

## A Reexamination of the Racemization of 1-Phenylbromoethane in Acetone

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In their original examination of the racemization of 1-phenylbromoethane by lithium bromide in anhydrous acetone which is one of the bulwarks of the S<sub>N</sub>2 mechanism for the bimolecular nucleophilic substitution at saturated carbon, Hughes and his colleagues reported the rate to be "nonlinear" with lithium bromide concentration. This racemization has been reexamined over a much wider concentration range, at constant ionic strength and as a function of ionic strength. On the basis of the empirical observations, the "nonlinearity" of the rate of racemization with lithium bromide concentration is assigned to ion pairing and aggregation by the lithium bromide. The alternative explanations based on competing uni- and bimolecular processes or the S<sub>N</sub>1 ion-pair mechanism for nucleophilic substitution at saturated carbon are shown to be untenable.

The recent publication of Beronius, Nilsson, and Holmgren,<sup>2</sup> in which they argue that neglecting ion association when one of the reactants is an ionic species can make a purely bimolecular reaction appear to have a unimolecular component, has prompted this publication of some initial results from a reexamination of the racemization of (+)- and (-)-1-phenylbromoethane. The racemizations of optically active 1-phenylbromoethane and 2-iodooctane were examined by Hughes and his colleagues<sup>3,4</sup> and the observation that the rates of racemization and of halide exchange were the same within experimental error was the basis for the postulation of the S<sub>N</sub>2 mechanism for the bimolecular nucleophilic displacement at saturated carbon.<sup>5</sup>

Hughes, *et al.*, reported that, for the racemization of optically active 1-phenylbromoethane in acetone containing lithium bromide, the racemization was not exactly first order in halide ion (see Table I). The

TABLE I  
RACEMIZATION OF *d*-1-PHENYLBROMOETHANE IN ACETONE  
CONTAINING LITHIUM BROMIDE AT 30.2°<sup>a</sup>

No. of runs	Concn, <i>M</i>		<i>k</i> (× 10 <sup>3</sup> l./msec)	Reaction velocity <sup>b</sup> (× 10 <sup>-5</sup> mol/l. sec)
	RBr	LiBr		
2	0.200	0.200	0.795	3.18
2	0.200	0.102	0.963	1.97

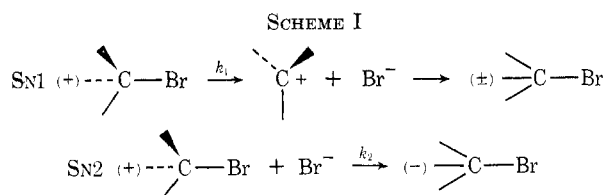
<sup>a</sup> E. D. Hughes, *et al.*, *J. Chem. Soc.*, 1173 (1936). <sup>b</sup> Reaction velocity (Ni) as calculated by the expression  $Ni = (A/2t) \ln \alpha_0/\alpha$ , where *A* = concentration of RBr, *t* the time in seconds, and  $\alpha_0$  and  $\alpha$  the initial angle of rotation of the plane of polarized light (*t* = 0) and at time *t*, respectively.

rate constant calculated assuming a bimolecular reaction, first order in each of 1-phenylbromoethane and lithium bromide, decreased with increasing concentration of the inorganic bromide. Thus, at 30.2° when the concentration of lithium bromide was halved from 0.200 to 0.102 *M*, the empirical second-order rate constant increased by over 20%. The reaction velocity or rate decreased, of course, when the concentration of lithium bromide was halved, but only to 62% rather than 50% of its former value. Similar behavior was

reported for the racemization of asymmetric 2-iodooctane.<sup>4,6</sup>

There are a number of possible explanations for such a variation of rate constant with the concentration of inorganic bromide. These include (1) unimolecular and bimolecular processes occur simultaneously; (2) the alkyl halide dissociates to an ion pair which may be intercepted by bromide at an early stage or as ion separation occurs; (3) ion pair formation by the lithium bromide. Empirical results are reported which permit a decision among these possibilities but first the three possibilities should be examined in more detail.

