on a Consolidated Model 21-103C instrument. Isotopic compositions of the propyl benzoates were derived from low-voltage measurements on the molecular ions.[21]

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(21) D. P. Stevenson and C. D. Wagner, *J. Amer. Chem. Soc.*, **72**, 5612 (1950).

Acknowledgment. We thank the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for generous support of the research carried out at Michigan State University.

Carbonium Ions. XII. Reaction Paths in the Isomerization of Bromopropanes with Aluminum Bromide[1a]

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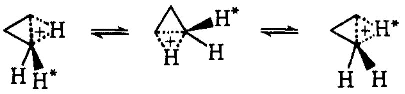
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan, and the Research and Development Department, American Oil Company, Whiting, Indiana. *Received August 26, 1968*

Abstract: The reactions of 1-bromopropane-1,1-d_2, -2,2-d_2, and -1-^{13}C with aluminum bromide, in 6:1 mol:mol ratios, at 0° for 5–6 min, yield mixtures of 1-bromopropane and 2-bromopropane. The recovered 1-bromopropanes show extensive hydrogen–hydrogen and carbon–carbon scrambling. The 2-bromopropanes are mainly isotope-position unrearranged, *i.e.*, they have arisen primarily from a nominally irreversible 1,2-hydride shift. The paths producing isotope-position rearranged 1-bromopropanes are shown to be reversible 1,2-hydride shifts and protonated cyclopropane intermediates. The results, however, do not firmly rule out 1,2-methyl shifts as an alternative to protonated cyclopropanes. Bimolecular reactions, elimination–addition reactions, and intermolecular hydride transfers do not occur under such reaction conditions. At longer reaction times, when the concentration of 2-bromopropane is large, intermolecular hydride transfers do occur. They were detected by the formation of propane and by isotopic analysis of the products. The rearrangement of 2-bromopropane to 1-bromopropane occurs by two paths—an intramolecular 1,2-hydride shift, which is the major path, and an intermolecular hydride transfer.

The question of the intermediacy of protonated cyclopropanes in carbonium ion reactions has recently received a good deal of attention, both theoretical[2] and experimental.[3] Up to now, however, most of the experimental evidence for the intervention of such species by the "σ route" has been restricted to reactions of a somewhat esoteric nature, such as amine deaminations,[3a] alcohol deoxidations,[4] or treatment of substrate with highly acidic media.[5] It is somewhat difficult to relate and extrapolate these findings to reactions more commonly encountered in organic chemistry, either because of the nature of the intermediate carbonium ions (vibrationally excited) in these reactions,[3a,4] or because of the nature of the reaction environment.[5] Because of this, we chose to study the propyl system under more common conditions, in order to ascertain whether protonated cyclopropanes intervene in these reactions. If so, we hoped to test the mechanism suggested[3a] for carbon–carbon and hydrogen–hydrogen scrambling (eq 1), *i.e.*, that a single process is responsible for both scramblings, and to ascertain whether or not the methyl-bridged ion I can be included at least as an intermediate preceding the formation of the edge-protonated cyclopropane.



(1)

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We report here our results and conclusions from the reactions of bromopropanes with aluminum bromide, and from the solvolysis of 1-propyl tosylate in aqueous 99% formic acid. As an adjunct to these reactions, we report also the results from the solvolysis of bromopropanes in water.

Results

I. Reaction of Aluminum Bromide with Unlabeled Bromopropanes. When either 1-bromopropane or 2-bromopropane was treated with aluminum bromide (5.8:1 molar ratio of bromopropane to aluminum bromide) at 0°, an equilibrium mixture was obtained that consisted of 6 ± 0.5% 1-bromopropane and 94 ± 0.5% 2-bromopropane.[6] The equilibrium was attained within 10–12 min when approached from the side of 1-bromopropane and within 6–7 min when approached from the side of 2-bromopropane. When the reaction of

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(1) (a) Part of this work was published as a preliminary communication: G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, **38**, 3735 (1967); (b) Research and Development Department, American Oil Company, Whiting, Ind.

(2) (a) J. D. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, **90**, 3338 (1968); (b) R. H. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (c) S. Ehrenson, *J. Amer. Chem. Soc.*, **86**, 847 (1964).

(3) For a discussion with leading references see (a) G. J. Karabatsos, C. E. Orzech, Jr., J. L. Fry, and S. Meyerson, *ibid.*, **92**, 606 (1970), and (b) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968).

(4) P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); *ibid.*, **82**, 2971 (1960); however, see also *ibid.*, **84**, 3962 (1962).

(5) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

(6) The equilibration of the two bromopropanes by the action of aluminum bromide on the neat liquid has been reported by W. Gerrard, H. R. Hudson, and W. S. Murphy, *J. Chem. Soc.*, 2314 (1964). For a review see W. Gerrard and H. R. Hudson, *Chem. Rev.*, **65**, 697 (1965).

Table I. Label Distributions[a] in the Trimethylsilyl Ethers of Labeled Propanols

No.	Compound	Parent less-methyl, % d_2	d_1	d_0	Parent less-ethyl, % d_2	d_1	d_0
A	$CH_3CH_2CD_2OSi(CH_3)_3$[b]	99.0	1.0	0.0	98.3	1.6	0.1
B	$CH_3CH_2CD_2OSi(CH_3)_3$[c]	99.0	1.0	0.0	98.2	1.6	0.2
C	$CH_3CD_2CH_2OSi(CH_3)_3$[d]	96.7	2.3	0.0	0.4	0.2	99.4
D	$CH_3CD_2CH_2OSi(CH_3)_3$[e]	98.4	1.6	0.0	0.6	0.3	99.1
E	$CH_3CH_2{}^{13}CH_2OSi(CH_3)_3$[f]	28.8(^{13}C, 71.2(^{12}C)			28.8(^{13}C), 71.2(^{12}C)		
F	$CH_3CH_2{}^{13}CH_2OSi(CH_3)_3$[g]	54.9(^{13}C), 45.1(^{12}C)			54.6(^{13}C), 45.4(^{12}C)		
G	$(CH_3)_2CDOSi(CH_3)_3$[h]	0.0	99.8	0.2			
H	$(CD_3)_2CHOSi(CH_3)_3$[i]	72.0 d_6, 2.6 d_5, 0.2 d_4, 25.2 d_3					

[a] Calculated from 70-V mass spectra. [b,c] Derivatives of 1-propanol samples prepared by reduction of propionic anhydride with lithium aluminum deuteride. [d,e] Derivatives of 1-propanols prepared by reduction of two samples of different isotopic enrichment of propionic-2,2-d_2 acid. [f,g] Derivatives of 1-propanols prepared by reduction of two samples of different isotopic enrichment of propionic-1-^{13}C acid. [h] Derivative of 2-propanol prepared by reduction of acetone with lithium aluminum deuteride. [i] Derivative of 2-propanol prepared by reduction of acetone-d_6 with lithium aluminum hydride.

