dried in vacuum to yield 5.2 g. (59%) of 3-*p*-anisyl-2-butanol, m.p. 58.8–59.2° (reported[31] 60° for the solid diastereoisomer).

3-*p*-Anisyl-2-butyl *p*-Toluenesulfonate.—4.0 g. (0.022 mole) of 3-*p*-anisyl-2-butanol was dissolved in 4.0 ml. of dry pyridine. The solution was cooled in ice, 4.3 g. (0.022 mole) of recrystallized *p*-toluenesulfonyl chloride, m.p. 68.5–69.0°, was added, and the mixture swirled in an ice-bath until the chloride dissolved. The mixture was allowed to stand overnight and then it was worked up in the conventional way. The bulk of the oily product was recrystallized from a dry ether–light petroleum mixture in a Dry Ice–acetone-bath, with the aid of seed crystals obtained by trituration of some of the oil with low-boiling pet. ether at −80°. There was obtained 4.2 g. (55%) of white product in several crops: seed crystals, m.p. 47.0–47.3°; 1st crop, m.p. 43.0—43.4°; 2nd crop, m.p. 43.0–45.0°; 3rd and 4th crops, more crude and sticky. The first crop was used almost immediately for rate determinations. The second crop of crystals was recrystallized from ether–petroleum ether in an attempt to obtain an analytical sample. A carbon and hydrogen analysis on some of the product, m.p. 48.5–50.0°, mixed m.p. with 3-*p*-anisyl-2-butanol 41–53°, was still poor. The *p*-toluenesulfonate used for acetolysis gave an infinity equivalent weight of 420.6 (calcd. 334.4).

Kinetic Measurements.—The procedures for determination of solvolysis rates in acetolysis,[44] ethanolysis,[13] and formolysis[16] were those previously described. The formic acid solvent contained 0.19% water by Karl Fischer titration and 99.95% acid by base titration. In ethanolysis and acetolysis the reactions were followed to 70–90% completion. This was true also in formolysis, except in the case of benzylmethylcarbinyl *p*-bromobenzenesulfonate whose reaction was followed to 40% completion. First order rate constants (Table II) were very satisfactory except in formolysis of *p*-methoxybenzylmethylcarbinyl *p*-toluenesulfonate where the mean deviation was higher (Table II) and a general downward drift in rate constant was apparent.

The formolysis rate of benzylmethylcarbinyl *p*-toluenesulfonate was also measured from the rate of increase of the conductance of a 0.01793 *M* solution of the ester as measured in a conductance cell with smooth platinum electrodes, using an impedance bridge (type 650-A, General Radio Co., Cambridge, Mass.) to measure resistance.

(44) Winstein, Grunwald and Ingraham, THIS JOURNAL, **70**, 821 (1948).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. X. Solvolysis of *endo*-Norbornyl Arylsulfonates[1,2,3]

BY S. WINSTEIN AND D. TRIFAN

Solvolysis of *endo*-norbornyl arylsulfonates proceeds in glacial acetic acid, aqueous acetone and aqueous dioxane to give completely the corresponding *exo*-derivative. That this *endo* to *exo* change involves rearrangement is clear from the complete resolution of *endo*-norbornyl alcohol and the solvolysis of optically active *endo*-norbornyl *p*-bromobenzenesulfonate in glacial acetic acid, ethanol and 75% aqueous acetone. Nearly complete loss of activity attends the formation of *exo*-products, first-order polarimetric rate constants agreeing with titrimetric rate constants within experimental error. The facts are most simply explained with carbon migration in the norbornyl cation. While the geometry in the *endo*-norbornyl *p*-bromobenzenesulfonate is unfavorable to participation of the C_1–C_6 bonding electron cloud in the ionization process, ionization is, for the most part, followed by rearrangement to the presumably more stable bridged structure. Solvent intervention, with 7–8% inversion, competes with carbon migration in acetolysis.

Among the norbornyl derivatives, the *exo*-configuration is the one associated with an enhanced rate of solvolysis.[3,4] Also, as reported previously in preliminary form[3] and in detail in the following paper,[5] the indications from stereochemical scrutiny of the solvolysis are that solvolysis proceeds with Wagner–Meerwein rearrangement. It would be instructive to know whether with the *endo* configuration, which is not associated with an enhanced solvolysis rate, rearrangement nevertheless accompanies solvolysis. The use of optically active *endo*-norbornyl derivatives represents one of the approaches to this problem, and, in this paper, we report the study of the solvolysis of *dl* and resolved *endo*-norbornyl arylsulfonates.

endo-Dehydronorbornyl acetate was prepared from cyclopentadiene and vinyl acetate with only slight modification of the method of Alder and Rickert.[6] Hydrogenation[6] of this material gave *endo*-norborneol (I) but this material was clearly not homogeneous, the Diels–Alder reaction being not completely stereospecific as was also noted recently by Roberts and co-workers.[7] The crude acid phthalate was a mixture and the crude toluenesulfonate (III, X = *p*-CH_3) was contaminated with material which solvolyzed much more rapidly than the *endo*-*p*-toluenesulfonate.

Solvolysis of the crude *endo*-*p*-toluenesulfonate (III) gave rise to products at least very largely *exo*. Thus acetolysis in glacial acetic acid gives acetate product IV (obtainable in 86% yield) which is at least largely *exo* as shown by comparison of the infrared spectrum of the acetolysis product (Fig. 1) with those of *endo*-norbornyl acetate (Fig. 1) and *exo*-norbornyl acetate.[5] Treatment of the acetate with lithium aluminum hydride and conversion of the carbinol product to 3,5-dinitrobenzoate gave 3,5-dinitrobenzoate of *exo*-norborneol (II) with no evidence of contamination with the *endo*-isomer. Similarly, hydrolysis in aqueous dioxane or aqueous acetone yielded *exo*-norborneol (II) either as the 3,5-dinitrobenzoate or as the acid phthalate in yields of 76–78% with no evidence for the presence of *endo*-isomer in the product. The results of solvolysis of pure *endo*-

(1) Supported in part by the Office of Naval Research and the Research Corporation.

(2) Much of the material of this paper was presented in summary: (a) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of Abstracts; (b) at Montpellier, France, April, 26, 1950, *Bull. soc. chim.*, [5] **18**, C55 (1951); (c) presented before Organic Division of American Chemical Society, Boston, Mass., April 2–5, 1951, page 54M of Abstracts.

(3) Preliminary communication, Winstein and Trifan, THIS JOURNAL, **71**, 2953 (1949).

(4) Winstein, Morse, Grunwald, Jones, Corse and Marshall, *ibid.*, **74**, 1127 (1952).

(5) Winstein and Trifan, *ibid.*, **74**, 1154 (1952).

(6) Alder and Rickert, *Ann.*, **543**, 1 (1940).

(7) Roberts, *et al.*, THIS JOURNAL, **72**, 3116 (1950).

