

**Test of Precision.**—In order to test the precision attainable, five separate determinations were made for toluene. These yielded values for Henry's law constant at  $-78.51^\circ$  of 298, 299, 299, 300, 299 mm. Representative data for four of these determinations are illustrated in Fig. 8. It was therefore concluded that the Henry's law constant could be obtained with a precision of 1 part in 300. Although refinements in technique might have improved the precision, we found it ample to distinguish between the different compounds whose basicities were of interest.

**Materials.**—The trimethyl- and tetramethylbenzenes were generously supplied by Professor Lee Irvin Smith of the University of Minnesota. The remaining compounds were commercial products, the purest available. Depending upon the quantity available, the compounds were distilled either through a Todd Micro Column (rated efficiency: 50 theoretical plates) or a helices packed column (rated

efficiency: 75 theoretical plates). Only materials which boiled constantly and exhibited constant refractive indices were utilized. The bromobenzene was a Bureau of Standards sample for styrene determinations by the freezing point method and was used without further purification. Physical data for these compounds are summarized in Table X.

**Acknowledgment.**—We wish to acknowledge our indebtedness to the Standard Oil Company (Indiana) for financial support of this investigation and to Professor L. I. Smith for his generous samples of the higher methylbenzenes. We are also indebted to Mr. Lionel Domash and Miss Martha Havill for assistance in calculating the dissociation constants for the aromatic-hydrogen chloride complexes.

LAFAYETTE, INDIANA

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

## The Thermal Racemization of Dimethyl (–)-Bromosuccinate

BY LAWRENCE J. ANDREWS AND JAMES E. HARDWICKE

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Contrary to a previous report it has been found that no extensive racemization occurs when optically active bromosuccinic acid is converted to its dimethyl ester with diazomethane. The ester does, however, lose activity when subjected to repeated distillation under reduced pressure. To demonstrate the sensitivity of this ester to thermal racemization a series of kinetic measurements of the rate of loss of optical activity of this compound at several temperatures has been made. Kinetic measurements of the dehydrobromination reaction, which occurs simultaneously with racemization, have also been made. Similar kinetic studies have also been carried out using optically active methyl esters of  $\alpha$ - and  $\beta$ -bromobutyric acids. The results are of interest as regards the mechanisms of the racemization and dehydrobromination reactions.

It is known that certain esters of optically active bromosuccinic acid undergo slow autoracemization at room temperature.<sup>1</sup> It has also been demonstrated that in acetone solution dimethyl (–)-bromosuccinate can be racemized in the temperature range of 0 to  $52^\circ$  by the addition of inorganic bromides.<sup>2</sup> However, little is known concerning the thermal racemization of pure esters of this type.

Interest in this problem has arisen as an outgrowth of attempts to check the report<sup>3</sup> that a racemic ester is formed when (–)-bromosuccinic acid is treated with diazomethane. All samples of dimethyl bromosuccinate which have been prepared by this method in this Laboratory have retained a high degree of optical activity comparable to that of samples prepared by esterification with methanol in the presence of anhydrous hydrogen chloride. It has, however, been noted that the optical rotation of the ester diminishes appreciably as the material is subjected to repeated distillation.

A series of measurements of the kinetics of racemization and dehydrobromination of dimethyl (–)-bromosuccinate at temperatures in the vicinity of  $100^\circ$  has been made to establish that the racemizations resulting from distillation of the ester are thermally induced. In addition similar studies have been made with the methyl esters of optically active  $\alpha$ - and  $\beta$ -bromobutyric acid. These results

are of interest in connection with a discussion of possible mechanisms for the racemizations.

**The Kinetic Measurements.**—In the course of preliminary measurements it was noted that a precipitate was formed in samples of the dimethyl bromosuccinate which had been heated for long periods of time. This precipitate, m.p.  $100$ – $101^\circ$ , was readily identified by mixed melting point determination as dimethyl fumarate. Walden<sup>1</sup> also recognized that this ester showed a tendency to form dimethyl fumarate on distillation, and Olson and Long<sup>4</sup> have observed in studying the halide ion catalyzed racemization of (–)-bromosuccinic acid the simultaneous occurrence of a dehydrobromination reaction.

