Table II. Effect of DME Concentration on Second-Order Alkaline Rate Constant

1,2-Dimethoxyethane (DME), % (v/v)	Second-order alkaline rate constant, 10^5k (M^{-1} sec^{-1})
8	3.45
12	2.69
16	1.95
20	1.45
24	1.21

constants observed was made, and extrapolation of these measurements to 0% 1,2-dimethoxyethane gave a value of 4.94×10^{-5} M^{-1} sec^{-1} for the rate constant (Table II and Figure 2.)

Thus, a comparison of the rate constants for the two sulfonates shows that the five-membered cyclic sulfonate (I) hydrolyzes 6.8×10^5 times faster than its open-chain analog (II). This is then the second observation of a very large rate enhancement for the hydrolysis of a five-membered cyclic sulfur-containing ester.

A comparison of the phosphorus and sulfur systems reveals an interesting trend; the ratios of the rates for the cyclic esters compared to their acyclic analogs are lower when a methylene group is directly attached to the hetero atom (phostonates and sultones) than those which have been observed for the phosphates and sulfates. Studies on the origin of the extraordinary lability of the cyclic sulfur-containing esters and the mechanism involved in their hydrolyses are being pursued.[13,14]

(13) X-Ray investigations on the structures of the sulfonate esters are in progress in the laboratory of Professor E. B. Fleischer at the University of Chicago.

(14) The support of the National Science Foundation is gratefully acknowledged. O. Z. wishes to thank the National Institutes of Health for a Predoctoral Fellowship.

Bridged Polycyclic Compounds. XXXVI. Rearrangements in the Acetolysis of *exo*-Dehydro-2-norbornyl *p*-Bromobenzenesulfonate[1]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received December 30, 1965*

Abstract: *exo*-3-Deuteriodehydro-2-norbornyl *p*-bromobenzenesulfonate (VIIb) solvolyzes in glacial acetic acid to give about 7% of an equimolar mixture of *exo*-3-deuteriodehydro-2-norbornyl acetate (VIId) and 7-deuteriodehydro-2-norbornyl acetate (VIIId), along with about 93% of deuterated 3-nortricyclyl acetate (IId). The acetolysis is accompanied by a considerably more rapid scrambling of the *p*-bromobenzenesulfonate by internal return to 7-deuteriodehydro-2-norbornyl *p*-bromobenzenesulfonate (VIIIb), without attendant formation of deuterated nortricyclyl *p*-bromobenzenesulfonate (IIb). The data are consistent with the assumption that ion pairs involving a symmetrical nonclassical cation such as IV are produced in the ionization process, or with the assumption that *rapidly* equilibrating nonsymmetrical cations such as V and VI are involved, but are not consistent with the suggestion made earlier that the nonsymmetrical cation V is formed in the ionization step and isomerizes relatively slowly to its Wagner–Meerwein isomer VI.

Solvolyses of derivatives of *exo*-dehydro-2-norborneol (Ia) and of its homoallylic isomer 3-nortricyclenol (IIa) have been of interest since the initial reports of their reactivities and interconversions,[2,3] in particular as one of the key examples of a homoallylic cationic system.[4] The high reactivity of the *exo*-*p*-bromobenzenesulfonate Ib compared with its *endo* epimer in acetolysis[3] or of the corresponding *exo* chloride in solvolysis in 80% aqueous ethanol[5] compared with its *endo* epimer has been attributed[2–6] to anchimeric assistance to ionization provided by the electron cloud of the 5,6 double bond (homoallylic interaction) at the developing cationic center at C_2. In addition, it has been suggested that a portion of the driving force for increased reactivity may be ascribed to participation of the σ 1,2 bond,[4b] similar to that assumed in the *exo*-2-norbornyl case,[7,8] where there is much evidence supporting the concept that the symmetrical nonclassical cation III[4] (or a variant thereof) is produced in the ionization process.