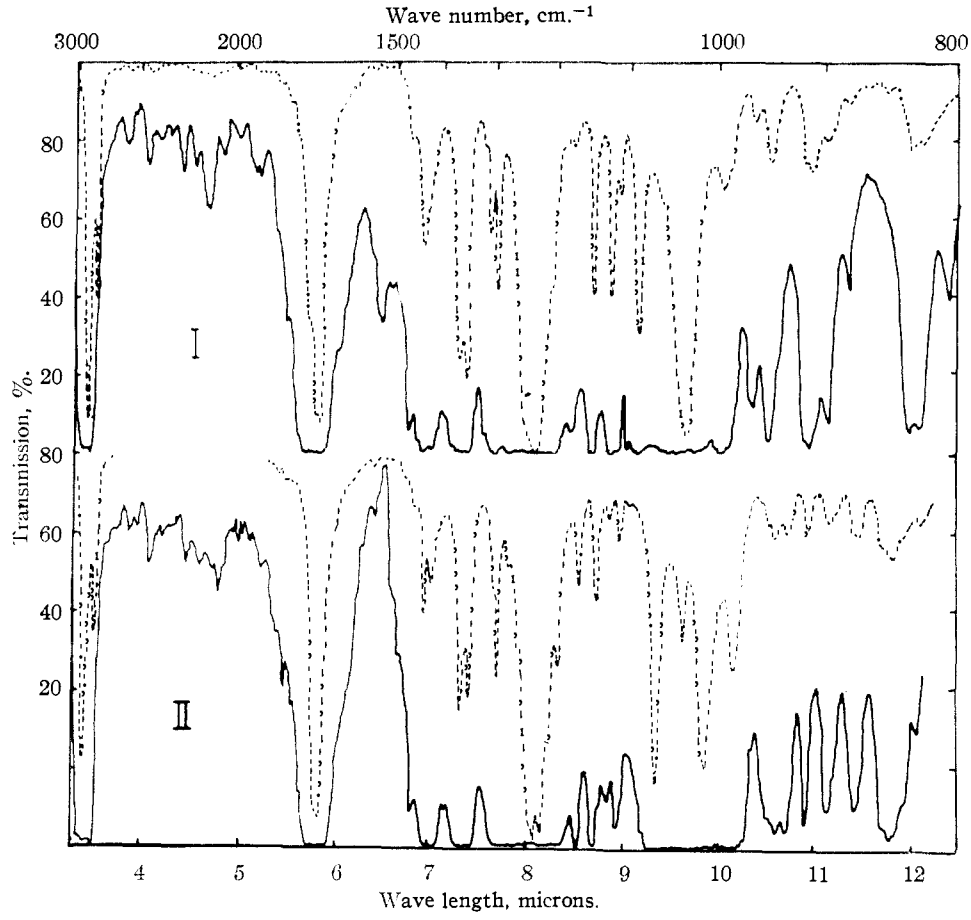
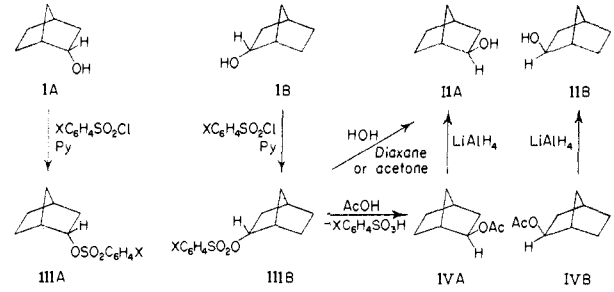


Fig. 1.—Infrared absorption spectra (Baird infrared spectrometer; 0.1 mm. cell length): I, *endo*-norbornyl acetate; II, acetolysis product from *endo*-norbornyl *p*-bromobenzenesulfonate; —, pure liquid; - - - 10% in CCl_4.

norbornyl *p*-bromobenzenesulfonate (III) (X = Br) were entirely analogous to those with the *p*-toluenesulfonate. Large scale solvolysis of the sulfonate esters in aqueous acetone and isolation of the norborneol II as acid phthalate was convenient for preparative purposes, saponification of the acid phthalate yielding pure *exo*-norborneol (II). A little more quantitative idea of the completeness of the change from *endo*- to *exo*-configuration accompanying the solvolysis is available from the refractive index of the product of acetolysis. The value $n^{25}D$ 1.4565 agreed perfectly with the value for authentic *exo*-norbornyl acetate.[5] Since the value for the *endo*-isomer is $n^{25}D$ 1.4583, the *exo*-product is pure within the experimental error of *ca.* 6%.

The most accurate estimate of the completeness of the *endo* → *exo* change in solvolysis depended on reconversion of the solvolysis product to *p*-bromobenzenesulfonate and scrutiny of the kinetics[4] of acetolysis of this material. This method was applied to the product of solvolysis of *endo*-*p*-bromobenzenesulfonate (III) (X = *p*-Br) in 75% acetone. The first order rate constant for acetolysis of the product was (9.02 ± 0.09) × 10^{-5} sec.$^{-1}$ at 25.10 ± 0.05°; (8.84 ± 0.21) × 10^{-5} sec.$^{-1}$ at 25.00 ± 0.05° in good agreement with the value reported previously[4] (8.79 ± 0.90) × 10^{-5} at 24.96° for *exo*-norbornyl-*p*-bromobenzenesulfonate. Furthermore, the acid liberation after 24 hours at 25° (11 half-lives for *exo*-material; 2% reaction for *endo*-isomer) was equal to that after 24 hours at 100° (complete reaction of *endo*-isomer). From this it is clear that the *endo* → *exo* change in the solvolysis in 75% acetone was at least 99.7% complete.



Other analogous transformations, which proceed with the *endo* → *exo* configurational change, have been reported although less quantitative evidence is available in these cases. This is true of the treatment of *endo*-norbornylamine with nitrous acid[8,9] and the hydrolysis of *endo*-norbornyl halides.[10]

For the work with optically active benzene-

(8) Alder and Stein, *Ann.*, **514**, 211 (1934).
(9) Komppa and Beckmann, *ibid.*, **512**, 172 (1934).
(10) Roberts, Bennett and Armstrong, THIS JOURNAL, **72**, 3329 (1950).

TABLE I

EFFECT OF SOLUTES ON ACTIVE MATERIALS IN ACETIC ACID SOLVENT AT 74.57°

Other solute	Active compound	*M*	Time, hr.	Observed α, degrees Initial	Final
None	*exo*- (A) acetate	0.370	13.0	−0.813	−0.815
None	*endo*- (A) acetate	.373	14.0	− .802	− .805
0.755 *M* HOTs[a]	*exo*- (A) acetate	*ca.* .370	1.30	− .751	− .073
.755 *M* HOTs	*exo*- (A) acetate	*ca.* .370	3.40	− .751	− .001
.758 *M* HOTs	*exo*- (B) acetate[c]	*ca.* .370	17.0	+ .726	+ .675
.758 *M* HOTs	*endo*- (A) acetate	*ca.* .373	14.0	− .763	− .758
.427 *M* KOAc	*exo*- (B) acetate	*ca.* .370	14.0	+ .743	+ .746
.666 *M* PyHOBs[b]	*exo*- (A) acetate	*ca.* .370	14.0	− .678	− .681
.673 *M* PyHOBs[b]	*endo*- (A) acetate	*ca.* .373	27.0	− .732	− .734
.453 *M* HOTs	*exo*- (A) alcohol[d]	*ca.* .302	3.55	+ .077	+ .078
.453 *M* HOTs	*exo*- (A) alcohol[d]	*ca.* .302	11.77	+ .077	+ .075

[a] *p*-Toluenesulfonic acid. [b] Pyridinium *p*-bromobenzenesulfonate. [c] Temperature was 24.96°. [d] Solvent was 75% acetone.