Table II. Label Distributions[a] in the Trimethylsilyl Ethers of Propanols[b] Prepared by Hydrolysis of the Corresponding Bromides

No.	Compound	Parent less-methyl, % d_2	d_1	d_0	Parent less-ethyl, % d_2	d_1	d_0
A	$CH_3CH_2CD_2OSi(CH_3)_3$[c]	98.9	1.1	0.0	98.0	1.8	0.2
A	$CH_3CH_2CD_2OSi(CH_3)_3$[d]	98.9	1.1	0.0	98.1	1.7	0.2
D	$CH_3CD_2CH_2OSi(CH_3)_3$[c]	98.4	1.6	0.0	0.3	0.2	99.5
D	$CH_3CD_2CH_2OSi(CH_3)_3$[d]	98.4	1.6	0.0	0.2	0.3	99.5
G	$(CH_3)_2CDOSi(CH_3)_3$[c]		99.5	0.5			

[a] Calculated from 70-V mass spectra. [b] The alcohols identified as A, D, and G are the hydrolysis products from the bromides that had been prepared from alcohols A, D, and G (Table I) by treatment with phosphorous tribromide. [c] Alcohol was obtained by hydrolysis of corresponding bromide with 15% aqueous silver nitrate solution at room temperature. [d] Alcohol was obtained by hydrolysis of corresponding bromide in hot 10% aqueous sodium hydroxide solution.

1-bromopropane with aluminum bromide was stopped at 5 or 6 min by quenching it with quinoline, the recovered bromopropanes accounted for 94–100% of the starting material. No other volatile compounds were detected by gas chromatographic analysis. Continued rapid stirring of the homogeneous, equilibrated mixture for 1–2 hr resulted in the evolution of hydrogen bromide and other gaseous material. The recovered bromopropanes, after a 2-hr reaction, accounted for 84% of the starting material. The remaining 16% was nonvolatile, resinous material of indeterminate composition and the gaseous material. The gas was trapped by passing it through chilled carbon tetrachloride or benzene. Nmr analysis of the resulting solutions revealed that the gas consisted of 2-bromopropane and propane.[7] We were unable to detect any propene or cyclopropane. Gas chromatographic analysis of the crude reaction mixture failed to establish the presence of any dibromopropane or any other volatile compounds, except propane.

II. Preparation of Labeled Bromopropanes. Labeled bromopropanes were prepared by treatment of appropriate alcohols with phosphorous tribromide. To make sure that no isotope-position rearrangement occurred during their preparation, the bromopropanes were converted back to the alcohols by treatment either with 15% aqueous silver nitrate solution at room temperature, or with hot 10% aqueous sodium hydroxide. The precursor and product alcohols were then converted to the trimethylsilyl ether derivatives for mass spectral analysis. In Tables I and II are summarized the label distributions in the parent less-methyl and parent-less-ethyl ions of the precursor and product alcohols, respectively (for a discussion of the fragmentation patterns see ref 3a). The good correspondence between label distributions in the precursor and product alcohols (A, D, and G) leads to the conclusion that no isotope-position rearrangement occurred either during the preparation of the bromopropanes or during the hydrolysis back to the alcohols. We could, thus, assess the isotopic composition of the bromopropanes both before and after reaction with aluminum bromide by converting them to the corresponding alcohols and analyzing the mass spectra of their trimethylsilyl ether derivatives.

III. Reactions of Labeled 1-Bromopropanes with Aluminum Bromide. Labeled 1-bromopropanes were treated with aluminum bromide, at 0°, to yield varying amounts of 2-bromopropane. The results are summarized in Table III. The presence of a small amount of diethyl ether in the 1-bromopropane sample used in run 1 resulted in only 14% conversion of 1-bromopropane to 2-bromopropane. The conversion of 1-bromopropane-2,2-d_2 to 2-bromopropane is slower than that of any of the other samples (compare runs 6 and 7 with any other run for the same period of time and same molar ratio of 1-bromopropane and aluminum bromide).

The recovered 1-bromopropane and 2-bromopropane products were converted to the corresponding alcohols for mass spectral analysis of the trimethylsilyl ether derivatives of the alcohols. The results are summarized in Tables IV and V. The excellent correspondence between label distributions in the parent less-methyl ions of the derivatives of the recovered and starting 1-bromopropanes (compare, for example, runs 1–4 of Table IV

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[7] For an early report of the formation of propane from the reaction of 1-iodopropane with aluminum chloride see B. Köhnlein, *Chem. Ber.*, **16**, 560 (1883).

