ABSTRACT

CARBONIUM ION REARRANGEMENTS IN
THE PROPYL SYSTEM

by James Leslie Fry

The purpose of this investigation was to study the mechanisms of several reactions whose conditions could potentially permit the formation of propyl cations. The reactions studied were: the 99% formic acid solvolysis of 1-propyl tosylate (1-propyl p-toluenesulfonate), the basic hydrolysis of 1-bromopropane, the aqueous silver ion-assisted hydrolyses of 1-bromopropane and 2-bromopropane, and the aluminum bromide catalyzed interconversion of the bromopropanes. In all cases, the fate of the propyl species was studied by using isotope-position labeled reactants and observing the position(s) of the isotope label in the products by means of mass spectrometry and nuclear magnetic resonance (n.m.r.) spectroscopy.

When solvolyzed in 99% formic acid at 75°, 1-propyl tosylates prepared from 1-propanol-1,1-d_2 gave 94% 1-propanol and 6% 2-propanol. The solvolysis of 1-propyl tosylate prepared from 1-propanol-2,2-d_2 gave 98% 1-propanol and 2% 2-propanol. Mass-spectral analysis of the trimethylsilyl ether derivatives proved the absence of isotope-position rearrangements in the 1-propyl product. This product was interpreted as arising from an S_N2 attack on the unionized tosylate or on the incipient tight-ion pair.

The identity of the mass spectra of the trimethylsilyl ethers of I and I' shown below proved that no isotope-position rearrangements had occurred during the preparation or hydrolysis of 1- and 2-bromopropanes in 15% aqueous silver nitrate solution (R = $CH_3CH_2CD_2$-, $CH_3CD_2CH_2$-, $(CH_3)_2CD$-). The hydrolysis was interpreted as occurring by an S_N2 attack on a bromopropane-silver ion complex.

$$\underset{\text{I}}{\text{ROH}} \xrightarrow{PBr_3} \text{RBr} \xrightarrow[\text{or 10\% aq. NaOH}]{\text{15\% aq. } AgNO_3} \underset{\text{I'}}{\text{ROH}}$$

A similar identity of the mass spectra of the trimethylsilyl ethers of I and I' was observed for hydrolysis in 10% aqueous sodium hydroxide at steam bath temperatures (R = $CH_3CH_2CD_2$-, $CH_3CD_2CH_2$-).

A thermodynamic equilibrium mixture of 1-bromopropane and 2-bromopropane in the ratio 6/94 was obtained at 0° when either bromopropane was isomerized with aluminum bromide in a 5.7/1 molar ratio.

$$\text{1-RBr} \xrightarrow[0^\circ]{AlBr_3} \text{1-R'Br} + \text{2-R'Br}$$

(R = $CH_3CH_2CD_2$-, $CH_3CD_2CH_2$-, $CH_3CH_2{}^{13}CH_2$-)

The above isomerization was run to various stages of completion and the products were converted to the alcohols by silver ion-assisted hydrolysis. N.m.r. and mass-spectral

analyses of the products and their derivatives showed that, for short reaction times, whereas the 2-propyl product was the result of a single intramolecular 1,2-hydride shift, the recovered 1-bromopropane was extensively intramolecularly isotope-position rearranged. This rearrangement was interpreted in terms of partially equilibrating edge-protonated cyclopropanes. The occurrence of intermolecular hydride transfers at longer reaction times was established.

The isomerization of 2-bromopropane to 1-bromopropane occurs primarily by an intramolecular 1,2-hydride shift.

$$2\text{-RBr} \xrightarrow[0^{\circ}]{AlBr_3} 1\text{-R'Br} + 2\text{-R'Br}$$

(R = $(CH_3)_2CD$-, $(CD_3)_2CH$-, and 1:1 mixture of both)

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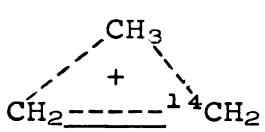
INTRODUCTION

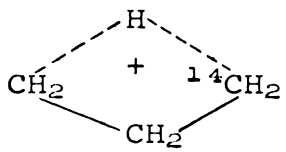
A few decades ago it was recognized that carbonium ions may exist as discrete intermediates in the course of certain chemical reactions and that during their more or less brief existence they may undergo internal rearrangements which lead to rearranged products (1,2,3). This discovery has provided the impetus for an enormous amount of work and discussion on the nature of such species and the manner in which they rearrange.

Of the many diverse systems which have been studied, the simplest one in which carbon skeletal rearrangements could compete with hydrogen shifts is the propyl system. In 1953, Roberts and Halmann reacted 1-aminopropane-1-^{14}C with nitrous acid and obtained 1-propanol along with other products (4). By partially degrading this product they found that 8.5% of the carbon-14 was at C-2 and C-3. Although they did not know if the label was at one carbon or both, they assumed that it was exclusively at C-2 and suggested that the initially formed 1-propyl cation had partially (17%) gone to the methyl-bridged cation I, which would lead to label at C-1 and C-2 upon attack by water.



I

I could be thought of as the simplest of non-classical carbonium ions. Roberts and Halmann considered the possible intervention of the 1,3-hydrogen-bridged ion II, which would lead



II

to label at C-3, but dismissed it as unimportant on the grounds that the 1,2-hydrogen-bridged ethyl cation had been found unimportant in the reaction of ethyl amine with nitrous acid (5).

In 1960, Reutov and Shatkina repeated the work of Roberts and Halmann. They degraded both the 1-propanol and 2-propanol products and reported that in both the label was at C-1 and C-3 only. They, therefore, suggested that the rearrangement proceeded either *via* a 1,3-hydride shift with a hydrogen-bridged transition state as II, or by successive 1,2-hydride shifts (6,7,8).

On the basis of an n.m.r. study of the 1- and 2-propanol products of the deamination of 1-aminopropane-1,1,2,2-*d*$_4$, Karabatsos and Orzech ruled out successive 1,2-hydride shifts and concluded that the rearrangement proceeded "mainly, if not exclusively" by way of a 1,3-hydride shift (9). This conclusion was corroborated by Reutov in a study of the deamination of 1-aminopropane-2-*t*, (10). Although no

experimental details were given (10), it was stated that the 2-propanol contained tritium at both C-1 and C-2, whereas the 1-propanol contained tritium at C-2 only.

Skell and his co-workers have generated carbonium ions in strongly basic media and observed related rearrangements (13,14,15). When alcohols were reacted with alkoxides, or hydroxide, and bromoform, olefins were formed and carbon monoxide was generated in yields depending on the structure of the alcohol ($1^{o}<2^{o}<3^{o}$). The following mechanism, which has been criticized (11,12), was proposed for this "deoxidation" reaction (13):

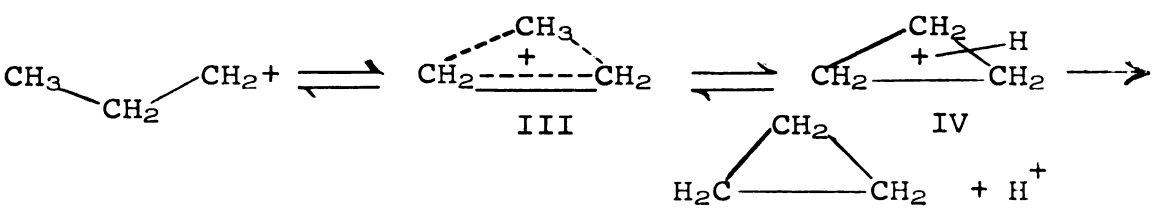
$$HCX_3 + RO^- \longrightarrow ROH + {}^-CX_3 \xrightarrow{-X^-} :CX_2$$

$$RO^- + :CX_2 \longrightarrow X^- + R\ddot{O}CX \longrightarrow R^+ + CO + X^-$$