TABLE II

TITRIMETRIC AND POLARIMETRIC SOLVOLYSIS RATES OF *endo*-NORBORNYL *p*-BROMOBENZENESULFONATE AT 74.57°

Solvent	Concn., *M*	Other solute	Procedure	Isomer	Observed α, degrees Initial	Final	*k* sec.$^{-1}$
AcOH	0.020[a]		Titrimetric	*dl*			(1.54 ± 0.02) × 10^{-4}
	.301		Polarimetric	(B)	1.260	0.001	(1.53 ± .08) × 10^{-4}
	.301		Titrimetric	(B)			(1.70 ± .10) × 10^{-4}
	.301		Titrimetric	*dl*			(1.71 ± .10) × 10^{-4}
	.301	0.409 *M* KOAc	Polarimetric	(B)	1.199	.043	(2.07 ± .08) × 10^{-4}
	.302	0.415 *M* KOAc	Titrimetric	(B)			(1.87 ± .06) × 10^{-4}
75% $(CH_3)_2CO$	.301		Polarimetric	(B)	1.076	.002[a]	(2.31 ± .19) × 10^{-4}
	.301		Titrimetric	(B)			(2.51 ± .13) × 10^{-4}
EtOH	.301		Polarimetric	(B)	1.139	.002[b]	(6.05 ± .23) × 10^{-5}
	.301		Titrimetric	(B)			(6.38 ± .20) × 10^{-5}

[a] 0.002 ± 0.005°. [b] 0.002 ± 0.004°.

sulfonates, *endo*-norborneol (I) was resolved in the conventional manner. Preliminary tests on *endo*-norbornyl acid phthalate using the organic bases cinchonidine, brucine, cinchonine, quinine and *l*-menthylamine failed to yield crystallizable salts with the last three compounds but indicated that the cinchonidine and brucine alkaloids concentrated the (A) and (B) enantiomorphs, respectively. After concentrating the (A) and (B) enantiomorphs to *ca.* 65–80% purity, final purification was possible by recrystallizations of the active acid phthalates until they were free of the less soluble racemic material. The rotations of the (A) and (B) enantiomorphs agreed well and there are other indications that the resolution was complete. Saponification of the (A) and (B) acid phthalates made available the *endo*-(A) and (B)-norborneols IA and IB which were converted to bromobenzenesulfonates III A and B.

Examination of the optical stability of *endo*-norbornyl acetate, *exo*-norborneol, whose resolution is described elsewhere,[5] and the corresponding acetate under conditions for solvolysis of *endo*-norbornyl *p*-bromobenzenesulfonate disclosed how much the stereochemical result of solvolysis could be influenced by racemization of the product subsequent to its formation. As summarized in Table I, *exo*-acetate is not optically stable at 75° in acetic acid solution 0.755 *M* in toluenesulfonic acid, being 90% racemized in 1.3 hours and completely racemized after 3.40 hours. On the other hand, it is only 7% racemized by the same solution after 17 hours at 25°. Both *exo*- and *endo*-acetates are completely optically stable at 75° in acetic acid alone or in the presence of potassium acetate or pyridinium *p*-bromobenzenesulfonate, while the *endo*-acetate is stable even in the presence of 0.758 *M* toluenesulfonic acid. The *exo*-norborneol is optically stable at 75° to the more weakly acidic medium represented by 0.453 *M* toluenesulfonic acid in 75% acetone.

Examination of the solvolysis of optically active *endo*-(B)-norbornyl *p*-bromobenzenesulfonate showed that it was attended by loss of optical activity to a very large extent. Some of the information is summarized in Table II, which includes initial and final rotation readings on solvolysis solutions. Hydrolysis in 75% acetone is attended by essentially complete loss of activity. However, because of the low specific rotation of *exo*-norborneol, complete survival of activity would have led in this case to a rotation of only *ca.* 0.080° (see Table I). Even so, with the accuracy obtainable with the polarimeter which was available for this work (see data, Table II), it is clear that racemization attending the hydrolysis to *exo*-norborneol is at least 90% complete. Activity is similarly lost in ethanolysis, but no work was carried out on norbornyl ethers which would permit more quantitative evaluation of this result.

In acetolysis, in the absence of potassium acetate, activity is completely destroyed, but this result loses most of its significance because of the optical instability of *exo*-acetate under the solvolysis conditions. However, in the presence of 0.409 *M* potassium acetate, under conditions where *exo*-acetate is completely optically stable, solvolysis of 0.301 *M* *endo*-norbornyl *p*-bromobenzenesulfonate is still

attended by nearly complete loss of activity, the rotation reading dropping from 1.199 to 0.043° (see Table II). From data in Table I it is clear that *ca.* 93% racemization attends the acetolysis to *exo*-acetate. The result was similar when 96.5% resolved *endo*-(B)-bromobenzenesulfonate was acetolyzed in 0.10 *M* solution, 0.12 *M* in potassium acetate and the acetate product isolated. The rotation $\alpha^{24}D$ +0.793° (1 dm.) of the acetate product, compared with the magnitude of 10.39° for pure *exo*-acetate,[5] indicates that *ca.* 92% racemization attends the acetolysis.

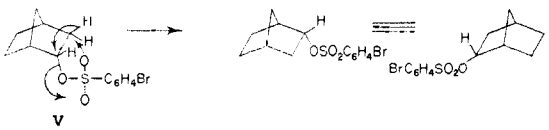
To verify that racemization is inherent in the solvolysis process and not due to racemization of the bromobenzenesulfonate, the change in rotation attending solvolysis was followed polarimetrically for comparison of polarimetric rate constants with titrimetric solvolysis rate constants. Polarimetric rate constants were calculated from equation 1, the change in rotation of the solutions following good first-order kinetics.

Table II summarizes the comparison between polarimetric and titrimetric solvolysis rate con-

$$2.303 \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty} = kt \qquad (1)$$

stants. At the top of Table II is listed the rate constant for acetolysis[4] of *endo*-norbornyl *p*-bromobenzenesulfonate in 0.02 *M* solution, and it is seen that titrimetric rates at higher concentration (appropriate for polarimetric observation) and with potassium acetate present are somewhat higher by about the magnitude of medium effects. In acetolysis with and without potassium acetate, as also in solvolysis in 75% acetone and in ethanolysis, the polarimetric rate constants agreed within experimental error with those from the titrimetric procedure.

Thus it is clear that the solvolysis of *endo*-norbornyl *p*-bromobenzenesulfonate is not complicated by a polarimetric rate constant in excess of the titrimetric one, as we observe in other cases, including *exo*-norbornyl *p*-bromobenzenesulfonate.[5] This means that no racemization of *endo*-norbornyl *p*-bromobenzenesulfonate takes place during or before solvolysis. This rules out such over-all processes, resulting in racemization of original *endo*-bromobenzenesulfonate, as the one symbolized in V (regardless of mechanism).



V

It is still necessary to inquire whether *endo*-norbornyl *p*-bromobenzenesulfonate somehow solvolyzes by way of the *exo*-isomer, which we know[3,5] does give racemic *exo*-product in solvolysis. *exo*-Norbornyl *p*-bromobenzenesulfonate is sufficiently more reactive in solvolysis[4] than the *endo*-isomer that formation of *exo*-isomer from *endo* would contribute to the measured solvolysis rate.

