical with β-(3 nortricyclyl)ethyl acetate (**17c**), prepared by heating β-(*anti*-7-norbornenyl)ethyl acetate (**3c**) with silica–alumina catalyst[42] at 170° according to the procedure of Schleyer.[43]

When the acetolysis of **3b** was allowed to proceed for 7 hr (*ca.* one half-life) the only product obtained was the acetate **3c**. When this acetate was heated for 80 hr in acetic acid[40] containing 0.005 *M* sodium acetate, the products isolated were **3c** (80%), **17c** (2%), and two compounds whose retention times corresponded to the *third* and *fourth* components of the acetolysis mixture of **3b**. It is evident from their retention times that the latter two products are diacetates formed by the addition of acetic acid to the norbornene double bond. They have not been isolated and characterized.

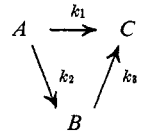
The Acetolysis of β-(7-Norbornyl)ethyl *p*-Bromobenzenesulfonate (4b). This reaction was carried out and the product mixture analyzed in the manner described for the brosylate **2b**. The only product found was β-(7-norbornyl)ethyl acetate (**4c**).

Nmr-Determined Acetolysis Rates of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (2b). Small, weighted samples of the brosylate **2b** were dissolved in 0.50 ml of anhydrous acetic acid,[40] 0.1–0.3 *M* in sodium acetate, contained in an nmr tube. The tube was capped and placed in a variable, controlled-temperature probe of a Varian A-60 nmr spectrometer, and the rate of reaction was followed by repeated 25-sec, upfield integral scans of the pertinent hydrogen-resonance regions: δ 7.9–7.7 for the four aromatic hydrogens of the alkyl brosylates, δ 7.7–7.5 for the four aromatic hydrogens of the *p*-bromobenzenesulfonate anion, and δ 6.0–5.7 for the two vinyl hydrogens of the unsaturated brosylate **2b**. The time was recorded for each scan when the pen crossed an arbitrary line drawn on the chart paper at δ ~8.5. No correction was made for the constant difference in scan time required for the pen to integrate the higher field vinyl hydrogens. The temperature of the probe was determined immediately before and after each run by measuring the chemical shift between the hydroxyl and the methyl(ene) hydrogen resonances of either methanol or ethylene glycol (*cf.* Table I, footnote *a*). Values of the integrals, read directly from the chart paper, ranged from about 60 to 5 mm. Rate constants were calculated from the data as described below.

Titrimetric Acetolysis Rates. The titrimetric acetolysis rates of the brosylates **3b**, **4b**, and **15b** were determined using the ampoule technique described previously.[40] The initial rate of brosylate ion formation was too fast in the case of **2b** to be measured titrimetrically at 25°. However, by waiting until 99% of **2b** had reacted—about 70 min at this temperature—the fraction of **2b** returning to **15b** and the acetolysis constant of the returned brosylate could be measured by following the formation of *p*-bromobenzenesulfonate ion titrimetrically in the usual manner.[40] Data from these runs were treated as described below.

Kinetic Treatment. Since **16b**, if formed, is too reactive to be detected kinetically,[26] solvolyzing **2b** may be treated according to Scheme IV

Scheme IV



where $A \propto$ [**2b**], $B \propto$ [**15b**], and $C \propto$ [BsO^-]. Scheme IV is described mathematically by eq i–iii, *viz.*

$$dA/dt = -(k_1 + k_2)A \quad \text{(i)}$$

$$dB/dt = k_2A - k_3B \quad \text{(ii)}$$

$$dC/dt = k_1A + k_3B \quad \text{(iii)}$$

which integrate to

$$A = A_0 \exp[-(k_1 + k_2)t] \quad \text{(iv)}$$

$$B = -(k_2A_0/\Delta) \exp[-(k_1 + k_2)t] + [(k_2A_0 + \Delta B_0)/\Delta] \exp(-k_3t) \quad \text{(v)}$$

$$C = -[(k_1 - k_3)A_0/\Delta] \exp[-(k_1 + k_2)t] - [(k_2A_0 + \Delta B_0)/\Delta] \exp(-k_3t) + A_0 + B_0 + C_0 \quad \text{(vi)}$$

where $\Delta = k_1 + k_2 - k_3$, and A_0, B_0, and C_0 represent the value of A, B, and C at $t = 0$.

