Solvolysis of β-(7-Norbornadienyl)ethyl *p*-Bromobenzenesulfonate. A Search for Unsymmetrical [$2^0 + 2^0 + 1^+$] Laticyclic Stabilization[1]

Robert S. Bly,* Ruta K. Bly,* George B. Konizer, and Satya P. Jindal

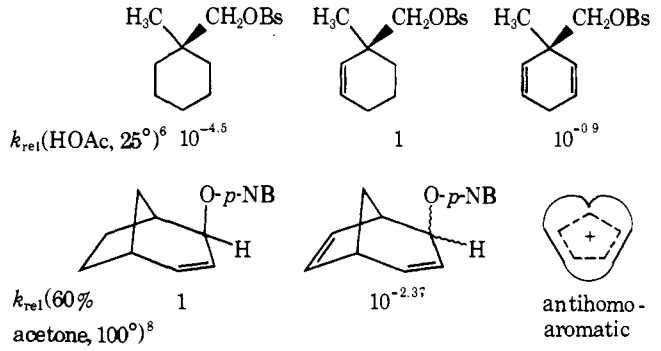
Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received September 20, 1974*

Abstract: β-(7-Norbornadienyl)ethyl *p*-bromobenzenesulfonate (**2**-OBs) has been synthesized and its solvolysis rates and products have been compared with those of β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs). At 25° **2**- and **19**-OBs have similar reactivities (k(HOAc) = ~1.4×10^{-3} s^{-1}, k(90% dioxane/H_2O) = ~2.5×10^{-4} s^{-1}) indicating that the anti double bond of the former provides little, if any, additional assistance to the ionization. The acetolysis of **2**-OBs at 35° ultimately produces ~2% deltacyclene (**7**), 28% 5-deltacyclyl (**8**-), 51% *exo*-2-brendenyl (**9**-), 6% *exo*-4-brexenyl (**10**-), and 13% *exo*-5-isodeltacyclyl (**11**-) acetate (-OAc) but is accompanied by extensive internal return to **9**-OBs and a tetracyclic brosylate presumed to be **8**-OBs. Alcohols of similar structure are formed in aqueous 90% dioxane though return is minimal in this solvent. The acetolysis of **9**-OBs, which is ~27 times less reactive (k(HOAc, 25°) = 5.9×10^{-7} s^{-1}) than *exo*-2-brendyl brosylate, produces ~65% **9**-OAc, ~35% **11**-OAc, traces of **7** and **10**-OAc, but no **8**-OAc. The nature of the solvolytic intermediates is discussed, and it is suggested that some or all of the non-hydrogen-migrated 5-deltacyclyl derivatives from the solvolysis of **2**-OBs may be formed from a [$2^0 + 2^0 + 1^+$] laticyclic cation and/or ion pair.

In this paper we report the preparation and solvolysis of β-(7-norbornadienyl)ethyl *p*-bromobenzenesulfonate (**2**-OBs). Our initial interest in this compound was twofold: we wished to determine whether both double bonds participate anchimerically in the rate-limiting step of its solvolysis and we wanted to compare the intermediates and products of the reaction with those of the monounsaturated counterpart β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (**19**-OBs).[2a]

The question of remote double bond participation in solvolysis had long been of interest to us[2,3] and to others.[4] One of the more intriguing aspects of the early work in this area was the question of whether each of two isolated or weakly interacting, appropriately situated double bonds can *simultaneously* act to accelerate the rate and stabilize the cationic intermediate(s). In cases where such stabilization would lead to antihomoaromatic[5] cations, theory and experiment were in good agreement; the second double bond has a destabilizing effect[6-8] (e.g., see Chart I). However, when the geometry of

Chart I



the system does not permit destabilizing antihomoaromatic interactions the available data were less clear. Doubly delocalized intermediates had been suggested in the solvolyses of both 7-norbornadienyl chloride[9a] and *endo,endo*-dimethanonaphthadienyl *p*-nitrobenzoate:[10] each is considerably more reactive than the comparable *anti*-7-norbornenyl derivative[11] and each gives unrearranged product exclusively under normal solvolysis conditions (Chart II). Although these suggestions were later confirmed in the former case[9b-e] and questioned in the latter,[12] they appeared at the time to contrast sharply with the observations of DePuy et al.[13] that both double bonds *do not* simultaneously participate in the acetolysis of either *exo*- or *endo*-7-isopropylidene-5-norbornen-2-yl tosylate. Even though positive charge is clearly developed at C-2 in the transition state and intermediate of each reaction, the products are discrete, indicating that there is no crossover from one homoallylic cation to the other under these conditions (Chart III). Clearly, simultaneous double bond participation in the

Chart II

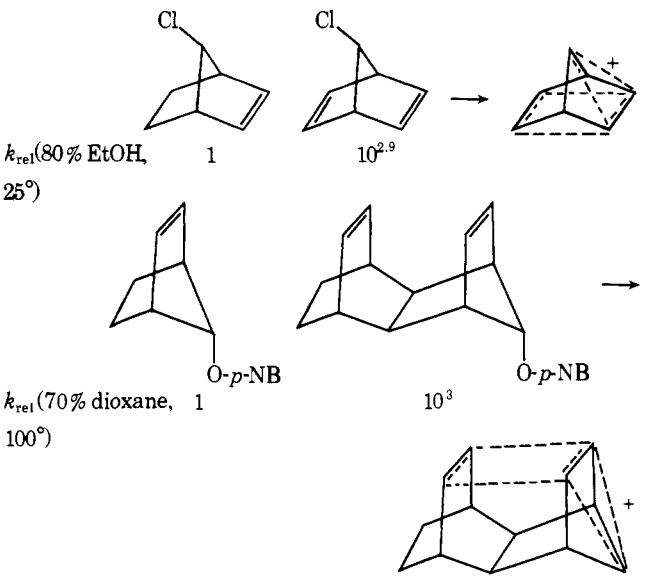


Chart III

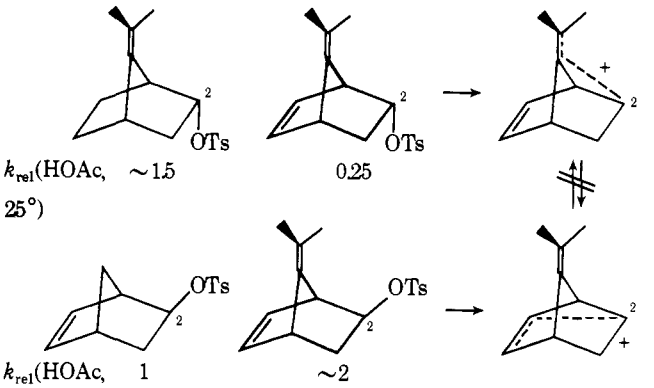


Chart IV

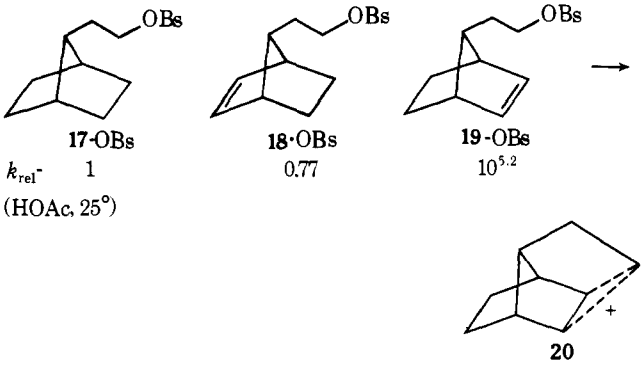
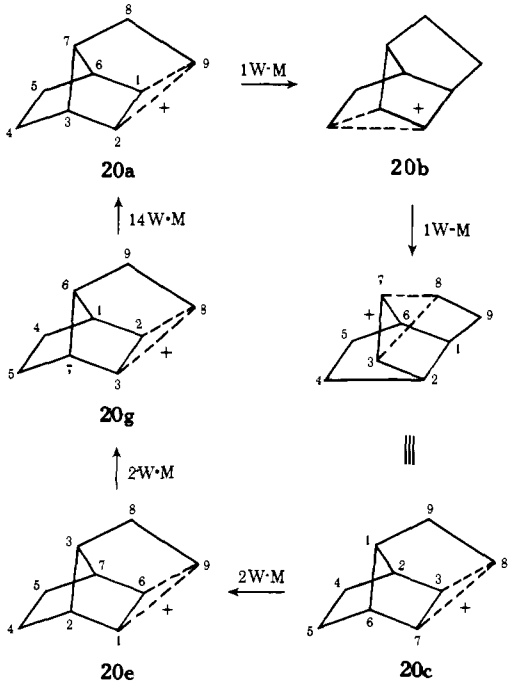
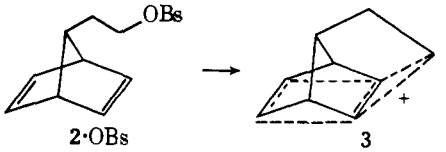


Chart V



sovolysis of doubly unsaturated derivatives is dependent upon both the symmetry and geometry of the overlap.

With this background in mind we decided to examine the rate and products from the solvolysis of the doubly unsaturated β-(7-norbornadienyl)ethyl brosylate (**2**-OBs) (eq 1). This



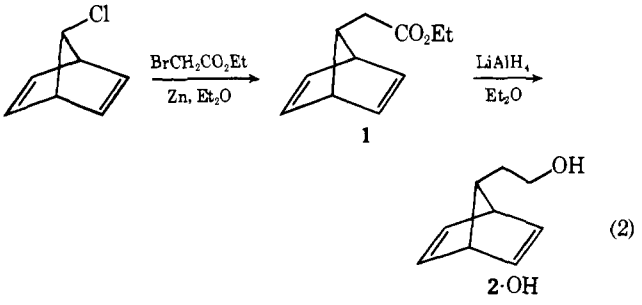
? (1)

seemed a particularly good case in which to search for simultaneous double bond participation because not only had extensive participation been observed in the monounsaturated analogue, β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs) (Chart IV),[2a] but there was also ample precedent for good overlap between both double bonds[9] and their simultaneous participation was not expected to be inhibited by antihomoaromatic interactions. Although we were not aware of it, at the time we were searching for $[2^0 + 2^0 + 1^+]$ laticyclic stabilization![14]

In addition to the question of participation by the second double bond of **2**-OBs in the rate-limiting step, we were interested in its effect upon the product-determining intermediates as well. We had inferred that Wagner-Meerwein rearrangement(s) precede product-determining hydride migration in the case of **19**-OBs and suspected that the initial 2-brexyl cation—shown here in its charge delocalized formulation—might well be structurally degenerate,[2] e.g., as shown in Chart V. In the doubly unsaturated case (**2**-OBs) carbon degeneracy is also a possibility with homoallyl-cyclopropylcarbinyl interactions playing an important part.