Table III. Isomerization of 1-Bromopropanes with Aluminum Bromide at 0°

Run	Precursor[a] alcohol	1-BrPr	1-BrPr:$AlBr_3$ (mol:mol)	Run time,[b] min	% BrPr[c] recovered	% 1-BrPr,[d] ±2%	% 2-BrPr,[d] ±2%
1	A	$CH_3CH_2CD_2Br$	10.1:1[e]	6.0	97	86	14
2	B	$CH_3CH_2CD_2Br$	10.5:1	6.0	95	55	45
3	B	$CH_3CH_2CD_2Br$	5.6:1	5.0	93	21	79
4	A	$CH_3CH_2CD_2Br$	5.6:1[e]	6.0	100	20	80
5	B	$CH_3CH_2CD_2Br$	5.6:1	120.0	84	6	94
6	C	$CH_3CD_2CH_2Br$	5.7:1	5.0	78	42	58
7	C	$CH_3CD_2CH_2Br$	5.7:1	6.0	94	35	65
8	E	$CH_3CH_2{}^{13}CH_2Br$	5.7:1	4.7	94	15	85
9	F	$CH_3CH_2{}^{13}CH_2Br$	5.7:1	5.0	100	20	80
10	F	$CH_3CH_2{}^{13}CH_2Br$	6.5:1	180.0	81	4.6 ± 1	95.4 ± 1

[a] For identification of alcohol see Table I. [b] Quenched with quinoline. [c] Sum of 1-bromopropane and 2-bromopropane. [d] By gc analysis. [e] Trace of diethyl ether present in starting 1-bromopropane.

Table IV. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 1-Propanols Obtained from Hydrolysis of 1-Bromopropanes Recovered From Reactions with Aluminum Bromide

Run	Bromide[b]	Parent less-methyl, %				Parent less-ethyl, %		
		d_3	d_2	d_1	d_0	d_2	d_1	d_0
1	A		98.8	1.2	0.0	97.1	2.0	0.9
2	B		99.0	1.0	0.0	95.4	2.2	2.4
3	B		98.7	1.3	0.0	82.7	5.0	12.3
4	A		98.9	1.1	0.0	78.2	6.4	15.4
5	B	6.1	87.0	6.5	0.4	36.0	22.3	41.7
6	C		98.1	1.9	0.0	1.8	3.3	94.9
7	C		98.0	2.0	0.0	2.4	6.2	91.4
9	F		54.6(^{13}C), 45.4(^{12}C)			46.9(^{13}C), 53.1(^{12}C)		
10	F		54.6(^{13}C), 45.4(^{12}C)			26.3(^{13}C), 73.7(^{12}C)		

[a] Calculated from 70-V mass spectra. [b] To identify the starting 1-bromopropanes in each run see Table III (run 1 in this table corresponds to run 1 in Table III, etc.)

Table V. Label Distributions[a] in the Trimethylsilyl Ether Derivatives of 2-Propanols Obtained from Hydrolysis of 2-Bromopropanes Recovered from Reactions with Aluminum Bromide

Run	Bromide[b]	Parent less-methyl, %			
		d_3	d_2	d_1	d_0
2	B		84.9	1.6	13.5
3	B		84.9	1.8	13.3
4	A		84.6	2.1	13.3
5	B	5.6	72.4	10.9	11.1
6	C		80.9	18.6	0.5
7	C		81.1	18.2	0.7
8	E		24.1(^{13}C), 75.9(^{12}C)		
9	F		45.6(^{13}C), 54.4(^{12}C)		

[a] Calculated from 70-V mass spectra. [b] To identify the starting 1-bromopropanes in each run see Table III (run 2 in this table corresponds to run 2 in Table III, etc.)

with A and B of Tables I and II), when the reaction time was short, establishes that both starting and recovered 1-bromopropanes have the same isotopic enrichment, *i.e.*, they contain the same number of doubly and singly labeled molecules. When the reaction was run for 2 hr (run 5) the recovered 1-bromopropane contained not only doubly and singly labeled molecules in different proportions than the starting 1-bromopropane, but also triply labeled and unlabeled molecules.

A. Isotope-Position Analysis of 1-Bromopropanes Recovered After Short Reaction Times. The results pertaining to the 1-bromopropane products recovered after short reaction times, *i.e.*, prior to establishment of equilibrium between the 1- and 2-bromopropane, when corrected and normalized to 100% d_2 isotopic purity,[3a] are summarized in Chart I.

The per cent conversion refers to the amount of 2-bromopropane in the recovered sum of 1- and 2-bromopropane. The results of run 8 were calculated from nmr (100 Mc) analysis of the 1-bromopropane and those of run 9 from a combination of mass spectral and nmr analysis. Integration of the nmr spectrum of the 1-propanol derived from the 1-bromopropane recovered from run 7 showed that the deuterium distribution in this alcohol (uncorrected for d_1 species) corresponded to 0.10 ± 0.03 deuterium atom at C-1, 1.72 ± 0.02 at C-2, and 0.18 ± 0.04 at C-3, in agreement with the mass spectral analysis (0.11 deuterium atom at C-1). The following features of the data will be pertinent to subsequent discussion: (a) the ratio II″:II′ from the reaction of the 1,1-d_2 labeled species is larger at low conversions, 4:1 in runs 1 and 2, than at high conversions, 3:1 in run 4. The corresponding ratio of the 1-propanol species from the deamination of 1-aminopropane-1,1-d_2 was [3a] about 2.5:1 to 3:1. (b) The ratio II′:II from the reaction of the 2,2-d_2 species, runs 6 and 7, is larger (2:1) than the corresponding ratio (1:1) of the 1-propanol species from the deamination of 1-aminopropane-2,2-d_2, and increases with increasing per cent conversion. (c) The conversion of 1-bromopropane-2,2-d_2 to 2-bromopropane is slower than those of the other isotope-position labeled 1-bromopropanes. (d) Of the rearranged ^{13}C label in the reaction of 1-bromopropane-1-^{13}C, about one-third is at C-2 and two-thirds at C-3. This observation should be contrasted with the finding[8] that the rearranged ^{14}C label in the 1-propanol product obtained from the deamination of 1-aminopropane-1-^{14}C was about equally distributed between C-2 and C-3. (e) More deuterium is at C-3 (0.18 atom) than at C-1 (0.10 atom) in the recovered 1-bromopropane from the reaction of the 2,2-d_2 species.

