

CARBONIUM IONS. X. PROTONATED CYCLOPROPANES IN THE REACTION
OF 1-BROMOPROPANE WITH ALUMINUM BROMIDE.

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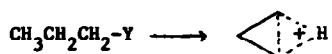
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We wish to report on the effect of Y ($Y = \overset{-}{\text{Br}}-\overset{+}{\text{AlBr}}_3$, OTs), on the extent of protonated



cyclopropane formation by the "σ-route" (1).

In Table I we have summarized the results of partial isomerization of labeled 1-bromopropanes to 2-bromopropanes (2). The isotopic distribution in the recovered bromides was determined by converting them to the corresponding alcohols and then mass-spectrally analyzing the trimethylsilyl ethers of the alcohols (3). The results are summarized in Table II.

The absence of any \underline{d}_3 species in the $[\text{P-Me}]^+$ ion rules out any intermolecular hydride transfers, bimolecular reactions, or elimination-addition reactions under the experimental conditions (4). This conclusion is further supported by the fact that the trimethylsilyl ether of 1-propanol, precursor to the bromide used in runs 1, 2, and 3, gave 99.0% \underline{d}_2 and 1.0% \underline{d}_1 ($[\text{P-Me}]^+$); 98.2% \underline{d}_2 , 1.6% \underline{d}_1 , and 0.2% \underline{d}_0 ($[\text{P-Et}]^+$).

TABLE I

Reaction of 1-Bromopropane with Aluminum Bromide at 0°

Run	RBr	RBr/AlBr ₃ mole/mole	Rxn. Time ^a (min.)	Recovered ^b		
				RBr, %	1-Br, %	2-Br, %
1	CH ₃ CH ₂ CD ₂ Br	10.5	6.0	95	55	45
2	CH ₃ CH ₂ CD ₂ Br	5.6	5.0	93	21	79
3	CH ₃ CH ₂ CD ₂ Br	5.6 ^c	6.0	100	20	80
4	CH ₃ CD ₂ CH ₂ Br	5.7	5.0	78	42	58
5	CH ₃ CD ₂ CH ₂ Br	5.6	6.0	94	35	65

- a. Quenched with quinoline.
 b. Sum of 1-bromo- and 2-bromopropanes
 c. Trace of diethyl ether in starting bromide.

TABLE II

Isotopic Analysis of [P-Me]⁺ and [P-Et]⁺ Ions in Mass Spectra of
 Trimethylsilyl Ethers of 1-Propanols Derived from

the Recovered 1-Bromopropanes

Run	[P-Me] ⁺		[P-Et] ⁺		
	% d ₂	% d ₁	% d ₂	% d ₁	% d ₀
1	99.0	1.0	95.4	2.2	2.4
2	98.7	1.3	82.7	5.0	12.3
3	98.9	1.1	78.2	6.4	15.4
4	98.1	1.9	1.8	3.3	94.9
5	98.0	2.0	2.4	6.2	91.4

Correcting and normalizing the results (5) of Table II gives the following:

	$\text{CH}_3\text{CH}_2\text{CD}_2\text{Br} \longrightarrow$	$\text{C}_2\text{H}_5\text{-CD}_2\text{Br}$	+	$\text{C}_2\text{H}_4\text{D-CHDBr}$	+	$\text{C}_2\text{H}_3\text{D}_2\text{-CH}_2\text{Br}$
Run	1	97.1%		0.6%		2.3%
	2	84.5%		3.3%		12.2%
	3	79.8%		5.0%		15.2%
$\text{CH}_3\text{CD}_2\text{CH}_2\text{Br} \longrightarrow$						
Run	4	1.5%		3.0%		95.5%
	5	2.1%		5.8%		92.1%

The 2-bromopropanes obtained in runs 1, 2, and 3 were converted to 2-propanols whose trimethylsilyl ethers gave the following $[\text{P-Me}]^+$ isotopic distributions: 84.9% \underline{d}_2 , 1.6% \underline{d}_1 , and 13.5% \underline{d}_0 (run 1); 84.9% \underline{d}_2 , 1.8% \underline{d}_1 , and 13.3% \underline{d}_0 (run 2); and 84.6% \underline{d}_2 , 2.1% \underline{d}_1 , and 13.3% \underline{d}_0 (run 3). Since the trimethylsilyl ether of authentic 2-propanol-1, 1- \underline{d}_2 (98.5% \underline{d}_2 and 1.5% \underline{d}_1) gave 84.5% \underline{d}_2 , 1.8% \underline{d}_1 , and 13.7% \underline{d}_0 ($[\text{P-Me}]^+$), these bromides are better than 97% isotope-position unrearranged, *i.e.*, derived from a nominally irreversible 1,2-hydride shift. This should be contrasted with the 15-20% isotope-position rearranged 1-bromopropane obtained in runs 2 and 3.