Results

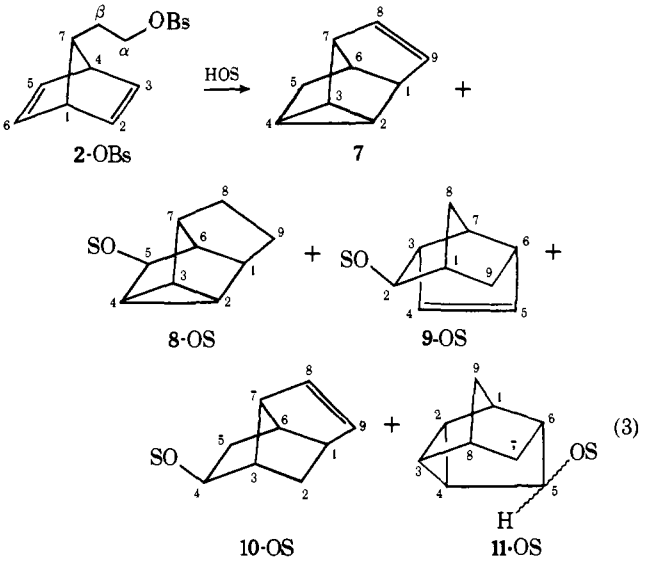
The doubly unsaturated alcohol **2**-OH was prepared as outlined in eq 2. Norbornadienyl chloride[15] was coupled with



(2)

ethyl bromoacetate in the presence of zinc to produce ethyl 7-norbornadienylacetate (**1**) in ~20% yield. Reduction of the ester with lithium aluminum hydride gave β-(7-norbornadienyl)ethanol (**2**-OH) which was converted to the brosylate (**2**-OBs) in the usual manner.[2a] Nuclear magnetic resonance spectra confirm that the norbornadienyl ring is preserved throughout the sequence.

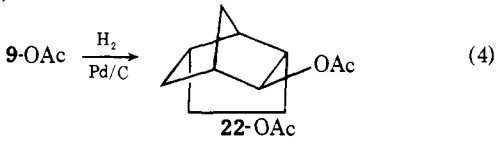
Solvolysis of **2**-OBs in anhydrous acetic acid buffered with sodium acetate and in 90% dioxane–water buffered with sodium bicarbonate gave product mixtures composed ultimately of deltacyclene[16] (**7**), and 5-deltacyclyl[16] (**8**-), *exo*-2-brendenyl[16] (**9**-), *exo*-4-brexenyl[16] (**10**-), and 5-isodeltacyclyl[17] (**11**-) acetates (-OAc) or alcohols (-OH), respectively. If solvolysis is interrupted prior to 100% completion, some internally returned, *exo*-2-brendenyl brosylate (**9**-OBs) can also be detected in each case.



(3)

OS = OBs, OAc, or OH

The identity of the hydrocarbon was established by spectral comparison with authentic samples.[18] The structures of the brendenyl and brexenyl derivatives were confirmed by catalytic hydrogenation of the acetates **9**- and **10**-OAc and the brosylate **9**-OBs to their known saturated brendyl and brexyl counterparts (eq 4-6).[2a]



(4)

$$\text{9-OBs} \xrightarrow[\text{Pd/C}]{H_2} \text{22-OBs} \qquad (5)$$

$$\text{10-OAc} \xrightarrow[\text{Pd/C}]{H_2} \text{AcO-}\langle\text{structure}\rangle \qquad (6)$$

23-OAc

Structures of the tetracyclic acetates **8**- and **11**-OAc were established in the following manner (see Scheme I). The entire acetolysis mixture was reduced with lithium aluminum hydride, oxidized with chromium trioxide, and separated by gas chromatography into the individual components. The more abundant of the two ketones, having no vinyl hydrogen resonances in the NMR and no C=C stretching bands in the ir, was shown by spectral comparisons to be identical with authentic 5-deltacyclanone (**12**) synthesized expressly for this purpose;[19,20] the less abundant ketone was shown to be 5-isodeltacyclanone (**15**) by similar comparisons with an authentic sample.[16b,22] Although the foregoing reaction sequences establish the structure of 5-deltacyclyl acetate (**8**-OAc) unequivocally, they leave unresolved the stereochemistry of the functional group in the isodeltacyclyl ester (**11**-OAc). Mechanistic considerations suggest that it is the exo isomer.

The hydrolysis products of **2**-OBs could not be analyzed by GLC because of poor resolution and isomerization in the chromatograph. Their structures and relative abundances[23] were determined by treating the mixture with acetic anhydride in pyridine, separating the resulting acetates by GLC, and comparing each with the previously identified acetolysis products (eq 7).

$$\text{2-OBs} \xrightarrow{H_2O/\text{dioxane}} \text{8-OH} + \text{9-OH} + \text{10-OH} + \text{11-OH}$$
$$\downarrow Ac_2O/\text{pyridine} \qquad (7)$$
$$\text{8-OAc} + \text{9-OAc} + \text{10-OAc} + \text{11-OAc}$$

In order to demonstrate that such a transformation can be accomplished without significant isomerization or loss of the alcohols, we reduced the *acetolysis* products of **2**-OBs with lithium aluminum hydride and reacetylated the resulting alcohols using the same procedure (eq 8). Except for a decrease in **11**-OAc, due presumably to its isomerization to **9**-OAc (vide infra), we found that the relative amounts[23] of the acetates did not change significantly.

$$\text{2-OBs} \xrightarrow[25^\circ]{\text{HOAc/AcO}^-} \underset{37\%}{\text{8-OAc}} + \underset{43\%}{\text{9-OAc}} + \underset{8\%}{\text{10-OAc}} + \underset{12\%}{\text{11-OAc}} \xrightarrow{LiAlH_4}$$
$$\text{Alcohols} \xrightarrow[\text{pyridine}]{Ac_2O/} (39\% \quad 45\% \quad 8\% \quad 8\%) \qquad (8)$$

Since it appeared that some of the products isolated from the solvolysis mixtures of **2**-OBs are probably formed from the returned brosylate **9**-OBs, we have examined its solvolysis separately. When heated for 14 days at 35° in buffered acetic acid, *exo*-2-brendenyl brosylate (**9**-OBs) yields **9**-OAc and **11**-OAc in an approximately 2:1 ratio, mere traces of **7** and **10**-OAc, and no detectable amount of **8**-OAc.

$$\text{9-OBs} \xrightarrow[35^\circ]{\text{AcOH/AcO}^-} \text{9-OAc (65\%)} + \text{11-OAc (35\%)} \qquad (9)$$

The composition of the volatile solvolysis products of β-(7-norbornadienyl)ethyl and *exo*-2-brendenyl brosylates (**2**- and **9**-OBs, respectively), determined by gas chromatography as described in the Experimental Section at differing reaction times, are summarized in Table I.

Although **9**-OBs was the only returned brosylate isolated from the acetolysis mixtures of **2**-OBs, we suspect that others may be involved. We note, for example, that **8**-OAc constitutes about 37% of the total acetates produced in the early stages of the reaction (run 1), increases to a maximum of ~42% at 3.5 h (run 3), then drops to a constant value of ~28–29% in the latter stages (runs 6 and 7) after all the brosylate has reacted. It is apparent from its constant abundance in runs 6 and 7 that 5-deltacyclyl acetate (**8**-OAc) is stable to the reaction conditions. A possible interpretation of these observations is that two internally returned brosylates are produced in the acetolysis: **9**-OBs which reacts slowly to produce **9**-, **11**-, and possibly **10**-OAc (vide supra) and another which reacts at an intermediate rate to produce **8**-OAc predominantly or exclusively. Since it may be estimated from the data of Schleyer and Leone on the corresponding tosylate[21] that **8**-OBs would be less reactive than **2**-OBs but more reactive than **9**-OBs (Table VI), and since the acetolysis of **8**-OTs at 75° produces **8**-OAc as the only detectable product,[21] we *presume* that **8**-OBs is, in fact, formed during the acetolysis of **2**-OBs at 25–35°, e.g., as shown in eq 10, where $k_1 + k_2 > k_4 > k_3$.

$$\text{2-OBs} \xrightarrow{k_1} \text{9-OAc} + \text{10-OAc} + \text{11-OAc} + \text{8-OAc}$$
$$\text{2-OBs} \xrightarrow{k_2} \text{9-OBs} \xrightarrow{k_3} \text{9-OAc} + \text{10-OAc} + \text{11-OAc} \qquad (10)$$
$$\text{9-OBs} \xrightarrow{k_4} \text{8-OBs}$$