B. Isotope-Position Analysis of 2-Bromopropanes Obtained After Short Reaction Times. In interpreting the data of Table V, the following must be taken into consideration: (a) the isotopic distribution of the parent less-methyl ions from the trimethylsilyl ether of authentic 2-propanol-1,1-d_2 (98.4% d_2 and 1.6% d_1) was 84.5% d_2, 1.8% d_1, and 13.7% d_0.[3a] Thus, about 27.4% of this ion yield arises by loss of methyl from the isopropyl group and 72.6% by loss from the trimethylsilyl group. (b) The parent less-methyl ion of the trimethyl-

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[8] C. C. Lee and J. E. Kruger, *J. Amer. Chem. Soc.*, 87, 3986 (1965).

Chart I

$$CH_3CH_2CD_2Br \longrightarrow C_2H_5\text{-}CD_2Br + C_2H_4D\text{-}CHDBr + C_2H_3D_2\text{-}CH_2Br$$

100% d_2		II, %	II', %	II'', %
Run 1	(14% conversion)	99.0	0.2	0.8
2	(45% conversion)	97.1	0.6	2.3
3	(79% conversion)	84.5	3.3	12.2
4	(80% conversion)	79.8	5.0	15.2

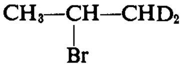
$$CH_3CD_2CH_2Br \longrightarrow \text{II, \%} + \text{II', \%} + \text{II'', \%}$$

100% d_2		II, %	II', %	II'', %
Run 6	(58% conversion)	1.5	3.0	95.5
7	(65% conversion)	2.1	5.8	92.1

$$CH_3CH_2{}^{13}CH_2Br \longrightarrow CH_3CH_2{}^{13}CH_2Br + CH_3{}^{13}CH_2CH_2Br + {}^{13}CH_3CH_2CH_2Br$$

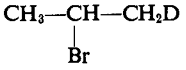
100% ^{13}C		$CH_3CH_2{}^{13}CH_2Br$	$CH_3{}^{13}CH_2CH_2Br$	$^{13}CH_3CH_2CH_2Br$
Run 8	(85% conversion)	80.2 ± 1.1%	6.5 ± 1.8%	13.3 ± 0.4%
9	(80% conversion)	85.7 ± 0.2	3.7 ± 0.9	10.6 ± 0.6

silyl ether of authentic 2-propanol-1-^{13}C (19.8% ^{13}C and 80.2% ^{12}C) gave 17.0% ^{13}C.[3a] These values imply that 28 ± 1% of this ion yield arises by loss of methyl from the isopropyl group and 72 ± 1% by loss from the trimethylsilyl group. Had the 2-bromopropanes in runs 2–4 (Table V) been exclusively isotope-position unrearranged, *i.e.*, had they arisen solely by a nominally irreversible 1,2-hydride shift (species III and IV), the isotopic distribution of the parent less-methyl ion should have been about 84.9% d_2, 1.3% d_1, and 13.8% d_0. The fact that the experimental d_1 and d_0 percentages are higher and lower, respectively, than the predicted percentages, means that species V and/or VI must also be present, as these species (or, more correctly, the trimethylsilyl ethers of their derivative 2-propanols) would cause the d_1 percentage to increase and the d_2 and d_0 percentages to decrease in the parent less-methyl ion. The data can thus be summarized, after correction for the initial isotopic impurity, in terms of the reaction



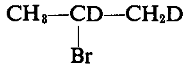
$\underset{\substack{|\\ Br}}{CH_3\text{—}CH\text{—}CHD_2}$

III



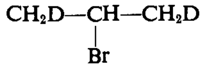
$\underset{\substack{|\\ Br}}{CH_3\text{—}CH\text{—}CH_2D}$

IV



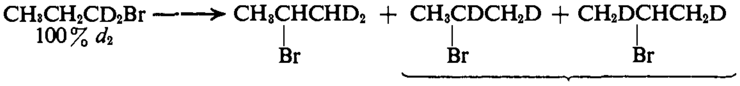
$\underset{\substack{|\\ Br}}{CH_3\text{—}CD\text{—}CH_2D}$

V



$\underset{\substack{|\\ Br}}{CH_2D\text{—}CH\text{—}CH_2D}$

VI



$$\underset{100\%\ d_2}{CH_3CH_2CD_2Br} \longrightarrow \underset{\substack{|\\ Br}}{CH_3CHCHD_2} + \underbrace{\underset{\substack{|\\ Br}}{CH_3CDCH_2D} + \underset{\substack{|\\ Br}}{CH_2DCHCH_2D}}$$

Run 2 (45% conversion)	>98.7%	<1.3%
Run 3 (79% conversion)	>98%	<2%
Run 4 (80% conversion)	>97%	<3%

Similar analysis of the results from runs 8 and 9 (Table V) leads to the conclusion that the 2-bromopropane is labeled solely at C-1, not at C-2. This conclusion was corroborated by nmr analysis of the 2-bromopropane products. The results, after normalization to 100% ^{13}C, may thus be summarized

$$\underset{100\%\ ^{13}C}{CH_3CH_2{}^{13}CH_2Br} \longrightarrow \underset{\substack{|\\ Br}}{CH_3CH^{13}CH_3} + \underset{\substack{|\\ Br}}{CH_3{}^{13}CHCH_3}$$

Runs 8 and 9	>99.5%	<0.5%

Accurate analysis and interpretation of the mass spectral results relevant to the 2-bromopropane obtained from the reaction of 1-bromopropane-2,2-d_2 (runs 6 and 7, Table V) is impossible, because of the k_H/k_D isotope effect associated with the 1,2-hydride shift leading to 2-bromopropane.[9] Thus, the 1-bromopropane-2-*d* species present (3.3%) will lead preferentially to 2-bromopropane-2-*d* rather than 2-bromopropane-1-*d*. Furthermore, proportionately more 2-bromopropane will result from this species than from the corresponding doubly labeled species 1-bromopropane-2,2-d_2. In any case, the nmr spectrum of the 2-propanol derived from the 2-bromopropane product of run 7 revealed, within the limits of detection, no protium at C-2, in agreement with the conclusion from the other results that the 2-bromopropane is mainly isotope-position unrearranged.