To study the racemization rates two series of measurements were made at each temperature investigated. In the first series the loss in optical activity of samples of the pure bromoester as a function of the heating time was determined. In a second set of measurements weighed samples of the ester were heated over various time intervals and were then analyzed for hydrogen bromide.

The following reactions have been considered in deriving a rate law for the interpretation of the data taken in following the loss of optical activity of the bromoester



(1) P. Walden, *Ber.*, **31**, 1416 (1898).

(2) (a) T. Wagner-Jauregg, *Monatsh.*, **53**, 791 (1929); (b) R. Kuhn and T. Wagner-Jauregg, *Naturwiss.*, **17**, 103 (1929); (c) E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937); (d) A. R. Olson, I. D. Frasier and F. J. Spieth, *J. Phys. & Colloid. Chem.*, **55**, 860 (1951).

(3) E. Bergmann and Y. Spruzak, *THIS JOURNAL*, **60**, 1998 (1938).

(4) A. R. Olson and F. A. Long, *ibid.*, **56**, 1294 (1934).

where  $l$  and  $d$  represent the enantiomeric forms of the bromoester,  $U$  is the ester dehydrobromination product and  $k_1 = k_2$ .

If the observed losses in optical activity result only from reactions (1)–(3), the rates of disappearance of the  $l$ - and  $d$ -isomers and of appearance of unsaturate are given by equations (4)–(6).

$$-d(l)/dt = k_1(l) - k_1(d) + k_3(l) \quad (4)$$

$$-d(d)/dt = k_1(d) - k_1(l) + k_3(d) \quad (5)$$

$$d(U)/dt = k_3[l + (d)] \quad (6)$$

The optical rotation of the heated samples at any time  $t$  is given by equation (7) in which the subscripts refer to times  $t$  and zero and  $C$  is a constant.

$$\alpha_t = C[(l)_t - (d)_t] = C[-2(d)_t + (d)_0 + (l)_0 - (U)_t] \quad (7)$$

Using equations (4)–(7) it can be shown that

$$-\frac{d\alpha}{dt} = C \left[ \frac{2d(d)}{dt} + \frac{d(U)}{dt} \right] = \alpha [2k_1 + k_3] \quad (8)$$

or that

$$2k_1 + k_3 = \frac{2.303}{t} \log \frac{\alpha_0}{\alpha_t} = k_{\text{obsd}} \quad (9)$$

where  $k_{\text{obsd}}$  is the rate constant calculated from the observed changes in rotation.

The constant  $k_3$  can be determined from the dehydrobromination rate measurements using the rate law

$$k_3 = \frac{2.303}{t} \log \frac{a}{a-x} \quad (10)$$

where  $a$  represents the number of moles of bromoester at zero time and  $x$  represents the moles of hydrogen bromide at time  $t$ .

The data were interpreted using equations (9) and (10) on the assumption that the volume of the samples did not change during the course of the reaction. A similar interpretation was applied to the results obtained in studies of the rates of loss of optical activity and of dehydrobromination of methyl (+)- $\beta$ -bromobutyrate. Typical data for individual runs are given in Tables I and II, and the rate constants are summarized in Table III.

TABLE I

THE RATES OF LOSS OF OPTICAL ACTIVITY OF DIMETHYL (-)-BROMOSUCCINATE AND METHYL (+)- $\beta$ -BROMOBUTYRATE AT 130.7°

Time, min.	$\alpha^a$	$k_{\text{obsd}} \times 10^4$ , min. <sup>-1</sup>
Bromosuccinate		
0	-31.8°	...
120	-20.2	37.5
250	-14.5	31.3
392	-7.02	38.5
486	-6.40	33.0
	Av.	35.1
$\beta$ -Bromobutyrate		
0	+11.1°	...
149	10.2	5.84
282	9.52	5.36
356	9.03	5.72
402	8.65	6.14
1370	5.09	5.67
	Av.	5.75

<sup>a</sup> Observed rotation in 0.5-dm. tube based on the average of several readings.