Scheme I

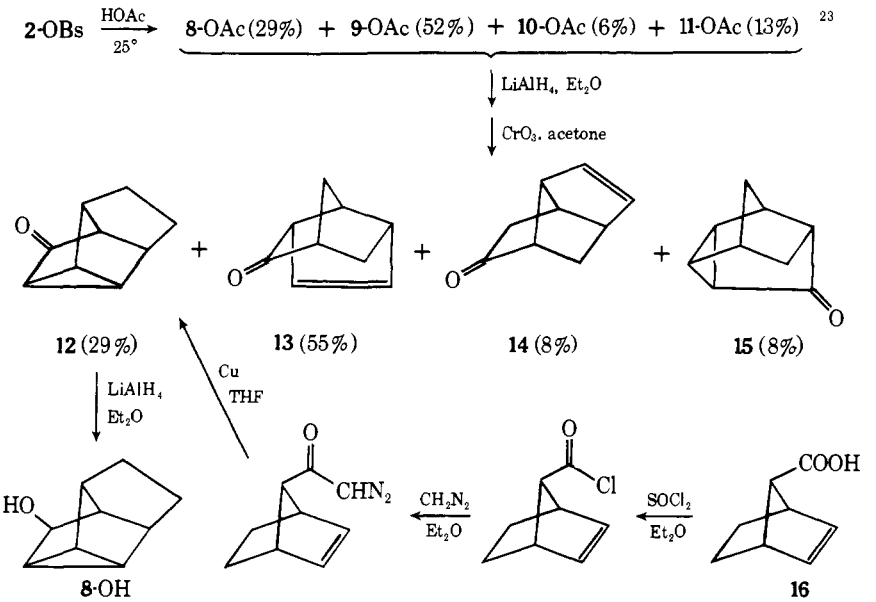


Table I. Volatile Products from the Solvolysis of β-(7-Norbornadienyl)ethyl and *exo*-2-Brendenyl *p*-Bromobenzenesulfonates[a]

Run	Compd	Solvent	Reaction time, h	Percent[b] (proportion[c]) of products				
				7[d]	8-OS	9-OS[e]	10-OS	11-OS[e]
1	2-OBs	HOAc[f]	~0.1	25	28 (37)	35 (47)	6 (8)	6 (8)
2			0.5	11	36 (40)	40 (45)	5 (6)	8 (9)
3			3.5	7	39 (42)	35 (38)	7 (8)	11 (12)
4			46	7	31 (33)	43 (46)	7 (8)	12 (13)
5			720[g]	2	28 (29)	51 (52)	6 (6)	13 (13)
6			~2500	0	28 (28)	58 (58)	5 (5)	9 (9)
7[h]			4	6	36 (38)	40 (42)	8 (9)	10 (11)
8[h]		Aq dioxane[i]	8[j]	3	27 (28)	43 (44)	17 (18)	10 (10)
9	9-OBs	HOAc[f]	336[k]	Trace	0 (0)	65 (65)	Trace	35 (35)
10[l]			71	0	16 (16)	43 (43)	6 (6)	35 (35)

[a] At 35°, unless otherwise specified. [b] Uncorrected for differences in thermal conductivity. [c] Hydrocarbon excluded; other volatile products normalized to 100%. [d] Must be considered approximate especially at short reaction times because the high volatility of 7 renders some loss inevitable and because entrained brosylate produces hydrocarbon when pyrolyzed in the heated injection port of the gas chromatograph. [e] Since 11-OAc isomerized to 9-OAc under our analytical conditions values reported here are probably low in the former and high in latter. [f] Containing ~1% acetic anhydride and sufficient sodium acetate to neutralize the *p*-bromobenzenesulfonic acid produced in the reaction; OS = OAc. [g] 9.7 half-lives of 9-OBs. [h] At 25°. [i] 90/10 v/v dioxane/water buffered with excess sodium bicarbonate; OS = OH. [j] ~8 half-lives of 2-OBs; ~0.006 half-life of 9-OBs. Fraction of 2-OBs returned to 9-OBs estimated to be less than 15%. [k] 4.5 half-lives of 9-OBs. [l] Starting material contains 80–85% 9-OBs and 20–15% of one or more rearranged brosylates of undetermined structure(s).

Table II. Products from the Rearrangement of β-(7-Norbornadienyl)ethyl *p*-Bromobenzenesulfonate in Carbon Tetrachloride at ~33°

Compd	Initial %[a]	Final %[b]
7	~17–0	~9–0
9-OBs	~52–63	~65–71
10-OBs	~0–21	~0–10
8- and/or 11-OBs	~30–16	~26–19

[a] After ~30 min at room temperature; relative proportions of products exclusive of 2-OBs which constitutes ~53–58% of the total mixture. [b] After an additional 60 min at ~33°; relative proportions of products exclusive of 2-OBs which constitutes ~5–6% of the total mixture.

Even though 9-OBs is the only returned brosylate which could actually be isolated from the solvolysis mixtures of 2-OBs, the formation of at least one tetracyclic brosylate can be observed by NMR in the nonnucleophilic solvent carbon tetrachloride. A solution of 2-OBs in this solvent containing a trace of *p*-toluenesulfonic acid was allowed to stand at room temperature for 30 min, then placed in the probe of an A-60 spectrometer at ambient temperature (~33°). When the integral was scanned from δ 7.0 to 3.2, we could observe the disappearance of the resonances at δ 6.63, 6.42, and 3.88 (due respectively to the two nonequivalent pairs of vinyl hydrogens and the two methylene hydrogens on the functionalized carbon of 2-OBs) and the simultaneous appearance of a multiplet at δ ~5.9 (=CH-), a singlet at δ 4.16 (>CH-O- of 9-OBs), and a broad resonance at δ ~4.7 which we attribute to the hydrogen(s) on the functionalized carbon(s) of the other rearrangement product(s). The relative areas of the three emerging resonances, i.e., δ ~5.9/4.16/~4.7, were initially 2.0/0.75/0.44, but changed to 2.0/0.88/0.35 after an additional hour at probe temperature (Table VII). Assuming that structures other than 7 and 8- through 11-OBs are not involved, the approximate composition of the solution can be calculated; cf. Table II. It is clear that at least one tetracyclic brosylate is formed and that an unsaturated material other than 9-OBs is also produced. In view of our previous experience with the monounsaturated brosylate 19-OBs,[2a] we suspect that at least a portion of the unsaturated material present under these conditions is, in fact, deltacyclene (7). The amount of *exo*-2-brendenyl brosylate (9-OBs) increases with time indicating that at least one of the other components isomerizes to it. The material recovered from the carbon tetrachloride solution and recrystallized from pentane consists of ~85% 9-OBs and ~15% of other rearrangement products as indicated by the NMR spectrum. When this recrystallized material was solvolyzed in buffered acetic acid at 25° for ~4 h, the reisolated unreacted brosylate was found to consist exclusivly of 9-OBs, cf. kinetic runs 23 and 24, Table IV. In other words, the unknown rearranged brosylate(s) produced in carbon tetrachloride is (are) *more* reactive than the major product, *exo*-2-brendenyl brosylate (9-OBs). These results are in accord with (though they do not confirm) our previous assumption that some 5-deltacyclyl brosylate (8-OBs) is formed by internal return during the solvolysis of 2-OBs.

The rate of disappearance of 2-OBs in acetic acid and in aqueous 90% dioxane could be followed by NMR since the norbornadienyl vinyl-hydrogen resonances at δ 6.63 and 6.42 do not overlap those of the solvents or the other products. The integral values at δ 6.7–6.4 were measured at known reaction times. Plots of ln [2-OBs], normalized with respect to total aromatic hydrogens (δ 7.9–7.5) at each point,[2a] vs. time gave reasonably good straight lines. The rate constants ($k_1 + k_2$), calculated from a single least-squares regression analysis of ln [2-OBs] on t,[2a] are given in Table III. The agreement of the computed rate constant between individual runs under similar conditions, though acceptable, is not remarkably good. We attribute these fluctuations to the rather poor temperature control in the probe of the spectrometer. The activation parameters for the acetolysis of 2-OBs were calculated from runs at similar acetate concentrations.

Although the rate of ionization, k_1, of 2-OBs is too fast to be followed in this manner, a first-order plot of the titrimetric rate of *p*-bromobenzenesulfonic acid formation, i.e., $(H^+)_\infty - (H^+)$, after all 2-OBs had disappeared gave a straight line from whence the acetolysis rate constant of the least reactive returned brosylate, 9-OBs, could be computed. As discussed previously,[2a] the intercept of such a plot, extrapolated to $t = 0$, is a measure of the fraction of 2-OBs returning to 9-OBs. Titrimetric data are summarized in Table IV.

It is worthy of note that the titrimetric acetolysis rate constant of 9-OBs, derived as described above from the acetolysis of 2-OBs at 35° ($k_3 = 2.37 \times 10^{-6}$ s^{-1}, runs 19 and 20) is *identical* with that determined directly from the acetolysis of pure 9-OBs under similar conditions (run 23) and in good agreement with the extrapolated value (35°) obtained spectrophotometrically (uv) at higher temperatures in much more dilute solution[24] (viz. 2.59×10^{-6} s^{-1}, cf. Table V).

Also notable is the fact that the titrimetric rate constant for the acetolysis of the ~85% pure 9-OBs, isolated as described previously from the treatment of a carbon tetrachloride solution of 2-OBs with acid for ~1.5 h at 25–33°, is identical within

Table III. NMR-Determined, First-Order Solvolysis Constants of β-(7-Norbornadienyl)ethyl and β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonates (**2**- and **19**-OBs, Respectively)

Run	Compd	Solvent	Temp, °C[a]	[ROBs], M	[NaOAc], M	$10^3 (k_1 + k_2)$, s^{-1}	n^b
1	**2**-OBs[c]	HOAc	18.0	0.17	0.20	0.63	34
2			18.6	0.18		0.56	40
3			23.3		0.00	1.09	30
4			23.8		0.20	1.42	37
5						1.48	34
6				0.17	0.30	1.23	37
7			24.6	0.18	0.00	1.13	40
8					0.10[d]	1.17	38
9					0.21	1.18	40
10					0.27	1.49	40
11			34.3		0.20	2.97	27
12			34.8			3.53	22
	19-OBs[e]		23.0		0.00	0.95	29
			23.7	0.19	0.19	1.10	31
			24.2	0.17	0.29	1.30	30
			24.7	0.19	0.20	1.18	30
13, 14	**2**-OBs	90% dioxane[f]	25.7	0.18	0.00	0.251 ± 0.0015	40
15	**19**-OBs		24.6			0.235	40

[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, i.e., data points per run. [c] ΔH^*(HOAc) = 17.2 ± 0.2 kcal/mol; ΔS^*(HOAc) = −13.9 ± 0.5 eu. [d] Sufficient to neutralize all the *p*-bromobenzenesulfonic acid produced during the period that the rate was followed kinetically. [e] Unnumbered runs are from ref 2a, Table I runs 3–5 and 7, respectively, ΔH^*(HOAc) = 16.3 ± 0.1 kcal/mol; ΔS^*(HOAc) = −17.0 ± 0.2 eu. [f] 90/10 v/v dioxane/water, unbuffered.