C. Isotope-Position Analysis of Bromopropanes Obtained After Long Reaction Times. Two reactions, runs 5 and 10, were carried out for 2 and 3 hr, respectively. Both the 1- and 2-bromopropane recovered from run 5 contain, in addition to doubly and singly labeled molecules, triply labeled (about 6%) and unlabeled (0.4% in the case of 1-bromopropane, from the parent less-methyl isotopic distribution, Table IV) molecules. Furthermore, the concentrations of the doubly and singly labeled molecules have decreased and increased, respectively. The increase of singly labeled molecules is 5.5%. The sum, therefore, of unlabeled (0.4%) and incremental singly labeled molecules (5.5%) is approximately equal to the concentration of the triply labeled molecules (6.1%). Significantly, no d_4 labeled molecules were detected, and the distribution of d_3, d_2, d_1, and d_0 molecules was not what would have been expected from complete statistical exchange of hydrogens among all propyl groups. The 1-bromopropane recovered from the reaction of 1-bromopropane-1-^{13}C, run 10, contains no doubly labeled ^{13}C molecules. Since the recovered sample was too small for nmr analysis, only the mass spectral data are available to assess the ^{13}C distribution at the various positions. Normalization of the results of 100% labeled material gives the following

$$\underset{100\%\ ^{13}C}{CH_3CH_2{}^{13}CH_2Br} \xrightarrow{180\ min} \underset{48\%}{CH_3CH_2{}^{13}CH_2Br} + \underset{52\%}{\overbrace{CH_3CH_2}^{13}CH_2Br}$$

As was the case with run 5, complete statistical scrambling among the three carbon atoms of the propyl system has not occurred. Had it occurred, only one-third, instead of 48%, would have been found at C-1. The absence of such statistical scrambling, even after pro-

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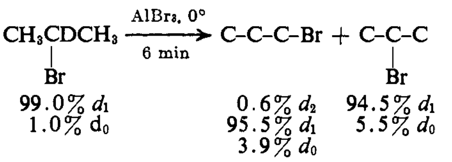
[9] In the isomerization of 1-bromopropane-2-*d*, hydrogen migrates 3.3 times faster than does deuterium; H. S. A. Douwes and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **83**, 276 (1964).

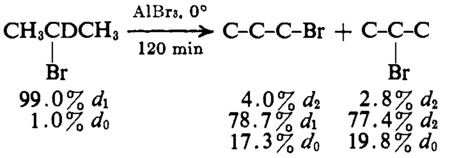
longed reaction times, is not surprising. Reactions between alkyl halides and Lewis acids are known to practically stop after a period of time, because of deactivation of the catalyst by—most probably—the polymer formed.[10]

IV. Reactions of 2-Bromopropane with Aluminum Bromide. As an adjunct to the studies of 1-bromopropane with aluminum bromide, we also studied the reactions of labeled 2-bromopropanes with aluminum bromide. The reaction of 2-bromopropane-2-*d* (99.0% d_1 and 1.0% d_0 by parent-ion mass spectral analysis) with aluminum bromide, 5.7:1 mol to mol ratio, at 0°, was quenched after 6 min with quinoline. The 74% recovered bromopropane product consisted of 4% 1-bromopropane and 96% 2-bromopropane. Mass spectral analysis (parent-ion) of the two bromides gave the results summarized



$$CH_3\underset{|\atop Br}{C}DCH_3 \xrightarrow[6\ min]{AlBr_3,\ 0°} C\text{-}C\text{-}C\text{-}Br + C\text{-}\underset{|\atop Br}{C}\text{-}C$$

When the reaction was run for 120 min, with a 6.3:1 mol to mol ratio, we recovered 52% bromopropane, consisting of 7% 1-bromopropane and 93% 2-bromopropane. Mass spectral analysis of these materials gave



$$CH_3\underset{|\atop Br}{C}DCH_3 \xrightarrow[120\ min]{AlBr_3,\ 0°} C\text{-}C\text{-}C\text{-}Br + C\text{-}\underset{|\atop Br}{C}\text{-}C$$

The following features of the results, when taken in conjunction with the formation of propane, will be pertinent to subsequent discussion: (a) the recovered bromopropanes contain less deuterium than the starting 2-bromopropane, *i.e.*, the concentration of unlabeled molecules is more than twice that of doubly labeled ones; (b) the 1-bromopropane contains more doubly labeled molecules than does the 2-bromopropane.

When 2-bromopropane-1,1,1,3,3,3-d_6 (96.0% d_6 and 4.0% d_5 by parent-ion analysis of the benzoate of its alcohol) was treated for 10 min with aluminum bromide at 0°, bromopropane recovery was essentially quantitative, consisting of 3% 1-bromopropane and 97% 2-bromopropane. The 1-bromopropane was 94% d_6.

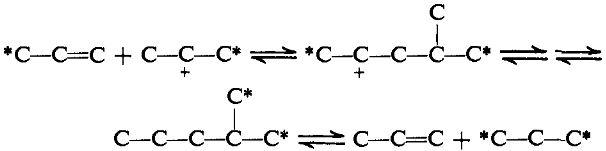
V. Solvolysis of 1-Propyl Tosylates. When 1-propyl tosylate, prepared from 1-propanol-1,1-d_2 (alcohol A, Table I), was solvolyzed in 99% aqueous formic acid at 75°, a 36% yield was obtained of a mixture consisting of 94 ± 2% 1-propanol and 6 ± 2% 2-propanol. Mass spectral analysis of the trimethylsilyl ether derivative of the product 1-propanol gave: parent less-methyl, 98.9% d_2 and 1.1% d_1, and parent-less-ethyl, 98.2% d_2, 1.7% d_1, and 0.1% d_0. The values are indistinguishable from those of A in Table I. The propanol product from the solvolysis of the tosylate is, therefore, exclusively isotope-position unrearranged. Similar solvolysis of the tosylate prepared from 1-propanol-2,2-d_2 (alcohol D, Table I) gave a 48% yield of a mixture of 1-propanol (97.7 ± 0.6%) and 2-propanol (2.3 ± 0.6%). Mass spectral analysis of the trimethylsilyl ether of the product 1-propanol gave: parent less-methyl, 98.4% d_2 and 1.6% d_1, and parent less-ethyl, essentially 100% d_0. Again, therefore, the 1-propanol product is exclusively isotope-position unrearranged. Our results disagree with the reported[11] 0.83% isotope-position rearranged 1-propyl formate obtained from the solvolysis of 1-propyl-1-^{14}C tosylate in redistilled, reagent grade acid (98–100% HCOOH) after refluxing for 18 hr.