If S<sub>N</sub>1 and S<sub>N</sub>2 processes are occurring simultaneously (Scheme I), the rate of the former will be independent



of, and the latter linearly dependent upon, bromide ion concentration. If any other effects of increasing the concentration of lithium bromide (*e.g.*, common ion and salt effects) can be ignored, the uni- and bimolecular components can be separated as shown in Figure 1.<sup>7</sup> Inclusion of a common ion effect on the reaction would result in a decreasing unimolecular component with increasing bromide ion concentration only if the common ion effect operated prior to racemization of the carbonium ion intermediate while the increased ionizing power of the solvent with increasing salt concentration could cause an increase in the unimolecular component despite any common ion effect. Thus instead of a constant contribution to the overall rate of the racemization, the S<sub>N</sub>1 contribution could increase or decrease (or first decrease, then increase<sup>8</sup>) with increasing lithium bromide concentration. Consequently, some curvature, either convex or concave, in the actual rate *vs.* concentration of bromide ion line could occur, but the racemization rate should be sig-

(1) Address to which correspondence should be sent.

(2) P. Beronius, A.-M. Nilsson, and A. Holmgren, *Acta Chem. Scand.*, **26**, 3173 (1972).

(3) E. D. Hughes, F. Juliusburger, A. D. Scott, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1173 (1936).

(4) E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

(5) J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

(6) E. Bergmann, M. Polanyi, and A. L. Szabo, *Z. Phys. Chem., Abt. B*, **20**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936).

(7) Such mixed kinetics need not be detectable by differences in the rates of racemization and halide exchange, since such differences would only occur if there were significant internal return after racemization in the unimolecular reaction.

(8) S. Winstein, P. E. Klinedinst, and E. Clippinger, *J. Amer. Chem. Soc.*, **83**, 4986 (1961).

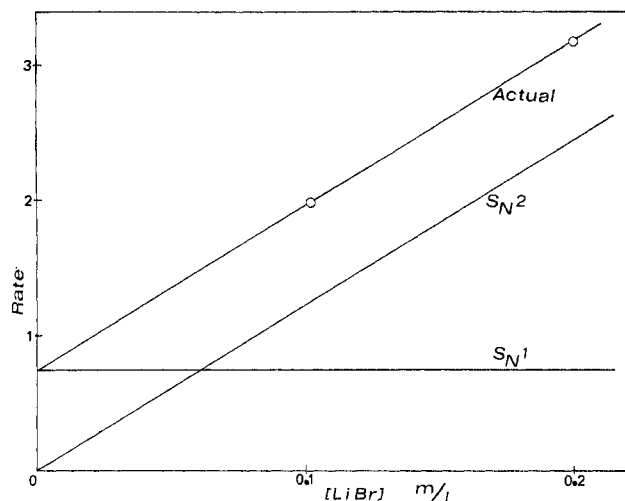
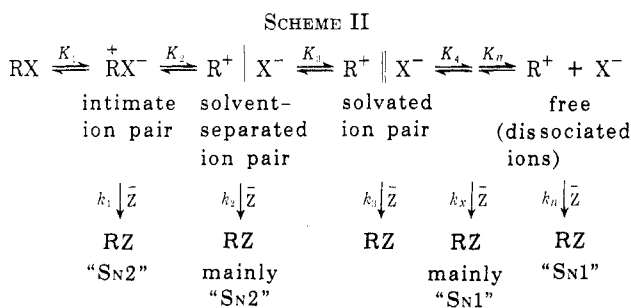


Figure 1.—Schematic representation of the racemization of (+)-1-phenylbromoethane with lithium bromide in anhydrous acetone assuming that both  $S_N1$  and  $S_N2$  processes are occurring. The actual rate of racemization (rate =  $[RBr]/2t \ln \alpha_0/\alpha$ ) could be considered to have a constant unimolecular component and a bimolecular component linearly dependent upon the concentration of the nucleophile (bromide ion). [Data from E. D. Hughes, *et al.*, *J. Chem. Soc.*, 1173 (1936)].

nificant at zero bromide ion concentration and the intercept or  $S_N1$  contribution would be greater, the greater the degree of curvature.

