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.

LOS ANGELES 24, CALIF. RECEIVED JUNE 11, 1951

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

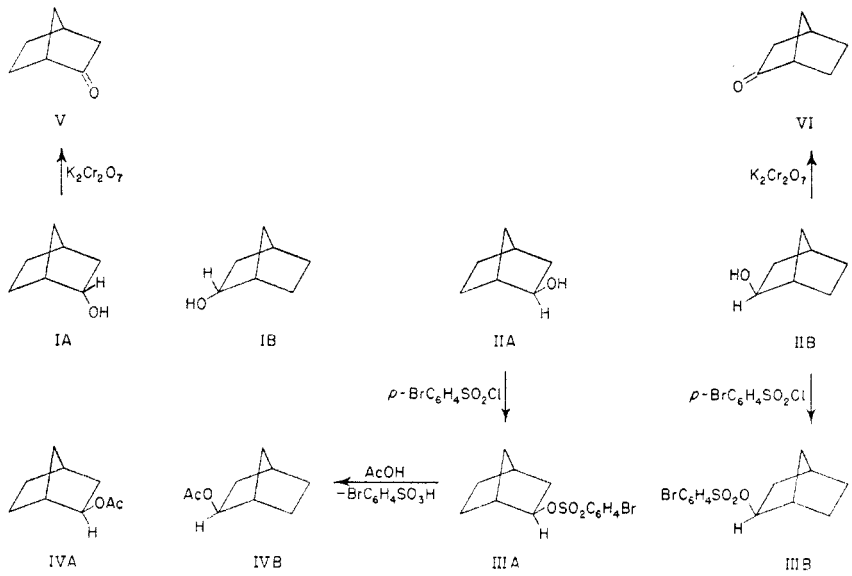
Neighboring Carbon and Hydrogen. XI. Solvolysis of *exo*-Norbornyl *p*-Bromobenzenesulfonate[1,2,3]

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).

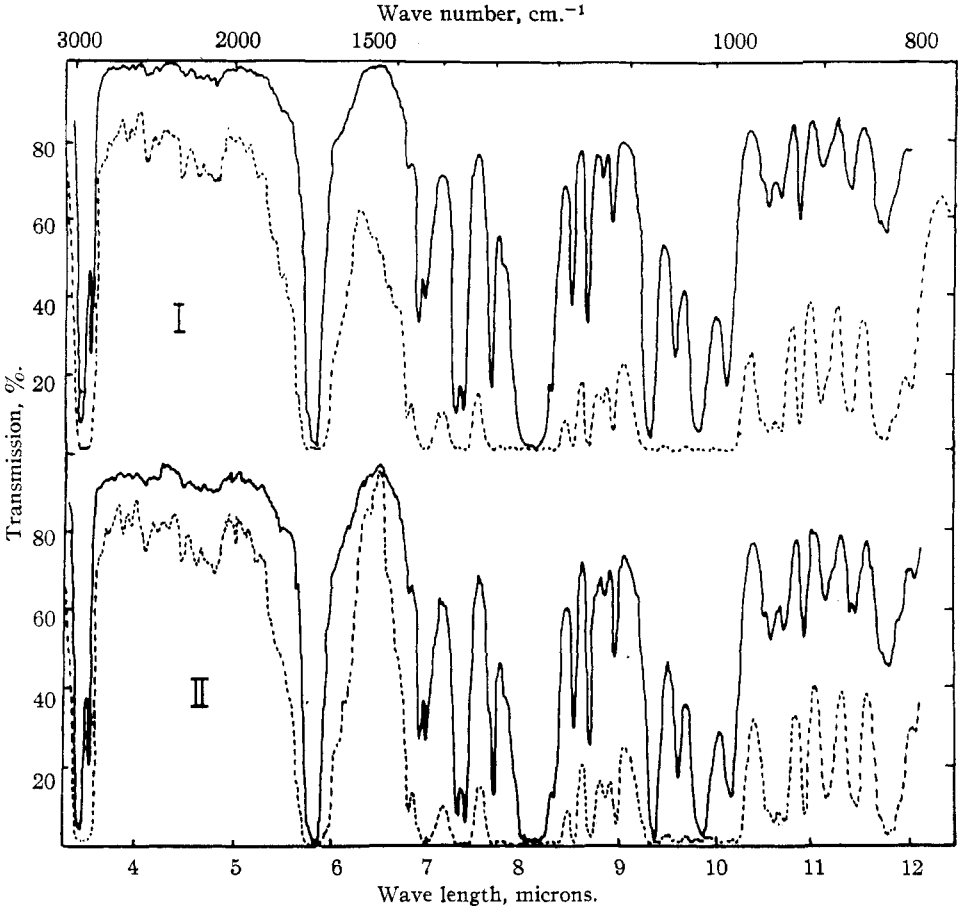


Fig. 1.—Infrared absorption spectra (Baird infrared spectrometer; 0.1 mm. cell length): I, *exo*-norbornyl acetate; II, acetolysis product from *exo*-norbornyl *p*-bromobenzenesulfonate; - - - - -, pure liquid; —— 10% solution in CCl_4.

As shown in Table I, the first-order acetolysis rate constant for this product agreed well with the previously[4] reported value for *exo*-*p*-bromobenzenesulfonate. Moreover, early and late infinity titers indicated that the proportion of *endo* derivative in the product was very small and possibly as large as 1.6 ± 0.5%. Thus the *exo*-configuration survived in hydrolysis at least to the extent of 98.4%.