TABLE II  
THE RATES OF DEHYDROBROMINATION OF THE ESTERS AT 130.7°

Time, min.	Bromoester, millimoles	HBr, millimole	$k_1 \times 10^4$ , min. <sup>-1</sup>
Bromosuccinate			
476	0.676	0.066	21.5
1290	.548	.143	23.4
2740	.861	.445	26.6
4490	.682	.397	19.4
		Av.	22.7
$\beta$ -Bromobutyrate			
653	1.093	0.145	21.8
1422	1.672	.427	20.7
2133	1.294	.509	23.4
3582	1.085	.574	21.0
5372	1.323	.901	21.3
		Av.	21.6

TABLE III

SUMMARY OF RATE CONSTANTS FOR LOSS OF ACTIVITY AND DEHYDROBROMINATION OF THE BROMOESTERS

Temp., °C.	$k_{\text{obsd}} \times 10^4$ , min. <sup>-1</sup>	$k_3 \times 10^5$ , min. <sup>-1</sup>	$k_1 \times 10^4$ , min. <sup>-1</sup>
Bromosuccinate			
100.0	4.09	2.03	1.94
110.0	7.61	4.63	3.57
130.7	35.1	22.7	16.4
Bromobutyrate			
110.0	0.79	2.72	0.26
130.7	5.75	21.6	1.79
140.0	12.6	38.8	4.36

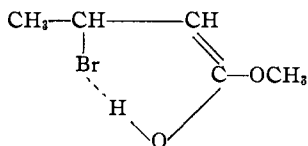
To check on the nature of the dehydrobromination product of methyl  $\beta$ -bromobutyrate, which was presumed to be methyl crotonate, fifteen grams of the bromoester was heated at atmospheric pressure for 17 hours at 160–180°. During this time only about 10% of the theoretical quantity of hydrogen bromide was evolved, and only small amounts of low boiling ester could be isolated by distillation of the heated material. However, an appreciable quantity of crotonic acid precipitated from the cooled high boiling residue. It seems likely that the methyl crotonate produced by the dehydrobromination reaction was subject to attack by the evolved hydrogen bromide to form crotonic acid and methyl bromide.

In the kinetic studies on the dehydrobromination reactions the rates were followed by titrating the contents of the reaction tubes for acidic substances. Therefore the occurrence of an ester cleavage reaction, producing crotonic acid at the expense of hydrogen bromide, should not affect the accuracy of the dehydrobromination rate constants reported for methyl  $\beta$ -bromobutyrate. It is noteworthy that no solid substances were observed to precipitate from the cooled methyl  $\beta$ -bromobutyrate rate samples.

Relatively few rate samples were run at any individual temperature because of the labor involved in preparing the active esters in large quantity. All reactions, however, were followed to better than 50% completion. Some difficulty was encountered in making these measurements because of darkening of individual rate samples and because, in the case



The rate determining step in this sequence is pictured as the formation of a carbonium ion from the enol form of the ester. The resultant carbonium ion could then recapture bromide ion or lose a proton to form, respectively, either of the enantiomeric forms of the bromoester or the unsaturated ester. It should also be noted that this cation might yield crotonic acid by reaction with bromide ion. The activated complex in the slow step of the reaction might be so constituted that the enolic hydrogen would assist in the rupture of the carbon-bromine bond by a process comparable to hydrogen bond formation as indicated below.



Evidence for the existence of the O-H-Br bond has been obtained in studies of *o*-bromophenol.<sup>8</sup> This cyclic structure for the activated complex is in accord with the frequency factors observed for these reactions. A similar process could be written to account for the reactions of the bromosuccinate. The thermodynamic data for the bromobutyrate, at least, do not contradict the supposition that both the racemization and dehydromination reactions proceed through the same activated complex. It is entirely possible that the two reactions of the bromosuccinate also proceed through a common activated complex since the differences in the reported activation energies may result entirely from experimental error.

### Experimental

**(-)-Bromosuccinic Acid.**—This was prepared from L-(+)-aspartic acid according to the method of Holmberg.<sup>9</sup> The product had the following properties: m.p. 170–171°;  $[\alpha]^{25D} -39.6^\circ$  (0.184 g./cc. in water); neut. equiv. calcd., 98.5; found, 98.6.