Solvolyses of Ib and IIb in methanol and in acetic acid have been shown to give mixtures of dehydronorbornyl and nortricyclyl ethers and esters containing largely II isomers.[9] These mixtures contained slightly

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(1) Previous paper in series: S. J. Cristol, J. K. Harrington, and M. S. Singer, *J. Am. Chem. Soc.*, **88**, 1529 (1966).

(2) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(3) S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950).

(4) (a) S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948); (b) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (c) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

(5) J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

(6) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(7) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

(8) For a recent summary of the evidence available on the norbornyl ion, see S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

(9) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962).

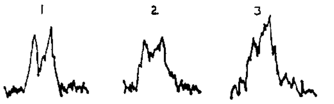
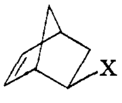


Figure 1. Multiplet of proton at C-2 in nmr spectra of deuterated *exo*-dehydronorbornyl *p*-bromobenzenesulfonates at successive stages of acetolysis: (1) starting material, (2) after 16 min at 28°, (3) after 36 min at 28° (multiplet is centered at τ 5.55 and the principal coupling is 7.5 cps).

more Ic and Id when Ib was solvolyzed than did those from the solvolyses of IIb.[10] Data of this sort have been used to support the suggestions[4c,9] that several intermediates (at least two) may be involved in such solvolyses, although these data may be accommodated on the basis that the several intermediates are ion pairs in which symmetrical cation IV has its gegenion disposed differently in the intermediates initially formed from Ib and from IIb. However, in order to interpret the report[11] that the acetolysis of Ib, labeled with ^{14}C at C_2 and C_3, gave scrambling of ^{14}C, but not as much as that required by the intermediate IV, it has been assumed[4c,11] that solvolysis of Ib does not lead directly to IV, but instead gives initially the unsymmetrical homoallylic cation V. The fact that ^{14}C scrambling does occur in acetolysis and is reported to be almost complete on formolysis of Ib suggests[11] that the initially formed unsymmetrical cation V is transformed either to the symmetrical cation IV (a second intermediate) or to the enantiomorphic unsymmetrical cation VI *via* a Wagner–Meerwein rearrangement process, presumably through a transition state (or an intermediate) resembling IV. In order to explain the ^{14}C data, it was assumed that, in the acetolysis, 24% of V was captured by acetic acid or acetate ion before transformation to IV or equilibration with VI.



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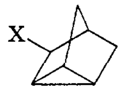

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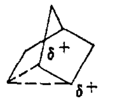

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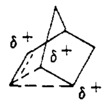
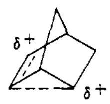
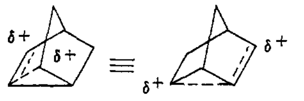


IV



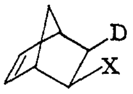
V



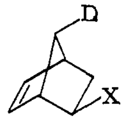
VI

a, X = OH
b, X = OBs
c, X = OCH_3
d, X = OAc

In connection with our interest in the nature of the mechanistic paths involved in solvolysis and addition reactions, we prepared the stereospecifically labeled *exo,cis*-3-deuteriodehydro-2-norborneol (VIIa) by oxidation of the product of addition of deuteriodiborane to norbornadiene.[12] Its stereochemical purity was shown by the nmr spectrum of the acetate VIId (prepared from the alcohol VIIa), in which a fairly clean doublet at τ 5.47 with J = 7 cps was observed for the proton at C_2 and also by that of the *p*-bromobenzenesulfonate VIIb, which had a doublet (with some minor splitting) at τ 5.55 with J = 7.5 cps (Figure 1). The location of the deuterium at C_3 (or possibly at C_2) was confirmed by mass spectral analysis in which the amount of deuterium not at C_2 and C_3 is correlated with the relative peak intensities at *m/e* 66 and *m/e* 67. These ratios, after correction for isotopic abundance and by comparison with undeuterated material (all of our compounds were converted to acetate esters for analysis), indicated that at most, 3% of the deuterium present was not at C_2 and C_3.[13]



VIIa, X = OH
b, X = OBs
d, X = OAc



VIIIa, X = OH
b, X = OBs
d, X = OAc

A portion of the work described below was carried out with the *p*-bromobenzenesulfonate sample described above, while another portion was carried out with samples of *p*-bromobenzenesulfonate richer in VIIb than in VIIIb and also containing undeuterated materials. These samples were prepared by addition of deuterioacetic acid to norbornadiene under various conditions. These preparations will be reported[12] but the pertinent data on the starting materials are indicated in the Experimental Section.