Other analogous transformations in which *exo* configuration is maintained, but where less quantitative evidence is available, are the conversion of *exo*-norbornylamine[7,8] to *exo*-norborneol (II) and the hydrolysis of *exo*-norbornyl halides.[9]

For the study of optically active *exo*-*p*-bromobenzenesulfonates (III) A and B, *exo*-norborneol (II) was resolved through the acid phthalate in the conventional manner. Small scale tests with brucine, strychnine, cinchonine, cinchonidine, quinine and *l*-menthylamine showed cinchonidine to be the most useful resolving agent. Using this alkaloid for partial resolution, fractional crystallization of the partially resolved acid phthalate as in the *endo*-case,[6] yielded completely resolved (A) and (B) isomers, the specific rotations of the enantiomorphs agreeing closely. Saponification of the (A) and (B) acid phthalates yielded the enantiomorphic *exo*-(A) and (B)-norborneols IIA and B from which *p*-bromobenzenesulfonate or acetate were prepared.

The stereochemical relationship between the *exo*-norborneols IIA and B and the *endo*-norborneols IA and B described in the preceding paper[6] was established by oxidation to norcamphor V and VI. *Ca.* 60–80% resolved *endo*-(A)-norborneol IA and optically pure *exo*-(B)-norborneol IIB were oxidized with potassium dichromate and sulfuric acid.[10] The norcamphor (predominantly V) from IA displayed a rotation $[\alpha]^{24}D$ −15.73°, while the norcamphor (predominantly VI) from IIB displayed a rotation $[\alpha]^{24}D$ +8.66. This proves that *endo*-(A) is related to *exo*-(A) and *endo*-(B) to *exo*-(B) and the representation of IAB and IIAB and their derivatives in this paper and the preceding one[6] takes account of this relationship. It is interesting that the 100% resolved *exo*-(B)-norborneol yielded a norcamphor of lower rotation than the one from the less fully resolved *endo*-(A)-norborneol. This is undoubtedly due to racemization of the *exo*-alcohol in the acidic medium prior to oxidation, this alcohol being more rapidly racemized.[6]

Solvolysis of optically active *exo*-(B)-norbornyl *p*-bromobenzenesulfonate IIIB proceeded with complete loss of optical activity, even under conditions toward which the solvolysis products are

(7) Alder and Stein, *Ann.*, **514**, 211 (1934).

(8) Komppa and Beckmann, *ibid.*, **512**, 172 (1934).

(9) (a) Roberts, Bennett and Armstrong, THIS JOURNAL, **72**, 3329 (1950); (b) Schmerling, *ibid.*, **68**, 195 (1946).

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

TABLE I

TITRIMETRIC AND POLARIMETRIC SOLVOLYSIS RATES OF *exo*-NORBORNYL *p*-BROMOBENZENESULFONATE AT 24.98 ± 0.02°

Solvent	Concn., *M*	Other solute	Isomer	Procedure	Rotations, degree Initial	Final	k(sec.$^{-1}$)	k_α/k_t
AcOH	0.020		*dl*	Titrimetric[4]			$(8.79 \pm 0.09) \times 10^{-5}$	
	.037		[a]	Titrimetric			$(8.64 \pm 0.08) \times 10^{-5}$	
	.037		[a]	Titrimetric			$(8.90 \pm 0.01) \times 10^{-5}$	
	.201	0.252 *M* KOAc	(B)	Polarimetric	0.265	−0.001	4.25×10^{-4}	
	.200	.249 *M* KOAc	(B)	Titrimetric			$(1.22 \pm 0.03) \times 10^{-4}$	3.46
EtOH	.300		(B)	Polarimetric	.279	− .003	7.83×10^{-5}	
	.300		(B)	Titrimetric			$(2.66 \pm 0.03) \times 10^{-5}$	2.94
75% $(CH_3)_2CO$	.200		(B)	Polarimetric	.119	.002	7.56×10^{-4}	
	.200		(B)	Titrimetric			$(5.41 \pm 0.35) \times 10^{-4}$	1.40

[a] *p*-Bromobenzenesulfonate of product of solvolysis in 75% acetone.

optically stable. This is shown in Table I which lists initial and final rotations for solvolysis runs in acetic acid, 75% acetone and absolute alcohol. In the case of the latter solvent, no rotation data are available on norbornyl ethers to give quantitative significance to the loss of optical activity. In acetolysis the high degree of completeness of the loss of optical activity was more quantitatively demonstrated by isolation of the acetate and measurement of the rotation of the homogeneous material. The acetate from a 1:1 mixture of *exo*-(B) and *dl-exo*-norbornyl *p*-bromobenzenesulfonates gave a rotation of 0.001 ± 0.004° whereas 50% active *exo*-acetate would have corresponded to a rotation of 5.20°.

To probe whether loss of activity was indeed to be ascribed to solvolysis and not to prior racemization of the bromobenzenesulfonate, the solvolyses were followed polarimetrically. In preliminary work,[3] there was some indication that the polarimetric drop in rotation in solvolysis of *exo*-norbornyl bromobenzenesulfonate III somewhat exceeded the titrimetric rate. Careful comparison of polarimetric rate constants, k_α, defined by equation 1, with titrimetric rate constants

$$2.303 \log \alpha_0/\alpha = k_\alpha t \qquad (1)$$

k_t brought to light an interesting disturbance, k_α indeed exceeding k_t.

Table I gives the titrimetric rate constants for solvolysis at 24.98° at concentrations of 0.200 to 0.300 *M* in III, high enough for polarimetric scrutiny. In the case of acetolysis, potassium acetate at 0.25 *M* was included, and the rate constant here was, as is proper, some 40% higher than the one previously reported.[4] The titrimetric rates displayed good first-order behavior, and the polarimetric rates were also nicely first-order. Figure 2 shows plots of log α *vs.* time for hydrolysis in 75% acetone, acetolysis and ethanolysis. The points fall nicely on first-order straight lines, especially when one considers that rotations down to 0.02° in acetolysis and 0.01° in aqueous acetone are involved. The polarimetric rate constants derived from the slopes of these plots are the ones given in Table I.