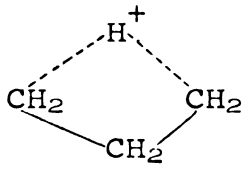
or,

$$RO^- + :CX_2 \longrightarrow 2X^- + ROC^+ \longrightarrow R^+ + CO$$

When 1-propanol was reacted under these conditions, the C_3H_6 products were found to be propylene and cyclopropane in a 9:1 ratio. Skell observed that this same ratio of propylene to cyclopropane was also obtained in the deamination of 1-aminopropane and suggested that a short-lived protonated cyclopropane intermediate might be common to both reactions (14):



Later, 1-propanol-1,1-$\underline{d}_2$ was deoxidated to yield cyclopropane which was 94 $\pm$ 2% $C_3H_4D_2$ and 5-6% C_3H_5D (15). It was thus established that the process was cationic and not carbenoid; however, in view of Reutov's deamination studies (6), the formation of cyclopropane was interpreted as proceeding $\underline{via}$ 1,3 ring closure with loss of a proton, rather than by way of protonated cyclopropane such as IV. The formation of cyclopropane-$\underline{d}$ was explained as a 1,3-interaction resulting in a 1,3-hydride shift which proceeded through the 1,3-hydrogen-bridged transition state V and was followed by ring closure with loss of a deuteron or proton.



V

In 1963, Baird and Aboderin revealed the fact that cyclopropane, when stirred with 7.5 M D_2SO_4, underwent hydrogen-deuterium exchange to give C_3H_5D and $C_3H_4D_2$ species in addition to undergoing solvolytic ring opening to $\underline{n}$-propyl products. The rate of solvolysis was about twice that of exchange (16). When the ring-opened products from solvolysis in 8.4 M D_2SO_4 were examined, they were found to consist of 1-propanol with traces of 2-propanol (<0.3%) and di-$\underline{n}$-propyl ether (17). The isotopic composition of the 1-propanol was examined by n.m.r. and found to correspond to a deuterium

distribution of 0.38 ± 0.03 deuterium atom at C-1, 0.17 ± 0.04 at C-2, and 0.46 ± 0.03 at C-3. (Deno and co-workers report equal amounts of deuterium at C-1 and C-2 (18).) 1-Propanol-1,1-$\underline{d}_2$ did not undergo isotope-position rearrangement when subjected to conditions more rigorous than those used in this experiment. The mechanism shown in Figure 1 was suggested to account for these results. (A variation of this mechanism has also been suggested by K. B. Wiberg (19).)

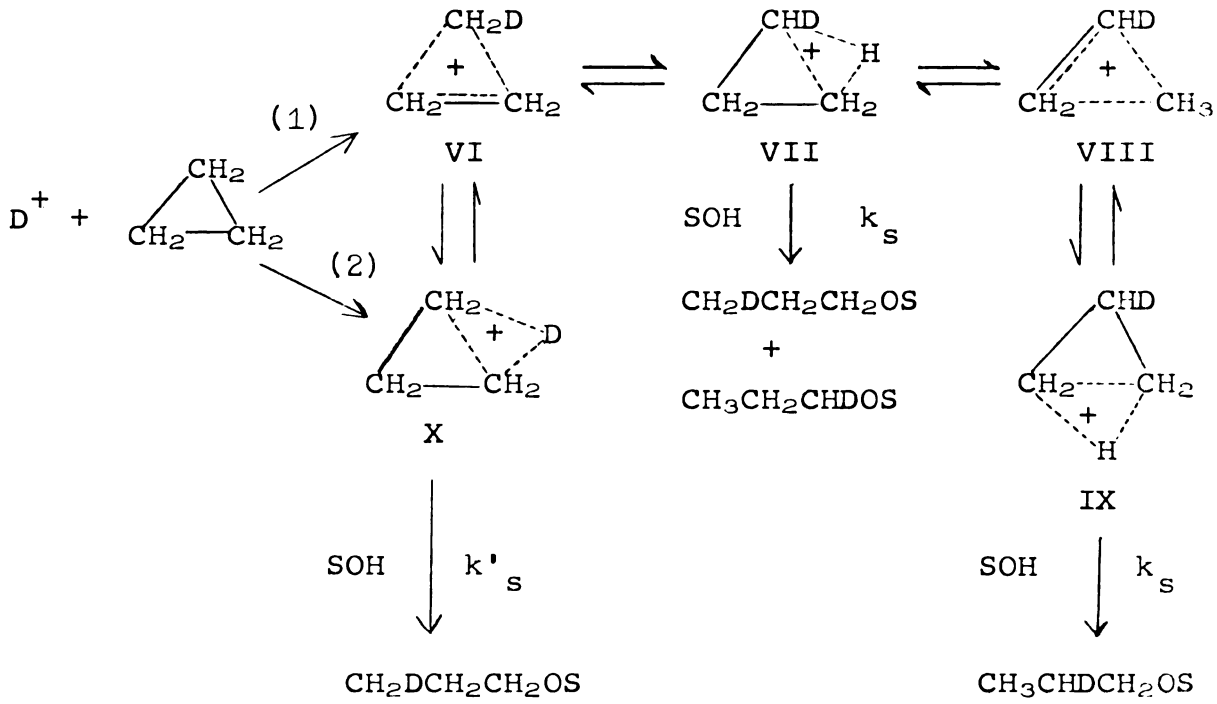
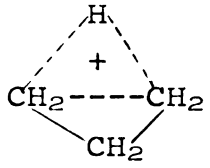


Figure 1. D_2SO_4 solvolysis of cyclopropane.

Baird and Aboderin state that the experimental results are best explained on the assumption that the solvolytic ring opening occurs with the hydrogen-bridged ions VII, IX, and X, rather than with the methyl-bridged ions VI and VIII.

This led to the postulation that a 1-propyl cation, or its immediate precursor (such as formed in deamination or deoxidation reactions), should be able to undergo a variety of reactions, including the loss of a proton, the addition of solvent, rearrangement to the 2-propyl cation, and cyclization to the hydrogen-bridged ion, XI, i.e., an edge-protonated cyclopropane.



XI

Ion XI could, of course, either undergo solvolytic ring opening, or lose a proton to form cyclopropane. Proton equilibration could occur as shown in Figure 1. The extent to which such equilibration could proceed would depend on how fast the ring protons could exchange into the hydrogen-bridging position compared with how fast the ion could undergo solvolysis or loss of a proton. If the former process were very fast compared with the latter two, then the intermediate might appear to be a symmetrically "face-protonated" cyclopropane IV, as originally postulated by Skell (14). Molecular orbital calculations indicate, qualitatively, that the methyl-bridged ion III is more stable than an open 1-propyl cation (20) and that the edge-protonated cyclopropane XI is, in turn, more stable than III (21).

The deamination of 1-aminopropane-3,3,3-$\underline{d}_3$ led to 43 ± 1% cyclopropane-$\underline{d}_2$ and 57 ± 1% cyclopropane-$\underline{d}_3$ (19). Baird and Aboderin argued that if the cyclopropane arose by the 1,3-interactions described by Skell (15), then no more than 6% cyclopropane-$\underline{d}_3$ should have been formed if there were no isotope effects on deprotonation, and only 31% if K_H/k_D were as large as 7. They rejected Skell's mechanism and stated that the results could be explained by equilibration of ions such as XI, by a mechanism like that in Figure 1, if an isotope effect of K_H/k_D = 2.7-3.0 were in operation for deprotonation. They concluded by postulating that 1,3-rearrangements could be more readily interpreted in terms of protonated cyclopropane intermediates than <u>via</u> equilibration of the primary cations. They warned, however, that care should be taken in extending this interpretation into other systems.