The ion-pair mechanism for nucleophilic substitution at saturated carbon, as proposed by Snee and Larsen,<sup>9</sup> is summarized in Scheme II. Here it is as-



sumed that there is a single or unified mechanism involving an initially formed ion pair which progressively dissociates as the individual ions are solvated. If the initially formed ion pair is intercepted by the nucleophile,  $S_N2$  kinetics and stereochemistry would be expected, while, at the other extreme, combination of a symmetrically solvated carbonium ion with a nucleophile would show  $S_N1$  kinetics and stereochemistry. As the average or median site of interception of the dissociating ion pair is shifted to the left, the "unimolecular" character of the reaction decreases and the "bimolecular" character increases. Increasing the concentration of the nucleophile, other things being equal, should have such an effect. Again a positive intercept for the reaction rate *vs.* bromide ion concentration curve would be expected and the rate constant of the reaction should decrease with increasing concentration of lithium bromide. Increasing the ion-supporting ability of the solution, by, for example, adding inert electrolyte, should accelerate the reaction

(9) R. A. Snee and J. W. Larsen, *J. Amer. Soc.*, **91**, 362, 6031 (1969).

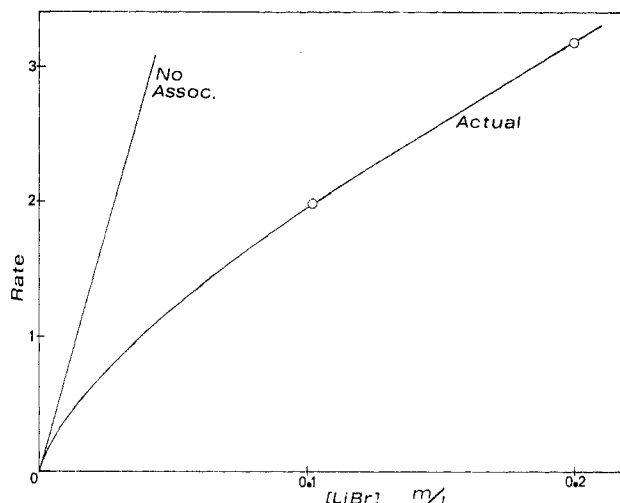


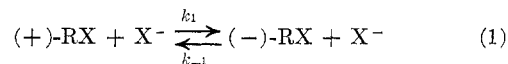
Figure 2.—Schematic representation of the effect of association of lithium bromide on the racemization of (+)-1-phenylbromoethane in anhydrous acetone (rate =  $[RBr]/2t \ln \alpha_0/\alpha$ ). [Data from E. D. Hughes, *et al.*, *J. Chem. Soc.*, 1173 (1936)].

if it involves an equilibrium ionization to even intimate ion pair.

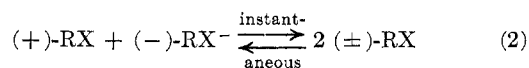
Finally, if association or ion-pair formation on the part of the lithium bromide is occurring, increasing the concentration of lithium bromide would increase the fraction of the salt associated. Since the reactivity of ion pairs and higher aggregates is generally much lower than that of dissociated ions,<sup>10,11</sup> the rate of the reaction would increase less rapidly than expected for a bimolecular reaction as the concentration of lithium bromide is increased. The anticipated behavior is illustrated in Figure 2, again with the limited data of Hughes, *et al.*,<sup>3</sup> included. Here the intercept should be zero (if there is no unimolecular component) and the tangent of the curve at zero bromide ion concentration would represent the rate behavior expected if no association of the added salt occurred.

## Results

Assuming that the reaction of optically active 1-phenylbromoethane [(+)-RX] with bromide ion ( $X^-$ ) is an equilibrium bimolecular process with inversion of stereochemistry [*i.e.*, giving (-)-RX], eq 1 can be written.



However, the product will, together with an equal molar quantity of unreacted alkyl halide, give racemic material [(±)-RX], so that a second, instantaneous "reaction," eq 2, can also be written. Since the reac-



tion of racemic product with bromide would have an equal probability of giving either stereoisomer, both the first and second equations can be considered to be irreversible (*i.e.*, racemic material does not spon-

(10) P. Beronius, L. Pataki, A.-M. Nilsson, and G. Wikander, *Radioanal. Lett.*, **6**, 333 (1971), and references cited therein.