**The Reaction of (-)-Bromosuccinic Acid with Diazomethane.**—To 7 g. of (-)-bromosuccinic acid was added excess diazomethane (prepared from nitrosomethylurea) in ether at 0°. The resultant solution was allowed to stand for 30 minutes and was then concentrated on the steam-bath at reduced pressure. The residual yellow oil ( $[\alpha]^{25D} -62.2^\circ$ ) was distilled under reduced pressure. The 6.6 g. of dimethyl (-)-bromosuccinate thus obtained had the following properties: b.p. 108–110° (10 mm.);  $[\alpha]^{25D} -55.8^\circ$ ;  $d^{20}_4$  1.501;  $n^{20D}$  1.4610; calcd. Br, 35.5; found Br, 35.2. After a second distillation (103–104° at 7 mm.) the ester showed a specific rotation  $[\alpha]^{25D} -48.6^\circ$ .

A sample of the ester prepared by reversing the order of mixing of reactants in a procedure similar to that used by Bergmann and Sprinzak<sup>3</sup> was still highly optically active. This ester sample (b.p. 103–108° at 7 mm.) gave  $[\alpha]^{25D} -54.1$  and Br, 35.3. These procedures were used several times to prepare small samples of the ester. The lowest specific rotation recorded for these samples was  $[\alpha]^{25D} -39.1^\circ$ .

**Esterification of (-)-Bromosuccinic Acid with Methanol.**—A solution of 43 g. of the acid in 200 ml. of methanol was cooled to 0° and saturated with anhydrous hydrogen chloride. The resultant solution was kept at refrigerator temperature for two days and was then concentrated under reduced pressure at 30°. The residue was washed with sodium bicarbonate and water, dried over calcium sulfate and

distilled to yield 27.8 g. of ester (b.p. 103–106° at 7 mm.) of  $[\alpha]^{25D} 63.2^\circ$ . Samples of ester prepared in this manner lost optical activity when subjected to redistillation in much the same manner as was observed with samples prepared by the diazomethane procedure.

One sample of the ester,  $[\alpha]^{25D} -65.6^\circ$ , was dissolved in an ether solution of diazomethane. After this solution had stood for four hours in the refrigerator, it was concentrated on the steam-bath at reduced pressure. The undistilled residue gave  $[\alpha]^{25D} -63.4^\circ$ . Therefore the ester is not appreciably racemized by contact with diazomethane.

**Dimethyl (-)-Chlorosuccinate.**—(-)-Chlorosuccinic acid was prepared from L-(+)-aspartic acid by the method of Holmberg.<sup>9</sup> The product gave m.p. 175–176° and  $[\alpha]^{25D} -20.9^\circ$  (0.0614 g./cc. in water). A solution of 5.3 g. of the acid in 20 ml. of ether and 15 ml. of methanol was cooled to 5° and treated with excess diazomethane in ether. After several hours the resultant solution was concentrated and the residual oil was distilled. The 4.2 g. of product had the following properties: b.p. 99–100° (11 mm.);  $[\alpha]^{25D} -42.3^\circ$ ; calcd. Cl, 19.64; found Cl, 19.55.

**Methyl (+)- $\alpha$ -Bromobutyrate.**—Racemic  $\alpha$ -bromobutyric acid was prepared by the procedure of Fischer and Mouneyrat<sup>10</sup> and was resolved by methods described previously.<sup>11</sup> After two resolutions the acid (b.p. 90–93° at 10 mm.) gave  $\alpha^{25D} +8.83^\circ$  (0.5-dm. tube). The acid was esterified using the diazomethane procedure described for preparation of dimethyl (-)-bromosuccinate. The product had the following properties: b.p. 48–51° (15 mm.);  $n^{27D}$  1.4497;  $d^{25}_4$  1.4022;  $[\alpha]^{25D} +13.5^\circ$ ; calcd. Br, 44.2; found, Br, 44.3.

**Methyl (+)- $\beta$ -Bromobutyrate.**— $\beta$ -Bromobutyric acid was prepared and resolved according to the directions of Olson and Miller.<sup>12</sup> The crude product,  $\alpha^{25D} +17.3$  (0.5-dm. tube), was esterified with diazomethane in ether solution. The resulting methyl (+)- $\beta$ -bromobutyrate had the following properties: b.p. 71° (15 mm.);  $[\alpha]^{25D} +10.85^\circ$ ;  $n^{25D}$  1.4524;  $d^{27}_4$  1.3858; calcd. Br, 44.15; found Br, 44.10.