The pure *exo,cis*-deuteriosulfonate VIIb was solvolyzed in acetic acid for periods of time less than those giving complete reaction, and the remaining *p*-bromobenzenesulfonate samples were recovered and subjected to scrutiny by nmr analysis in the τ 5.55 region. Samples were taken after approximately 16 and 36 min of reaction time at 28°. The results observed made several things clear. These were (a) solvolysis was accompanied by significant scrambling of deuterium in the *p*-bromobenzenesulfonate from *exo*-C_3 presumably to C_7; (b) rearrangement to nortricyclyl *p*-bromobenzenesulfonate IIb is not an observable companion to solvolysis; and (c) while the scrambling noted in a is significant, it would not be enough to explain the completely scrambled distribution of the deuterium in the product acetates (Figure 1 and Table I), if cation V were captured by solvent (or acetate) before rearrangement to its enantiomorph VI or to IV. The appropriate portions of nmr spectra are given in Figure 1.

The results just noted permit certain simple deductions. One of these is that there is internal return[15] in

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(10) Similar unpublished data of S. Winstein and H. J. Schmid have also been alluded to in the literature; see footnote 23, in ref 4c.

(11) J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, 77, 3034 (1955).

(12) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, unpublished work.

(13) Dehydronorbornyl derivatives fragment in the mass spectrometer in such a fashion that the principal ion intensity is usually that due to $C_5H_6^+$ (*m/e* 66).[14] This appears to be largely due to cleavage between C_1 and C_2 and between C_3 and C_4, although the results with VIId (apparent marking at C_2 and C_3 of 97–98% D and of 2–3% D in atoms C_1, C_4, C_5, C_6, and C_7) suggests that there is a strong possibility that a small portion of the apparent retrograde Diels–Alder reaction occurring in the mass spectrometer occurs after mixing of all seven carbon atoms. Thus it seems possible that the sample of VIId prepared by deuterioboration was cleanly labeled at C_3 and that the 2–3% D indicated by mass spectrometry in the $C_5H_6^+$ (or $C_5H_5D^+$) peak comes from scrambling in the analysis. On this basis, all of the results obtained by us may have small corrections calculated on the assumption that the indicated deuterium at C_2 and C_3 is 97–98% of the actual amount.

(14) (a) Details of the mass spectral analytical procedure will be described elsewhere by R. A. Sanchez and D. C. Sheesley; (b) E. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, 30, 2886 (1965).

(15) See, for example, ref 7 and S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, 74, 2156 (1952).

Table I. Acetolysis of Deuterated *exo*-Dehydro-2-norbornyl *p*-Bromobenzenesulfonate at 24.0°

	Deuterium anal. in initial *p*-bromobenzenesulfonate[a]							Deuterium anal. in product acetate		
Expt no.	at C_7[b]	at C_3[c]	% at C_3[d]	Time, hr	[ROBs], *M*	[NaOAc], *M*	Estd %[e] reaction	at C_7[b]	at C_3[c]	% D at C_7[d]
1[f]	1.8	95.0	98	44	0.130	0.00	>99	50.7	45.6	52.6
2	*g*	*g*	96	4	0.0364	0.364	48	37.6	39.8	48.6
3a	2.8	90.1	97	11	0.0304	0.304	82	45.3	47.2	49.0
3b	2.0	38.0	95	11	0.0258	0.258	82	18.3	20.2	47.5
4a	1.3	32.5	96	52.5	0.0282	0.282	>99	13.1	11.5	53.2
4b	2.0	38.0	95	52.5	0.0258	0.258	>99	20.0	17.9	52.8
5a	2.0	38.0	95	72	0.0302	0.0334	>99	18.5	19.0	49.3
5b	2.8	90.1	97	72	0.0242	0.0268	>99	40.2[h]	40.0	50.1