(11) (a) S. G. Smith and M. P. Hanson, *J. Org. Chem.*, **36**, 1931 (1971); (b) G. H. Barlow and H. E. Zangg, *ibid.*, **37**, 2246 (1972), and references cited therein; (c) J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11**, 112 (1972), and references cited therein.

TABLE II  
RACEMIZATION OF 1-PHENYLBROMOETHANE IN ANHYDROUS ACETONE CONTAINING LITHIUM BROMIDE AND LITHIUM NITRATE AT 40.38°

Run no.	Concn of LiBr, mol/l.	Concn of LiNO <sub>3</sub> , mol/l.	Ionic strength, mol/l. of Li <sup>-</sup>	$\frac{\Delta \log \alpha_0/\alpha}{\Delta t, \text{ sec}}$	$k \times 10^3, \text{ l./mol sec}$
1	0.000	0.000	0.000	$<0.008 \times 10^{-4}$	
2	0.0025	0.000	0.0025	2.19	10.09
3	0.0050	0.000	0.0050	2.95	6.79
4	0.0100	0.000	0.0100	4.36	5.02
5	0.0200	0.000	0.0200	6.66	3.83
6	0.0300	0.000	0.0300	9.17	3.52
7	0.0500	0.000	0.0500	12.89 <sup>a</sup>	2.97
8	0.0700	0.000	0.0700	16.74	2.75
9	0.1000	0.000	0.1000	21.04 <sup>b</sup>	2.42 (2.39) <sup>e</sup>
10	0.0000	0.100	0.1000	0.15 <sup>d</sup>	(0.0173) <sup>d</sup>
11	0.0050	0.0950	0.1000	1.34	3.09 (2.37) <sup>e</sup>
12	0.0100	0.0900	0.1000	2.37 <sup>c</sup>	2.73 (2.37) <sup>e</sup>
13	0.0300	0.0700	0.1000	6.47	2.48 (2.36) <sup>e</sup>
14	0.0500	0.0500	0.1000	10.77	2.48 (2.41) <sup>e</sup>
15	0.0700	0.0300	0.1000	14.79	2.43 (2.38) <sup>e</sup>
16	0.0100	0.0200	0.0300	3.58	4.12
17	0.0100	0.0400	0.0500	2.90	3.34
18	0.1000	0.0600	0.0700	2.69	3.10

<sup>a</sup> Average of two runs. <sup>b</sup> Average of four runs. <sup>c</sup> Average of three runs. <sup>d</sup> Initial rate constant for NO<sub>3</sub><sup>-</sup> as the nucleophile. The rate of racemization increases as Br<sup>-</sup> is liberated. <sup>e</sup> Values in brackets are corrected for the nonzero intercept which represents the rate of reaction 10 plus the contribution to the rate by the Br<sup>-</sup> so liberated.

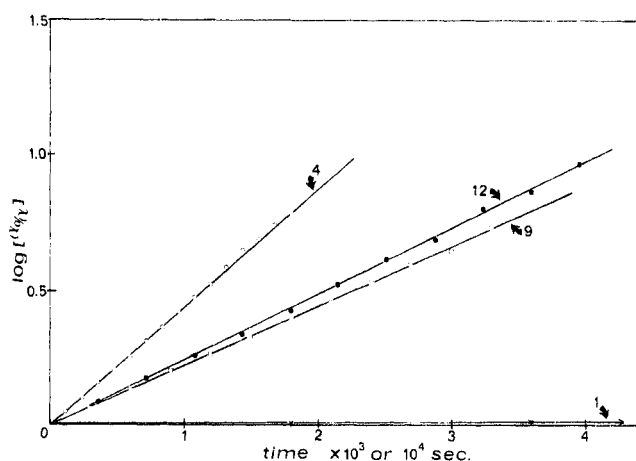
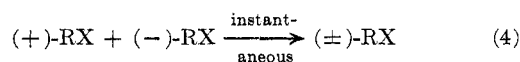
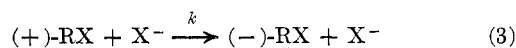