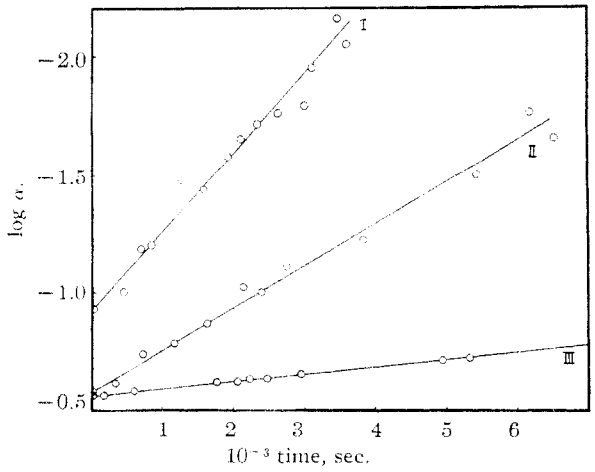


Fig. 2.—Polarimetric observation of solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate: I, in 75% acetone; II, in AcOH; III, in EtOH.

The available data (Table I) show that steady first-order polarimetric rate constants k_α exceed the steady first-order titrimetric rate constants k_t by factors of 3.46, 2.94 and 1.40 in acetolysis, ethanolysis and hydrolysis in 75% acetone, respectively. The data also show that in this extra racemization *exo*-bromobenzenesulfonate (III) remains *exo*, for *endo*-ester is so much less reactive[4] in solvolysis that the titrimetric rate constant would reflect any *exo* → *endo* change.

It is evident from the kinetic behavior that the excess racemization of the *exo*-norbornyl *p*-bromobenzenesulfonate does not involve external *p*-bromobenzenesulfonate ion. The process is, kinetically, an intramolecular one. The rate of the so-called internal racemization is very dependent on the ionizing character of the solvent, as shown, for example, by the optical stability of *exo*-norbornyl *p*-bromobenzenesulfonate in the solvent pyridine which is used in the preparation of the material. Thus the *exo*-(B)-norbornyl *p*-bromobenzenesulfonate (IIIB) possessed the identical rotation whether isolated after 16 hours or 7 days in the pyridine solvent. This whole phenomenon is discussed[11] more fully in the following article and the concern here will be with the effect of the excess racemization of the *p*-bromobenzenesulfonate concurrent with solvolysis on the quantitative significance to be attached to the racemic character of the final solvolysis product.

We can calculate what fraction of the final solvolysis product has come from *exo*-(B)-material (IIIB), and what fraction has arisen from *dl-exo*-bromobenzenesulfonate IIIAB. Taking $k_\alpha - k_t$ as a rate constant for the extra racemization of *p*-bromobenzenesulfonate not associated with sol-

(11) Winstein and Schreiber, THIS JOURNAL, in press.

volysis, the optical purity **P**, starting with optically pure material, of residual *p*-bromobenzenesulfonate at time *t* is given by equation 2.

$$\mathbf{P} = e^{-(k_\alpha - k_t)t} \qquad (2)$$

This is the optical purity of the *p*-bromobenzenesulfonate undergoing solvolysis at time *t*. The average optical purity $\bar{\mathbf{P}}$ of the *p*-bromobenzenesulfonate which has solvolyzed over a long interval is given by equation 3.

$$\bar{\mathbf{P}} = \frac{\int \mathbf{P}[-\mathrm{d(ROBs)}]}{\int -\mathrm{d(ROBs)}} = \frac{\int e^{-(k_\alpha - k_t)t} k_t (\mathrm{ROBs})_0 e^{-k_t t} dt}{\int k_t (\mathrm{ROBs})_0 e^{-k_t t} dt} \qquad (3)$$

At time *t*, $\bar{\mathbf{P}}$ is given by equation 4, and at total reaction, $\bar{\mathbf{P}}$ is expressed by equation 5.

$$\bar{\mathbf{P}} = (k_t/k_\alpha)(1 - e^{-k_\alpha t})/(1 - e^{-k_t t}) \qquad (4)$$

$$\bar{\mathbf{P}} = k_t/k_\alpha \qquad (5)$$

Another way to put it is that, on complete solvolysis, the fraction of solvolysis product which has arisen from prior racemized bromobenzenesulfonate is $(1 - k_t/k_\alpha)$, while the fraction which has arisen from active material is (k_t/k_α).

Thus we see from the rate constants in Table I that in solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate (III), the solvolysis product arises from active material only to the extent of 29, 34 and 71% in acetolysis, ethanolysis and hydrolysis in 75% acetone, respectively.

In Table II are given the data relating to the loss in activity attending solvolysis in acetic acid and 75% acetone. In the third column are given the rotations ($\alpha_{\text{theor.}}$) which would be expected from previous[6] and present data if III did not racemize and solvolysis proceeded with complete retention of configuration. In the next column this figure is corrected for racemization of the III. The values of $\bar{\mathbf{P}}$ $\alpha_{\text{theor.}}$ are still sufficiently large compared to the uncertainties in reading with the instrument available for this work, that it is clear that loss in activity attends solvolysis itself to within *ca.* 10% in 75% acetone and within 0.3% in acetic acid.