[a] Analyses of deuteration were based on fragmentation results of acetate prepared from alcohol from which sulfonate ester was prepared. A more complete analytical mass spectral method for such acetates will be reported. [b] Calculated from relative intensities of *m/e* peaks 67 and 66 after correction for isotopic abundances. [c] Calculated from the difference between the deuterium content of the molecular ion (obtained from *m/e* peak 152 and 153) and the result of *b*. [d] $b/(b + c) \times 100 = \%$ D at C_7, $c/(c + b) \times 100 = \%$ D at C_3. The assumption is made that deuterium is distributed solely between C_3 and C_7, based upon mechanistic preconceptions. [e] Based on the rate constant reported in ref 16. [f] Experiment 1 was carried out at 28°; all others were at 24.0°. [g] The alcohol used for this experiment was a mixture of the samples used for expt 3a and 4a. [h] A check on the deuterium analysis can be made by comparing the total deuterium analysis ($b + c$) for the starting sulfonate ester with the analysis for the product acetate. The failure of such a comparison to be consistent for experiment 5b is the result of using a fairly large amount of undeuterated sulfonate ester for seed crystals in the preparation of the starting material.

this system. Rough calculations from the data of Figure 1 suggest that the half-life for scrambling in the bromobenzenesulfonate at 28° is about 20 min, while that for solvolysis is about 4 hr.[16] The internal return results in Wagner–Meerwein rearrangement (1,2 shift), as in the norbornyl system,[8,15] and may be accommodated by an ion pair between *p*-bromobenzenesulfonate ion and a symmetrical nonclassical ion such as IV (or a variant of IV), or a system in which IV is simulated by a rapidly interconverting set of V and VI ions. The second is that return from the IV–OBs⁻ ion pair is too fast to allow significant migration of the *p*-bromobenzenesulfonate ion to C_5 to give IIb.

As noted above, acetolysis of Ib (or of mixtures of VIIb and VIIIb) leads to mixtures containing about 7% of Id acetate (or mixtures of VIId and VIIId) and 93% of IId (or the deuterated equivalents). Fortunately the dehydronorbornyl esters are readily separable from the nortricyclyl esters by vapor phase chromatography,[9] and analysis by mass spectroscopy requires only very small samples. Accordingly, samples of deuterium-labeled bromobenzenesulfonates were solvolyzed in glacial acetic acid at 24.0°, and the deuterium distribution determined. Data and results are given in Table I.

Before the results in Table I may be considered meaningful, one must be assured that they represent kinetic control rather than equilibration. Our experience with addition of deuterioacetic acid to norbornadiene,[12] where deuterium is (generally) not distributed equally between C_3 and C_7, made it clear that first-formed products would be stable under solvolysis conditions. To confirm this, a sample of deuteriodehydronorbornyl acetate (0.004 *M*) containing 97% deuterium, 98% of which was VIId and 2(±1)% was VIIId (*i.e.*, 2(±1)% of the deuterium content was analyzed as being on C_7) was allowed to stand at 27° for 161 hr in glacial acetic acid containing 0.464 *M* sodium acetate and 0.0516 *M* sodium *p*-bromobenzenesulfonate. The acetate was reisolated (no nortricyclyl acetate IId was formed) and had the following mass spectral analysis: total D, 97%; D at C_3, 99%; D at C_7, 1(±1)%. These results show that, within the limit of error of the procedure, the initially formed acetate mixture is stable.