Figure 3.—Typical racemization results for (+)- or (-)-1-phenylbromoethane with lithium bromide in anhydrous acetone at 40.38 ± 0.03°. Curve numbers refer to Table II and the conditions, concentration of lithium bromide, and ionic strength (sum of the concentration of lithium bromide and nitrate) in moles per liter and time scale, are, respectively, run 4, 0.01 M, 0.01 M, × 10<sup>4</sup> sec; run 12, 0.01 M, 0.10 M, × 10<sup>4</sup> sec; run 9, 0.10 M, 0.10 M, × 10<sup>3</sup> sec; run 1, 0.00 M, 0.00 M, × 10<sup>4</sup> sec.

taneously convert to one enantiomer). The observable process can then be represented by eq 3 and 4.



For eq 3, a rate expression can be written

$$-\frac{d[(+) \text{-RX}]}{dt} = k[\text{X}^-][(+) \text{-RX}]$$

However, for every molecule of (+)-RX reacting *via* eq 3, a second molecule is "used up" *via* eq 4, so the overall or actual rate expression can be written

$$-\frac{d[(+) \text{-RX}]}{dt} = 2k[\text{X}^-][(+) \text{-RX}]$$

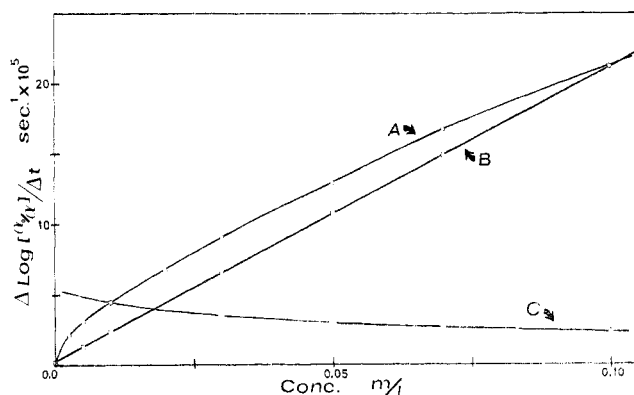


Figure 4.—Racemization rate as a function of concentration of lithium bromide and ionic strength in anhydrous acetone at 40.38°. Curve A: rate *vs.* concentration of lithium bromide. Curve B: rate *vs.* concentration of lithium bromide at constant ionic strength (sum of the concentrations of LiBr and LiNO<sub>3</sub> equal to 0.100 M). Curve C: rate *vs.* ionic strength with fixed (0.0100 M) lithium bromide concentration.

The concentration of the halide ion is a constant throughout, so that on integration the following expression is obtained.

$$\ln [(+) \text{-RX}] = -2k[\text{X}^-]t$$

or

$$\log \frac{[\text{RX}]_t}{[\text{RX}]_0} = \frac{2k}{2.303} [\text{X}^-]t$$

This last expression was used to evaluate the rate constants reported in Table II. Because the optical purity of the 1-phenylbromoethane varied somewhat from batch to batch and was, in fact, unknown in any case, the angle of rotation,  $\alpha$ , of plane-polarized light was used directly as a measure of the concentration of the asymmetric material, [(+) -RX]. That this procedure is valid can be seen from Figure 3, where not atypical plots of  $\log \alpha_0/\alpha$  *vs.* time are shown. The linearity shows the racemization process to be first order with respect to the optically active reactant.

In Figure 4 are plotted some rate data for the racemization of optically active 1-phenylbromoethane at

40.38° in anhydrous acetone. Curves are shown for the rate as a function of concentration of ionic bromide both at constant (curve B) and at varying ionic strengths (curve A). Also shown is the curve for constant concentration of ionic bromide (0.0100 M) but with changing ionic strength, *i.e.*, concentration of lithium ion where that concentration is the sum of the concentrations of lithium bromide and of lithium nitrate (curve C).