**The Thermal Decomposition of Methyl  $\beta$ -Bromobutyrate.**—For this study a sample of the inactive ester (b.p. 111–113° (93 mm.),  $n^{25D}$  1.4520) prepared from  $\beta$ -bromobutyric acid and methanol using anhydrous hydrogen bromide as a catalyst, was employed. The procedure was closely similar to that used in the methylation of bromosuccinic acid. Fifteen grams (0.083 mole) of methyl  $\beta$ -bromobutyrate was heated at 160–180° on an oil-bath for 17 hours. Evolved gases were trapped in a known volume of standard sodium hydroxide. Analysis of the trap contents indicated that only about 10% of the theoretical quantity of hydrogen bromide was evolved.

The heated sample was subjected to distillation at atmospheric pressure. A small low boiling fraction weighing 0.37 g. was collected from 120–155°. This material had a characteristic ester-like odor and gave  $n^{25D}$  1.4330. It absorbed bromine from carbon tetrachloride solution and was water insoluble. This material was undoubtedly methyl crotonate.

From the cooled residue in the distilling flask a large quantity of crystalline material precipitated. The crystals were filtered (weight 2.2 g.) and recrystallized from Skellysolve C. The recrystallized material was identified as crotonic acid in terms of its melting point, 68–70°, and mixed melting point, 69–71°, with an authentic sample. The isolated crotonic acid gave a neut. equiv. of 85.7; theoretical for  $C_5H_7COOH$ , 86.1.

The possibility that hydrogen bromide liberated in the thermal decomposition of the bromoester might have cleaved some of the unreacted material to form  $\beta$ -bromobutyric acid was considered. Any attempt to separate small amounts of this acid from the mixture of crotonic acid and methyl  $\beta$ -bromobutyrate seemed futile. It is significant that the unpleasant odor of the bromoacid could not be detected in the reaction product. Also it should be noted that no further hydrogen bromide elimination occurred after nine hours of heating the bromoester, whereas crotonic acid precipitation was not observed until after a 17-hour heating period. These facts suggest that once methyl crotonate develops to an appreciable amount in the reaction mixture, the liberated hydrogen bromide is consumed to form crotonic acid.

(10) E. Fischer and A. Mouneyrat, *ibid.*, **33**, 2387 (1900).

(8) O. R. Wulf, U. Liddel and S. B. Hendricks, *THIS JOURNAL*, **58**, 2289 (1936).

(9) B. Holmberg, *Ber.*, **60**, 2194 (1927).

(11) (a) P. A. Levene, T. Mori and L. A. Mikeska, *J. Biol. Chem.*, **75**, 342 (1927); (b) P. A. Levene and M. Kuna, *ibid.*, **141**, 391 (1941).

(12) A. R. Olson and R. J. Miller, *THIS JOURNAL*, **60**, 2687 (1938).

A consideration of the mechanism of the ester cleavage reaction suggests that methyl crotonate would be much more susceptible than methyl  $\beta$ -bromobutyrate to reaction with hydrogen bromide.

**The Kinetic Studies.**—For the optical rotation studies samples of the pure bromoesters were sealed in small Pyrex glass tubes. The tubes had previously been exposed for 24 hours to hot concentrated nitric acid, washed with distilled water, dried and stored in a desiccator over phosphorus pentoxide. The rate samples were immersed in the vapor of a refluxing liquid of appropriate boiling point. Substances such as water, toluene, chlorobenzene and *n*-butyl ether were used. The tubes were removed from time to time, quenched in ice water and opened. The optical rotations of the contents were determined using a 0.5-dm. micropolarimeter tube. Samples were ordinarily allowed to equilibrate to bath temperature for one hour before the first sample was withdrawn. The optical rotation of this sample was used as  $\alpha_0$  in the calculation of rate constants,  $k_{\text{obsd}}$ , reported in Table I.

To follow the kinetics of dehydrobromination weighed samples of the bromoesters were heated in the Pyrex tubes as described above. Tubes removed for analysis were broken in a beaker of ice-water, and the contents of the

beaker were titrated with 0.1 *N* sodium hydroxide to the phenolphthalein end-point using a microburet.

The reaction tubes were again allowed to equilibrate to bath temperature for at least one hour before withdrawal of the first sample. The time of withdrawal of this sample was chosen as zero time in calculating rate constants. Analyses of samples withdrawn subsequently were corrected on the assumption that all samples underwent the same per cent. dehydrobromination during the equilibration period.