Since the acetolysis of **2b** produces no unsaturated products the concentration of **2b** ([**2b**]) is proportional at all times to the number of vinyl hydrogens present in the mixture. The over-all first-order rate constant for the disappearance of **2b** ($k = k_1 + k_2$) can be calculated from the integral values in the vinyl hydrogen region (δ 6.0–5.7) of the nmr spectra determined as described previously by fitting A_n = (integral δ 6.0–5.7) at $t = t_n$ to eq iv. Since the precision of the method is not high, many integral determinations were made for each of the runs and a FORTRAN IV programmed,[44] single least-squares regression analysis of A on t was used to calculate the best value of k, the normal equations for such a treatment being[45]

$$\ln A_0 \Sigma A_n^2 - \Sigma A_n^2 \ln A_n - k\Sigma A_n^2 t_n = 0 \quad \text{(vii)}$$

and

$$\ln A_0 \Sigma t_n A_n^2 - \Sigma t_n A_n^2 \ln A_n - k\Sigma A_n^2 t_n^2 = 0 \quad \text{(viii)}$$

where n = the number of integral determinations per run and the summations are over $n = 1 \rightarrow n$. Values of k obtained in this manner are included in Table I, runs 1–3, 9, and 10.

In an effort to reduce the variable temperature induced scatter of the integral values, the total aromatic hydrogen integral (δ 7.9–7.5) was normalized to 1.00 for each individual integral trace on several runs. Best values of k, determined by fitting values of A_n = [2(integral δ 6.0–5.7)/(integral δ 7.9–7.5)] at $t = t_n$ to eq iv, are included in Table I, runs 4–8.

Since **15b** is about 50-fold less reactive than **2b** at 25°, *i.e.*, $(k_1 + k_2) \approx 50k_3$, its concentration during that portion of the acetolysis that can be successfully followed by measuring the vinyl hydrogen integral of **2b** in the nmr, *e.g.*, up to about two half-lives of **2b**, is adequately represented by the expression

$$B = -[k_2/(k_1 + k_2)]A + [k_2/(k_1 + k_2)]A_0 + B_0 \quad \text{(ix)}$$

The concentration of **15b** is proportional to the integral of the total aromatic hydrogens of the alkyl brosylates (δ 7.9–7.7) minus twice the total vinyl hydrogen integral (δ 6.0–5.7). Thus k_2 can be de-

(42) Synthetic Silica Alumina Catalyst, Type S-90. We thank the Houdry Process and Chemical Co. for a generous sample of this material.

(43) P. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(44) K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, Inc., New York, N. Y., 1965.

(45) (a) R. Livingston in "Investigations of Rates and Mechanisms of Reactions, Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, pp 193–195; (b) J. B. Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins Press, Baltimore, Md., 1930, pp 370–374.

termined by substituting values of B_n = [(integral δ 7.9–7.7) − 2(integral δ 6.0–5.7)]/(integral δ 7.9–7.5) and A_n = [2(integral δ 6.0–5.7)]/(integral δ 7.9–7.5) at $t = t_n$ into eq ix. Since the precision of the values B_n and A_n is approximately equal but not high, many integral determinations were made for each run and a FORTRAN IV programmed,[44] double least-squares regression analysis[46] was used to calculate the best value of k_2. The normal equations for such an analysis are[46]

$$(k/n\alpha)\Sigma B_n + (k_2/n\alpha)\Sigma A_n - 1 = 0 \quad \text{(x)}$$

$$[(k_2^2 - k^2)/\alpha^2]\Sigma A_n + [(k)(k^2 - k_2^2)/\alpha^3]\Sigma A_n B_n + (2kk_2/\alpha^2)\Sigma B_n - (k^2k_2/\alpha^3)[\Sigma A_n^2 - \Sigma B_n^2] + (nk_2/\alpha) = 0 \quad \text{(xi)}$$

where $\alpha = (k_2A_0 + kB_0)$, $k = (k_1 + k_2)$, n = the number of integral determinations per run, and the summations are over $n = 1 \rightarrow n$. From the values of k (which had been determined previously) and k_2, k_1 could then be calculated. Values of k_1 and k_2 determined in this manner from runs 4 to 8 are recorded in Table I, together with $k_2/(k_1 + k_2)$, the fraction of **2b** which returns to **15b** during the acetolysis.