TABLE II

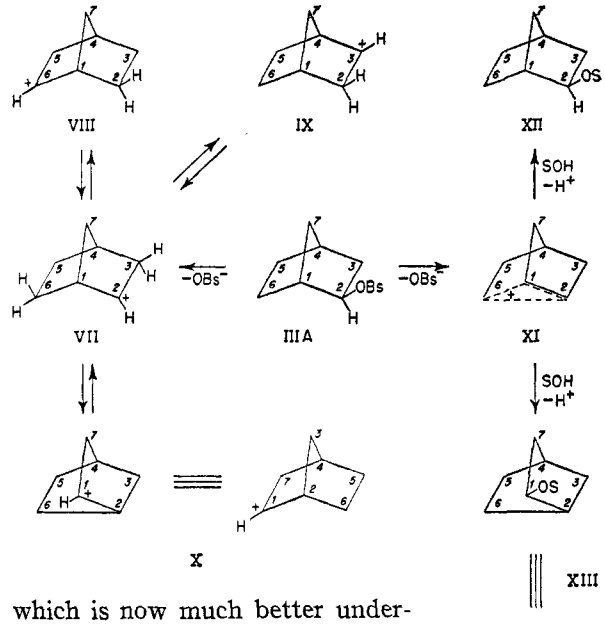
SUMMARY OF EXTENT OF RACEMIZATION ATTENDING ACETOLYSIS AND HYDROLYSIS OF *exo*-NORBORNYL *p*-BROMOBENZENESULFONATE

Solvent	ROBs concn.	α theor.	$\bar{\mathbf{P}}\alpha$ theor.	α obsd.	% Rac. att. solv.
AcOH	0.201	0.440	0.127	−0.001	100 ± 4
AcOH	.100[a]	5.20	1.51	+ .001	100 ± 0.3
75% acetone	.200	0.051	0.036	.002	100 ± *ca.* 10

[a] Acetate isolated and α_D (1 dcm.) of homogeneous material taken.

Actually, there are several possible rearrangements which could conceivably account for the racemization that attends the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate by way of a carbonium ion. One of them involves C_2, C_6 equivalence by 2,6-hydrogen equilibration as shown in VII⇄VIII. This is the type shift once called on[12] to explain the isobornyl chloride racemization

(12) Meerwein and Montfort, *Ann.*, **435**, 207 (1924).



which is now much better understood on the basis of the Nametkin rearrangement.[13] Another possible racemization mode involves C_2, C_3 equivalence by 2,3-hydrogen equilibration as shown in VII ⇄ IX. Still another involves C_1, C_2 equivalence by carbon migration as, for example, in VII ⇄ X. While other labelling techniques in addition to the polarimetric one are necessary, there are reasons to favor carbon migration.

Stereo-electronically, carbon migration is more likely than hydrogen for C_6, C_1 and C_2 are more nearly in the favorable situation of planarity with the axis of the vacant *p*-orbital on C_2 than is the case for a 3-hydrogen atom, C_3 and C_2. Further, there is the example of the cation from camphene hydrochloride or isobornyl chloride, where the Nametkin rearrangement,[13] involving a methyl migration analogous to the 3-hydrogen migration, competes only poorly with other reactions of the cation. Thus it is expected that hydrogen migration will be slower and subsequent to carbon involvement in the system in hand.

On the basis of carbon migration, racemization alone could be due to a dynamic equilibrium between two one-sided cationic species VII and X. Further qualifications regarding these species and their reactions would be necessary to account for the other striking aspects of the present results, namely, the essentially exclusive formation of *exo*-product, and the enhanced solvolysis rate of the *exo*-*p*-bromobenzenesulfonate.[4] While our precise chemical and thermodynamic knowledge of bicyclic systems is still limited, it is attractive to account for all of these results by way of the bridged formulation[14] XI for the norbornyl cation. This structure would, in this system,[4] be more stable[15] than the classical one VII. The *exo*-norbornyl

(13) W. Hückel, "Theoretische Grundlagen der Organischen Chemie," Vol. I, Akademische Verlagsgesellschaft m. B. H., Leipzig, 1940, pp. 295–299.

(14) Winstein and Morse, THIS JOURNAL, **74**, 1133 (1952).

(15) One of the contributory causes of this could be relief of strain attending the greater flattening of the $C_{1,2,3,4,7}$ ring in the species XI.

p-bromobenzenesulfonate III has the proper geometry for delocalization of the C_1–C_6 bonding electron pair directly in the rate determining ionization process, and thus is the more reactive isomer. Like the *cis*-2-butene bromonium ion,[2,16] the bridged ion XI is internally compensated, attack on C_2 giving original configuration XII, attack on C_1 giving inverted configuration XIII.

In the present system, favorable to carbon participation, the dominance of this over solvent intervention is very large and greater than in solvolysis of the *endo*-*p*-bromobenzenesulfonate. In 75% acetone, the indications are that *ca.* 1.5% of *endo*-norborneol is produced in solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate. This is being investigated further, but it would seem that carbon participation has not yet taken over completely in 75% acetone. More complete dominance of carbon participation could be expected[17] in the less nucleophilic acetic acid solvent and the facts seem to be in line with this. While the technique for disclosing small amounts of *endo* material in *exo* has not yet been applied to the acetolysis product, the polarimetric results indicate that any proportion of active *endo*-acetate in the *exo*-acetate product must be very small indeed. Starting with *exo*-(B)-norbornyl *p*-bromobenzenesulfonate (IIIB), the acetate product IV A B is completely optically inactive. Now, either no active acetate of *endo*-(B)-norborneol[6] (IB) is present, or its activity is just balanced, by coincidence, by that due to active *exo*-acetate. The *exo*-acetate cannot be the *exo*-(B) for its sign of rotation is the same as that of *endo*-(B). It would need to be the inverted *exo*-(A)-acetate. On the whole, the cancellation of activities seems likely than the absence of active materials in the *exo*-acetate product and, on this basis, allowing for the possible error in rotation reading and multiplying by (k_α/k_t), the proportion of *endo*-(B)-acetate in the solvolysis product must be less than 5 parts per thousand.