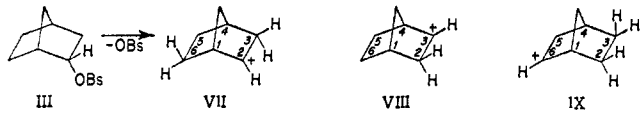
One of the conceivable disturbances is a bimolecular displacement by *p*-bromobenzenesulfonate ion (OBs^-) on IIIA to yield *exo*-bromobenzenesulfonate as symbolized in VI. This can be ruled out because it requires the titrimetric solvolysis rate constant to climb as OBs^- builds up in a run. Also, were racemization attending solvolysis due to this cause, there would be no agreement between polarimetric and titrimetric rate constants early in a run.

VI

Another conceivable disturbance which can be ruled out on the basis of the observed kinetics, is the formation of *exo*-bromobenzenesulfonate from an intermediate cation and external *p*-bromobenzenesulfonate ion.

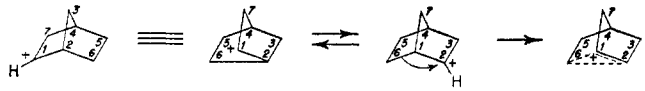
Still another conceivable route to *exo*-norbornyl *p*-bromobenzenesulfonate is by way of an ion pair from ionization of IIIA which achieves the proper orientation to give back *exo*-bromobenzenesulfonate. This does not involve external OBs^- and cannot be dismissed on simple kinetic grounds. However, the extent of a similar kind of return to *exo*-*p*-bromobenzenesulfonate is known in the much more favorable case where one start with *exo*-*p*-bromobenzenesulfinate.[5,11] Even this much return either to active or inactive *exo*-*p*-bromobenzenesulfonate (which then gives racemic solvolysis product) is far from sufficient to account for the racemization which attends solvolysis of *endo*-norbornyl *p*-bromobenzenesulfonate (III).

The data on the stereochemical outcome of solvolysis of III and the previous discussion make it clear that racemization is due to some rearrangement of the cation VII produced by ionization of III. In this system, racemization would result either from H: shifts (VII ⟶ VIII or VII ⟶ IX) or from migration of the C-6 ring member. There is conceivable even further structural reshuffling



III VII VIII IX

by H: and carbon shifts, either consecutive or coupled, and other tracer work is necessary here. We are informed that some of this is being carried out by Dr. J. D. Roberts of the Massachusetts Institute of Technology. Pending results of this work, the simplest interpretation[5] of the presently observed racemization attending solvolysis of *endo*-norbornyl *p*-bromobenzenesulfonate (III) involves C-6 migration in the cation VII giving either the bridged[12] intermediate X or the mirror image ion XI, the former being preferred.[5]



XI VII X

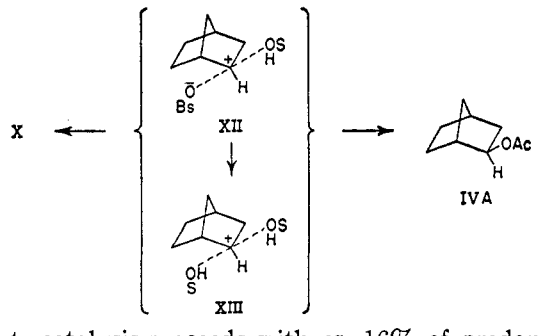
On this basis, the solvolysis of *endo*-norbornyl *p*-bromobenzenesulfonate (III) illustrates re-

(11) Winstein and Schreiber, THIS JOURNAL, in press (1952).
(12) Winstein and Morse, *ibid.*, **74**, 1133 (1952).

arrangement, not associated with a driving force, which follows a rate-determining ionization. The geometry of III is unfavorable[4] for delocalization of the C-1–C-6 bonding electron cloud in the rate-determining ionization. The bromobenzenesulfonate ion, departing with the pair of electrons previously shared with C-2, leaves the developing *p*-orbital on C-2 in just the direction unfavorable to participation by the C-1–C-6 bonding pair. Essentially after ionization, however, this involvement does occur. The behavior here parallels that in the solvolysis of bornyl derivatives.[4]

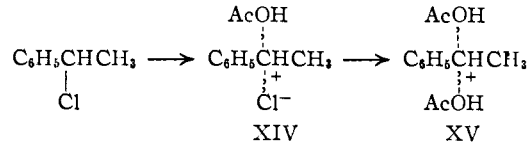
It is interesting how well rearrangement competes with solvent intervention—in other words how little do the stereochemical results of solvolysis differ from complete racemization. Examination of the small amount of activity which survives in acetolysis with the aid of the stereochemical relationships brought out in this paper and the following one[5] shows that it is in accord with a slight excess of either simply inverted product [*exo*-(A)-acetate IVA from IIIA and *exo*-(B)-acetate IVB from IIIB], or product with retained configuration [slight amount of *endo*-(A)-acetate from IIIA or *endo*-(B)-acetate from IIIB]. That the surviving activity is associated with *exo* or inverted product is clear from the fact that the product is completely racemized by toluenesulfonic acid in glacial acetic acid under conditions toward which *endo*-acetate is completely optically stable (Table I). On this basis, the proportion of predominantly inverted acetate in the product of acetolysis of active *p*-bromobenzenesulfonate III is calculated to be *ca.* 7% in the experiment employing 0.409 *M* potassium acetate and *ca.* 8% in the one employing 0.12 *M* potassium acetate. Thus the 7–8% inversion in the acetolysis is not due to acetate ion attack, but is inherent in the solvolysis.

Writing the first intermediate VII to include the 2 species most important in the solvation sphere,[13] we have XII which can give XIII, SOH indicating a solvent molecule. Involvement of the C-1–C-6 bonding electron pair gives eventually racemic product. Prior collapse gives active *exo*-acetate IVA. Even with α-phenylethyl chloride, we estimate from the data of Steigman and Hammett[14]



that acetolysis proceeds with *ca.* 16% of predominant inversion. Thus the participation of carbon is more serious in the later steps of the acetolysis process for IIIA than the process XIV → XV is in acetolysis of α-phenylethyl chloride.

(13) Winstein, Grunwald and Jones, THIS JOURNAL, **73**, 2700 (1951).
(14) Steigman and Hammett, *ibid.*, **59**, 2536 (1937).



Experimental

endo-**Dehydronorbornyl Acetate.**—A typical batch run in a steel bomb with a glass liner consisted of 164 g. of freshly distilled cyclopentadiene and 322 g. of distilled vinyl acetate (molar ratio of 1.00:1.50 instead of the 1.00:1.15 molar ratio[15] employed by Alder and Rickert[6]) and a reaction time of 10–19 hours at 168–178° was employed instead of 10 hours at 185–190°. It was noted that the crude reaction mixture was very dark in cases where the heating period was 10–12 hours but was markedly lighter when the heating period was extended to 15–19 hours. In two separate preparations, each involving four and six batches, respectively, yields of the 1:1 dehydronorbornyl adduct (b.p. range 73–77° at 14 mm.) were 45.0 and 44.8% (reported[6] 43.5%).

endo-**Norbornyl Acid Phthalate.**—In a typical preparation, 194 g. (1.274 moles) of crude *endo*-dehydronorbornyl acetate was hydrogenated in 300 ml. of glacial acetic acid with 0.07 g. of platinic acid and agitated with external air cooling for 18 hours, the major hydrogen uptake occurring during the first hour. The solution was diluted with 1 l. of water, the salted aqueous phase extracted six times with ether, and the combined ether extracts washed with aqueous potassium carbonate and dried over anhydrous magnesium sulfate. The ether solution of the crude *endo*-norbornyl acetate was directly reduced with lithium aluminum hydride.[16] The reaction mixture was treated with excess dilute sulfuric acid in ice and the aqueous phase, heavily salted with sodium choride, was extracted seven times with 50–100-ml. portions of ether. After washing the combined ether extracts with aqueous potassium carbonate and drying over anhydrous magnesium sulfate, the ether solution was concentrated using a fractionating column. When the volume was reduced to *ca.* 250 ml., 125 ml. of anhydrous pyridine was added and the distillation continued until ethyl alcohol was completely expelled.