Soon after this, both Lee and Karabatsos and their coworkers published data from reinvestigations of the 1-aminopropane deamination. Lee found (22) that the deamination of 1-aminopropane-1-<u>t</u> produced 1-propanol containing 1.2-1.3% of the tritium label at C-2 and 1.6-1.7% at C-3. 1-Aminopropane-1-^{14}C was once again deaminated (23), yielding 1-propanol containing 2.2% carbon-14 at C-2 and 1.9% at C-3. These data ruled out the possibilities of successive 1,2-hydride shifts or a 1,3-hydride shift and it was postulated that 4-6% of the 1-propanol product was formed from a protonated cyclopropane intermediate or transition state.

The experimental data did not allow a distinction to be made between a face-protonated species such as IV or a rapidly equilibrating edge-protonated species such as XI.

Karabatsos and co-workers studied the isotopic composition of C-1 of the 1-propanol products from the deamination of deuterated 1-aminopropanes by mass spectrometry (24). Thus, 1-aminopropane-1,1-$\underline{d}_2$ and -2,2-$\underline{d}_2$ gave the following product compositions:

$$CH_3CH_2CD_2NH_2 \xrightarrow{40^\circ} C_2H_5\text{-}CD_2OH + C_2H_4D\text{-}CHDOH + C_2H_3D_2\text{-}CH_2OH$$

100% $\underline{d}_2$	95.7%	1.0%	3.8%

$$CH_3CD_2CH_2NH_2 \longrightarrow$$

100% $\underline{d}_2$	1.2%	0.9%	97.9%

These data were explained in terms of the equilibration of edge-protonated cyclopropanes through a mechanism like that of Baird and Aboderin in Figure 1.

The intervention of protonated cyclopropane intermediates has been suggested for a wide variety of reactions and conditions, such as the acylation (25) and bromination (18) of cyclopropane, the hydrogen bromide catalyzed gas phase rearrangement of cyclopropane to propene (26), and in various rearrangements occurring in the mass spectrometer (27,28). The reported moist aluminum bromide catalyzed isomerization of propane-1-^{13}C to a mixture containing 33% propane-2-^{13}C may also proceed by such a mechanism (46). The formation of bicyclo[3.1.0]hexane (2%) from the deamination of cyclohexyl amine has been

interpreted as going *via* a protonated cyclopropane intermediate, as have various rearrangements observed upon deamination of alicyclic α-aminoketones (29). Although it has not been interpreted as such, an intermediate of this type could serve to explain the 1,3-hydride shifts reported to accompany the solvolysis of cyclohexyl tosylate (10,30) and the deamination of cyclohexyl amine (10,31). The formation of tricyclo[4.3.1.0] decane systems from the deamination of *trans*-9-decalylcarbinyl amines could also involve a protonated cyclopropane (32).

It is well, however, to heed the warning of Baird and Aboderin, urging caution in the broad generalization of such a mechanism into other systems. Friedman and his co-workers have studied the deamination of various systems in aprotic solvents (33,34) and have found that cations generated under such conditions are of a higher energy than the same cations formed under conditions in which they may be stabilized through solvation. Such high energy cations have a tendency to give products of kinetic, rather than thermodynamic, control. Thus, *n*-, *sec*-, and isobutylamine (but not *t*-butyl) all gave methylcyclopropane, along with other products, when deaminated under these conditions (35,36). This product has been explained as arising from edge-protonated cyclopropane intermediates common to all three reactions. Both *n*- and isobutyl (but not *sec*- or *t*-butyl) alcohol gave methylcyclopropane under deoxidation conditions (13).

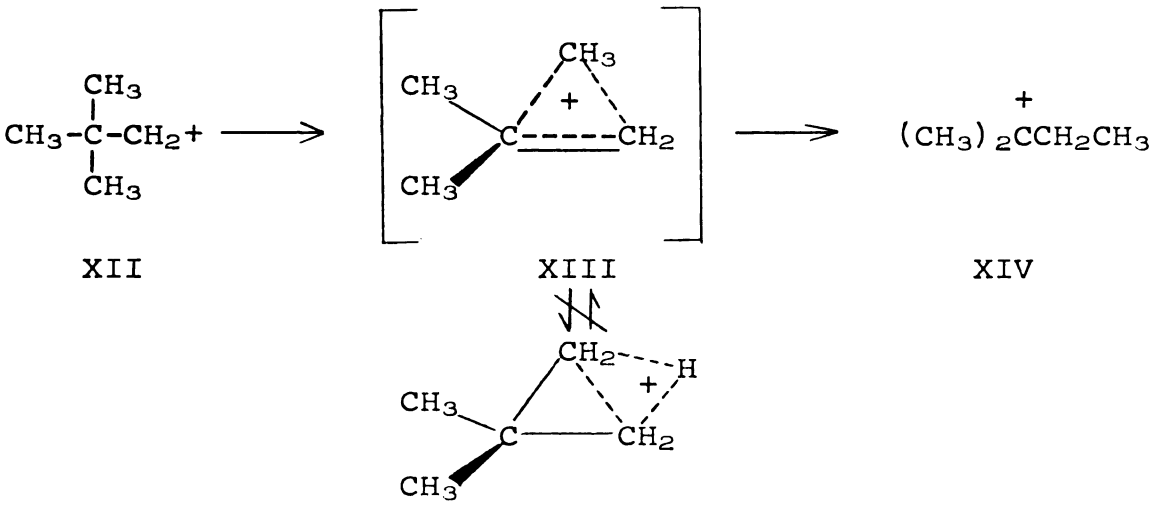
Significantly, Karabatsos and co-workers have shown, by using isotopically labeled amines, that in aqueous media pathways involving protonated cyclopropane intermediates can not be important to the formation of the alcoholic solvolysis products from the deamination of either n-butyl or isobutyl amine (37,38).

Small amounts of ethylcyclopropane and dimethylcyclopropane have been reported in the deoxidation of 2-methyl-1-butanol (39). Although an appreciable quantity of dimethylcyclopropane is produced on deamination of 3-methyl-2-aminobutane in anhydrous acetic acid, the solvolysis of 3-methyl-2-butyl tosylate under the same conditions produces none (40,41). It seems very likely that this difference may be ascribed to the lack of formation of a "free" 3-methyl-2-butyl cation in the tosylate solvolysis. It may be that a cation formed by the loss of a small, stable molecule, such as nitrogen on deamination or carbon monoxide on deoxidation, is "freer" in the sense that it is less strongly solvated ("hot" carbonium ion) and, hence, tends to give more products of kinetic, rather than thermodynamic, control, much as observed in Friedman's study of poorly solvated cations.

The neopentyl (2,2-dimethyl-1-propyl) system undergoes many reactions in which t-pentyl (2-methyl-2-butyl) products are formed. Since this rearrangement formally proceeds by a 1,2-methyl shift, it would seem possible that protonated cyclopropanes might be involved. This does not appear to be

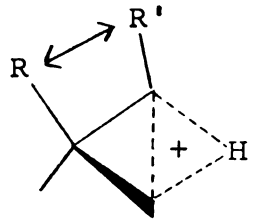
the case, since neither substituted cyclopropanes, nor evidence for anything occurring other than a simple 1,2-methyl shift to the tertiary cation have been observed while studying deoxidations (13,42), deaminations, solvolyses (43,44), or acid treatment of neopentyl alcohol (45).

In general then, the possibility of protonated cyclopropane species intervening appears to be greatest for the propyl system and diminishes for higher homologs. Thermodynamically, this would seem to indicate that unsubstituted protonated cyclopropane must have a stability intermediate between the 1-propyl cation and the 2-propyl cation, and so can compete favorably with both for product control. Apparently, the substituted protonated cyclopropane is not as stable, in relation to the other ions potentially formed, and so it intervenes to a much lesser extent, being detected only by formation of cyclopropane products, if at all. In the extreme case, that of the neopentyl cation XII rearranging to the t-pentyl cation XIV, the substituted protonated cyclopropane must be much less stable than the tertiary ion; so much so that the methyl-bridged ion XIII could now be at, or close to, the maximum free energy on the reaction coordinate. Thus, it never equibrates ring protons at all, but instead proceeds directly to the more stable tertiary ion XIV.