The results displayed in Table I indicate that deuterium in the product acetate is distributed essentially equally between C_3 and C_7, and that in the course of the acetolysis reaction, C_3 and C_7 become completely scrambled (and suggest correspondingly that C_1 and C_2 also become completely scrambled). These results are consistent with the formulation of the intermediate cation as the symmetrical nonclassical species IV or as a pair of *rapidly* equilibating ions such as V $\rightleftharpoons$ VI, but are not consistent with slowly equilibrating unsymmetrical cations (classical or nonclassical).[11] Our results are thus consistent with the studies using ^{14}C labeling where the solvent was formic acid, but are not in agreement with reports for solvolysis in acetic acid.[11]

However, regretably, in view of the fact that VIIb and VIIIb were so rapidly interconverted in the course of the solvolysis, we would be unable to detect small differences in yields of VIId and VIIId, and our experiments therefore do not completely rule out moderately rapidly equilibrating V $\rightleftharpoons$ VI ion intermediates. We hope to do solvolyses in other solvents and under other conditions where we would hope to find solvolysis competing somewhat better with internal return than in these acetolysis experiments.

The problem[9] of the number of intermediates formed by *both* Ib and IIb also still remains. We hope that the problem of whether IIb in fact leads to an unsymmetrical cation will yield to experiments now in progress in this laboratory.

Experimental Section

Preparation of *exo,cis*-3-Deuteriodehydro-2-norbornyl *p*-Bromobenzenesulfonate (VIIb). A crude sample (*ca.* 2.5 g, 0.022 mole) of *exo,cis*-3-deuteriodehydro-2-norborneol (VIIa, contaminated with some *endo,cis*-3-deuteriodehydro-2-norborneol) was used, the preparation of which will be described.[12] This sample was dissolved in 5.0 ml of pyridine and cooled to 0°. A solution of 8.6 g (0.034 mole) of *p*-bromobenzenesulfonyl chloride in 16 ml of cold (ice bath) pyridine was added rapidly with stirring to the alcohol–pyridine mixture. The mixture was stored at −10° for 18 hr.

An unsuccessful attempt to crystallize the arenesulfonate product was made by pouring the reaction mixture on crushed ice. The resulting brown, solid material was extracted from the ice–water

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(16) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, 78, 595 (1956).

mixture by three 30-ml portions of ether. These ether extracts were combined and washed successively with 10 ml of cold water, 5 ml of 10% sodium bicarbonate, and 10 ml of cold water. Drying of the ether solution was carried out over magnesium sulfate for 2 hr at 0°.

Filtration of the ether solution was followed by solvent removal (rotary evaporator). Two 20-ml extractions with boiling pentane were made upon the material left after solvent removal. These extracts were filtered (through glass wool and sodium sulfate) and refrigerated at −10° for 20 hr. A yield of 1.3 g (17% of theoretical maximum) of arenesulfonate was obtained, mp 68–72°.

Preparation of *exo,cis*-3-Deuteriodehydro-2-norbornyl Trideuterioacetate. A 4-ft, heavy-walled glass tube was charged with 25 g (0.391 mole) of acetic acid-d_4 (Columbia Chemical Co.) and 142 ml of norbornadiene (freshly distilled, 3.56:1.00 mole ratio of diene to carboxylic acid). The tube contents were frozen (Dry Ice) and the tube was sealed. After the tube was heated for 161 hr at 200° (±20°), the contents was again frozen and the tube was opened. After filtration, the crude reaction mixture was poured into 300 ml of cold water. The resulting suspension was extracted with three 250-ml portions of pentane; the extracts were combined and washed with 100 ml of 10% sodium carbonate solution and 100 ml of cold water. Drying was carried out overnight using magnesium sulfate. Filtration and solvent removal resulted in a crude reaction mixture which was used for the subsequent saponification step. Gas chromatographic analysis of the ester mixture indicated a ratio of 97:3 = *exo,cis*-3-deuteriodehydro-2-norbornyl trideuterioacetate:deuterionortricyclyl trideuterioacetate. Identification was on the basis of equivalence of the retention times to that of the undeuterated analogs. No absolute yield was determined at this point.

Preparation of *exo,cis*-3-Deuteriodehydro-2-norborneol (VIIa). One-third of the crude ester from above (0.13 mole of theoretical maximum amount) was used as starting material. This ester was treated with 200 ml of a 1.0 *M* solution of potassium hydroxide in methanol (0.20 mole of base) at ice-bath temperature for 18 hr. Pouring of the crude reaction mixture into 500 ml of cold water was followed by extraction of the resulting suspension with three 200-ml portions of ether. The ether extracts were combined and washed with 200 ml of cold water and dried overnight with magnesium sulfate.