Better values of the fraction of brosylate returning could be obtained titrimetrically. Since **2b** is much more reactive than **15b**, its concentration in the acetolysis mixture becomes negligibly small while that of **15b** is still fairly large. After 99% of **2b** has reacted (*e.g.*, after eight half-lives) the first term in eq vi approaches zero and the concentration of brosylate anion in the mixture is adequately represented by

$$C = -[(k_2A_0 + \Delta B_0)/\Delta] \exp(-k_3t) + A_0 + B_0 + C_0 \quad \text{(xii)}$$

At $t = \infty$, $C = C_\infty = A_0 + B_0 + C_0$ and, since $k_3 << (k_1 + k_2)$, xii may be written as

$$(C_\infty - C) = \{[k_2/(k_1 + k_2)]A_0 + B_0\} \exp(-k_3t) \quad \text{(xiii)}$$

Equation xiii is of the same general form as iv and a FORTRAN IV programmed,[44] single least-squares regression analysis of $C_\infty - C_n$ (where C_n equals the titrimetric brosylate ion concentration at time t_n) on t_n, similar to that performed on iv,[45] yields the best value of $[k_2/(k_1 + k_2)]A_0 + B_0$ (where $A_0 = [\mathbf{2b}]_0$ and $B_0 = [\mathbf{15b}]_0$). Since $B_0 = 0$ and A_0 is known, $k_2/(k_1 + k_2)$ (the fraction of **2b** returning to **15b** during the acetolysis) and k_3 (the first-order acetolysis constant of **15b**) can be computed from titrimetric data taken after greater than 99% of **2b** has reacted. Values of $k_2/(k_1 + k_2)$ and of k_3 obtained in this manner are recorded in Table II.

First-order acetolysis constants of pure **15b** and of **3b** and **4b** were determined in the usual manner[47] from the slope of the best straight line drawn by inspection through the points on a plot of log [ROBs] *vs.* t, and are recorded in Tables III and IV, respectively. The activation parameters ΔH^* and ΔS^* recorded in Table VI were computed from eq xiv[48]

$$\ln(k_r/T) = -\Delta H^*/RT + \Delta S^*/R + \ln(b/h) \quad \text{(xiv)}$$

(where b = the Boltzman constant, h = the Plank constant, R = the molar gas constant and T = absolute temperature) by a FORTRAN IV programmed,[44] single least-squares regression analysis[45] of ln (k_r/T) on $1/T$ from values of the first-order acetolysis constants, k_r, of **2b**, **3b**, **4b**, and **15b** determined at similar ionic strengths; $\mu \approx 0.20$ for **2b**, $\mu \approx 0.03$ for **3b**, **4b**, and **15b**.

The Rearrangement of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (2b) in Carbon Tetrachloride. A solution of 160 mg of **2b** and 0.4 ml of carbon tetrachloride contained in a capped nmr tube was placed in the probe of a Varian A-60 nmr spectrometer at 33°, and the integral was scanned repeatedly from δ 6.0 to 3.5, The relative concentrations of **2b** and **16b** could be observed directly from the vinyl hydrogen resonance at δ 5.8 and the >C*H*O resonance at δ 4.4, respectively. The concentration of **15b** could be calculated from the difference between the integrals at δ 4.1–3.9 (C*H*$_2$O of **2b** + >C*H*O of **15b**) and at δ 5.8 (C*H*=C*H* of **2b**). The results of several such scans are shown in Table IX. After 8 hr, the solvent was evaporated under aspirator pressure. The infrared spectrum of the residue (mp 89.5–91.5°) was identical with that of authentic **15b**.

Table IX. Nmr-Determined Rearrangement of β-(*syn*-7-Norbornenyl)ethyl and *exo*-4-Brexyl *p*-Bromobenzenesulfonates (**2b** and **16b**, respectively) in Carbon Tetrachloride at 33°

Compd	Time, min	% 2b	% 15b	% 16b
2b	1	100	0	0
	4	100	0	0
	7	62	25	13
	10	36	48	16
	15	23	60	17
	30	8	81	11
	60	4	88	8
	90	2	91	7
	240	0	95	5
16b	96	0	95	5
	580	0	100	Trace

When **2b** was dissolved in 0.5 ml of carbon tetrachloride which had been buffered with a drop of pyridine, only unrearranged **2b** could be detected by nmr after 2 hr at 33°; however, a small amount of a water-soluble precipitate, presumably pyridinium *p*-bromobenzenesulfonate, appeared in the nmr tube.

The Rearrangement of *exo*-4-Brexyl *p*-Bromobenzenesulfonate (16b) in Carbon Tetrachloride. Authentic **16b** was dissolved in unbuffered carbon tetrachloride and its rearrangement observed in the manner described for **2b**. The results are recorded in Table IX. After 24 hr, the solvent was evaporated as before. The infrared spectrum of the solid residue (mp 89–91°) was identical with that of authentic **15b**.

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(46) J. B. Scarborough, ref 45b, pp 380–383.
(47) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 2nd ed, 1961, p 12 ff.
(48) Reference 47, p 99, eq 49.