The pyridine solution of the crude *endo*-norbornyl alcohol was diluted with an additional 75 ml. of the pyridine and heated with 189.0 g. (1.274 moles) of phthalic anhydride at 100° for four hours. The reaction mixture was diluted with several volumes of water and shaken with a mixture of excess dilute sulfuric acid and benzene. After five additional extractions, the combined benzene extract was washed several times with water, dried, and evaporated to an oil. Crystallization from ethyl acetate–petroleum ether (30–60°) gave 242 g., 73.1%, of crude *endo*-norbornyl acid phthalate.

The crude acid phthalate, on fractional crystallization, indicated the presence of a small but definite amount of a second acid phthalate. The principal isomer present was purified by recrystallization six times from ethyl acetate–petroleum ether followed by an effective recrystallization from warm aqueous acetic acid to yield 122 g. of pure *endo*-norbornyl acid phthalate, m.p. 109.1–109.9° (reported[6] 109–110°).

endo-**Norbornyl Alcohol.**—In a typical experiment for liberation of pure *endo*-norbornyl alcohol from the corresponding *endo*-norbornyl acid phthalate, *endo*-norbornyl acid phthalate, 20.0 g., m.p. 109.1–109.9°, was dissolved in a solution of 25 g. of sodium hydroxide in 100 ml. of water and steam distilled at once. The liberated alcohol, which distilled rapidly, was collected together with *ca.* 100 ml. of water, and the water phase was quickly decanted from the 5.86 g. of solid alcohol. The aqueous decantate was saturated with sodium chloride and extracted with five portions of pet. ether (b.p. 20–40°), which were combined, dried, and concentrated with the aid of a fractionating column to yield 2.58 g. of additional alcohol. The combined 8.44 g. of pure *endo*-norbornyl alcohol, m.p. 152.0–153.0° (reported[6,9] 149–150°), corresponded to a yield of 97.8%.

Racemic *endo*-**Norbornyl Acetate.**—A mixture of 0.9 g. (0.008 mole) of *endo*-norbornyl alcohol, 20 cc. of acetic acid, and 5 cc. of acetic anhydride was kept at 75° for 8 hours. The reaction mixture was diluted with water and extracted

(15) Incorrectly reported as 1:1.5.
(16) Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

with pet. ether (30–40°); the pet. ether solution was washed with water, aqueous sodium bicarbonate and dried by filtration through magnesium sulfate. The solvent was removed and the residue was distilled *in vacuo* to yield 1.2 g. (0.007 mole, 89%) of product, $n^{25}D$ 1.4583. The infrared spectrum was taken on this material.

***endo*-Norbornyl *p*-Toluenesulfonate.**—This material was prepared in one instance from 10.1 g. of crude *endo*-norbornyl alcohol. A quantitative yield of crude oil was obtained from which 14.9 g. of solid *endo*-norbornyl *p*-toluenesulfonate, m.p. 28.1–29.2°, was crystallized with difficulty from ethyl ether–low boiling petroleum ether. The equiv. wt. of this material in acetolysis was 266.3, 267.2 (calcd. 266.3). The solvolysis kinetics of this material indicated contamination with *ca.* 19% *exo*-norbornyl *p*-toluenesulfonate. The figure of 19% is not perfectly representative, however, since the crude *endo*-norbornyl alcohol was derived from the first 53% of dehydronorbornyl acetate obtained in distillation of the Diels–Alder reaction product.

Solvolyses of *endo*-Norbornyl *p*-Toluenesulfonate. Glacial Acetic Acid.—Solvolysis of 4.78 g. of the crude *endo*-norbornyl *p*-toluenesulfonate was carried out in 187.6 g. of dry glacial acetic acid for 99.5 hours at 45° followed by 22 hours at 100°. The solvolysis product was extracted with seven portions of ethyl ether after dilution and neutralization of the acetic acid reaction medium. The combined ether extract was dried after several washings with aqueous potassium carbonate and water and the ester product reduced directly with 0.45 g. of lithium aluminum hydride. After working up the resulting alcohol product in the usual manner and concentrating the ether solution to an oil through use of a fractionating column, the oil was converted to the corresponding 3,5-dinitrobenzoate by reaction with 6.00 g. of 3,5-dinitrobenzoyl chloride in 30 ml. of dry pyridine for 10 minutes at *ca.* 80–100°. Cooling and dilution with several volumes of water precipitated a solid which was washed with dilute aqueous sodium carbonate, water and dried to yield 2.64 g. (48.1% yield from *p*-toluenesulfonate) crude *exo*-norbornyl 3,5-dinitrobenzoate, m.p. 99.5–102°, m.p. 104–105° (needles) after recrystallization from acetic acid–water (reported[6] for *exo*-norbornyl 3,5-dinitrobenzoate 105°). No isomeric *endo*-norbornyl 3,5-dinitrobenzoate (thin, pearly plates) was detectable.

65% Aqueous Dioxane.—Solvolyses in 65% aqueous dioxane (Eastman Kodak Co., white label dioxane) were carried out in sealed flasks at *ca.* 0.1 *M* for 148 hours at 45° and 6 hours at 100° on 2.750- and 2.879-g. quantities of *endo*-norbornyl *p*-toluenesulfonate. Each solution was diluted with *ca.* 400 ml. of water, extracted five times with 75-ml. portions of ethyl ether and converted to the 3,5-dinitrobenzoates in the same manner already described. Over-all yields based on the crude derivatives for the 45 and 100° solvolyses were 76.6% (needles, m.p. crude, 94.5–98.0°) and 69.2% (needles, m.p. crude, 100–103°), respectively. Recrystallization from acetic acid–water again gave in both cases with good recovery pure *exo*-3,5-dinitrobenzoate, m.p. 104–105° with no evidence for the presence of any of the *endo*-derivative.

65% Aqueous Acetone.—Solvolysis of 1.94 g. of crude *p*-toluenesulfonate in 75 ml. of 65% aqueous acetone (*ca.* 0.1 *M*) in the presence of excess powdered calcium carbonate for 18 hours at 63–64° yielded in the usual manner 1.73 g. (77.5%) *exo*-norbornyl 3,5-dinitrobenzoate (m.p. crude, 98–101°).