Table IV. Titrimetric First-Order Acetolysis Rates[a]

Run	Compd	Temp, °C	$[ROBs]_i$, M	$[NaOAc]_i$, M	Intercept[b]	$10^6 k_3$, s^{-1}
16	**2**-OBs	25.2	0.0235	0.0310	0.37	~0.48
17			0.0224		0.39	~0.60
18				0.0297	0.35	~0.53
19		35.1	0.00446	0.00615	0.39	2.27
20			0.00224	0.00614	0.39	2.46
	19-OBs[c]	25.0	0.0235	0.0309	0.42	13.3
21		35.1	0.00447	0.00662	0.47	56.6
22			0.00452	0.00666	0.47	58.3
23	**9**-OBs[d]		0.00443	0.0287	1.00	2.37
24[e]			0.00456		0.85[f]	2.45
	22-OBs[g]	25.0	0.0230	0.0292	1.00	15.0

[a] Buffered with sodium acetate. [b] Equal to $k_2/(k_1 + k_2)$. [c] Reported previously, ref 2a, Table II, run 16; contains 0.0309 M sodium *p*-bromobenzenesulfonate. [d] Recovered from acetolysis of **2**-OBs, see text. [e] Recovered from NMR run in carbon tetrachloride; see text. [f] Intercept indicates the presence of 15% of one or more reactive brosylates other than **2**-OBs; see text. [g] Reported previously, ref 2a, Table III, run 19.

Table V. Spectrophotometric First-Order Acetolysis Rates of *exo*-2-Brendenyl *p*-Bromobenzenesulfonate (**9**-OBs)[a]

Run	Temp, °C[b]	$10^4 k_3$, s^{-1}
25	62.1	0.90
26		0.90
27	74.4	3.9
28		4.0
29	88.2	17
30		19
	35.0[c]	0.0259

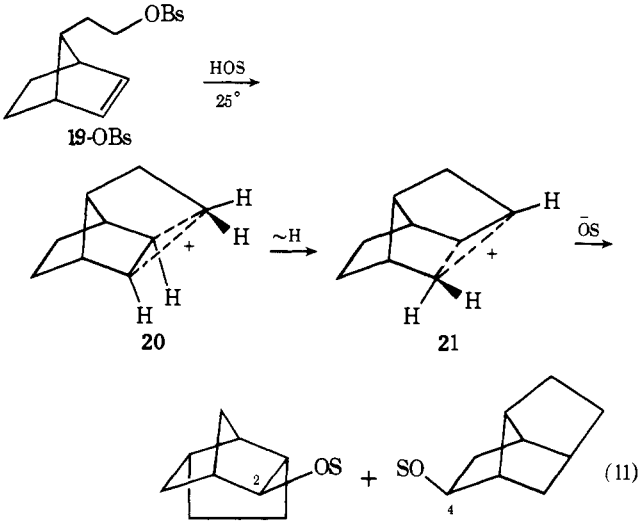
[a] 0.005 M in ROBs, 0.006 M in sodium acetate. [b] Controlled to ±0.5°. [c] Extrapolated from data at higher temperature, ΔH^*(HOAc) = 26.5 kcal/mol; ΔS^*(HOAc) = 1.95 eu.

the limits of our experimental accuracy ($k = 2.45 \times 10^{-6}$ s^{-1}, 35°) to the titrimetric acetolysis constant of pure **9**-OBs, even though the intercept of the first-order rate plot at $t = 0$ (run 24) indicates the presence of ~15% of a much more reactive brosylate. Since we know from the NMR spectra of this impure **9**-OBs that **2**-OBs is not a contaminant, this observation confirms our earlier conclusion based on product analyses that a brosylate of intermediate reactivity is produced in addition to **9**-OBs by internal return during the acetolysis of **2**-OBs.

Since we have not been able to isolate any returned brosylate other than **9**-OBs, our conclusion that **8**-OBs is the only kinetically detectable one produced, is inferential in this sense, and is not intended to preclude the formation of *small* amounts of other more reactive brosylates such as **10**-OBs or possibly even **11**-OBs.

Discussion

The introduction of a second double bond into β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs) has a significant effect upon the course of solvolysis. The monounsaturated brosylate, **19**-OBs, ultimately produces, in addition to deltacyclane whose origin is obscure, only hydrogen-shifted products, viz., *exo*-2-brendyl and *exo*-4-brexyl derivatives (**22**- and **23**-OS), in roughly similar amounts (eq 11). Acetolysis of the doubly



(11)

	22-OS	23-OS
HOS = $HOAc^{2a,23}$	54%	46%
HOS = H_2O/acetone	45%	55%

unsaturated brosylate **2**-OBs, in contrast, yields a substantial fraction of 5-deltacyclyl acetate (**8**-OAc), a *non-hydrogen-shifted product*, a relatively large amount of *exo*-2-brendenyl acetate (**9**-OAc) but very little *exo*-4-brexenyl ester (**10**-OAc), and a hydrogen-shifted tetracyclic product, 5-isodeltacyclyl

Scheme II. The Solvolytic Course of β-(7-Norbornadienyl)ethyl *p*-Bromobenzensulfonate[27]

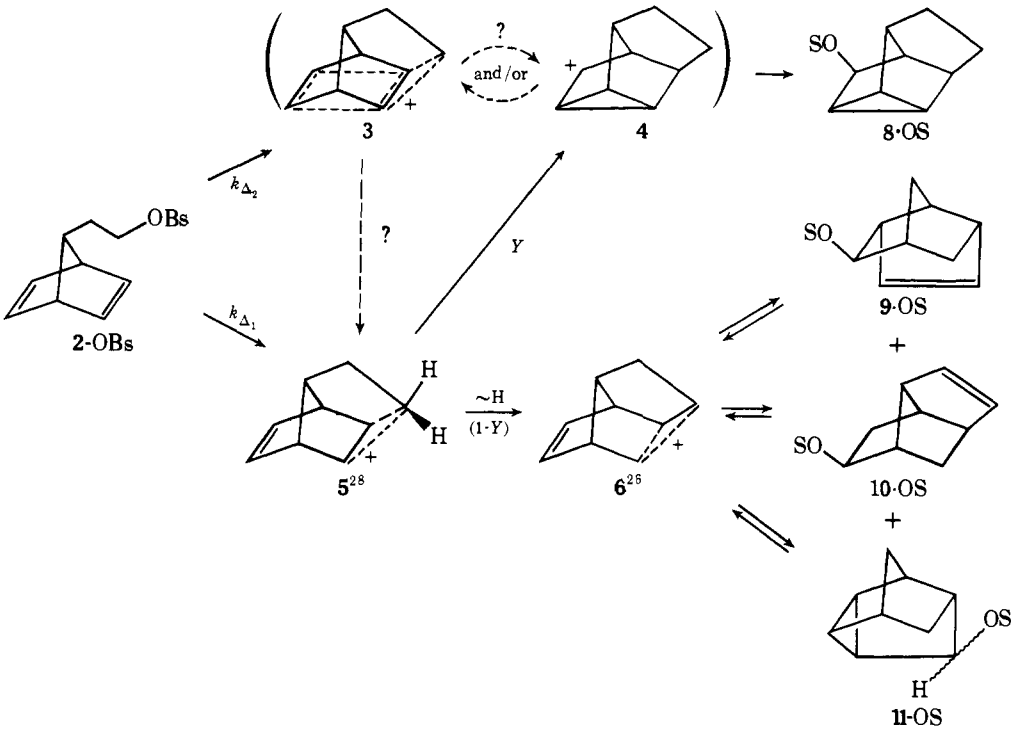


Table VI. Acetolysis Constants and Activation Parameters

Compd	k, s^{-1} 25°	k, s^{-1} 75°	ΔH^*, kcal/mol	ΔS^*, eu
2-OBs[a]	1.4×10^{-3} [b]	1.0×10^{-1} [c]	17.2	−13.9
19-OBs[d]	1.3×10^{-3} [b]	8.1×10^{-2} [c]	16.3	−17.0
18-OBs[d]	4.8×10^{-9} [c]	1.9×10^{-6}	23.9	−16.3
17-OBs[d]	6.4×10^{-9} [c]	2.0×10^{-6}	23.0	−18.8
9-OBs[a]	5.86×10^{-7}	4.25×10^{-4}	26.5	1.95
22-OBs[d]	1.56×10^{-5}	5.65×10^{-3}	23.7	−1.14
8-OTs[e]		7.38×10^{-3}		
8-OBs		(2.2×10^{-2})[f]		

[a] This work; ~0.02 M ROBs, ~0.02 M NaOAc unless otherwise indicated. [b] By NMR, ~0.18 M ROBs, 0.20 M NaOAc, "*b*" ≈ 2–3. [c] Extrapolated from data at other temperatures. [d] Reference 2a. [e] Reference 21a. [f] Estimated as 3.0 × ROTs.

acetate (**11**-OAc). Since this latter ester is converted slowly to **9**-OAc under acetolysis conditions (cf. runs 6 and 7, Table I), it is apparent that the double bond not only stabilizes the brendenyl carbon skeleton relative to the brexenyl, but also acts as an internal nucleophile to trap the homoallylic 2-brendenyl cation (**6**)[26] and kinetically divert some of the products to 5-isodeltacyclyl derivatives; cf. Scheme II. As in the case of **19**-OBs,[2b] relatively more of the tricyclo[4.3.0.0^{3,7}]-type derivative **10**-OH is formed during hydrolysis; cf. Table I.