The evidence for an unclassical structure XI for the norbornyl cation lends credence to the earlier suggestion of Christopher Wilson[18] of a possible mesomeric cation from camphene hydrochloride. Such a formulation (XIV), while again not uniquely required by any one result, takes account the most simply of products and reactivities. On this basis, one can understand: (a) the formation from the cation of isobornyl and camphene hydrate derivatives and not bornyl and methylcamphenilol derivatives[13]; (b) the formation of traces of tricyclene from the cation[19]; (c) the rate sequences, isobornyl > bornyl,[4] and camphene hydrate > methylcamphenilol,[20] to electrophilic reagents.

There are similar but less well known cations which may be best described by a bridged structure. One of these, for example, would be the internally compensated species XV from 2-methylisofenchol.[21] Another would be the species XVI from either methylborneol or methylfenchyl alcohol.[22]

XIV XV XVI

The number of known cases of carbonium ions[23] the stereochemistry of whose reactions is best accounted for, under some circumstances, by so-called non-classical structures, is still small. The known examples mostly have the special feature of the bicyclic ring structure in the systems discussed in this article or the feature that the neighboring group is an unsaturated electron source, vinyl, as in cholesteryl cation,[2,24] or phenyl, as in the benzylmethylcarbinyl[17] or 3-phenyl-2-butyl cations.[25] Thus it remains to be seen how general this situation may become.

ADDED IN PROOF.—Since our first publications[3,24] dealing with neighboring carbon, Hughes and Ingold have also recognized the possibility of acceleration of ionization due to carbon participation. They reported several cases of such acceleration (2,2,2-triphenylethyl chloride, isobornyl chloride and possibly camphene hydrochloride) at the Conference on the Walden Inversion and Molecular Rearrangements at Montpellier, France, April, 1950, which paralleled some of the results in the present series of papers presented at the same time.[2b] More recently they have discussed the possibility of bridged structures for certain ions, for example, the one from camphene hydrochloride (XIV) [F. Brown, E. D. Hughes, C. K. Ingold and J. F. Smith, *Nature*, 168, 65 (1951)]. Hughes and Ingold employ the terms, "synartetic acceleration" and "synartetic ions."

Very recently further evidence has appeared on the question of 2,6-hydrogen shifts[12] in [2,2,1]bicycloheptane systems. J. D. Roberts and C. C. Lee report that solvolysis of *exo*-norbornyl-2,3-C_2[14] *p*-bromobenzenesulfonate in 75% acetone results in a shuffling of carbon atoms slightly more than expected on the basis of the structure XI, while the extra shuffling is increasingly drastic in acetic and formic acid solvents [J. D. Roberts, Paper at 120th Meeting of the American Chemical Society, New York, N. Y., September 3–7, 1951, page 24M of Abstracts; J. D. Roberts and C. C. Lee, THIS JOURNAL, 73, 5009 (1951)]. The equivalent of 2,6-hydrogen shifts are required to account for the extra shuffling. Similarly, some 2,6-type hydrogen shift occurs in the dehydration of β-fenchol [W. Doering and A. P. Wolf, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10–13, 1951, page 437 of Abstracts].

The action of nitrous acid on camphenilyl amine has now been reported to give, in addition to camphenilol and the Wagner rearrangement product apoisoborneol, a small amount of a material which could owe its formation to 2,6-type hydrogen shift, namely, β-isofenchocamphorol, the quantity of the latter decreasing markedly under the mildest conditions [S. Beckmann and R. Bamberger, *Ann.*, 574, 65 (1951)]. In the hydration of para-santen, addition of hydrogen chloride, followed by hydrolysis with lime-water, gives no α-santenol (which may arise from a 2,6-type hydrogen shift), whereas the action of acetic acid-sulfuric acid gives some α-santenol and formic acid gives α-santenol essentially completely [S. Beckmann and R. Bamberger, *Ann.*, 574, 76 (1951)].

While we are now investigating related sulfonic acid esters, all of the above results are perhaps most simply explained by prior formation of a structure of the type XI which can rearrange further if the conditions are conducive

(16) Winstein and Lucas, THIS JOURNAL, **61**, 1576, 2845 (1939).

(17) Winstein, Brown, Schreiber and Schlesinger, *ibid.*, **74**, 1140 (1952).

(18) Nevell, de Salas and Wilson, *J. Chem. Soc.*, 1188 (1939).

(19) Moycho and Zienkowski, *Ann.*, **340**, 25 (1905).

(20) Hückel, "Theoretische Grundlagen der Organischen Chemie," Vol. I, Akademische Verlagsgesellschaft m. B. H., Leipzig, 1940. p. 291.

(21) Komppa and Nyman, *Ann.*, **533**, 290 (1938).

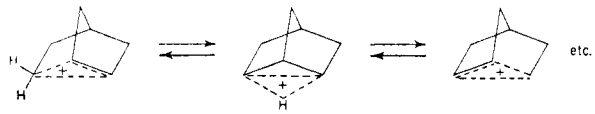
(22) Ruzicka, *Helv. Chim. Acta*, **1**, 110 (1918).

(23) Excluding cations with functional neighboring groups.

(24) (a) Winstein and Adams, THIS JOURNAL, **70**, 838 (1948); (b) Winstein and Schlesinger, *ibid.*, **70**, 3528 (1948).

(25) Cram, *ibid.*, **71**, 3863 (1949).

to long life of the carbonium ion, perhaps by way of intermediates like XVII.