### Discussion

The shape of the curve for the racemization of 1-phenylbromoethane (curve A, Figure 4) is analagous to that commonly obtained for reactions in nonpolar solvents where the reactant whose concentration is being varied is ionic (see, for example, ref 12). Such a curve with a zero intercept is inconsistent with there being bimolecular and unimolecular processes in competition. (Had SN1 and SN2 racemizations been occurring simultaneously, a result analagous to that shown in Figure 1 would have been expected.) Thus the first of the three possible explanations for the "nonlinearity" with lithium bromide concentration reported by Hughes, *et al.*,<sup>3</sup> can be discarded.

Similarly, the zero intercept for the racemization rate *vs.* the concentration of lithium bromide is inconsistent with the mechanism of Sneen, *et al.*,<sup>9</sup> being the explanation for the nonlinearity. That this second explanation can be discarded is confirmed by the fact that the rate constant of the racemization decreases rather than increases with increasing ionic strength of the solution, an observation inconsistent with an ionization process.

The only one of the three explanations not inconsistent with the empirical observations is the third one, ion-pair formation by the lithium bromide. Analagous conclusions as to the source of apparent non-zero intercepts have been reached by other workers.<sup>2,12,13</sup>

The concentration of dissociated bromide ion will be given by the expression

$$[\text{Br}^-] = \frac{K_{\text{dis}}[\text{LiBr}]}{[\text{Li}^+]}$$

where  $[\text{Br}^-]$  and  $[\text{Li}^+]$  are, respectively, the concentrations of dissociated bromide and lithium ions,  $[\text{LiBr}]$  is the concentration of associated lithium bromide, and  $K_{\text{dis}}$  is the applicable dissociation constant. If a second salt, for example lithium nitrate, is added so that the total concentration of lithium ion (associated plus dissociated) is kept constant as the amount of lithium bromide is varied, the concentration of dissociated lithium ion will remain approximately constant. At the high salt concentrations employed in the weakly ionizing solvent, acetone, a relatively small fraction of the lithium bromide will be dissociated, so that, under the conditions employed at constant total lithium ion concentration, the concentration of dissociated bromide ion should be linearly dependent upon the total amount of lithium bromide present. Consequently, at constant ionic strength a linear correla-

tion between rate of racemization and total concentration of lithium bromide would be anticipated. This is observed and shown as curve B in Figure 4, a further confirmation that the "nonlinear" increase in rate with increasing concentration of lithium bromide observed by Hughes, *et al.*,<sup>3</sup> is caused by association of the salt.

Finally, in conclusion it should perhaps be emphasized that the present study does not disprove the ion pair dissociative mechanism proposed by Sneen and Larsen<sup>9</sup> as an alternative to the Hughes-Ingold SN1-SN2 mechanisms. Rather it has been shown that by far the major source of inconsistency in the earlier results with 1-phenylbromoethane was ion pairing of the ionic reactants. The observed decrease in reaction rate with ionic strength is attributable to a decrease in activity of the bromide ion with increasing concentration of lithium ions. Unfortunately, solubility and dissociation problems precluded the use of other obvious electrolytes to determine whether this is a true salt effect or a cation concentration effect.

### Experimental Section

**Solvent.**—The acetone employed was "Analar" quality solvent (BDH) that was stored for several days over molecular sieves (Davison, Type 4A) and, immediately before preparation of the solutions, was distilled through a short Vigreux column from fresh molecular sieves in oven-dried glassware in a dry nitrogen atmosphere.

**Salts.**—Hydrated lithium nitrate (BDH) was twice recrystallized from anhydrous acetone and dried at room temperature and finally at 200° (0.1 mm) for 36 hr. The salt was stored under dry nitrogen and was reevacuated overnight at 200° immediately before use. Anhydrous, reagent grade (BDH) lithium bromide was dried and stored in an analagous manner. Both salts were off-white, microcrystalline solids.

**(+)- and (-)-1-Phenylbromoethane.**—By the procedure of Downer and Kenyon,<sup>14</sup> 1-phenylethanol (Aldrich) was resolved and the resolved material was converted to (+)- or (-)-1-phenylbromoethane by the procedure of Hughes, *et al.*,<sup>3</sup> with toluene as the solvent. On a 0.05-molar scale, for example, (+)-1-phenylethanol,  $[\alpha]_{\text{D}}^{20} +40^\circ$  (lit. 44.1°), gave after two distillations at 87° (10.5 mm) an 87% yield of (-)-1-phenylbromoethane,  $[\alpha]_{\text{D}}^{20} -12.6$  (lit. 12.8°). Both the (+) and (-) bromides were employed in this study and had molecular rotations of 11.7–12.9°. At high concentrations in CCl<sub>4</sub>, no hydroxylic absorption was observable in the infrared spectra nor were aliphatic protons of the corresponding alcohol detectable by nmr.