It is apparent from the kinetic data summarized in Table VI that the anti double bond of β-(7-norbornadienyl)ethyl brosylate (**2**-OBs) provides little or no *additional* kinetic assistance over that associated with the syn double bond alone. None of the hydrogen-migrated products, **9**-, **10**-, and **11**-OBs or -OAc yield 5-deltacyclyl derivatives (**8**-OS) upon buffered acetolysis at 35°; thus, all this non-hydrogen-migrated material must be derived from either the [$2^0 + 2^0 + 1^+$] laticyclic and/or the cyclopropylcarbinyl-type intermediate(s) **3** and **4**, respectively, as illustrated in Scheme II. One or both of these ions or ion pairs could conceivably be formed either directly by the simultaneous participation of both double bonds[29] (k_{Δ_2}) or indirectly by π-trapping of a 2-brexenyl intermediate (**5**)[28] formed by syn double-bond participation (k_{Δ_1}). Schleyer and Leone's report that the acetolysis of 5-deltacyclyl tosylate (**8**-OTs) at 75° produces no unsaturated or rearranged products makes it extremely unlikely that any of the hydrogen-migrated acetates, **9**-, **10**-, and **11**-OAc, observed at 35° arise via the cyclopropylcarbinyl-type intermediate **4**. If we assume for the moment that **3** and **4** represent either canonical forms of the same ion or discrete ions separated by a very low energy barrier, then the ratio of non-hydrogen-shifted to hydrogen-shifted acetates in the solvolysis mixture after all alkyl brosylate has disappeared is given by

$$\frac{[\textbf{8}\text{-OAc}]}{[\textbf{9}\text{-} + \textbf{10}\text{-} + \textbf{11}\text{-OAc}]} = \frac{k_{\Delta_2} + Yk_{\Delta_1}}{(1 - Y)k_{\Delta_1}}$$

where Y is the fraction of 2-brexenyl cations or ion pairs (**5**) converted to 5-deltacyclyl acetate (**8**-OAc) (cf. Scheme II). At 35°, $k_{\Delta_1} + k_{\Delta_2}$, the total rate of disappearance of **2**-OBs, equals 3.3×10^{-3} s^{-1} (Table III, runs 11 and 12), **8**-OAc/(**9**- + **10**- + **11**-OAc) ultimately equals 0.28/0.72, or 0.39 after all the alkyl brosylate has reacted (Table I, run 5 and 6), and

$$k_{\Delta_1} = \frac{3.3 \times 10^{-3}}{1.39 - 1.39Y}$$

Thus, if *none* of the 2-brexenyl intermediate (**5**) is converted to a 5-deltacylyl derivative (i.e., $Y = 0$), then k_{Δ_1} and k_{Δ_2} must equal 2.4×10^{-3} and 9×10^{-4} s^{-1}, respectively, in order to account for the observed product distribution. Alternately, if *all* of the observed **8**-OAc is formed via **5** ($Y = 0.28$), then $k_{\Delta_1} \approx 3.3 \times 10^{-3}$ s^{-1} and k_{Δ_2} is negligibly small.

As Winstein[30] and Schleyer[31] have emphasized, the absence of a large kinetic effect does not necessarily rule out the occurrence of substantial neighboring group participation. In the present example it is likely, in fact, that some or all of the non-hydrogen-migrated product *is* formed via the k_{Δ_2} route. If *all* of the 5-deltacyclyl product were formed via the k_{Δ_1} process exclusively (i.e., $Y = 0.28$), it is necessary to conclude that the nonparticipating anti double bond of **2**-OBs either causes no inductive retardation to the k_{Δ_1} process or destabilizes the ground state relative to the k_{Δ_1} transition state by an amount coincidentally equal to the inductive retardation, since k_{Δ_1} would then approximate the acetolysis constant of **19**-OBs

under comparable conditions (cf. Table VI). This latter possibility seems unlikely in view of the fact that proximate nonparticipating double bonds normally cause a two- to tenfold solvolytic retardation.[2a,6,32] Alternately, if *all* the observed 5-deltacyclyl derivatives are formed via the k_{Δ_2} path, then $k_{\Delta_2} = 2.3 \times 10^{-3}$ s^{-1} or 0.7 times the acetolysis constant of β-*syn*-7-norbornenyl brosylate (**19**-OBs)—a more reasonable expectation.

All of the above conclusions are predicated on the assumption, vide supra, that little or no energy barrier separates the $[2^0 + 2^0 + 1^+]$ laticyclic and cyclopropylcarbinyl-type intermediates **3** and **4**, respectively. If such is not the case, then the observation that **8**-OTs produces no hydrogen-migrated products upon acetolysis[21a] does not necessarily rule out the formation of such products from the laticyclic intermediate **3**, and it is possible that the k_{Δ_2} route is the exclusive reaction path, i.e., that $k_{\Delta_2} = 3.3 \times 10^{-3}$ s^{-1} and k_{Δ_1} is negligible. We view this as unlikely, but are presently investigating this possibility.

Although it is clear that our present data do not provide the ultimate answer to the questions of $[2^0 + 2^0]$ laticyclic participation or of $[2^0 + 2^0 + 1^+]$ laticyclic stabilization, they do suggest that the kinetic assistance attributable to such an effect is not larger than that provided by a single double bond alone. In the present case the laticyclic cation **3** appears at best to be only marginally more stable than the bis(homocyclopropenyl) type (**20**) formed in the solvolysis of β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs).[33]

Experimental Section[34]

Ethyl 7-Norbornadienylacetate (1). To a mixture of 15 g (0.23 mol) of 20-mesh zinc (activated by washing successively with 2% hydrochloric acid, acetone, and ether) and 7.6 g (0.060 mol) of 7-norbornadienyl chloride[15] in 300 ml of ether were added 9 ml (0.08 mol) of ethyl bromoacetate and a trace of iodine. The suspension was heated under reflux in a nitrogen atmosphere for 5 h and then cooled, and enough 50% aqueous acetic acid (~4 ml) was added to dissolve the precipitated salts. The ethereal solution was decanted from the unreacted zinc, washed three times with 5% sodium bicarbonate, once with water, once with saturated sodium chloride, and dried over a mixture of anhydrous potassium carbonate and sodium sulfate. The solvent was removed by distillation at atmospheric pressure and the residue was distilled in a short-path still to yield 2.52 g (23.6%) of product, bp 35–95 °C (2 mm). A GLC analysis on the 8-ft Carbowax column at 150° showed the product to be 85% pure. The ester was separated by collection from the 20-ft Carbowax column at 190°; ir (CCl_4) 3063, 731, 722 (-CH=CH-), 1745 (C=O), 1294, 1155 cm^{-1} (-CO-O-); NMR (CCl_4) δ 6.69 (triplet, J = 2 Hz, 2 =CH-), 6.48 (triplet, J = 2 Hz, 2 =CH-), 3.98 (quartet, J = 8 Hz, $-OCH_2CH_3$), 3.36 (broad sextet (?), 2 >CH, bridgehead), 2.76 (broad asymmetric triplet, J = 7 Hz, $>CHCH_2-$), 2.25 (asymmetric doublet, J = 7 Hz, $>CHCH_2-$), 1.22 (triplet, J = 8 Hz, $-CH_2CH_3$).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.24; H, 8.22.

β-(7-Norbornadienyl)ethanol (2-OH). To a nitrogen-blanketed suspension of 377 mg (9.93 mmol) of lithium aluminum hydride in 60 ml of anhydrous ether was added dropwise over a period of 20 min a solution of 3.05 g (17.2 mmol) of the ester **1** in 60 ml of anhydrous ether. The mixture was stirred at room temperature for 2 h, and the excess hydride was decomposed by the successive dropwise addition of 1 ml of water, 1 ml of 15% sodium hydroxide, and 3 ml of water.[35] The ethereal solution was decanted and the inorganic salts were washed with three portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and the solvent removed under atmospheric pressure. The residue was distilled under reduced pressure giving 2.16 g 15.9 mmol, 92%) of **2**-OH, bp 69.5–70.5 °C (1.0 mm); ir (CCl_4) 3627, 3339 (OH), 3065, 724 (-CH=CH-), 1056, 1041 cm^{-1} (C-O); NMR (CCl_4) δ 6.62 (triplet, J = 2 Hz, 2 =CH-), 6.40 (irregular triplet, 2 =CH-), 3.32 (triplet, J = 7 Hz, $-CH_2CH_2O-$) superimposed on a broad singlet (?) at δ ~3.3 (2 >CH, bridgehead), 2.52 (broad triplet, J = 7 Hz, $>CHCH_2-$), ~2 (broad, concentration dependent singlet, −OH), 1.45 (quartet, $J_1 = J_2$ = 7 Hz, $>CHCH_2CH_2-$).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.02; H, 9.03.

β-(7-Norbornadienyl)ethyl *p*-Bromobenzenesulfonate (2-OBs). A solution of 497 mg (3.65 mmol) of the alcohol **2**-OH in 6 ml of anhydrous pyridine was cooled to −10°, and 980 mg (3.84 mmol) of *p*-bromobenzenesulfonyl chloride was added in one portion. The mixture was swirled to effect solution and then allowed to stand at −20° for 5 h. The solution was poured over 25 ml of cracked ice and the crystalline product separated by suction filtration. The product was washed with ice-water and dried under high vacuum at 0°. The crude material was dissolved in 250 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 reduced pressure until the product crystallized. The crystallized material was filtered quickly, washed with a small volume of chilled pentane, and dried under high vacuum at 0° giving 699 mg of pure **2**-OBs, mp 38.5–39 °C. Further concentration of the pentane mother liquor gave a second crop of 100 mg, mp 37–38 °C, for an overall yield of 799 mg (2.25 mmol, 62%). The infrared spectrum (KBr) had characteristic peaks at 3060, 742 (-CH=CH-), 1190, 1178, ($-SO_2O-$), and 618 cm^{-1} (CBr); NMR (CCl_4) δ 7.61 (singlet, 4 =CH-, aromatic), 6.63 (triplet, J = 2 Hz, 2 =CH-), 6.42 (triplet, J = 2 Hz, 2 =CH-), 3.88 (triplet, J = 6.5 Hz, $-CH_2CH_2O-$), 3.22 (broad sextet (?), 2 >CH, bridgehead), 2.46 (broad triplet, J = 6.5 Hz, $>CHCH_2-$), 1.72 (quartet, $J_1 = J_2$ = 6.5 Hz, $>CHCH_2CH_2-$).