Similarly, solvolysis of 98.5 g. (0.370 mole) of crude *endo*-norbornyl *p*-toluenesulfonate was carried out in 2310 ml. of 65% aqueous acetone (0.16 *M*) for 40.0 hours at 63.5° under reflux in the presence of excess powdered calcium carbonate. The *exo*-norbornyl alcohol was extracted with ether, concentrated through use of a fractionating column with dry pyridine as a chaser for the ether and ethanol, and reacted with 0.370 mole of phthalic anhydride in a *ca.* two-fold molar excess dry pyridine for four hours at 96°. Dilution and neutralization of the pyridine with dilute hydrochloric acid in ice, followed by extraction with benzene and isolation of the acid phthalate in several crops from ethyl acetate–petroleum ether gave a yield of 75.6% crude *exo*-norbornyl acid phthalate, m.p., on one recrystallization from the same solvent pair, 80.5–83.5° (reported[6] 80–81°, 102–103°[9,17]). Saponification of a 20.0-g. portion of the *exo*-norbornyl acid phthalate and isolation *via* steam distillation, gave directly very pure *exo*-norbornyl alcohol, m.p. 127.6–128.5° (reported 128–129°,[8] 127–128°[6]) in 95% yield.

Solvolyses of *endo*-Norbornyl *p*-Bromobenzenesulfonate in 75% Aqueous Acetone.—In a manner identical to that described above for the preparation of *endo*-norbornyl acid phthalate from crude *endo*-dehydronorbornyl acetate, 421 g. of this same latter material was carried through to the pyridine solution of the crude *endo*-norbornyl alcohol at which point it was treated in the usual manner with 727 g. of *p*-bromobenzenesulfonyl chloride (5% excess of theoretical) to yield six crops of crude *endo*-norbornyl *p*-bromobenzenesulfonate totaling 795.4 g. with a calculated yield of 88.8% from the starting dehydronorbornyl acetate.

The entire 795.4 g. of the *p*-bromobenzenesulfonate was solvolyzed in 74.9% aqueous reagent acetone at 0.76 *M*, the approximate maximum concentration permitted by solubility of the *p*-bromobenzenesulfonate in the medium, in the presence of excess powdered calcium carbonate for 44 hours at 61.5–62.0° under reflux. Isolation of the resulting *exo*-norbornyl alcohol as the acid phthalate as in the case of the solvolysis of the *p*-toluenesulfonate gave rise to 448.9 g. (71.7%) of crude *exo*-norbornyl acid phthalate.

Pure *endo*-norbornyl *p*-bromobenzenesulfonate (4.50 g.) was dissolved in 68 ml. of 75% aqueous acetone (0.20 *M*), sealed in a pressure tube, and immersed in a 75° thermostat for 14.5 hours. Shaking with several portions of anhydrous potassium carbonate served to remove the water from the solution and, after a final overnight drying over anhydrous magnesium sulfate, the solution was concentrated through a fractionating column and the acetone removed using dry pyridine as a chaser. An equimolar amount of *p*-bromobenzenesulfonyl chloride was added to the cold pyridine solution containing the product alcohol and after standing 37 hours in the ice-box, the resulting *p*-bromobenzenesulfonate was isolated by diluting the pyridine with several volumes of ice and scratching. The *p*-bromobenzenesulfonate separated from the solution as a clean white solid and was washed thoroughly on a sintered glass funnel and promptly dried *in vacuo* over phosphorus pentoxide. In this manner, 3.27 g. (72.6%) of *exo*-norbornyl *p*-bromobenzenesulfonate was obtained. The solvolysis rate of this product in dry acetic acid was measured at concentrations of *ca.* 0.03 to 0.037 *M*. In two runs the infinity titers in ml. of base were: I, calcd. 3.679, 3.546 after 24 hr. at 25°, 3.556 after 24 hr. at 100°; II, calcd. 4.391, 4.251 after 24 hr. at 25°, 4.243 after 24 hr. at 100°. The material assays 96.7–96.8% *exo*, 0.0% *endo* and 3.2–3.3% inert materials.[18]

Complete Resolution of *endo*-Norbornyl Acid Phthalate.—69.3 g. of pure racemic *endo*-norbornyl acid phthalate, m.p. 109.1–109.9°, was dissolved in 350 ml. of hot acetone followed by an equivalent amount of brucine (104.8 g.). The initial 79.7 g. (45.7%) of brucine salt was recrystallized from hot acetone with overnight standing an additional four times, the amount of starting alkaloid salt at this stage having decreased to 28.6 g. (16.4% of theoretical).

At the same time, the combined mother liquors from the first two brucine salt crystallizations were combined, shaken with 150 ml. of 2 *N* hydrochloric acid, diluted considerably with water, and extracted with seven portions of chloroform. The combined extract, after washing with dilute acid and water was concentrated and evaporated to dryness (36.1 g.). This partially active *endo*-(A)-norbornyl acid phthalate was in turn dissolved in 180 ml. of hot acetone together with an equimolar quantity of 40.75 g. of cinchonidine and also crystallized slowly, with overnight standing, four times to yield a 25.5-g. quantity (19.3% of theoretical) of cinchonidine salt.

Polarimetric examination of the liberated acid phthalates from 5-g. portions of the brucine and cinchonidine salts gave rotations of $[\alpha]^{25}D$ −3.96° (chloroform, *c* 0.97) and $[\alpha]^{25}D$ +3.28° (chloroform, *c* 10.00) corresponding (on the basis of later data) to only 79.2 and 65.5% resolution, respectively, at this stage. The remaining amounts of partially resolved acid phthalates were liberated from their brucine and cinchonidine salts by shaking the benzene solutions several times in turn with excess dilute hydrochloric acid and water. The acid phthalates were further purified through their sodium salts by extraction of the benzene solution with excess aqueous sodium bicarbonate, acidifi-

(17) This crystalline form of *exo*-norbornyl acid phthalate was also prepared and is described in the following paper.[5]

(18) We are indebted to Dr. Kurt Schreiber for this analysis.

cation with excess dilute sulfuric acid to reliberate the acid phthalates, extraction with five portions of reagent benzene, washing, and evaporation of the benzene solvent to dryness with a 95–98% recovery of the partially active acid phthalates. Fractional crystallization of the individual enantiomorphs away from the racemate was then carried out with each of the partially resolved *endo*-acid phthalates. The crystalline racemate was slightly but sufficiently less soluble in ethyl ether–petroleum ether (20–40°) mixtures than the crystalline enantiomorphs (m.p. 98.3–99.7°) to permit successful separation, although a considerable number of fractionations, recombinations of fractions, and refractionation cycles were necessary to achieve a successful complete resolution of both the (A) and (B) enantiomorphs. The melting point was used on all fractions to indicate the progress of the fractionation and polarimetric checks were required only at the last stages in these separations. To keep mechanical losses at a minimum all fractions were separated, washed, etc., by decantation procedures and quantitatively recovered from all glassware. In this manner, starting with 11.45 g. of 65.5% initially resolved *endo*-(A)-acid phthalate, 4.01 g. 100% resolved (A) enantiomorph, together with 4.28 g. of low activity acid phthalate (and 2.94 g. of middle fractions) were finally obtained through manipulation of *ca.* 56 intermediate fractions with a loss of only 1.9% material.

The completeness of this resolution was indicated by the fact that the last three crops of a total of five obtained at a late stage of the fractionation had rotations of $[\alpha]^{24}D$ +5.02° (chloroform, *c* 10.03), $[\alpha]^{24}D$ +5.00° (chloroform, *c* 10.02), and $[\alpha]^{24}D$ +4.97° (chloroform, *c* 10.00). The first two crops which had rotations of $[\alpha]^{24}D$ +4.27° (chloroform, *c* 10.01) and $[\alpha]^{24}D$ +4.84° (chloroform, *c* 10.00) on further multiple recrystallization yielded an additional amount of enantiomorph $[\alpha]^{23}D$ +4.97° (chloroform, *c* 10.03).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found for *endo*-(A)-norbornyl acid phthalate: C, 69.16; H, 6.34.