**Rate Studies.**—In anhydrous acetone, 0.1000 M stock solutions of LiBr and LiNO<sub>3</sub> were prepared. The appropriate quantity of each solution was pipetted into a 10-ml volumetric flask which was made up to volume with anhydrous acetone if appropriate. After equilibration to the bath temperature, 40.38 ± 0.03° throughout this study, 0.1 ml (0.13–0.14 g, 7.3 × 10<sup>-4</sup> mol) of the optically active 1-phenylbromoethane was added, the solution was shaken and the 10.000-cm jacketed quartz cell (capacity 6.6 ml) of the Perkin-Elmer Model 141 polarimeter was filled. The angle of rotation as a function of time was determined from the Servowriter potentiometric recorder connected to the polarimeter. The initial rotation at the 365-nm wavelength employed was 0.200–0.215° and the infinity value was 0.000 ± 0.003° (owing to instrument zero wandering). Typical results are shown graphically in Figure 3.

**Acknowledgments.**—The author wishes to thank Memorial University of Newfoundland for the financial support that made this research possible and the Department of Chemistry, King's College, University of

(12) P. Beronius, U. Isacson, and A.-M. Nilsson, *Acta Chem. Scand.*, **24**, 189 (1970).

(13) R. W. C. Broadbank, A. H. E. Harhask, and S. Kanchanalai, *Radioisotop. Phys. Sci. Ind. Proc. Conf., Copenhagen, 1960*, **3**, 179 (1962).

(14) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).

London, for the use of their polarimeter and other laboratory facilities for the kinetic measurements. Finally, the author wishes to sincerely thank Martin Grossel at King's College for so generously sharing his limited laboratory and fumehood space, glassware,

solvents, and routine laboratory chemicals and apparatus with a visitor from the "colonies."

Registry No.—(+)-1-Phenylbromoethane, 1459-14-9; (−)-1-phenylbromoethane, 3756-40-9.

## Methyl-Substituted Fluorine-Containing Cyclobutenes. Establishment of the HF Coupling Constants between a Vinylic Methyl Group and the Ring Fluorines<sup>1a</sup>

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Halogen interchange reactions with aluminum chloride on 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene and 1-methyl-2,3,3,4,4-pentafluorocyclobutene have been shown to lead to 1,2-dimethyl-3,3-difluoro-4,4-dichlorocyclobutene (2) and 1-methyl-3,3-difluoro-2,4,4-trichlorocyclobutene (5), respectively. The assignment of the HF coupling constants between the vinylic methyl group and the allylic ring fluorines in the nmr spectra for these materials was aided by compounds produced by alternate synthetic pathways. Thus, 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutene (7), prepared by a thermal codimerization technique, served as the starting material for the synthesis of 1-methyl-2-chloro-3,3-difluorocyclobutene (8) and 1-methyl-3,3-difluoro-4,4-dichlorocyclobutene (9).

Fluorocyclobutenes are known to undergo a facile substitution of the vinylic halide with methyl lithium<sup>2a-c</sup> and methyl Grignard reagents<sup>2d</sup> to yield monomethyl- or dimethylperfluorocyclobutenes. Studies on the chemical reactivity of these materials have been concerned with hydrolysis of the ring fluorines,<sup>2c</sup> the halogenation of the vinylic methyl group,<sup>2b</sup> and elimination reactions which occur in the presence of alkoxide ions.<sup>3</sup> This paper reports on a halogen interchange reaction with aluminum chloride to produce methyl-substituted fluorochlorocyclobutenes and chlorocyclobutenes and the assignment of the HF coupling constants between the vinylic methyl group and the allylic ring fluorines in the nmr spectra.