Discussion

Accurate assessment of the role that protonated cyclopropane intermediates may play in the isomerization of 1-bromopropane to 2-bromopropane is rendered difficult by the fact that 2-bromopropane rearranges back to 1-bromopropane under the reaction conditions, and, therefore, part of the isotope-position rearranged 1-bromopropane must arise from this path. Before embarking on a detailed discussion of the relative merits of the various rearrangement paths, let us first draw some firm, general conclusions regarding these paths.

(1) Reversible 1,2-hydride shifts cannot be the sole path responsible for the formation of isotope-position rearranged 1-bromopropanes, as such shifts account neither for the scrambling between C-1 and C-2 (runs 8 and 9) nor for the relatively high ratio II:II′ in run 6.

(2) Bimolecular reactions, such as eq 2, are excluded



(2)

as mechanistic paths responsible for the isotope-position rearranged products, as no doubly labeled carbon-13 species were detected, even after reaction for 180 min (run 10, Table IV). Such bimolecular reactions constitute a significant path in the isotope-position rearrangement of *t*-amyl chloride with aluminum chloride.[10]

(3) The identity of label distribution in the parent less-methyl ions of the trimethylsilyl ethers derived from precursor and product 1-bromopropanes, when the contact time between 1-bromopropane and aluminum bromide is short, rules out under these conditions not only bimolecular reactions, but also elimination–addition reactions[12] and intermolecular hydride transfers.

(4) The large amounts of d_3 and d_1 species in the recovered 1- and 2-bromopropane product from run 5 (Tables IV and V) show that intermolecular hydride shifts become important at prolonged reaction times when the reaction mixture consists predominantly of 2-bromopropane. That the 2-bromopropane, rather than the 1-bromopropane, is the species primarily involved in intermolecular hydride transfers is further supported by finding d_2 and d_0 species after 6 min of reacting 2-bromopropane-2-*d* with aluminum bromide.

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[10] See G. J. Karabatsos, F. M. Vane, and S. Meyerson, *J. Amer. Chem. Soc.*, **83**, 4297 (1961).

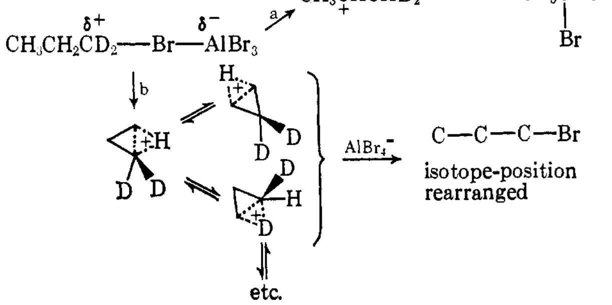
[11] C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966).

[12] An elimination–addition mechanism was previously ruled out for the isomerization of 1-chloropropane to 2-chloropropane with aluminum chloride by L. M. Nash, T. I. Taylor, and W. von E. Doering, *J. Amer. Chem. Soc.*, **71**, 1516 (1949). The 13% 2-propyl products obtained from the mercuric ion-assisted solvolysis at 25° of 1-bromopropane in 90% aqueous formic acid-*t* contain no tritium according to J. S. Coe and V. Gold, *J. Chem. Soc.*, 4940 (1960).

Mechanisms for the Formation of Isotope-Position Rearranged 1-Bromopropanes. At least two paths are required to explain the isotope-position rearrangement of 1-bromopropane at short contact times with aluminum bromide. Since the isomerization of 2-bromopropane to 1-bromopropane involves primarily intramolecular hydride shifts (*vide infra*), one of the mechanistic paths may be simply viewed as occurring through reversible 1,2-hydride shifts.[13] The need for a second path to account for the scrambling of carbon-2 with the two terminal carbons of the 1-propyl system has already been mentioned. The simplest representation of this path is as 1,2-methyl shifts. In view of the reversibility of the reactions under the experimental conditions, it is difficult to unambiguously rule out this mechanism. The absence of any ^{13}C label at C-2 of the product 2-bromopropane is certainly inconsistent with such a mechanism.

An alternative interpretation of the results involves protonated cyclopropane intermediates in the second path, as shown in Scheme I. The initially formed 1-bromopropane–aluminum bromide complex can proceed along either of two separate and discrete pathways. Path a involves a 1,2-hydride shift and results in the formation of 2-bromopropane; path b involves the partial equilibration of protonated cyclopropanes before their capture by nucleophile to give isotope-position rearranged 1-bromopropanes. The two questions raised in the introduction to this paper—namely, what are the relative rates of edge–edge equilibration and nucleophilic attack on the protonated cyclopropane, and what is the place of the methyl-bridged ion I in the mechanistic scheme—cannot be answered with any degree of certainty, because of the competing 1,2-hydride shift path. In order to answer these questions, the relative extents of isotope-position rearrangement through the 1,2-hydride shift and through the protonated cyclopropane must be known. Such information requires comparison of isotope-position rearranged 2-bromopropane and II′ (C_2H_4D-CHDBr). Although the concentration of the latter has been determined accurately, that of the former can only be estimated as small. In any case, the results argue against a significant contribution from the methyl-bridged species I (as an intermediate preceding the formation of the edge-protonated cyclopropanes) to the isotope-position rearranged 1-bromopropane. Such a species would lead to at least as much ^{13}C at C-2 as at C-3 of the 1-propyl system. These questions and arguments become irrelevant if one were to accept 1,2-hydride and 1,2-methyl shifts as the rearrangement paths. Insofar as can be judged from the present results, acceptance or rejection of the protonated cyclopropane path in the reaction of 1-bromopropane with aluminum bromide is a matter of personal taste. On the basis of finding no ^{13}C at C-2 of the product 2-bromopropane, and on the basis of the deamination results,[3] we prefer the protonated cyclopropane mechanism.