XII XIII XIV

Karabatsos and co-workers have pointed out (37,38) that as hydrogens on the ring of various protonated cyclopropanes are replaced by alkyl groups, the protonated cyclopropane may become progressively less stable due to unfavorable steric interactions caused by eclipsing of adjacent groups.

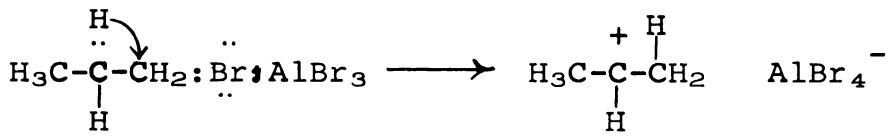


The purpose of the work reported in this thesis was to obtain a better understanding of the nature of rearrangements occurring through cationic species in the propyl system under widely different conditions. For this reason the solvolysis of 1-propyl tosylate in nearly anhydrous formic acid and the aluminum bromide catalyzed isomerization of bromopropanes were chosen for study by means of isotope-position labeling. Published work regarding the former reaction will be discussed later.

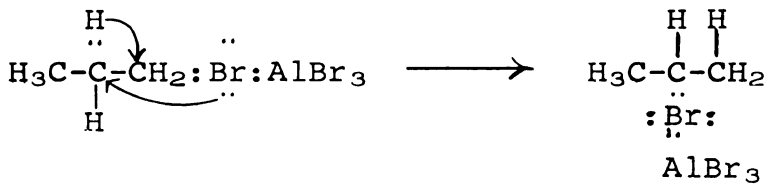
The isomerization of 1-bromopropane (1-BrPr) to 2-bromopropane (2-BrPr) by the action of aluminum bromide has been known since the 1870's and has been extensively studied since then (47). Brown and Wallace found that at 0° only 2-bromopropane was obtained if either 1-bromopropane or 2-bromopropane were reacted with aluminum bromide for 9 hours in a ca. 4:1 molar ratio (48). Hydrogen bromide was evolved during the isomerization, but addition of it to the starting material did not affect the reaction. Doering and his coworkers (49) had earlier reported that the addition of deuterium chloride did not affect the aluminum chloride catalyzed isomerization of 1-chloropropane to 2-chloropropane at 0°, and that no deuterium was found in the product. It was also shown that under these conditions the rate of addition of hydrogen chloride to propene to form 2-chloropropane was slower than the observed rate of isomerization, thus ruling out reversible dehydrochlorination as a mechanism. It was suggested

$$CH_3CH_2CH_2Cl \rightleftharpoons CH_3CH{=}CH_2 + HCl \rightleftharpoons CH_3CHClCH_3$$

that the reaction could proceed by the formation of a carbonium ion or its equivalent, followed by an intramolecular hydride shift and recombination with chloride from the catalyst. In view of these facts, Brown postulated that the 1- to 2-bromopropane isomerization could proceed by one of two paths; either ionization "assisted" by a 1,2-hydride shift,



or by a sort of concerted hydrogen-bromine shift with no ionization occurring.



The latter mechanism would not appear to be valid, however, in view of the report that bromine exchange between ^{82}Br labeled 1-bromopropane and aluminum bromide in carbon disulfide solution occurs much faster than the formation of 2-bromopropane (the exchange reaction is one-half order with respect to 1-bromopropane and second order with respect to aluminum bromide) (50).

Douwes and Kooyman have studied the kinetics of this reaction in carbon disulfide solution at -20° and found that it was quite complex, with the molecularity depending on the initial molar ratios of the reactants (51). Unlabeled 1-bromopropane isomerized 3.4 times faster than did 1-bromopropane-2,2-$\underline{d}_2$ and in the presence of deuterium bromide no deuterium was incorporated into the 2-bromopropane product. Furthermore, in 1-bromopropane-2-$\underline{d}$, the hydrogen shifted 3.3 times faster than the deuterium atom. They also observed that when the labeled reactants were used the mass spectra

of both the 1- and 2-bromopropanes recovered contained the same number of deuterium atoms as did the starting materials. The mass spectrum of the recovered 1-bromopropane was identical to that of the starting material. They interpreted these results as ruling out intermolecular deuterium exchange or intramolecular scrambling, including carbon skeletal isomerization. They noted, however, that 1,3-hydride shifts were not excluded, and suggested the following mechanism:

$$n\text{-}AlBr_3 + \underline{n}\text{-propyl bromide} \underset{\text{fast}}{\rightleftharpoons} (\underline{n}\text{-propyl}^+ Al_nBr_{3n+1}^-)$$

$$(\underline{n}\text{-propyl}^+ Al_nBr_{3n+1}^-) \xrightarrow{\text{slow}} \text{isopropyl bromide}$$

They pointed out that the "$\underline{n}$-propyl$^+$ should not be regarded as a fully developed cation but may be merely a $\underline{n}$-propyl fragment carrying a significantly greater positive charge than in free $\underline{n}$-propyl bromide."

Adema and co-workers studied this same isomerization in carbon disulfide solution at 24° by a microwave technique (52). They found that both bromopropane isomers formed 1:1 complexes with aluminum bromide under these conditions.

$$2(1\text{-BrPr}) + Al_2Br_6 \rightleftharpoons 2(1\text{-BrPr}\cdot AlBr_3) \quad ; \quad K_1 = 1.3\pm0.3 \text{ l/mole}$$

$$2(2\text{-BrPr}) + Al_2Br_6 \rightleftharpoons 2(2\text{-BrPr}\cdot AlBr_3) \quad ; \quad K_2 = 7.30\pm0.14 \text{ l/mole}$$

The following three kinetic expressions could be obtained for the isomerization:

$$v = k[1\text{-BrPr}][Al_2Br_6]$$

$$v = k'[1\text{-BrPr}\cdot AlBr_3][Al_2Br_6]^{1/2}$$

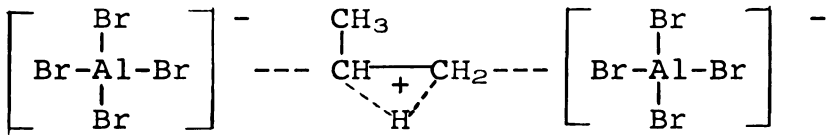
$$v = k''[1\text{-BrPr}\cdot AlBr_3]^2[1\text{-BrPr}]^{-1}$$

Although several mechanisms were compatible with these rate expressions, they favored the one shown below.

$$Al_2Br_6 \underset{\text{fast}}{\rightleftharpoons} AlBr_2^+ + AlBr_4^-$$

$$1\text{-BrPr}\cdot AlBr_3 + AlBr_4^- \underset{\text{slow}}{\rightleftharpoons} 2\text{-BrPr}\cdot AlBr_3 + AlBr_4^-$$