Filtration was followed by solvent removal (rotary evaporator). Ether was added to the solid left upon solvent removal. This solution was treated with Darco and filtered through magnesium sulfate and coarse filter paper with ether washing. Solvent was removed (rotary evaporator) giving a yield of 7.0 g of alcohol (VIIa, 49% of theoretical maximum based on acetic acid-d_4 of the first step).

Alternate Preparation of *exo,cis*-3-Deuterio-*exo*-dehydro-2-norbornyl *p*-Bromobenzenesulfonate (VIIb). Seven grams (63 mmoles) of alcohol VIIa from the preceding experiment was treated with 24 g (94 mmoles) of *p*-bromobenzenesulfonyl chloride in the same manner as described in the first experiment of this paper. Pouring the crude reaction mixture into 300 ml of ether was followed by extracting the ether solution with 200 ml of cold water, with four portions of cold 10% hydrochloric acid and with an additional 200-ml portion of cold water. Darco treatment was carried out at room temperature for 5 min and the resulting mixture was filtered through magnesium sulfate and coarse grade filter paper. Solvent was removed (rotary evaporator) and a solid crystalline material appeared. This material was dried by aspirator-aided filtration, resulting in a yield of 10 g (48% of theoretical, based on alcohol). An nmr spectrum of this material was identical with the arenesulfonate obtained in the first experiment of this paper. This is indicative of a highly deuterated arenesulfonate, with a preponderance of the deuterium in the *exo*-vicinal position (see text of paper).

Typical Solvolysis Run (Experiment 3a, Table I). To a 1-l. volumetric flask was added 10.0 g (0.0304 mole) of the arenesulfonate VIIb obtained from the preceding experiment. To this flask was added 24.9 g (0.304 mole) of anhydrous sodium acetate and the flask was filled to the mark with glacial acetic acid. The contents were dissolved with shaking, and the flask was placed in a constant-temperature bath at 24.0 ± 0.1°. At the end of 11 hr the reaction mixture was worked up as described in the preparation of *exo,cis*-3-deuterio-*exo*-dehydro-2-norbornyl trideuterioacetate. Gas chromatographic analysis (20 M Carbowax, on firebrick, 2 m, $^3/_8$ in., 142°, 150 ml/min) indicated a ratio of 8:92 = deuterio-*exo*-dehydro-2-norbornyl acetate (VIId and VIIId): deuterionortricyclyl acetate. A sample of the VIId–VIIId mixture was collected and subjected to mass spectroscopic analysis. Samples of dueterated *exo*-2-dehydronorbornyl *p*-bromobenzenesulfonate were taken after 16 and 36 min of reaction time in a similar experiment at 28°. Spectral analysis indicated significant deuterium scrambling (nmr of 1 in Figure 1) and no homoallylic rearrangement (no deuterated nortricyclyl bromobenzenesulfonate detected by infrared or nmr analysis).

Rough Calculations for Estimating the Degree of Scrambling of Recovered *p*-Bromobenzenesulfonate. These calculations were based upon the nmr spectra of the proton at C_2 for the various deuterated arenesulfonates (Figure 1) and the spectrum of the undeuterated sulfonate ester which displays a triplet centered at τ 5.55. An arbitrary point was selected in each multiplet (the center of a line connecting the tips of the doublet peaks) and the degree of the return to the baseline was measured. This measurement, since the undeuterated sulfonate ester (assumed to be the same as would be found for VIIIc) has the least return to base line and the *cis*,-*exo*-labeled sulfonate has the greatest return, is then the basis for the estimation of the amount of "scrambled" sulfonate composing the substrate. Calculations of such a nature indicated 46% scrambling (% scrambled sulfonate (VIIIc) × 2) at the end of 16 min and 70% scrambling at the end of about 36 min. This implies a half-life of scrambling of about 20 min at 28°.

Acknowledgments. Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.