Scheme I



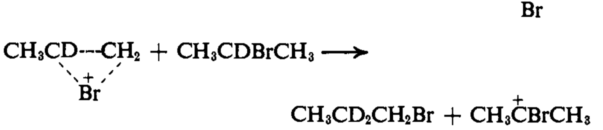
Although the results just discussed do not resolve the question of the intermediacy of protonated cyclopropanes in the reaction of 1-bromopropane with aluminum bromide, those from the solvolysis of 1-propyl tosylate in 99% formic acid unambiguously rule out the intervention of such species in this reaction. If such a species is an intermediate in the formation of any 1-propanol product, it must be responsible for less than 0.1%. In view of the not quite limiting mechanism under these conditions,[14] this finding is not surprising.

Mechanisms of the Rearrangement of 2-Bromopropane to 1-Bromopropane. The results from the reactions of 2-bromopropane-2-*d* and 2-bromopropane-1,1,1,3,3,3-d_6 with aluminum bromide shed some light on the mechanism of the conversion of 2-bromopropane to 1-bromopropane. The major path is intramolecular in nature, as attested by the fact that the 3% 1-bromopropane obtained from the reaction of 2-bromopropane-1,1,1-3,3,3-d_6 (96.0% d_6 and 4.0% d_5) is 94.1% d_6 species. The apparent loss of some of the deuterium label is much more pronounced in the reaction of 2-bromopropane-2-*d*. Not only have the recovered 1- and 2-bromopropane products lost deuterium label, but in addition doubly labeled molecules are detected, first in the 1-bromopropane—even at such short contact times as 6 min—and later in the 2-bromopropane. These observations, coupled with the formation of propane, imply the intervention of intermolecular hydride transfers. A sequence of reactions, as depicted in eq 3–7,

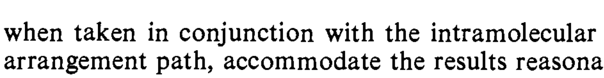
$$CH_3CDBrCH_3 + AlBr_3 \rightleftharpoons CH_3\overset{+}{C}DCH_3 + AlBr_4^- \quad (3)$$

$$CH_3CDBrCH_3 + CH_3\overset{+}{C}DCH_3 \longrightarrow CH_3CD_2CH_3 + CH_3\overset{+}{C}BrCH_3 \quad (4)$$

$$CH_3\overset{+}{C}BrCH_3 + CH_3CDBrCH_3 \rightleftharpoons CH_3CDBrCH_3 + CH_3\overset{+}{C}BrCH_3 \quad (5)$$



$$CH_3\overset{+}{C}BrCH_3 + CH_3CDBrCH_3 \rightleftharpoons CH_3CHBrCH_3 + CH_3\underset{\overset{+}{Br}}{CD{=}CH_2} \quad (6)$$



$$CH_3\underset{\overset{+}{Br}}{CD\text{---}CH_2} + CH_3CDBrCH_3 \longrightarrow CH_3CD_2CH_2Br + CH_3\overset{+}{C}BrCH_3 \quad (7)$$

when taken in conjunction with the intramolecular rearrangement path, accommodate the results reasonably well. The hydride or deuteride abstractions in eq 4 and 5 have a precedent in the hydride abstraction of the methine hydrogen of 2-propanol by the trityl cation.[15,16]

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[13] Discrete carbonium ion intermediates are not necessarily needed for such shifts. They may occur within the alkyl halide–aluminum halide complex. See, for example, ref 9 and (a) H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, **75**, 6279 (1953); (b) E. H. Adema, A. J. J. M. Teunissen, and M. J. J. Tholen, *Rec. Trav. Chim. Pays-Bas.*, **85**, 377 (1966).

[14] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

The propylenebromonium ion has been recently observed by nmr.[17] Presumably the 2-bromo-2-propyl cation could also lose a proton and polymerize. Such a polymer would eventually lead to catalyst deactivation—a likely process in view of the fact that in no case was a statistical distribution of label found in the products—and could serve as a hydride source for the formation of propane.

Experimental Section

Nmr spectra at 60 Mc were obtained either on a Varian A-60 or on a JEOLCO C-60-H instrument. A Varian HA-100 was used to obtain spectra at 100 Mc. Mass spectra were measured with a Consolidated Model 21-103C instrument.

Synthesis of Labeled Compounds. All compounds were prepared according to well-established procedures. Trimethylsilyl ether derivatives of alcohols were prepared by warming overnight a 2:1 molar mixture of the alcohol and hexamethyldisilazane (Metallomer Laboratories) with a drop of trimethylchlorosilane (Stauffer). Purification was achieved by gas chromatography on a 20 ft × $^1/_4$ in. 20% Carbowax 20M on 60–80 Chromosorb W column at 60–80°.

1-Propanol-1,1-d_2 was prepared by lithium aluminum deuteride (Metal Hydrides) reduction of propionic anhydride.

1-Propanol-2,2-d_2 was prepared by the repeated exchange of methylmalonic acid with deuterium oxide, followed by decarboxylation to propionic acid and reduction with lithium aluminum hydride.

1-Propanol-1-^{13}C was prepared by carboxylation of ethylmagnesium bromide with carbon-^{13}C dioxide to form propionic-1-^{13}C acid, followed by lithium aluminum hydride reduction. The carbon-^{13}C dioxide was generated by dripping 35% aqueous perchloric acid onto barium carbonate-^{13}C (Merck Sharp and Dohme of Canada, 56.5 atom % ^{13}C).

2-Propanol-2-*d* was prepared by the lithium aluminum deuteride reduction of acetone (Baker Analyzed Reagent, dried over magnesium sulfate).

2-Propanol-1,1,1,3,3,3-d_6 was prepared by the lithium aluminum hydride reduction of acetone-d_6 (Merck Sharp and Dohme of Canada, >99.5 atom % D).