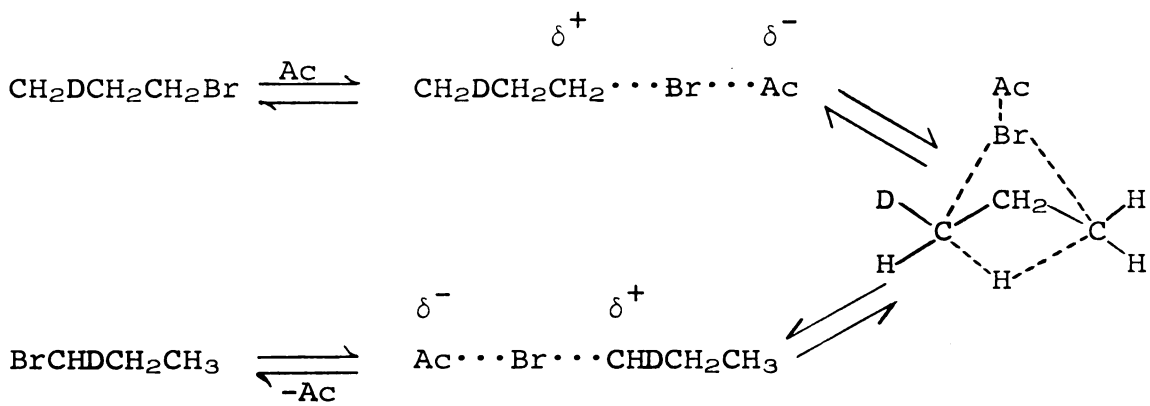
The transition state was pictured as:



1-Chloropropane-1-^{14}C is reported to be rapidly converted to 2-chloropropane-1-^{14}C (10) when treated with aluminum chloride. In contrast to this, when treated with an excess of zinc chloride and concentrated hydrochloric acid, 1-chloropropane-1-^{14}C was partially converted into 1-chloropropane-3-^{14}C with only traces of 2-chloropropane being formed (53). No 1-chloropropane-2-^{14}C was found and the reaction proceeded only in the presence of hydrochloric acid. The amount of 1-chloropropane-3-^{14}C formed depended on the reaction time, varying from 2.5% for reaction at 50° for 20 hours, to 16% for reaction at 20° for 1,500 hours. 1-Chloropropane-3-d was also partially converted to 1-chloropropane-1-d under

these conditions. When 1-chloropropane was treated with zinc chloride and concentrated hydrochloric acid containing deuterium chloride, no deuterium was incorporated into it. Under the same conditions, deuterium was exchanged into 2-chloropropane (10).

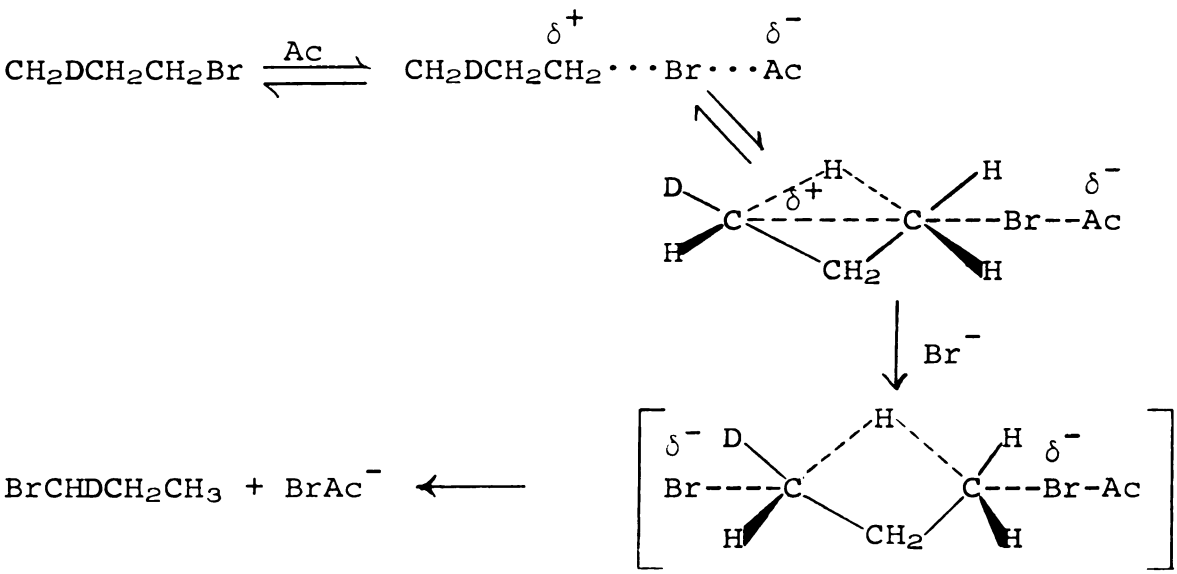
When 1-bromopropane-3-d was treated with zinc chloride in concentrated hydrochloric acid, a mixture of products including 2-chloropropane, 2-bromopropane, 1-chloropropane-1-d, and -3-d, and 1-bromopropane-1-d, and -3-d was formed (no percentages or experimental details were reported) (54,10). It was argued that since chloride was present in large excess, the 1-bromopropane-1-d wouldn't have been formed if a free cation were an intermediate, and so the 1,3-shift must have proceeded by the mechanism shown below.



(Ac = Lewis Acid, ZnX_2 or H^+)

Since no quantitative data were given, it is difficult to judge the merits of such a proposal. However, if the amount of 1-bromopropane-1-d formed were small, it seems conceivable that the rearrangements could also have proceeded by

nucleophilic attack on a bridged intermediate, as shown below, with the small amount of bromide ion present competing with chloride ion.



RESULTS

I. Formic Acid Solvolysis of 1-Propyl Tosylates

When 1-propyl tosylate (1-propyl p-toluenesulfonate) was heated in anhydrous formic acid at 50° for 40 hr. and then worked-up (see Experimental), 85% of it was recovered and no other products were observed. The same results were obtained when 1-propyl tosylate was heated in formic acid which was 0.556 M in water (0.86% by weight) at 60° for 72 hr. However, when heated in the latter solvent at 75° for 115 hr., a mixture of 1-propanol (93 ± 2%) and 2-propanol (7 ± 2%) was obtained in 30-35% yield. The absence of formate esters in the product was established by vapor phase chromatography (v.p.c.). This absence may have been due to the basic conditions used in the product work-up, which could have caused the hydrolysis of any esters formed to their respective alcohols.

Only 1-propanol was recovered (36%) when it was heated with an equimolar amount of p-toluenesulfonic acid in the nearly anhydrous formic acid at 75° for 40 hr.

A. 1-Propyl-1,1-d_2 Tosylate

1-Propyl-1,1-d_2 tosylate was solvolyzed in formic acid (0.556 M in H_2O) at 75 ± 1° for 144 hr. A mixture of 1-propanol (94 ± 2%) and 2-propanol (6 ± 2%) in 36% yield

was obtained. Trimethylsilyl ethers of the alcohols were prepared and subjected to mass-spectral analysis. Both ethers were prepared from run 2, while only the 1-propyltrimethylsilyl ether was prepared from run 1. The results are shown in Tables I-VI. In all of the reported mass spectra, the monoisotopic peak heights have been corrected for the presence of contaminating hexamethyldisiloxane (HMDS). The peak at m/e 147 was used for this correction.

Under the mass-spectral conditions used, the parent-less-methyl ion $[(P-Me)^+]$ is produced solely from silicon-carbon bond cleavage in 1-propyltrimethylsilyl ether (24). Analysis of this ion gives the isotopic composition of the entire propyl group. The parent-less-ethyl ion $[(P-Et)^+]$ arises from cleavage of the carbon-1-carbon-2 bond of the propyl group. Analysis of this ion gives the isotopic composition of the α-methylene group of the propyl moiety.