XI XVII XVIII

Considering the wave-mechanical description of the cyclopropane ring, structure XVII illustrates one of the attractive ways to protonate a cyclopropane, and changes of the type XI ⇄ XVII could be important in certain closures and openings of the cyclopropane ring. Also, the distance between Cα and a γ-hydrogen atom in a carbonium ion is substantially decreased in the bridged structure of type XI, and changes of the type XI → XVII → XVIII may represent one general way in which so-called 1,3-shifts could arise.

Experimental

***exo*-Norbornyl Alcohol and *exo*-Norbornyl Acid Phthalate.**—The solvolysis of *endo*-norbornyl *p*-toluenesulfonate to *exo*-norborneol isolated as the acid phthalate in the 80–81° crystalline form described by Alder and Rickert[10] has been described already.[6] In the second large preparation, the 448.9 g. of crude *exo*-norbornyl acid phthalate proved to be this same crystalline form. After several recrystallizations from ethyl acetate–petroleum ether, which failed to effectively remove the phthalic acid impurity, recrystallization from aqueous acetic acid yielded a second crystalline form, m.p. 98.6–99.7° (probably corresponding to the 102–103° form reported by Komppa and Beckmann[5]), m.p. unchanged on recrystallization from ethyl acetate–petroleum ether.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.21; H, 6.44.

exo-Norbornyl acid phthalate (20.0 g.), m.p. 80.5–83.5°, and *exo*-norbornyl acid phthalate (10.0 g.), m.p. 98.6–99.7°, gave, on saponification,[6] 8.37 g. (98.0%) and 4.17 g. (96.9%) of the same *exo*-norbornyl alcohol, m.p. 127.8–128.5°.

Solvolysis of *exo*-Norbornyl *p*-Bromobenzenesulfonate. Glacial Acetic Acid.—*exo*-Norbornyl *p*-bromobenzenesulfonate[4] (1.50 g.) was allowed to solvolyze in dry glacial acetic acid at 25° for 24 hours. Extraction from the neutralized acetic acid solvent with ether, reduction with lithium aluminum hydride, and conversion of the norborneol to the 3,5-dinitrobenzoate yielded 0.828 g. (59.3%) of *exo*-norbornyl 3,5-dinitrobenzoate, m.p., crude, 97–102°, m.p. 103.4–105.0° after recrystallization from aqueous acetic acid.

A 0.60 *M* *exo*-norbornyl *p*-bromobenzenesulfonate[4] solution in dry acetic acid and a solution 0.60 *M* in *exo*-norbornyl *p*-bromobenzenesulfonate and 0.70 *M* in potassium acetate in dry acetic acid were each allowed to solvolyze to completion at 25° and then examined for unsaturation by quantitative bromination. Carefully weighed amounts of the solvolyzed solution (*ca.* 0.15–0.24 g.) were added to 15 ml. of acetic acid containing 2 ml. of 10% aqueous sulfuric acid in bromination flasks followed by 10 ml. of standard bromate–bromide solution delivered by pipet. The bromination was allowed to proceed in the dark for 12–40 minutes, excess solid potassium iodide introduced after sufficient water (*ca.* 30 ml.) was added to reduce acidity, and then the solution was titrated with standard 0.0509 *M* thiosulfate to a starch end-point.

In the absence and presence of potassium acetate, bromine consumption equivalent to 0.27 ± 0.27 mole % and 4.53 ± 0.22 mole % norbornylene was observed, respectively.

75% Aqueous Acetone.—*exo*-Norbornyl *p*-bromobenzenesulfonate[4] (3.4 g.) was dissolved in 75% aqueous acetone to a concentration of 0.30 *M* and the solution held at 25° for *ca.* 12 hours. Isolation of the norborneol as in the case of the analogous experiment with the *endo*-*p*-bromobenzenesulfonate[6] and conversion to the *p*-bromobenzenesulfonate gave 1.45 g. (42.6%) of *exo* ester. A portion of this *exo*-norbornyl *p*-bromobenzenesulfonate product was then solvolyzed in dry glacial acetic acid in duplicate runs at 0.037 *M* (Table I). Early and late infinity titers[6] yielded assays of the material of 2.1, 0.9 and 1.9% *endo*-derivative.

Complete Resolution of *exo*-Norbornyl Acid Phthalate.—Racemic *exo*-norbornyl acid phthalate (207.0 g.) was refluxed in 1000 ml. of acetone with an equivalent amount of cinchonidine alkaloid (234 g.) and allowed to stand overnight in the cold room. The initial 387.6 g. of alkaloid salt (87.9% theoretical) was recrystallized from warm acetone with overnight standing three more times, ending with 165.6 g. (37.5%) of cinchonidine salt. A 5-g. quantity of this salt was dissolved in 25 ml. of hot benzene, extracted with excess 2 *N* hydrochloric acid, washed and dried, and the liberated *exo*-norbornyl acid phthalate was isolated in two crops after addition of 20–40° petroleum ether to the concentrated benzene solution. Polarimetric examination of the two successive crops of 1.15 g. and 0.88 g. acid phthalate gave rotations of $[\alpha]^{25}D$ +0.89° and +8.39° (chloroform, *c* 10.04), respectively.