A less thorough but sufficient separation of the (B) enantiomorph yielded from an initial 10.66 g. of 79.2% resolved *endo*-acid phthalate only 2.33 g. of 100% resolved (B) enantiomorph, $[\alpha]^{24}D$ −4.99° (chloroform, *c* 10.03), 6.82 g. of several combined fractions corresponding to 81.8% resolution, together with 1.36 g. of low activity acid phthalate with an over-all 98.6% recovery of material through an intermediate *ca.* 31 fractions. The concentration of the *endo*-(B)-norbornyl acid phthalate was discontinued at this point and the 2.33 g. of pure enantiomorph combined with the 6.82-g. quantity above to give optically active compound of known per cent. resolution (calcd. 86.5%).

Conversion of *endo*-Acid Phthalate Enantiomorphs into the Corresponding Alcohols and *p*-Bromobenzenesulfonates.—By methods described above, 3.47 g. of optically pure *endo*-(A)-acid phthalate, m.p. 98.3–99.7°, $[\alpha]^{24}D$ +5.00° (chloroform, *c* 10.0) and 8.33 g. of 86.5% resolved *endo*-(B)-acid phthalate were saponified and steam distilled to yield 1.44 g. (96.3% yield) of optically pure *endo*-(A)-norbornyl alcohol, m.p. 151.2–152.5°, $[\alpha]^{24}D$ −1.89° (chloroform, *c* 10.05) and 3.46 g. (96.4% yield) *ca.* 86.5% resolved *endo*-(B)-norbornyl alcohol.

Anal., *endo*-(A)-norbornyl alcohol. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.67; H, 10.74.

0.95 g. of *endo*-(A)-norbornyl alcohol and 3.00 g. of *ca.* 86.5% resolved *endo*-(B)-norbornyl alcohol were converted in the usual manner to 2.73 g. (97.4%) of pure *endo*-(A)-norbornyl *p*-bromobenzenesulfonate, recrystallized, m.p. 60.6–62.0°, $[\alpha]^{24}D$ −11.78° (chloroform, *c* 9.97), $[\alpha]^{24}D$ −13.52° (glacial acetic acid, *c* 10.09) and 96.5% resolved *endo*-(B)-norbornyl *p*-bromobenzenesulfonate.

Anal., *endo*-(A)-norbornyl *p*-bromobenzenesulfonate. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.14; H, 4.57. Found: C, 46.98; H, 4.72. Mol. wt. Calcd.: 331.23. Found by ∞ titration in solvolysis: 332.9, 331.4.

Acetolysis of Active *endo*-(A)-Norbornyl *p*-Bromobenzenesulfonate in Glacial Acetic Acid and Examination of Product.—A mixture of 1.00 g. of optically pure *endo*-(A)-norbornyl *p*-bromobenzenesulfonate and 3.00 g. of racemic *endo*-norbornyl *p*-bromobenzenesulfonate was solvolyzed in 120 ml. of dry glacial acetic acid (0.10 *M*) containing potassium acetate (0.085 *M*, inadvertently insufficient) in a 75° thermostat for 18.5 hours. The acetic acid solution was diluted to four times its volume with water; then it was extracted four times with 50-ml. portions of petroleum ether (b.p. 34–39°). The combined extract was washed with water and aqueous sodium bicarbonate, then dried over magnesium sulfate. The petroleum ether solution was concentrated through a fractionating column and the residue distilled *in vacuo* to give 1.60 g. (85.9%) of *exo*-norbornyl acetate, $n^{25}D$ 1.4565, $\alpha^{25}D$ −0.129°. This material was completely racemized (α 0.000 ± 0.002°) by 0.75 *M* toluenesulfonic acid in gl. acetic acid after 10 hours at 75°.

When the acetolysis was repeated on 4.00 g. of 96.5% resolved *endo*-(B)-norbornyl *p*-bromobenzenesulfonate in 0.10 *M* solution, 0.12 *M* in potassium acetate, for 17.3 hours at 75°, there was obtained 1.38 g. (74%) *exo*-norbornyl acetate, $n^{25}D$ 1.4565, $\alpha^{24}D$ 0.793° (1 dcm.).

Active *exo*- and *endo*-Norbornyl Acetates in Acetic Acid.—0.2076 g. of active *exo*-norbornyl alcohol[5] and 0.2094 g. of active *endo*-(A)-norbornyl alcohol were each weighed into 5-ml. volumetric flasks and dissolved in *ca.* 1 ml. of dry glacial acetic acid. Then 0.328 g. and 0.325 g. (*ca.* 50% excess of theoretical) of acetic anhydride (Baker's Analyzed) were also weighed into each volumetric flask, respectively, followed by *ca.* 0.03 g. of dry pyridine. The characteristic odor of the norbornyl acetates could be detected at once. The flasks were stoppered and warmed at 40° for *ca.* 24 hours and then made up to volume with more dry acetic acid to produce 0.370 *M* and 0.373 *M* stock solutions of the respective *exo*-norbornyl acetate, $[\alpha]^{24}D$ 14.20° (acetic acid, *c* 5.72) and *endo*-(A)-norbornyl acetate, $[\alpha]^{24}D$ −14.00° (acetic acid, *c* 5.73).

Effect of Solutes on Active Acetates in Acetic Acid and on Active *exo*-Alcohol in Aqueous Acetone.—Appropriate quantities of *p*-toluenesulfonic acid monohydrate, anhydrous potassium acetate and pyridinium *p*-bromobenzene-sulfonate (prepared by reaction of reagent pyridine with *p*-bromobenzenesulfonic acid monohydrate) were weighed out to 0.1 mg. and made up to the mark at room temperature in a calibrated constricted test-tube (1.628 ml.) with either the stock 0.370 *M* active *exo*-norbornyl acetate or 0.373 *M* active *endo*-norbornyl acetate in acetic acid. The solutions were homogenized with the aid of a drawn-out medicine dropper and the initial observed rotation measured in the polarimeter in a 1-decimeter, semimicro polarimeter tube. The solution was then sealed in a clean ampoule and immersed in the 74.57° thermostat for a measured period of time, after which the ampoule was opened and the optical rotation remeasured.

The corresponding test on active *exo*-norbornyl alcohol with *p*-toluenesulfonic acid in 75% aqueous acetone was performed similarly (Table I).

Solvolysis Rate Measurements.—The solvents and procedures for acetolysis[19] and ethanolysis[13] rate measurements were the same as those previously employed.

In acetolysis involving high salt concentrations, the difficulty resulting from the gradual color change of the brom phenol blue indicator was minimized by diluting the 1-ml. aliquots during the first half of the run with 5 ml. of glacial acetic acid prior to titration and with 10 ml. of glacial acetic acid during the last half of the run. The measurements were carried out by first titrating with standard *p*-toluenesulfonic acid in acetic acid beyond the equivalence point to colorless followed by backtitration with standard sodium acetate to the usual yellow end-point color.