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 but is unstable at room temperature.

The Acetolysis of β-(7-Norbornadienyl)ethyl *p*-Bromobenzenesulfonate (2-OBs). Solutions of the brosylate (~0.17 M) in anhydrous acetic acid[3b] containing an excess of sodium acetate (~0.2 M) were heated at 35° for varying lengths of time (Table I). The products were isolated as described earlier in the case of β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs).[2a] Analysis of the product mixture by GLC on the 8-ft Carbowax column at 130° revealed the presence of five components with relative retention times of 1.0, 8.5, 10.0, 10.7, and 12.7, respectively. The relative abundance of these products at different reaction times is given in Table I. The individual components were isolated by GLC and their structures were established as follows.

The first component had infrared and NMR spectra identical with those of authentic deltacyclene (**7**) prepared independently by Cannell[18a] and by Katz.[18b]

The second component had ir absorptions (CCl_4) at 3056, 725 (-CH=CH-), 1735 (C=O), 1240, and 1027 cm^{-1} (-CO-O-), and NMR signals (CCl_4) at δ 5.90 (slightly irregular singlet, -CH=CH-), 4.18 (singlet, >CHO-), 2.88 (broad multiplet, >CH, bridgehead), 2.58–2.12 (broad multiplet, 3 >CH, bridgehead), and 2.12–0.92 (complex multiplet, 4 $>CHH + >CHH$, superimposed on a singlet at 1.92, $-COCH_3$).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.94; H, 8.11.

Catalytic hydrogenation of a 20-mg sample in ethyl acetate with a palladium-on-charcoal catalyst gave 11 mg (55%) of a product identical in all respects with authentic *exo*-2-brendyl acetate (**22**-OAc).[2a]

The third component had ir absorptions (CCl_4) at 3058, 712 (-CH=CH-), 1737 (C=O), 1244, and 1051 cm^{-1} (-CO-O-), and NMR signals (CCl_4) at δ 6.18–5.84 (broad multiplet, -CH=), 5.84–5.55 (broad multiplet, =CH-), 4.90 (broad doublet, J = 7 Hz, >CHO-), 3.03–2.76 (broad multiplet, >CH, bridgehead), 2.52–2.05 (broad multiplet, 2 >CH, bridgehead), and 2.05–0.82 (complex multiplet, 5 H, >CH, bridgehead + 4 $>CHH + >CHH$ superimposed on a sharp singlet at 1.95, $-COCH_3$).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.82; H, 8.09.

A small sample (<10 mg) of the collected product was hydrogenated in ethyl acetate with palladium-on-charcoal catalyst. Only a very small amount of the hydrogenation product was isolated. Its ir spectrum (very dilute) was in good agreement with that of *exo*-4-brexyl acetate (**23**-OAc).[2a] The structure **10**-OAc, *exo*-4-brexenyl acetate, has been therefore assigned to the third acetolysis component. Since the amount of this material that could be isolated was small, the ir and NMR spectra are of dilute solutions and this assignment must be regarded as tentative.

The fourth component had ir absorptions (CCl_4) at 3057 (C-H,

cyclopropyl), 1736 (C=O), 1239, and 1041 cm^{-1} (-CO-O-), and NMR signals at δ 4.80 (irregular singlet, >CHO-), 2.42 (broad singlet, >CH, bridgehead), 2.13 (broad singlet, >CH), 1.93 (singlet, $-COCH_3$), 1.73 (broad singlet, >CH, superimposed on a complex multiplet δ ~1.8-0.8 (4 >CHH + >CHH, ethano bridge + 3 >CH)).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.87; H, 8.27.

Lithium aluminum hydride reduction of a 45-mg sample gave 14 mg (40%) of an alcohol identical in all respects with 5-deltacyclanol (**8**-OH) prepared by an independent route (vide infra).[20] We conclude that the fourth component is 5-deltacyclyl acetate (**8**-OAc).

The fifth component had ir absorptions (CCl_4) at 3048 (C-H, cyclopropyl ?), 1736 (C=O), 1244, 1024 (-CO-O-), and 726 cm^{-1} (-CH=CH-), and NMR (CCl_4) at δ 5.91 (broad singlet, =CH-), 4.94 (broad singlet, >CHO-), 4.20 (broad singlet, >CHO-), and 3.00-0.75 (multiplet superimposed over sharp singlets at 1.95 and 1.92, $-COCH_3$ + secondary and tertiary alkyl hydrogens). Since the integrals of the low-field signals gave fractional values for the number of hydrogens corresponding to each peak, we suspected that this component was a mixture of two acetates, one containing a double bond. Reinjection of a small sample on the 10-ft Carbowax column revealed the presence of two well-resolved peaks corresponding to the second component, *exo*-2-brendenyl acetate (**9**-OAc, ~60%) and the fifth component (~40%). It is apparent that isomerization takes place in the gas chromatograph. This component was subsequently identified as 5-isodeltacyclyl acetate (**11**-OAc) by conversion to the known ketone **15**[22] prior to separation by GLC, vide infra.

When the acetolysis was interrupted prior to completion (runs 1-4, Table I) a returned brosylate could be recovered in 10-20% yield (cf. ref 2a). Recrystallization from pentane gave a crystalline product, mp 67-68 °C: ir (CCl_4) 3059, 725 (-CH=CH-), 1186, 1175 ($-SO_2O-$), and 610 cm^{-1} (CBr); NMR (CCl_4) δ 7.61 (singlet, 4 =CH-, aromatic), 5.84 (perturbed octet (?), -CH=CH4-), 4.16 (singlet, >CHO-), 2.92 (broad multiplet, >CH, bridgehead), 2.64-0.90 (broad complex multiplet, 3 >CH, bridgehead + 4 >CHH + >CHH).

Anal. Calcd for $C_{15}H_{15}BrO_3S$: C, 50.71; H, 4.26; Br, 22.49; O, 13.51; S, 9.03. Found: C, 50.84; H, 4.39; Br, 22.67; S, 9.04.

A small sample of the product was hydrogenated at atmospheric pressure in ethyl acetate using a palladium-on-charcoal catalyst. The hydrogenated material was identical in all respects with authentic *exo*-2-brendyl brosylate (**22**-OBs).[2a] This product must therefore be *exo*-2-brendenyl brosylate (**9**-OBs).

5-Deltacyclanone (12). To 218 mg (1.58 mmol) of *syn*-7-norbornenecarboxylic acid (**16**)[36] in 10 ml of anhydrous ether were added 250 mg (2.10 mmol) of thionyl chloride and a drop of dry pyridine. The solution was heated under reflux in a nitrogen atmosphere for 2.25 h. The ether and excess thionyl chloride were removed under reduced pressure (~100 mm) at room temperature. To the residue was added 10 ml of ether and ethereal diazomethane until a pale yellow color persisted. The ethereal solution was allowed to stand overnight at room temperature in a loosely stoppered flask. The solvent was removed under reduced pressure (~80 mm) and the residue dissolved in 10 ml of anhydrous tetrahydrofuran. The THF solution was added over a period of 2 h to a rapidly stirred, refluxing suspension of 200 mg of copper powder and 30 ml of an anhydrous THF. The reaction mixture was stirred and heated under reflux for an additional 2 h then cooled, dried over magnesium sulfate, and filtered. Analysis on the 10-ft Carbowax column (column temp 140°; helium flow, 120 ml/min) after concentration of the solution to ~0.5 ml by a distillation at atmospheric pressure revealed that one component (retention time, 14.5 min) accounted for 93% of the mixture, exclusive of the solvent peak. Several other components with short retention times accounted for the other 7%. Collection of the ketone yielded 115 mg (0.860 mmol, 54%) of **12**: ir (CCl_4) 3058 (C-H, cyclopropyl), 1760 (C=O), 859, 841 cm^{-1}; NMR (CCl_4) δ 2.83-2.40 (broad singlet, 2 -COCH<, bridgehead), 1.89-1.90 (broad absorption with sharp resonance at 1.68, 4 >CH, + 4 >CHH + >CHH, ethano bridge).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.76; H, 7.73.

5-Deltacyclanol (8-OH). To a stirred slurry of 14 mg (0.38 mmol) of lithium aluminum hydride and 5 ml of anhydrous ether was slowly added 25 mg (0.19 mmol) of the ketone **12** dissolved in 5 ml of anhydrous ether. After being stirred for 2.5 h at room temperature, the reaction mixture was hydrolyzed with 15% aqueous sodium hydroxide. The ethereal solution was decanted and the precipitated salts thoroughly washed with ether. The combined ethereal solution was dried over sodium sulfate and concentrated to ~0.5 ml by distillation at atmospheric pressure. Collection from the 10-ft Carbowax column (column temp 160°; helium flow, 120 ml/min) yielded 18 mg (0.13 mmol, 70%; retention time, 16.0 min) of alcohol.