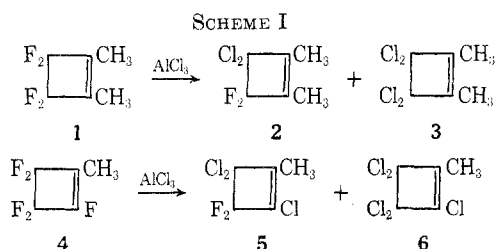
Halogen interchange with aluminum halides has been observed to take place with fluorinated cyclobutenes with particular ease.<sup>4</sup> Application of this convenient technique to 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene led to the characterization of two major products, 1,2-dimethyl-3,3-difluoro-4,4-dichlorocyclobutene (2) and 1,2-dimethyl-3,3,4,4-tetrachlorocyclobutene (3), as indicated in Scheme I. The proton nmr spectrum of 2

consisted of a triplet at  $\tau$  8.29 with a coupling constant  $J = 1.6$  Hz and a triplet at  $\tau$  8.17,  $J = 3.2$  Hz, as indicated in Table I along with the nmr data obtained

TABLE I  
NMR SPECTRA FOR CYCLOBUTENES

Compd	$\phi^*$	$\tau$	Group	Coupling
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{CH}_3$		8.29	$\text{CH}_3$	t, $J = 1.6$ Hz
		8.17	$\text{CH}_3$	t, $J = 3.2$ Hz
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{Cl}$	110.4	8.03	$\text{CH}_3$	t, $J = 3.1$ Hz
			Ring $\text{CF}_2$	q, $J = 3.1$ Hz
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{H}$		7.99	$\text{CH}_3$	d, t, $J = 1.5$ , 3.2 Hz
		4.04	Vinyl H	m, $J = 1.5$ , 2.2 Hz
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{Cl}$	104.6		Ring $\text{CF}_2$	d, q, $J = 2.2$ , 3.2 Hz
		8.09	$\text{CH}_3$	t, t, $J = 3.3$ , 1.3 Hz
$\text{H}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{Cl}$		7.15	Ring $\text{CH}_2$	t, q, $J = 2.7$ , 1.3 Hz
		111.3	Ring $\text{CF}_2$	t, q, $J = 2.7$ , 3.3 Hz
$\text{H}_2 \square \text{Cl}^a$ $\text{F}_2 \square \text{CH}_3$		8.29	$\text{CH}_3$	t, t, $J = 1.6$ , 2.3 Hz
		6.92	Ring $\text{CH}_2$	t, q, $J = 2.7$ , 2.3 Hz
	112.5	Ring $\text{CF}_2$	t, q, $J = 2.7$ , 1.6 Hz	

<sup>a</sup> Data obtained from ref 8. Compound prepared from  $\text{CH}_3\text{Li}$  and 1-chloro-2,3,3-trifluorocyclobutene.



(1) (a) Taken in part from the Ph.D. dissertation of T. S. Croft, University of Colorado, 1967. (b) To whom inquiries should be sent. Address correspondence to Central Research Laboratories, 3M Co., St. Paul, Minn. 55133.

(2) (a) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956); (b) A. T. Blomquist and P. P. Nicholas, *ibid.*, **32**, 863, 866 (1967); (c) A. T. Blomquist and R. A. Vierling, *Tetrahedron Lett.*, 655 (1961); (d) J. D. Park and R. Fontanelli, *J. Org. Chem.*, **28**, 258 (1963).

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for all of the methyl-substituted fluorocyclobutenes discussed in this report. Since the cross ring allylic fluorines would be expected to deshield the vinylic methyl protons more than do adjacent fluorines,<sup>5</sup> this resonance should occur at a lower field position and the coupling constant for the vinylic methyl protons coupled with cross ring allylic fluorines must be 3.2 Hz, thus

(5) (a) Unpublished results, this laboratory: J. H. Adams, Ph.D. Dissertation, University of Colorado, 1965; (b) J. D. Park, J. R. Dick, and J. H. Adams, *J. Org. Chem.*, **30**, 400 (1965); (c) J. D. Park, G. Groppelli, and J. H. Adams, *Tetrahedron Lett.*, 103 (1967).