2-Propanol-1,1-d_2 was prepared by the lithium aluminum deuteride reduction of *n*-octylformate to methanol-d_2, conversion of the methanol to methyl-d_2 iodide by treatment with red phosphorus and iodine, formation of methyl-d_2-magnesium iodide, and addition of acetaldehyde to it.

1-Propyl toluenesulfonates were prepared by the reaction of the appropriate 1-propanol with p-toluenesulfonyl chloride in pyridine.[18]

Both 1-bromopropanes and 2-bromopropanes were prepared by the reaction of the appropriate alcohol with phosphorous tribromide. In a typical example, 3.3 ml (0.035 mol) of phosphorus tribromide was slowly added with moderate stirring at 0° to 5.00 g (0.081 mol) of 1-propanol-1,1-d_2 in a 50-ml 3-necked flask equipped with a "Drierite" drying tube fitted to a water-cooled reflux condenser, a 50-ml addition funnel with equalizing tube, a stopper, and a small Teflon-covered magnetic stirring bar. Stirring was continued for 23 hr at room temperature, during which time hydrogen bromide was evolved. At the end of this time, 10 ml of water was added at 0°. The upper aqueous layer was extracted twice with 8 ml of pentane. The pentane extracts were combined with the colorless lower organic layer, washed with 10 ml of ice-cold 5% aqueous sodium carbonate solution, and dried over magnesium sulfate. Distillation through a 4-in. glass spiral-packed column yielded 5.56 g (56%) of 1-bromopropane-1,1-d_2, bp 69–70°, that was pure by gas chromatography except for a trace of pentane.

Hydrolysis of 1-Propyl *p*-Toluenesulfonates. Anhydrous formic acid[14] was added to water to bring the water concentration to 0.556 *M* (*ca.* 0.86 wt %). In a typical experiment, 4.52 g (0.021 mol) of 1-propyl-1,1-d_2 *p*-toluenesulfonate was dissolved in 50 ml of the aqueous formic acid in a 100-ml flask equipped with a calcium chloride drying tube fitted to a water-cooled reflux condenser and maintained at 75 ± 1° for 143.5 hr. At the end of this time, the straw-colored liquid was carefully diluted with 100 ml of water at 0° and the pH adjusted to 11 by addition of 65 ml of 50% sodium hydroxide solution. After addition of 40 ml of diethyl ether the aqueous layer was saturated with sodium chloride. At this point, the salted-out sodium tosylate was removed by means of a glass wool filter, the layers were separated, and the aqueous layer was extracted twice with 20-ml portions of ether. The combined ether extracts were then washed once with 25 ml of saturated sodium chloride solution and dried over magnesium sulfate. Distillation produced 0.47 g of product boiling above 36°, which was shown by gas chromatography to be composed of 6% 2-propanol and 94% 1-propanol, with a trace of diethyl ether.

Silver Ion Assisted Hydrolysis of Bromopropanes. In a typical experiment, 4.89 g (0.0392 mol) of 1-bromopropane-1,1-d_2, 8.69 g (0.0511 mol) of silver nitrate, 50 ml of water, and a small Teflon-covered magnetic stirring bar were placed in a 100-ml flask equipped with a water-cooled reflux condenser. The entire apparatus was wrapped with aluminum foil to exclude light. The mixture was stirred for 82 hr at room temperature and the pale yellow-green silver bromide (6.85 g, 0.0364 mol) was filtered out on a glass sinter. After addition of 50 g of potassium fluoride, the aqueous filtrate was extracted with 50 ml of diethyl ether in three portions. The combined ether extracts were dried (over magnesium sulfate) and distilled to yield 1.63 g of product boiling above 80°, which was found by gas chromatography to be 1-propanol with a trace of diethyl ether.

Alkaline Hydrolysis of Bromopropanes. In a typical experiment, 4.14 g (0.0331 mol) of 1-bromopropane-1,1-d_2, 5.00 g (0.125 mol) of sodium hydroxide, and 50 ml of water were placed in a 100-ml flask fitted with a water-cooled reflux condenser and heated over a steam bath for 71.5 hr. After addition of 50 g of potassium fluoride, the clear, aqueous layer was extracted with 50 ml of diethyl ether in three portions. The combined ether extracts were dried and distilled to yield 0.74 g of product boiling above 70°, which was found by gas chromatography to be 1-propanol containing a trace of diethyl ether.

Aluminum Bromide Catalyzed Isomerizations of Bromopropanes. Both 1- and 2-bromopropanes were allowed to react with aluminum bromide by the following technique: a small, round-bottomed flask (*ca.* 20 ml) equipped with two side arms, one sealed at the end and bent downward and the other topped with a rubber septum, was charged under a dry nitrogen atmosphere with a weighed amount of aluminum bromide (Fisher "Anhydrous") and a small Teflon-coated magnetic stirring bar and connected to a vacuum line. The flask was evacuated and the aluminum bromide was distilled onto the Dry Ice cooled flask bottom by gentle heating of the downward-bent side arm with a small, cool flame. Dry air was then admitted to the system and the flask was surrounded with an ice–water bath. Stirring was commenced and timing began as the bromopropane was injected with a calibrated syringe through the septum onto the aluminum bromide. Timing was stopped upon addition of quinoline to the pale yellow, homogeneous reaction mixture. The flask was closed to the atmosphere and surrounded by a warm water bath and the volatile reaction products distilled under vacuum into a liquid nitrogen-cooled receiver. They were weighed, immediately analyzed by gas chromatography, and then converted to their respective alcohols by hydrolysis in 15% aqueous silver nitrate solution.

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(15) P. D. Bartlett and J. D. McCollumn, *J. Amer. Chem. Soc.*, 78, 1441 (1956).

(16) For a recent review of intermolecular hydride shifts see C. D. Nenitzescu in "Carbonium Ions," Vol. II, G. A. Olah and P. Von R. Schleyer, Ed., Interscience-Wiley Publishers, New York, N. Y., 1968, Chapter 13.

(17) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, 90, 2587 (1968).

(18) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1941).