The NMR spectrum of the product was in reasonable agreement with that of authentic **8**-OH prepared by Schleyer and Leone.[21]

Ketones Derived from the Acetolysis Mixture of 2-OBs. A sample of **2**-OBs was solvolyzed in buffered acetic acid for 30 days (cf. Table I, run 5). The crude product mixture was reduced with lithium aluminum hydride in the usual manner. The ethereal solution of the reduced products was concentrated to ~0.25 ml and combined with ~4 ml of anhydrous acetone. The acetone solution was oxidized with chromium trioxide reagent[37] as described elsewhere.[2b] Analysis of the oxidation mixture on a 10-ft Carbowax column (160°; He flow 120 ml/min) revealed four components with the following retention times (min) and relative abundance (given in parentheses): 10.2 (55%), 13.3 (8%), 16.1 (29%), and 25.9 (8%). The third and fourth components were identified as 5-deltacyclanone (**12**) (vide supra) and 5-isodeltacyclanone (**15**)[16b,17] by comparison with authentic samples. Although the first and second components were not collected and identified separately, a comparison of their relative abundance in the oxidized mixture with the amount of the acetates **9**-OAc and **10**-OAc obtained in the solvolysis prior to reduction and oxidation (run 5, Table I) clearly indicates that these products must be 2-brendenone (**13**) and 4-brexenone (**14**), respectively.

Acetolysis of Products of *exo*-2-Brendenyl *p*-Bromobenzenesulfonate (9-OBs). Samples of pure **9**-OBs were solvolyzed at 35° for 14 days in buffered acetic acid containing: (1) 32 mg (~0.01 M) of brosylate and 160 mg (0.2 M) of sodium acetate in 10 ml of anhydrous[3b] acetic acid and (2) 16 mg (~0.005 M) of brosylate and 6 mg (0.006 M) of sodium acetate in 10 ml of anhydrous acetic acid. The products were isolated and analyzed as described for **2**-OBs. The compositions of both product mixtures were found to be identical: **9**-OAc (65%), **11**-OAc (35%), and a trace of **7** and **10**-OAc (cf. Table I, run 9).

Hydrolysis of β-(7-Norbornadienyl)ethyl *p*-Bromobenzenesulfonate (2-OBs) in Aqueous Dioxane. A solution of 650 mg (1.81 mmol) of **2**-OBs in 500 ml of 90/10 (v/v) dioxane/water containing 188 mg (2.24 mmol) of sodium bicarbonate was stirred at room temperature (~25°) for 8 h (~7.5 half-lives of **2**-OBs) (cf. Table I, run 8). The reaction mixture was poured into 2 l. of ice-water and extracted with six 250-ml portions of pentane. The pentane extract was washed with water and dried over anhydrous sodium sulfate. The solvent was carefully removed through a fractionating column. Analysis of the product mixture by GLC on the 8-ft Carbowax column showed two poorly resolved, broad peaks whose relative areas were dependent upon the GLC conditions (column temperature, flow-rate of the carrier gas, etc.). In order to avoid the apparent isomerization during GLC analysis, the hydrolysis products were converted to the corresponding acetates.

Acetylation of the Hydrolysis Products of 2-OBs. The crude hydrolysis mixture of **2**-OBs (Table I, run 8) was combined with 20 ml of anhydrous pyridine and 12 g of acetic anhydride and heated under reflux for 4 h. The solution was poured into 100 ml of ice-water and extracted with four 200-ml portions of pentane. The pentane extract was washed successively with two 20-ml portions of aqueous 2% hydrochloric acid and with one 20-ml portion of aqueous 10% sodium bicarbonate. The solution was dried (Na_2SO_4) and concentrated to ~1 ml by removal of the solvent through a fractionating column. The concentrate was cooled to −20° and filtered, giving 29 mg (4.9%) of a crystalline product identical in all respects with the **9**-OBs isolated previously from the acetolysis mixture of **2**-OBs. The volatile products, contained in the filtrate, were identified by comparison of GLC retention times and infrared spectra with the acetolysis products of **2**-OBs, the structures of which have been established; vide supra. Analysis by GLC showed the presence of one highly volatile component (3%) identical with authentic deltacyclene (**7**) and four other volatile components: **9**-OAc (43%), **10**-OAc (17%), **8**-OAc (27%), and **11**-OAc (10%).

In order to determine the extent to which the composition of the acetate mixture represents that of the original hydrolysis mixture, the following control experiment was carried out.

A solution of 573 mg of **2**-OBs in 43 ml of anhydrous buffered acetic acid (0.05 M in sodium acetate) was allowed to stand at room temperature (25°) for 4 h (cf. Table I, run 7). The acetate mixture (iso-

lated as described previously and analyzed by GLC), which consisted of[23] **9**-OAc (42%), **10**-OAc (9%), **8**-OAc (38%), and **11**-OAc (11%), was reduced with an excess of lithium aluminum hydride in the usual manner. After alkaline workup[35] the solvent was removed and the crude alcohol mixture reconverted to acetates by heating under reflux for 4 h with 20 ml pyridine and 15 g acetic anhydride. The product mixture, isolated and analyzed as described for the acetylated hydrolysis products of **2**-OBs, had the following composition: **9**-OAc (45%), **10**-OAc (8%), **8**-OAc (39%), and **11**-OAc (8%) (cf. run 7, Table I).

Rearrangement of 2-OBs in Carbon Tetrachloride. A tiny crystal of *p*-toluenesulfonic acid was added to a solution of 298 mg (0.842 mmol) of the brosylate **2**-OBs in 1 ml of carbon tetrachloride contained in a capped NMR tube. The solution was allowed to stand at room temperature for ~30 min and then placed in the probe of a Varian A-60 NMR spectrometer at 33°. The integral was scanned repeatedly between δ 7.0 and 3.2. The progress of the reaction was followed by observing the disappearance of the triplets at δ 6.63, 6.42 (=CH of **2**-OBs), and 3.88 (-CH_2O-) and the simultaneous appearance of a multiplet centered at δ 5.9 (=CH), a broad singlet at δ 4.16 (>CHO- of **9**-OBs), and a broad resonance at δ ~4.7 due to >CHO- of other rearrangement products. The integral values of these NMR signals at different reaction times are given in Table VII.

The *exo*-2-brendenyl brosylate (**9**-OBs) contained in this carbon tetrachloride solution was isolated in the following manner. A drop of pyridine was added to the solution and the solvent was removed under reduced pressure. The oily residue was dissolved in the minimum amount of pentane, treated with activated charcoal, filtered, and cooled to −20°. The precipitate was filtered to give 171 mg (0.482 mmol, 57%) of crystalline product. The ratio of the signals at δ 4.16 and 4.7 in the NMR spectrum of the crude product indicates that it consists of ~89% **9**-OBs and ~11% of other returned brosylate(s). The mother liquors show ~65% **9**-OBs and ~35% other brosylate(s). The absence of resonances at δ 6.63, 6.43, and 3.88 indicates that no **2**-OBs is present.

The **9**-OBs thus obtained was used in most of the acetolysis rate studies (cf. runs 24-30, Tables III and IV) without further purification.[38] Uncontaminated **9**-OBs could be most conveniently prepared as follows.

The crude rearrangement product recovered from carbon tetrachloride, vide supra (0.164 g, 0.46 mmol), was dissolved in 35 ml of anhydrous acetic acid containing an excess of sodium acetate (0.03 M) and the solution was heated at 36° for 6 h. The unreacted **9**-OBs was recovered as described previously for the incomplete acetolysis runs of **2**-OBs. Recrystallization from pentane gave 89 mg (54%) of pure **9**-OBs containing (by NMR) *none* of the other rearranged brosylate(s).

NMR-Determined Solvolysis Rates of 2- and 9-OBs.[2a] Small weighed samples (25-30 mg) of the brosylates were placed in NMR tubes and quickly dissolved in 0.5 ml of the appropriate rate solvent: (a) anhydrous acetic acid containing 0.0-0.3 M sodium acetate or (b) unbuffered 90/10 v/v dioxane/water. Each of the samples was *immediately* placed in the variable-temperature-controlled probe of a Varian A-60 NMR spectrometer and the integral was scanned repeatedly over the δ 9-5.5 region. The time was recorded with a stopwatch for each scan when the pen crossed a line drawn at δ 8.5.

The rate of disappearance of the starting material was determined from the ratio of the decreasing integral amplitudes of the norbornenyl-type vinyl hydrogen signals (at δ ~6.0-5.7 for the monounsaturated and ~6.8-6.3 for doubly unsaturated brosylate) to the theoretically constant total aromatic hydrogen signals (δ 7.9-7.5).[2a] By using the ratio rather than the absolute values of the norbornenyl hydrogen integrals, we hoped to compensate for any fluctuations in all integral amplitudes between individual runs and a slight steady downward drift which was occasionally observed throughout a given run.[2a] A total of 30 to 40 scans were recorded for each rate run. The probe temperature was determined before and after every run by measuring the difference in chemical shift between the hydroxy and the methyl hydrogens of methanol (*cf.* Table III, footnote *a*). The data, treated as described previously,[2a] are summarized in Table III.

Titrimetric acetolysis rates of 2- and 9-OBs were determined as described previously.[2a] In the case of **2**-OBs, the initial rate of brosylate ion formation was too fast to be measured in this manner but the fraction of **2**-OBs which returns to the less reactive **9**-OBs could be determined from the intercept of the first order plot at $t = 0$ extrapolated from the final linear portion of the rate of brosylate ion formation (i.e., after 60% reaction or ~1 h at 35°).[2a] Rate constants calculated from the slope of the final linear portion of the first-order plot were identical with those obtained for pure **9**-OBs under similar conditions (cf. Table IV).

Table VII. Intensities of Absorptions in the NMR Spectrum during Acid-Catalyzed Rearrangement of 2-OBs in Carbon Tetrachloride

Time, min	Intensity, mm				
	δ 6.63–6.42[a]	δ 5.9[a]	δ 4.7[a]	δ 4.16[b]	δ 3.88[b]
0[c]	52	16	3.5	6	26
5	37	20	4	8	19
10	25	29	6	12	14
15	19	29	6	12	10
20	15	32	5	12	9
30	11	32	6.5	13	8
40	8	34	6	14	6
50	6	35	6	14	5
60	4	34	6	15	3

[a] Estimated to be accurate to ±1 mm on the integral trace. [b] Because of partial overlap estimated to be accurate within ±2 mm on the integral trace. [c] In the probe at ~33° after 30 min at ~25°.