Both pure *exo*-norbornyl acid phthalate enantiomorphs were obtained by fractionally crystallizing the liberated partially active acid phthalates from the recrystallized cinchonidine salt and from the combined mother liquors. The procedure used in working up the active *exo*-(A)-norbornyl acid phthalate enantiomorph from the combined mother liquors from the alkaloid salt recrystallization is typical and the results were strictly analogous to those obtained in the isolation of the (B) isomer. In the former case, the four mother liquors were combined, diluted with water and 100% excess dilute hydrochloric acid and extracted with chloroform seven times. The combined chloroform phase was washed several times with dilute hydrochloric acid and then several times with water and finally dried over magnesium sulfate. The chloroform solution was evaporated under suction to a concentrated oil, dissolved in ethyl acetate and petroleum ether added to turbidity. Overnight standing in the ice-box yielded a first crop of 77.25 g. of *exo*-norbornyl acid phthalate which was essentially pure racemic compound, $[\alpha]^{25}D$ −0.04° (chloroform, *c* 9.98). The next three crops were combined and refractionated several times to remove racemic impurity and all of the remaining acid phthalate fractions (33.6 g.) were combined and purified through the sodium salt by extracting the compound from an ether solution with excess aqueous sodium carbonate. After the addition of excess dilute sulfuric acid, the liberated acid phthalate was extracted thoroughly with ether, washed, dried and evaporated to dryness. The resulting 32.85 g. of acid phthalate was crystallized from ether–petroleum ether and 31.66 g. of pure *exo*-(A)-norbornyl acid phthalate was obtained in five successive crops, m.p. 89.3–90.3°. The specific rotations, $[\alpha]^{24}D$, of crops 1, 2, 3 and 5 were −8.49°, −8.49°, −8.42° and −8.46° (chloroform, *c* 10), respectively.

In like manner, the *exo*-(B)-norbornyl acid phthalate enantiomorph was obtained by fractional crystallization of the partially active acid phthalate obtained from the recrystallized cinchonidine salt to yield in this case 29.15 g. of pure enantiomorph, m.p. 89.0–90.2°, $[\alpha]^{25}D$ +8.45° (chloroform, *c* 10.02).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found for *exo*-(A)-norbornyl acid phthalate: C, 69.35; H, 6.30. Found for *exo*-(B)-norbornyl acid phthalate: C, 69.19; H, 6.45.

Conversion of *exo*-Norbornyl Acid Phthalate Enantiomorphs into the Corresponding Alcohols and *p*-Bromobenzenesulfonates.—Employing the usual procedure,[6] 28.29 g. of *exo*-(A)-norbornyl acid phthalate and 28.15 g. of *exo*-(B)-norbornyl acid phthalate were saponified and steam distilled to give 11.93 g. (97.8%) of *exo*-(A)-norbornyl alcohol, m.p. 126.0–126.6°, $[\alpha]^{24}D$ +2.44° (chloroform, *c* 9.99) and 11.36 g. (93.7%) of *exo*-(B)-norbornyl alcohol, m.p. 126.0–126.8°, $[\alpha]^{24}D$ −2.41° (chloroform, *c* 10.04).

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found for *exo*-(A)-norborneol: C, 74.93; H, 10.57. Found for *exo*-(B)-norborneol: C, 74.90; H, 10.88.

exo-(B)-Norborneol (6.0 g.) was dissolved in *ca.* 40 ml. of dry pyridine and 14.32 g. (5% excess) of *p*-bromobenzenesulfonyl chloride was added with cooling of the flask in an ice-bath. The flask was left in the ice-box for seven days and the *exo*-(B)-norbornyl *p*-bromobenzenesulfonate was then isolated by dilution of the pyridine solution with several volumes of ice in the original flask. The product was induced to crystallize and then promptly collected on a sintered glass funnel, washed thoroughly with water and dried without delay over phosphorus pentoxide in a vacuum desiccator. A 16.31-g. yield (92.2%) of *exo*-(B)-norbornyl *p*-bromobenzenesulfonate, m.p. 55.3–56.4°, was thus directly obtained, $[\alpha]^{24}D$ +1.89° (chloroform, *c* 10.15).

Anal. Calcd. for $C_{13}H_{15}O_3SBr$: C, 47.14; H, 4.57. Found: C, 46.88; H, 4.71.

Repetition of the above procedure with 2.0 g. of *exo*-(B)-norbornyl alcohol, 4.77 g. (5% excess) of *p*-bromobenzene-

sulfonyl chloride and 15 ml. of dry pyridine and a reaction time of 16 hours yielded 5.16 g. (87.5%) of *exo*-(B)-norbornyl *p*-bromobenzenesulfonate with the identical optical activity, $[\alpha]^{24}D$ +1.85° (chloroform, *c* 10.21).

Relation of Configuration of *exo*- and *endo*-Norbornyl Enantiomorphs by Oxidation to Active Norcamphor.—1.93 g. of *ca.* 60–80% resolved *endo*-(A)-norbornyl acid phthalate[6] from middle fractions was saponified and steam distilled. The combined solid and *ca.* 20 ml. of aqueous distillate was treated with 8 ml. of acetic acid followed by 1.4 g. of potassium dichromate and 1.8 g. of concentrated sulfuric acid. After one hour standing with occasional warming to *ca.* 40°, excess sodium hydroxide was added and the norcamphor steam distilled. Only the 0.32 g. of solid norcamphor in the distillate was saved and dried *in vacuo* over potassium hydroxide, m.p. 95.5–96.2°, $[\alpha]^{24}D$ −15.73° (chloroform, *c* 9.79).

Anal. Calcd. for $C_7H_{10}O$: C, 76.29; H, 9.16. Found: C, 76.08; H, 9.37.

In similar manner, 1.42 g. of optically pure *exo*-(B)-norborneol was oxidized and 0.68 g. of solid norcamphor separated by decantation from the steam distillate and dried, m.p. 107.1–109.3°, $[\alpha]^{24}D$ +8.66 (chloroform, *c* 10.00).