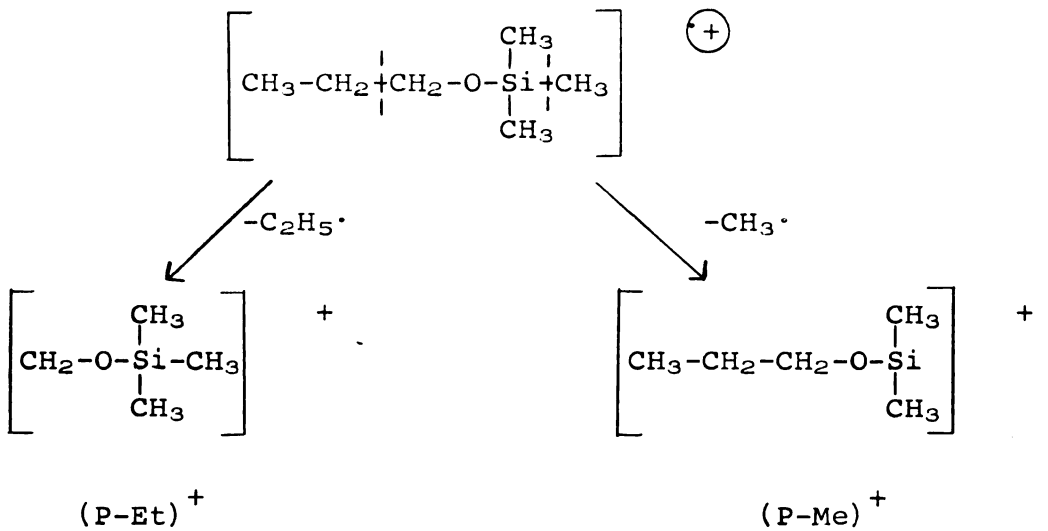


Table I. Mass spectrum of unlabeled $CH_3CH_2CH_2OSi(CH_3)_3$

M/e	Pk. Ht.	Mono.	
122	0.1	0.0	
121	0.9	0.3	
120	6.5	0.9	
119	93.0	11.5	
118	222.0	1.7	$(P-Me)^+$
117	2050.0	2054.2	99.3% at mass 117
116	2.9	1.6	
115	12.1	12.1	
		Σ 2067.9	
106	1.3	0.4	
105	18.0	1.5	
104	42.2	1.5	$(P-Et)^+$
103	424.0	422.7	91.0% at mass 103
102	4.6	1.7	
101	30.0	29.6	
100	1.3	0.3	
99	10.4	10.4	
		Σ 464.7	
147	4.0	Conc. HMDS = 0.08 vol. percent	

Table II. Mass spectrum of $CH_3CH_2CD_2OSi(CH_3)_3$ from precursor for 1-propyl-1,1-$\underline{d}_2$ tosylate used in runs 1 and 2, and 1-bromopropane-1,1-$\underline{d}_2$ used in runs 4, 10, and 13.

M/e	Pk. Ht.	Mono.			
122	5.0	0.1			
121	91.2	0.7		$(P\text{-}Me)^+$	
120	246.6	0.4		Mono.	Dist'n.
119	2286.0	2282.8	99.3% of	2282.8	99.0% $\underline{d}_2$
118	28.8	28.0	Σ = 2307.0	24.2	1.0% $\underline{d}_1$
117	5.6	4.8		2307.0	
116	7.1	7.0			
115	0.7	0.7			
		Σ 2323.3			
108	0.6	-.2			
107	17.2	0.0		$(P\text{-}Et)^+$	
106	42.7	-.3		Mono.	Dist'n.
105	446.0	444.3	91.4% of	444.3	98.3% $\underline{d}_2$
104	9.9	7.2	Σ = 452.1	7.2	1.6% $\underline{d}_1$
103	26.8	26.1		0.6	0.1% $\underline{d}_0$
102	5.7	5.1		452.1	
101	5.1	4.5			
100	5.7	5.6			
99	1.3	1.3			
98	0.3	0.3			
97	0.2	0.2			
		Σ 494.6			
147	1.0	Conc. HMDS = 0.017 vol. percent			

Table III. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 1.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	Dist'n.
122	3.1	0.4			
121	51.4	0.3			
120	138.0	-.7			
119	1290.0	1288.1	99.3% of	1288.1	98.8% d_2
118	17.0	16.5	Σ = 1303.5	15.4	1.2% d_1
117	3.9	3.5		1303.5	
116	4.0	3.9			
115	0.7	0.7			
		Σ 1312.7			
108	0.6	0.5			
107	10.1	0.6			
106	24.0	0.2			
105	246.3	245.1	90.6% of	245.1	97.8% d_2
104	7.3	5.7	Σ = 250.7	5.6	2.2% d_1
103	16.1	15.7		250.7	
102	3.5	3.1			
101	3.0	2.7			
100	3.0	2.9			
99	0.9	0.8			
98	0.7	0.7			
		Σ 276.7			
147	1.8	Conc. HMDS = 0.04 vol. percent			

$(P\text{-}Et)^+$

Mono.	Dist'n.
245.1	97.8% d_2
5.6	2.2% d_1
250.7	

Table IV. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 2.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	5.1	-.1			
121	96.0	-2.4			
120	263.7	-3.7			
119	2487.0	2483.5	99.3% of	2483.5	98.9% d_2
118	31.7	30.8	Σ = 2510.6	27.1	1.1% d_1
117	6.5	5.5		2510.6	
116	7.7	7.6			
115	0.7	0.7			
114	0.2	0.2			
		Σ 2528.3			
107	18.2	0.2		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
106	44.2	-1.1			
105	468.0	466.1	91.0% of	466.1	98.2% d_2
104	10.9	7.9	Σ = 474.4	7.9	1.7% d_1
103	30.2	29.4		0.4	0.1% d_0
102	6.2	5.5		474.4	
101	5.7	5.1			
100	6.1	6.0			
99	1.3	1.3			
		Σ 521.3			
147	6.3	Conc. HMDS = 0.13 vol. percent			

Table V. Mass spectrum of unlabeled $(CH_3)_2CHOSi(CH_3)_3$

M/e	Pk. Ht.	Mono.	
122	0.1	0.1	
121	0.2	0.2	
120	5.0	0.3	
119	89.2	0.1	
118	240.3	-1.1	$(P-Me)^+$
117	2250.0	2248.3	99.1% at mass 117
116	8.2	6.7	
115	13.5	13.2	
		Σ 2268.2	
106	0.1		
105	0.5		
104	0.9		
103	3.1		
102	5.2		
101	37.1		
100	1.0		
99	3.6		
147	39.7	Conc. HMDS = 0.79 vol. percent	

Table VI. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol product of run 2.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	$(P\text{-}Me)^+$ Dist'n.
122	0.2	-.1			
121	5.0	-.1			
120	14.9	0.6			
119	129.6	126.9	99.1% of	126.9	76.7% d_2
118	18.2	15.5	= 165.5	15.5	9.4% d_1
117	24.5	24.0		23.1	13.9% d_0
116	0.7	0.6		165.5	
115	0.2	0.0			
		Σ 167.0			
106	0.2				
105	2.1				
104	1.0				
103	7.0				
102	1.0				
101	1.0				
147	29.0	Conc. HMDS = 0.71 vol. percent			

The cracking pattern of 2-propyltrimethylsilyl ether is more complex and will be discussed later.

B. 1-Propyl-2,2-d_2 Tosylate

1-Propyl-2,2-d_2 tosylate was solvolyzed as in runs 1 and 2 to give a mixture of 1-propanol (97.7 ± 0.6%) and 2-propanol (2.3 ± 0.6%) in *ca*. 48% yield (run 3). The trimethylsilyl ether derivatives were prepared and analyzed by mass spectrometry. The results are shown in Tables VII-IX.

No meaningful data were obtained for the isotopic composition of the 2-propanol product. From the ratio of Σ 103/Σ 117 for the 2-propyltrimethylsilyl ether (Table IX), it seems probable that it was contaminated with an indeterminate amount of what may be 1-propyltrimethylsilyl ether and therefore the calculated distribution is not valid. The benzoate ester of the 2-propanol was analyzed, but it was found to contain an unknown impurity which contributed to m/e 166. An accurate isotopic distribution was thus impossible.