The 75% aqueous acetone was prepared by mixing 60 ml. of reagent grade acetone and 20 ml. of distilled water, each delivered by pipet. The solvolysis in this solvent was followed by titration with standard 0.05 *N* methanolic sodium methoxide using brom thymol blue as indicator.

Polarimetric Measurements.—Polarimetric determinations carried out in this work were done with the aid of a new Hilger polarimeter, with Lippich triple-field polarizer reading directly to 0.01 and estimating to 0.001°, and a *ca.* 1.2-ml. semimicro 1-dcm. polarimeter tube. In a completely dark room, individual settings made with care seldom varied more than ±0.005° and the average of five or six readings invariably were reproducible to 0.002–0.004° or better when the solutions were completely colorless. Decreased accuracy resulting from slight thermal gradients, developing in the solution during measurements, was avoided by intentionally introducing a small air bubble in the polarimeter tube during filling. Between readings the solution was occasionally mixed with the aid of the bubble by inverting the tube a number of times and then returning the air bubble to

(19) Winstein, Grunwald and Ingraham, THIS JOURNAL, **70**, 821 (1948).

a recess provided in the glass wall at the middle of the polarimeter tube.

Polarimetric Racemization Rates of *endo*-(B)-Norbornyl *p*-Bromobenzenesulfonate.—In these rate runs, the 96.5% resolved *endo*-(B)-norbornyl *p*-bromobenzenesulfonate was employed and the appropriate quantities of reagent involved were weighed out to 0.1 mg. and made up to the mark in a 10-ml. volumetric flask with the corresponding solvent. Approximate volumes (*ca.* 1.4–1.6 ml.) were introduced by means of a roughly calibrated medicine dropper into carefully cleaned Pyrex ampoules. The ampoules were simultaneously introduced into the 74.57 ± 0.01° thermostat in a wire basket which was then rocked for 6–8 minutes before the first ampoule ($t = 0$) was removed and quenched in ice and the time recorded. Soon thereafter, the ampoule was brought to room temperature in a water-bath, opened, and the polarimeter tube filled and the rotation measured.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

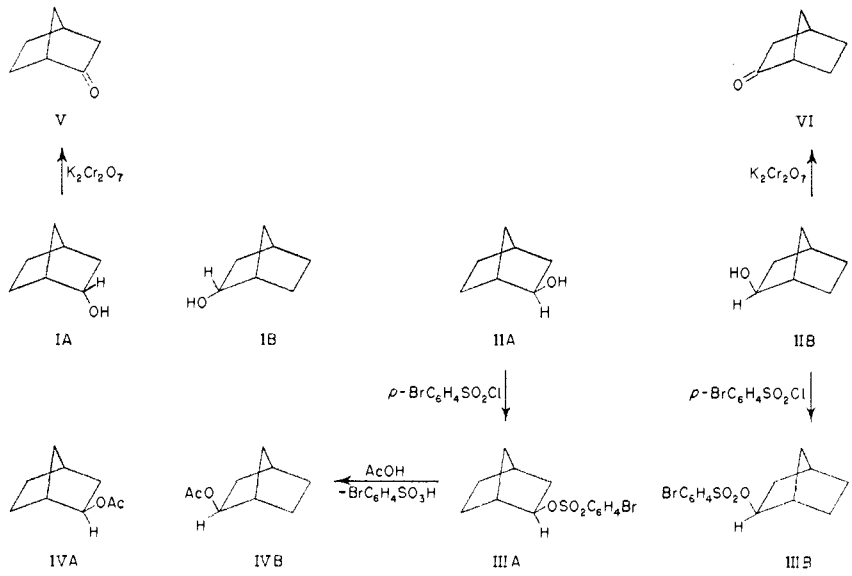
Neighboring Carbon and Hydrogen. XI. Solvolysis of *exo*-Norbornyl *p*-Bromobenzenesulfonate[1,2,3]

BY S. WINSTEIN AND DANIEL TRIFAN

Solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate in acetic acid and aqueous acetone gives the corresponding *exo*-derivatives with great steric specificity. Complete resolution of *exo*-norborneol has been carried out and the solvolysis of active *exo*-norbornyl *p*-bromobenzenesulfonate shown to proceed with complete loss of optical activity. Part of the loss in activity attending solvolysis is due to internal rearrangement, involving racemization, of the *exo*-norbornyl *p*-bromobenzenesulfonate, for first-order polarimetric rate constants exceed titrimetric first-order solvolysis rate constants by factors of 3.46, 2.94 and 1.40 in acetic acid, ethanol and 75% acetone, respectively. The facts are most readily interpretable in terms of a bridged structure for the norbornyl cation. The *exo*-norbornyl *p*-bromobenzenesulfonate with the favorable geometry for participation of the C_1–C_6 bonding electron pair in the rate-determining ionization process, giving it an enhanced ionization rate, ionizes to the bridged carbonium ion. This intermediate, with a plane of symmetry, leads to racemic *exo*-product.

Isobornyl chloride (*exo*), with the proper geometry for delocalization of the neighboring β-bonding electron cloud in the rate-determining ionization, is more reactive in solvolysis[4] by 5 powers of ten relative to bornyl chloride (*endo*). In the simpler analogous norbornyl system, a gap in rate between *exo* and *endo* configurations still persists, the *exo*-norbornyl *p*-bromobenzenesulfonate being 350 times as rapid in acetolysis at 25° as the *endo*-isomer.[4] For our understanding of participation of carbon[5] in displacement reactions, it is necessary to know whether Wagner–Meerwein rearrangement attends the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate. As in the case of the *endo*-isomer,[6] we studied the solvolysis of *dl*- and active *exo*-norbornyl *p*-bromobenzenesulfonate[3] and this work is reported in the present paper. This study, together with the previous one,[6] furnishes a picture of the nature of the solvolysis of the simple pair of isomers with the geometrical features of the more heavily substituted isobornyl–bornyl pair.

Solvolysis of the arylsulfonates of *endo*-norborneol (I), most conveniently carried out in 75% acetone as already described,[6] provided useful quantities of *exo*-norborneol (II) and its derivatives.



The solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate (III), as in the case of the *endo*-isomer,[6] gave rise essentially exclusively to *exo*-products. Thus the acetolysis product IV (obtainable in 80% yield) was at least 94% *exo*, as shown by infrared spectrum[6] (Fig. 1), refractive index,[6] and saponification and conversion to the 3,5-dinitrobenzoate. In the case of solvolysis in 75% acetone, a more quantitative estimate of the completeness of maintenance of the *exo*-configuration was obtained from reconversion of the crude norborneol to *p*-bromobenzenesulfonate and kinetic analysis of the latter.

(1) Supported in part by Office of Naval Research and Research Corporation.

(2) Much of the material of this paper was presented in summary (a) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of Abstracts; (b) at Montpellier, France, April 26, 1950 (*Bull. soc. chim.*, [5] **18**, C55 (1951)). Presented before Organic Division of American Chemical Society, Boston, Mass., April 2–5, 1951, page 53 M of Abstracts.

(3) Preliminary communication, Winstein and Trifan, THIS JOURNAL, **71**, 2953 (1949).

(4) Winstein, *et al.*, *ibid.*, **74**, 1127 (1952).

(5) Winstein, Morse, Grunwald, Schreiber and Corse, *ibid.*, **74**, 1113 (1952).

(6) Winstein and Trifan, *ibid.*, **74**, 1147 (1952).