To establish that unreacted bromoester did not consume standard base under the conditions of the titration approximately 0.2 g. of the pure esters were treated with cold aqueous hydrochloric acid in amounts approximating the hydrogen bromide content of some of the rate samples. By titration with sodium hydroxide the added hydrochloric acid could be accounted for with an accuracy of  $\pm 0.5\%$ .

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DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## Rearrangement of 2-Methylbutane-1-C<sup>14</sup> over Aluminum Bromide<sup>1,2</sup>

BY JOHN D. ROBERTS AND GEORGE R. CORAOR

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Liquid-phase rearrangement of 2-methylbutane-1-C<sup>14</sup> at room temperature over water-promoted aluminum bromide appears to yield 2-methylbutane-4-C<sup>14</sup> considerably more rapidly than 2-methylbutane-2(or 3)-C<sup>14</sup>. Very extensive rearrangement of C<sup>14</sup> was observed in the conversion of 2-methylbutane-1-C<sup>14</sup> to *t*-amyl bromide by treatment with *t*-butyl bromide and aluminum bromide even with a contact time of about 0.005 sec. Photochemical vapor-phase halogenations of isopentane were found to give essentially pure *t*-amyl bromide with bromine and a serious mixture of products with chlorine.

In an earlier investigation,<sup>3</sup> isotope-position rearrangements of C<sup>14</sup>-labeled *t*-amyl and *t*-butyl chlorides over aluminum chloride were found to proceed as would be expected on the basis of the carbonium ion theory of molecular rearrangements. The pattern of results was quite unlike that obtained in the isomerization of C<sup>13</sup>-labeled butanes over water-promoted aluminum bromide<sup>4</sup> and it seemed possible that the discrepancy was due to differences in: (1) the behavior of halides and hydrocarbons; (2) the natures of the catalysts; (3) four- and five-carbon systems; or (4) liquid- and vapor-phase operations. The last possibility seemed very likely since, if hydrocarbon isomerizations involve carbonium ion chain mechanisms,<sup>5</sup> a given cation, at the surface of a solid catalyst, would have a far better chance in a vapor-phase than a liquid-phase system to undergo several isotope position rearrangements before encountering a hydrocarbon molecule and being converted to isomerized hydrocarbon and a new cation in the very rapid exchange reaction demonstrated by Bartlett,

Condon and Schneider.<sup>6</sup> The purpose of the present research was to study the isomerization of 2-methylbutane-1-C<sup>14</sup> over water-promoted aluminum bromide in liquid and vapor phases. The work has had to be indefinitely suspended and we report at this time some interesting preliminary experiments on liquid-phase systems.

2-Methylbutane-1-C<sup>14</sup> (I) was synthesized from 2-methyl-2-butanol-1-C<sup>14</sup> by dehydration and hydrogenation. Treatment with permanganate was employed to remove the last traces of olefin. Location of the tracer atoms in I required a route to *t*-amyl halides or trimethylethylene, either of which could be further degraded as described previously.<sup>3</sup> The aluminum bromide-catalyzed halogen-hydrogen exchange between *t*-butyl halides and isopentane to yield *t*-amyl bromide seemed well suited for the purpose since the reaction appears to be clean and fast.<sup>6</sup> However, when this type of exchange was carried out with I using a contact time of 0.2 sec. it was found that complete isotopic equilibrium was established between C-1 and C-4 of the *t*-amyl bromide (*cf.* Table I). Even with a contact time as short as 0.005 sec., the C<sup>14</sup> was completely equilibrated between C-1 and C-4 and a total degradation showed some radioactivity at C-2 and C-3. The speed of these reactions compared with the rearrangements of labeled *t*-amyl chloride over aluminum chloride is probably partly due to

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(2) Presented at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

(3) J. D. Roberts, R. E. McMahon and J. S. Hine, *THIS JOURNAL*, **71**, 1896 (1949); **72**, 4237 (1950).

(4) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *J. Chem. Phys.*, **16**, 745 (1948).

(5) H. S. Bloch, H. Pines and L. Schmerlug, *THIS JOURNAL*, **68**, 153 (1946).

(6) P. D. Bartlett, P. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).