II. Bromopropane Hydrolyses

As a prerequisite for additional studies, it was necessary to demonstrate that isotopically labeled propanols could be converted to bromopropanes and back to the respective propanols without undergoing isotope-position rearrangements.

Table VII. Mass spectrum of $CH_3CD_2CH_2OSi(CH_3)_3$ from precursor for 1-propyl-2,2-$\underline{d}_2$ tosylate used in run 3, and 1-bromopropane-2,2-$\underline{d}_2$ used in run 5.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.[a]
122	3.8	0.3			
121	60.8	3.7			
120	156.0	0.6			
119	1443.0	1440.0	99.3% of	1440.0	98.3% $\underline{d}_2$
118	27.1	26.5	Σ = 1465.6	25.6	1.7% $\underline{d}_1$
117	4.6	4.1		1465.6	
116	4.9	4.9			
115	0.4	0.4			
		Σ 1475.9			
107	0.6	0.5		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
106	0.9	0.2			
105	12.0	1.9	90.6% of	1.9	0.8% $\underline{d}_2$
104	27.0	2.2	Σ = 247.5	2.2	0.9% $\underline{d}_1$
103	256.8	256.2		243.4	98.3% $\underline{d}_0$
102	5.0	4.5		247.5	
101	3.8	3.4			
100	3.6	3.5			
99	0.9	0.8			
98	0.7	0.7			
		Σ 273.2			
147	2.3	Conc. HMDS = 0.05 vol. percent			

[a]Another sample prepared from this same alcohol gave the following distribution: $(P-Me)^+$, 98.4% $\underline{d}_2$, 1.6% $\underline{d}_1$; $(P-Et)^+$, 0.6% $\underline{d}_2$, 0.3% $\underline{d}_1$, 99.1% $\underline{d}_0$ (55).

Table VIII. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 3.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	3.9	0.1			
121	72.0	-.3			
120	195.3	-1.4			
119	1827.0	1823.4	99.3% of	1823.4	98.4% $\underline{d}_2$
118	32.6	32.0	Σ = 1853.5	30.1	1.6% $\underline{d}_1$
117	4.1	3.4		1853.5	
116	6.0	5.8			
115	2.0	2.0			
		Σ 1866.6			
106	0.9	0.3			
105	13.1	0.6			
104	31.5	0.3			
103	323.0	322.2	91.2% of		
102	5.5	4.9	Σ = 307.0[a]		
101	4.8	4.4			
100	4.2	4.1			
99	0.9	0.9			
		Σ 336.6			
147	2.2	Conc. HMDS = 0.06 vol. percent			

$(P-ET)^+$ Mono. 307.0 — $(P-ET)^+$ Dist'n. 100.0% $\underline{d}_0$

[a]Less than m/e 103.

Table IX. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol product of run 3.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	2.1	0.1			
121	38.3	-.3			
120	118.5	0.7			
119	999.0	951.5	99.1% of	951.5	65.0% $\underline{d}_2$
118	407.0	393.2	Σ = 1465.8	393.2	26.9% $\underline{d}_1$
117	126.9	124.9		118.1	8.1% $\underline{d}_0$
116	5.0	4.4		1462.8	
115	2.6	1.7			
114	0.1	0.1			
113	0.7	0.3			
		Σ 1476.1			
106	1.0	0.4			
105	9.0	3.9			
104	12.6	2.4			
103	102.0	99.5[a]			
102	13.0	11.5			
101	5.9	4.9			
100	0.9	0.0			
99	0.9	0.9			
		Σ 116.8			
147	117.0	Conc. HMDS = 3.21 vol. percent			

[a]The large m/e 103 peak suggests the presence of an unknown amount of contaminating $CH_3CH_2CH_2OSi(CH_3)_3$ which casts serious doubt on the validity of the calculated distribution.

A. Silver Ion-Assisted Hydrolysis

1- and 2-Bromopropanes were prepared by phosphorous tribromide treatment of their respective alcohols. The bromides were stirred in 15% aqueous silver nitrate solutions at room temperature for 70-93 hr. Trimethylsilyl ether derivatives of the alcoholic products were prepared for mass-spectral analysis.

1-Bromopropane-1,1-$\underline{d}_2$ (98.7% $\underline{d}_2$ and 1.3% $\underline{d}_1$ by parent ion analysis) produced 1-propanol in 72% yield (run 4). The results are shown in Table X. Table II gives the isotopic composition of the 1-propanol-1,1-$\underline{d}_2$ precursor to the 1-bromopropane-1,1-$\underline{d}_2$.

1-Bromopropane-2,2-$\underline{d}_2$ (98.4% $\underline{d}_2$ and 1.6% $\underline{d}_1$ by parent ion analysis) produced 1-propanol in 59% yield (run 5). The results are shown in Table XI. Table VII gives the isotopic composition of the 1-propanol-2,2-$\underline{d}_2$ precursor to the 1-bromopropane-2,2-$\underline{d}_2$.

2-Bromopropane-2-$\underline{d}$ (99.0% $\underline{d}_1$ and 1.0% $\underline{d}_0$ by parent ion analysis) produced 2-propanol in $\underline{ca}$. 80% yield (run 6). The mass spectrum of the trimethylsilyl ether of this product is shown in Table XIII. The mass spectrum of the trimethylsilyl ether of the 2-propanol-2-$\underline{d}$ precursor (98.8 ± 0.2% $\underline{d}_1$ and 1.2 ± 0.2% $\underline{d}_0$ by parent ion analysis of the benzoate ester) to the 2-bromopropane-2-$\underline{d}$ is shown in Table XII.

Table X. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 4.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	4.3	-.6			
121	92.1	1.2			
120	247.0	-.1			
119	2298.0	2294.7	99.3% of	2294.7	98.9% $\underline{d}_2$
118	29.6	28.8	Σ = 2319.7	25.0	1.1% $\underline{d}_1$
117	6.0	5.2		2319.7	
116	7.1	7.1			
115	0.3	0.3			
		Σ 2336.1			
108	1.0	0.2			
107	17.1	0.0		$(P-Et)^+$	
106	42.7	-.3		Mono.	Dist'n.
105	446.0	444.2	91.4% of	444.2	98.0% $\underline{d}_2$
104	10.8	8.1	Σ = 453.2	8.1	1.8% $\underline{d}_1$
103	27.0	26.3		0.9	0.2% $\underline{d}_0$
102	5.8	5.1		453.2	
101	5.3	4.7			
100	5.8	5.7			
99	1.3	1.3			
98	0.2	0.2			
97	0.2	0.2			
		Σ 495.8			
147	3.0	Conc. HMDS = 0.05 vol. percent			

Table XI. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 5.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	4.7	0.1			
121	86.4	0.1			
120	235.5	0.6			
119	2181.0	2176.6	99.3% of	2176.6	98.4% d_2
118	40.5	39.8	Σ = 2212.1	35.5	1.6% d_1
117	4.9	4.1		2212.1	
116	7.0	7.0			
115	0.2	0.2			
		Σ 2227.7			
				$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
106	1.0	0.2			
105	16.2	1.1	91.4% of	1.1	0.3% d_2
104	38.6	0.9	Σ = 374.0	0.9	0.2% d_1
103	390.0	389.2		372.0	99.5% d_0
102	7.0	6.3		374.0	
101	5.7	5.2			
100	5.0	4.9			
99	1.1	1.1			
98	0.3	0.3			
97	0.2	0.2			
		Σ 409.2			
147	1.0	Conc. HMDS = 0.017 vol. percent			

Table XII. Mass spectrum of $(CH_3)_2CDSi(CH_3)_3$ from precursor for 2-bromopropane-2-$\underline{d}$[a] used in runs 6, 19-21.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	$(P\text{-}Me)^+$ Dist'n.
122	0.2	0.2			
121	4.3	-.2			
120	83.9	-1.1			
119	228.0	-2.7			
118	2148.0	2146.4	99.1% of	2146.4	99.8% $\underline{d}_1$
117	19.9	13.9	Σ = 2151.2	4.8	0.2% $\underline{d}_0$
116	3.8	2.9		2151.2	
115	7.8	7.5			
		Σ 2170.7			
106	0.9				
105	2.6				
104	5.2				
103	26.0				
102	8.9				
101	2.0				
100	1.2				
99	0.2				
147	35.3	Conc. HMDS = 0.69 vol. percent			

[a]Parent ion analysis of this bromide gave an isotopic distribution of 99.0% $\underline{d}_1$ and 1.0% $\underline{d}_0$.

