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

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We wish to report on the effect of Y (Y = $\overset{-}{Br}$—$\overset{+}{Al}Br_3$, OTs), on the extent of protonated

$CH_3CH_2CH_2\text{-}Y \longrightarrow$ 

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 $[P\text{-}Me]^+$ 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% $\underline{d}_1$ $\left([P\text{-}Me]^+\right)$; 98.2% $\underline{d}_2$, 1.6% $\underline{d}_1$, and 0.2% $\underline{d}_0$ $\left([P\text{-}Et]^+\right)$.

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	$CH_3CH_2CD_2Br$	10.5	6.0	95	55	45
2	$CH_3CH_2CD_2Br$	5.6	5.0	93	21	79
3	$CH_3CH_2CD_2Br$	5.6[c]	6.0	100	20	80
4	$CH_3CD_2CH_2Br$	5.7	5.0	78	42	58
5	$CH_3CD_2CH_2Br$	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

	[P-Me]$^+$		[P-Et]$^+$		
Run	% 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:

	$CH_3CH_2CD_2Br \longrightarrow$	$C_2H_5\text{-}CD_2Br$	+	$C_2H_4D\text{-}CHDBr$	+	$C_2H_3D_2\text{-}CH_2Br$
Run	1	97.1%		0.6%		2.3%
	2	84.5%		3.3%		12.2%
	3	79.8%		5.0%		15.2%
	$CH_3CD_2CH_2Br \longrightarrow$					
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 $[P\text{-}Me]^+$ 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% $\underline{d}_0$ ($[P\text{-}Me]^+$), 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:

$CH_3CH_2{}^{13}CH_2Br \longrightarrow$	$CH_3CH_2{}^{13}CH_2Br$	+	$CH_3{}^{13}CH_2CH_2Br$	+	$^{13}CH_3CH_2CH_2Br$
100% ^{13}C	85.7 ± 0.2%		3.7 ± 0.9%		10.6 ± 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-$\underline{d}_2$, whose trimethylsilyl ether gave 99.0% $\underline{d}_2$ and 1.0% $\underline{d}_1$ $\left([P-Me]^+\right)$; 98.3% $\underline{d}_2$, 1.6% $\underline{d}_1$, and 0.1% $\underline{d}_0$ $\left([P-Et]^+\right)$, yielded 1-propanol whose trimethylsilyl ether gave 98.9% $\underline{d}_2$ and 1.1% $\underline{d}_1$ $\left([P-Me]^+\right)$; 98.2% $\underline{d}_2$, 1.7% $\underline{d}_1$, and 0.1% $\underline{d}_0$ $\left([P-Et]^+\right)$. 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'

$$\underset{\text{I}}{\text{ROH}} \xrightarrow{\text{Pbr}_3} \text{RBr} \xrightarrow[\text{or 10\% aq. NaOH}]{\text{15\% aq. AgNO}_3} \underset{\text{I'}}{\text{ROH}}$$

$$[R = CH_3CH_2CD_2-,\ CH_3CD_2CH_2-,\ (CH_3)_2CD-]$$

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 $\underline{d}_3$ 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-$\underline{d}_2$ 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).