Nmr and mass-spectral analysis of the 1-bromopropane recovered from the reaction of 1-bromopropane-1- ^{13}C (45.4% ^{12}C and 54.6% ^{13}C) with aluminum bromide after 80% conversion (20% 1-bromopropane and 80% 2-bromopropane) gave the following result:

$\text{CH}_3\text{CH}_2\text{}^{13}\text{CH}_2\text{Br} \longrightarrow$	$\text{CH}_3\text{CH}_2\text{}^{13}\text{CH}_2\text{Br}$	+	$\text{CH}_3\text{}^{13}\text{CH}_2\text{CH}_2\text{Br}$	+	$^{13}\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
100% ^{13}C	85.7 \pm 0.2%		3.7 \pm 0.9%		10.6 \pm 0.6%

Nmr and mass-spectral analysis of the 80% 2-bromopropane revealed no ^{13}C at C-2. Thus, whereas the 1-bromopropane is extensively isotope-position rearranged, the 2-bromopropane has undergone essentially no rearrangement.

Interpretation of these results requires that the bulk of the isotope-position rearranged 1-bromopropane arise from an edge-protonated cyclopropane intermediate (5). The 2-bromopropane arises from a nominally irreversible 1,2 hydride shift (6).

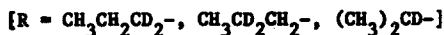
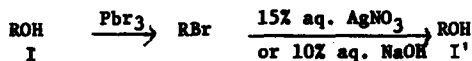
In contrast to the extensive rearrangement observed in the above reactions, the hydrolysis of 1-propyl tosylate in 99% formic acid at 75° gave 1-propanol (7) with no

measurable isotope-position rearrangement. Thus, 1-propyl tosylate prepared from 1-propanol-1,1- d_2 , whose trimethylsilyl ether gave 99.0% d_2 and 1.0% d_1 ($[P-Me]^+$); 98.3% d_2 , 1.6% d_1 , and 0.1% d_0 ($[P-Et]^+$), yielded 1-propanol whose trimethylsilyl ether gave 98.9% d_2 and 1.1% d_1 ($[P-Me]^+$); 98.2% d_2 , 1.7% d_1 , and 0.1% d_0 ($[P-Et]^+$). In view of the not quite limiting mechanism under these conditions (8), this finding is not surprising (9).

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References

- (1) For the notation " σ -route" and " π -route" to nonclassical carbonium ions, see S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).
- (2) The 1-Br/2-Br equilibrium ratio under our reaction conditions was 6/94.
- (3) The identity of the mass spectra of the trimethylsilyl ethers of I and I'



proves that the preparation of the bromides from the alcohols and their hydrolysis back to the alcohols proceed without isotope-position rearrangements.

- (4) Longer reaction times eventually lead to d_3 species.
- (5) See G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Am. Chem. Soc.*, **87**, 4394 (1965).
- (6) Our results differ from those reported for similar systems or for the same system under different experimental conditions. For example, the reaction of 1-chloropropane-1- ^{14}C with zinc chloride in concentrated hydrochloric acid at 20° and 50° gave 1-chloropropane with the label distributed exclusively between C-1 and C-3, according to O. A. Reutov and T. N. Shatkina, *Bull. Acad. Sci., USSR, Div. Chem. Sci.*, **180** (1963). This 1,3-hydride shift was supported by deuterium label experiments, according to O.A. Reutov, *Pure Appl. Chem.*, **7**, 203 (1963). The 1-bromopropane recovered from the reaction of 1-bromopropane-2,2- d_2 with aluminum bromide in carbon disulfide, at -20°, was isotope-position unrearranged according to H. S. A. Douwes and E. C. Kooyman, *Rec. Trav. Chim.*, **83**, 276 (1964).
- (7) Under our reaction conditions, the alcohol fraction consisted of 94% 1-propanol and 6% 2-propanol. 1-propanol did not isomerize to 2-propanol under these conditions.
- (8) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).
- (9) In 100% formic acid, at reflux, less than 1% isotope-position rearrangement was reported by C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966).