Active (B) and Racemic *exo*-Norbornyl Acetates.—Optically pure *exo*-(B)-norborneol (1.00 g.) was dissolved in a mixture of 5 ml. of acetic anhydride and 20 ml. of dry glacial acetic acid in a 50-ml. volumetric flask and heated in a 75° bath for 10.0 hours. The solution was diluted with *ca.* five volumes of water, extracted four times with 50-ml. portions of pet. ether (b.p. 34–39°) and the extract washed in turn with water, aqueous sodium bicarbonate, and water. It was dried over anhydrous magnesium sulfate, and then concentrated to *ca.* 5 ml. through a fractionating column. The residue was carefully distilled *in vacuo* through a small all-glass apparatus to give 1.24 g. (90.2%) of *exo*-(B)-norbornyl acetate, $\alpha^{25}D$ +10.39° (1 dcm.), $n^{25}D$ 1.4565.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.95; H, 9.25.

The same procedure was used to prepare a sample of pure racemic *exo*-norbornyl acetate whose infrared spectrum was taken (Fig. 1).

Acetolysis of Active *exo*-(B)-Norbornyl *p*-Bromobenzenesulfonate in Glacial Acetic Acid.—Optically pure *exo*-(B)-norbornyl *p*-bromobenzenesulfonate (2.00 g.) was mixed with 2.00 g. of racemic *exo*-norbornyl *p*-bromobenzenesulfonate and the combined 4.00 g. dissolved in 120 ml. of dry glacial acetic acid (0.10 *M*) to which was added potassium acetate (0.085 *M* inadvertently insufficient) and the solution warmed in a 40° bath for 18 hours. The acetate was isolated as in the preparation from norborneol to yield 1.50 g. (80.5%) racemic *exo*-norbornyl acetate, $\alpha^{24}D$ +0.001° (1 dcm.), $n^{25}D$ 1.4565, infrared spectrum in Fig. 1.

Actually, the amount of excess acid prevailing in this solvolysis because of the deficiency of potassium acetate employed in the run was insufficient to cause more than several per cent. racemization of the final acetate. This is clear from control experiments previously described[6] on the behavior of *exo*-acetate toward much more concentrated (0.76 *M*) toluenesulfonic acid at 75 and 25°, and also from the effect even at 75° of just this excess acid concentration on the surviving activity in the *exo*-acetate product from solvolysis of the *endo*-*p*-bromobenzenesulfonate.[6]

Kinetic and Polarimetric Measurements.—The general procedures for the titrimetric rate measurements were those previously employed.[4,6]

In most of the acetolysis runs, the solution aliquot was drained directly into at least an equal volume of pure pet. ether (b.p. 30–60°) which served to reduce the solvolysis rate very markedly. Cooling the pet. ether-diluted aliquot further slowed the solvolysis reaction so that titration could be postponed for at least an hour without error. Tests showed that the brom phenol blue indicator color and color change at the equivalence point were identical in 1:1 acetic acid–pet. ether and acetic acid.

In the case of the rapid solvolysis in 75% acetone, room temperature was kept close to 25° and the titrations concluded without delay. Time was taken at the titration endpoint.

Routine polarimetric measurements were carried out with the Hilger instrument[6] in semimicro or micro 1 dcm. polarimeter tubes.

Polarimetric racemization rates of *exo*-(B)-norbornyl *p*-bromobenzenesulfonate in various solvents were carried out in a specially constructed 4-dcm. all-glass jacketed polarimeter tube of *ca.* 22-ml. capacity with sealed-on optically plane 1/4-inch Pyrex end pieces. Water from a 24.98 ± 0.01° thermostat was continuously circulated through the outer jacket during the course of the racemization rate runs. In each such rate run, solvent first brought to temperature in the thermostat was used to dissolve the weighed quantity of the active *p*-bromobenzenesulfonate to the mark in a 25-ml. volumetric flask. The resulting solution was then transferred as rapidly as possible to the polarimeter tube through the glass-stoppered opening at the center of the tube and then carefully located in place in the polarimeter trough. Readings were taken at appropriate intervals.

LOS ANGELES 24, CALIF. RECEIVED JUNE 11, 1951

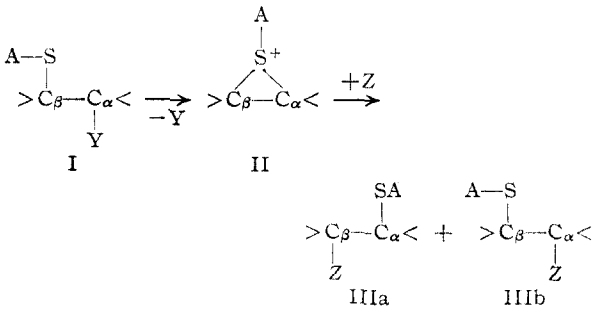
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. XVIII. Migration of the Methoxyl Group[1]

BY S. WINSTEIN AND L. L. INGRAHAM[2]

A simple recognizable result of participation of a functional neighboring group in a replacement process is migration of the neighboring group. Such a migration of a methoxyl group is shown to occur in solvolysis of 2-methyl-2-methoxy-3-bromobutane. This secondary bromide with a tertiary methoxyl group solvolyzes to give 3-methoxy-2-methyl-2-butanol, a tertiary alcohol containing a secondary methoxyl group.

Participation by functional neighboring groups in nucleophilic replacement processes, as in I → III, may control stereochemical results[3] and reactivity,[4] or give rise to the formation of unusual products, such as an orthoester[3c] in the case of the neighboring



(1) Much of the material of this paper was presented in summary: (a) before the Organic Division of the American Chemical Society, St. Louis, September, 1948; (b) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of abstracts; (c) at Montpellier, France, April 26, 1950 [*Bull. soc. chim.*, [5] **18** 55C (1951)]. Paper XVII, THIS JOURNAL, **72**, 4669 (1950).

(2) From the Ph.D. Thesis of L. L. Ingraham, U. C. L. A., 1949.

(3) *E.g.*, (a) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576, 2845 (1939); (b) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942); (c) S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943).

(4) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).