The kinetic treatment of the data is similar to that employed for the solvolysis of β-(*syn*-7-norbornenyl)ethyl brosylate (**19**-OBs) described in an earlir publication.[2a]

Uv-Determined Acetolysis Rates of *exo*-2-Brenenyl *p*-Bromobenzenesulfonate (9-OBs). Teflon-stoppered uv cells (1 cm) containing anhydrous acetic acid 6×10^{-3} M in sodium acetate were allowed to equilibrate in a Perkin-Elmer Model 202 spectrophotometer equipped with a variable-temperature cell holder and an ordinate scale expander. Small samples of the brosylate were introduced (~5×10^{-3} M) and the absorbance at 268 mμ (ROBs) was automatically plotted vs. time. These plots were converted to ln $(A - A_\infty)$ vs. time and the rate constants determined by a single least-squares regression analysis. These data are presented in Table V. The actual temperature of the solution in the cell was determined by measuring the difference in temperature between the sample cell, containing ethylene glycol, and the constant-temperature bath with an iron-constantan thermocouple. We believe the temperature fluctuation to be less than ±0.5°.

Acknowledgment. It is a pleasure to acknowledge our debt to those investigators, mentioned by name in the footnotes, who helped with the product identifications and to the National Science Foundation who generously supported a portion of this work.

References and Notes

(1) Portions of this work have been presented before the 156th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1968, Abstract ORGN 97; (b) abstracted in part from the Ph.D. thesis of G.B.K., University of South Carolina, 1968.
(2) (a) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967); (b) R. S. Bly, R. K. Bly, J. B. Hamilton, and S. P. Jindal, *ibid.*, in press; (c) R. S. Bly, R. K. Bly, and J. N. C. Hsu, *ibid.*, in press; (d) R. S. Bly, R. K. Bly, J. B. Hamilton, and J. N. C. Hsu, unpublished results.
(3) Cf. (a) R. S. Bly and H. L. Dryden, *Chem. Ind. (London)*, 1287 (1959); (b) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965); (c) R. K. Bly and R. S. Bly, *ibid.*, **31**, 1577 (1966); (d) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Am. Chem. Soc.*, **89**, 6993 (1967); (e) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292 (1969).
(4) For summaries see: (a) S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 1411 (1969); (b) P. R. Story and B. C. Clark, Jr. in "Carbonium Ions", Vol. III, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 23, and references cited therein.
(5) (a) S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959); (b) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).
(6) S. Winstein, M. Battiste, and R. Panda, 6th Report on Research, Petroleum Research Fund, American Chemical Society, 1961, p 178.
(7) O. L. Chapman and P. Fitton, *J. Am. Chem. Soc.*, **85**, 41 (1963).
(8) A. F. Diaz, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970).
(9) (a) S. Winstein and C. Ordronneau, *J. Am.-Chem. Soc.*, **82**, 2084 (1960); (b) P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962); (c) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); (d) *ibid.*, **89**, 6352 (1967); (e) *ibid.*, **89**, 6354 (1967).
(10) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 1293 (1968).
(11) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).
(12) (a) L. A. Paquette and I. R. Dunkin, *J. Am. Chem. Soc.*, **96**, 1220 (1974); (b) *ibid.*, **97**, 2243 (1975).

(13) C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *J. Am. Chem. Soc.*, **82**, 2397 (1960); **83**, 1668 (1961).
(14) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).
(15) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).
(16) (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. D. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613 (1965); (b) *ibid.*, **87**, 1615 (1965).
(17) P. K. Freeman, B. K. Stevenson, D. M. Balls, and D. H. Jones, *J. Org. Chem.*, **39**, 546 (1974).
(18) (a) L. G. Cannell, *Tetrahedron Lett.*, *5967 (1966)*; (b) *T. J. Katz, J. C. Carahan, and R. Boecke, J. Org. Chem.*, **32**, 1301 (1967). We thank Drs. Cannell and Katz for their willingness to make this comparison and to provide spectra of authentic deltacyclene.
(19) Cf. R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968); **92**, 4883 (1970).
(20) While we have not compared our material with that prepared independently by Coates and Kirkpatrick,[19] we have shown that its reduction product, 5-deltacyclanol (**8**-OH), is identical with an authentic sample prepared in a different manner.[21]
(21) (a) P. v. R. Schleyer and R. E. Leone, *J. Am. Chem. Soc.*, **90**, 4164 (1968). (b) We thank Professor Schleyer for volunteering his help in the confirmation of this structure.
(22) We are indebted to Professor P. K. Freeman for spectra of the authentic material.
(23) The percentages given are relative proportions of the nonhydrocarbon products normalized to 100%.
(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed., Wiley, New York, N.Y., 1961, pp 28–30.
(25) The actual intermediate is probably a pool of structurally degenerate, charge-delocalized cation–brosylate ion pairs of C_s symmetry.[2b-d]
(26) Charge delocalization in the rearranged cation is not required by our data; cf. footnote 5, ref 2b.
(27) Does not include deltacyclene (**7**), the provenance of which is uncertain.
(28) Depicted as charge-delocalized by analogy to the 2-brexyl cation **20**.[2c]
(29) Just as symmetric double bond participation in **19**-OBs produces the bishomocyclopropenyl cation (**20**),[2c] simultaneous, symmetric $2^0 + 2^0$ laticyclic participation of both double bonds in **2**-OBs would lead to the "unsymmetric" $[2^0 + 2^0 + 1^+]$ laticyclic cation **3**.[14] A dissymmetric participation of both double bonds which results in the formation of the cyclopropylcarbinyl-type cation **4** would not be classified as laticyclic participation under the Goldstein–Hoffmann definition.[14]
(30) (a) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953); (b) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (c) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958); (d) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).
(31) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in ref 4b, Chapter 27, p 1461, and references cited therein.
(32) (a) J. A. Berson in "Molecular Rearrangements", Vol. 1, P. deMayo, Ed., Wiley-Interscience, New York, N.Y., 1963, Chapter 3, pp 192 ff, and references cited therein; (b) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964); (c) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in ref 4b, Chapter 26, p 1336, and footnote 149; (d) N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964); (e) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).
(33) Other studies suggest that in systems where both are possible, laticyclic stabilization is liable to be less important than homoaromatic; cf. (a) ref 12b, footnote 45; (b) M. V. Moncur and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 6449 (1973), and references cited therein; (c) M. J. Goldstein and S. Natowsky, *ibid.*, **95**, 6451 (1973).
(34) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, either Model 337 or Model 257, the NMR spectra on a Varian A-60 spectrophotometer equipped with a variable-temperature probe using tetramethylsilane (δ 0.00) and chloroform (δ 7.31) as internal standards. Gas chromatography was carried out in an F & M Model 500 chromatograph equipped with a hot-wire detector using 8 or 10 ft × 0.25 in. coiled copper tubes packed with 20% Carbowax 20 M on 60–80 mesh Chromosorb Cl. Preparative gas chromatography was performed in an Aerograph Autoprep Model 700-A using a 20 ft × $\frac{3}{8}$ in. aluminum column packed with 20% Carbowax 20 M on 60–80 mesh Chromsorb W.
(35) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).
(36) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).
(37) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).
(38) Since the unidentified minor component(s) solvolyze much more rapidly than **9**-OBs, first-order rate plots using this mixture show different intercepts at $t = 0$ but slopes identical with those obtained using **9**-OBs of 100% purity.

Entering Chloride Kinetic Isotope Effects in Protic and Aprotic Solvents

Thomas H. Cromartie[1] and C. Gardner Swain*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 31, 1975*

Abstract: Chlorine kinetic isotope effects for the reaction of ethylene oxide and chloride ion are normal ($^{35}Cl/^{37}Cl$ greater than unity) in protic solvents and in acetone and dimethylformamide (DMF) in the presence of 1 equiv of 2,6-lutidinium ion. In the presence of 0.1 equiv of this cation (and 0.9 of Li^+) the isotope effect in DMF is inverse (0.9922). This is the first observation of an inverse entering-group heavy-atom isotope effect. The reaction of chloride ion with dimethyl sulfate is normal in water but inverse in DMF. The "normal" isotope effects are shown to be due in large measure to the dominance of changes in hydrogen bonding to chlorine over changes in carbon–chlorine bonding.

As noted in a previous paper,[2] kinetic chlorine isotope effects of organic reactions do not show as wide a variation in magnitude with changes in transition state structure as might have been expected.[3-6] One explanation that has been advanced is a leveling effect on the isotope effect by the hydroxylic solvents in which the reactions were studied.[7] As the chlorine at the transition state becomes more like a chloride ion, the isotope effect due to loss of carbon–chlorine bonding increases. The hydrogen bonding to this chloride ion may also increase, however, and this increase of bonding might lower the observed isotope effect. The simultaneous operation of these two opposing effects could lead to an insensitivity of the chlorine isotope effect to transition state structure. In support of this proposal, it has been noted that kinetic chlorine isotope effects measured in hydroxylic solvents are smaller than isotope effects for identical reactions in dipolar aprotic solvents.[8,9] Because the structural changes in the transition state for these reactions on transfer from hydroxylic solvents to dipolar aprotic solvents are not known, however, these observations do not prove that hydrogen bonding to chlorine at the transition state is responsible for the smaller isotope effects in protic solvents.

We recently reported kinetic and equilibrium chlorine isotope effects for the interconversion of ethylene oxide and 2-chloroethanol in the solvents H_2O, D_2O, ethanol, and *tert*-butyl alcohol.[2] One of the conclusions of that study was that, at least for equilibrium chlorine isotope effects, differences in solvation of chloride ion in those protic solvents are required to account for the experimental observations. We have now extended that study to entering group chlorine kinetic isotope effects in aprotic solvents and have found a striking dependence of such isotope effects on hydrogen bonding to chloride ion.

Results and Discussion

Heavy atom kinetic isotope effects are the product of two