Table XIII. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol product of run 6.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$	
				Mono.	Dist'n.
122	0.3	0.3			
121	5.0	0.2			
120	90.0	-.7			
119	243.0	-4.0			
118	2292.0	2289.6	99.1% of	2289.6	99.5% d_1
117	22.4	21.5	Σ = 2300.9	11.3	0.5% d_0
116	3.6	2.6		2300.9	
115	8.2	8.0			
114	0.1	0.1			
		Σ 2321.8			
106	1.0				
105	2.0				
104	12.3				
103	9.5				
102	28.8				
101	9.9				
100	2.0				
99	1.4				
147	20.4	Conc. HMDS = 0.40 vol. percent			

B. Basic Hydrolysis

1-Bromopropanes were hydrolyzed by heating in 10% aqueous sodium hydroxide solution at steam bath temperature for 70 hr.

1-Bromopropane-1,1-$\underline{d}_2$ (same as used in run 4) produced 1-propanol in 35% yield (run 7). The mass spectrum of the trimethylsilyl ether of the product is given in Table XIV.

1-Bromopropane-2,2-$\underline{d}_2$ (same as used in run 5) produced 1-propanol in 49% yield (run 8). The results are shown in Table XV.

III. Aluminum Bromide Catalyzed Isomerizations of Bromopropanes

1-Bromopropane and 2-bromopropane may be interconverted by the action of aluminum bromide on the neat liquid. Results from a study of this interconversion at 0° are shown in Tables XVI and XVII. As may be seen, an equilibrium mixture containing 6% 1-bromopropane and 94% 2-bromopropane was attained from either side within an hour when a mixture of bromopropane and aluminum bromide in a ca. 5.8/1 molar ratio was used.

$$CH_3CH_2CH_2Br \underset{}{\overset{AlBr_3,\,0^\circ}{\rightleftharpoons}} CH_3CHBrCH_3$$

$$\Delta F_{273^\circ} = -1.5 \pm 0.1 \text{ kcal./mole}$$

By approach from the 2-bromopropane side, this equilibrium mixture was attained after 6 minutes; from the 1-bromopropane side, after about 10 minutes.

Table XIV. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 7.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$	
				Mono.	Dist'n.
122	4.6	-.3			
121	91.8	0.6			
120	248.1	0.3			
119	2304.0	2300.7	99.3Σ of	2300.7	98.9% d_2
118	30.0	29.1	Σ = 2326.6	25.9	1.1% d_1
117	6.2	5.4		2326.6	
116	7.0	6.9			
115	0.9	0.9			
		Σ 2343.0			
108	1.0	0.2			
107	17.2	0.0			
106	43.0	-.1			
105	447.0	445.2	91.4% of	445.2	98.1% d_2
104	10.6	7.9	Σ = 454.0	7.9	1.7% d_1
103	27.0	26.0		0.9	0.2% d_0
102	5.9	5.3		454.0	
101	4.9	4.3			
100	5.7	5.5			
99	1.6	1.6			
98	0.3	0.3			
97	0.3	0.3			
		Σ 496.7			
147	1.7	Conc. HMDS = 0.03 vol. percent			

Table XV. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol product of run 8.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	4.9	0.0			
121	92.4	0.8			
120	249.3	-.1			
119	2316.0	2311.3	99.3% of	2311.3	98.4% d_2
118	42.4	41.7	Σ = 2348.6	37.3	1.6% d_1
117	5.0	4.2		2348.6	
116	7.5	7.4			
115	0.6	0.6			
		Σ 2365.2			
				$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
106	1.0	0.2			
105	17.0	0.9	91.4% of	0.9	0.2% d_2
104	41.2	1.1	Σ = 398.1	1.1	0.3% d_1
103	415.0	414.2		396.1	99.5% d_0
102	7.3	6.6		398.1	
101	6.0	5.4			
100	5.8	5.7			
99	1.2	1.2			
98	0.3	0.3			
97	0.2	0.2			
		Σ 435.6			
147	2.0	Conc. HMDS = 0.035 vol. percent			

Table XVI. 1-Bromopropane + aluminum bromide reaction at 0°.

Run	1-BrPr/$AlBr_3$ (mole/mole)	Rxn. Time[a] (min.)	Recovered[b] BrPr, percent	1-BrPr, ±2%[f]	2-BrPr, ±2%
8A	14.9[c]	6.0	93	65	35
B	14.9[c]	5.6	33	48	52
C	13.8[c]	6.0	96	69	31
D	13.2[c]	6.0	94	72	28
E	13.2[d]	6.0	--	100	0
F	13.2[d]	6.0	--	100	0
G	13.2	6.0	89	58	42
H	10.4[e]	12.0	93	93	7
I	5.8	6.0	87	13	87
J	5.8	60.0	85	5.9±0.5	94.1±0.5
K	7.4	5.0	99	16	84

[a] Quenched with quinoline.
[b] Sum of 1-BrPr and 2-BrPr.
[c] Trace of diethyl ether in starting 1-BrPr.
[d] More than molar equivalent of diethyl ether added to $AlBr_3$ before addition of 1-BrPr.
[e] More than molar equivalent of quinoline added to $AlBr_3$ before addition of 1-BrPr.
[f] It did not contact some $AlBr_3$ in upper part of flask.
[f] By v.p.c. analysis.

Table XVII. 2-Bromopropane + aluminum bromide reaction at 0°.

Run	2-BrPr/$AlBr_3$ (mole/mole)	Rxn. Time[a] (min.)	Recovered[b] BrPr, percent	1-BrPr, ±2%[c]	2-BrPr, ±2%
9A	5.8	6.0	57	7	93
B	5.9	6.0	95	6	94
C	5.9	60.0	96	6.1±0.5	93.9±0.5
D	5.9	120.5	80	7	94
E	5.6	1.0	100	2	98
F	5.6	2.0	100	3	97
G	5.7	3.0	100	3	97
H	5.6	4.0	100	4	96

[a]Quenched with quinoline.
[b]Sum of 1-BrPr and 2-BrPr.
[c]By v.p.c. analysis.

Attempts were made to determine other products, in addition to the 1- and 2-bromopropanes, that might have formed. For reaction times of 6 minutes or less, no evidence for any other products could be found. After reaction times of 1 hour, many small, indistinct peaks resembling baseline noise could be detected in the vapor phase chromatograms of the reaction mixtures. These peaks could be obtained regardless of whether 1-bromopropane or 2-bromopropane was used as the reactant. The retention times were not reproducible, however, and the compounds were present in such trace amounts that they could not be isolated or identified even when mixtures from scaled-up reactions were fractionated. Small amounts of brown, polymeric residues were formed in all of these reactions.

There are large discrepancies in the literature regarding the formation of gaseous products in this reaction. Some workers have reported large amounts of hydrogen bromide being evolved (48,56), while others have reported the complete absence of any gaseous products (57). In the present study, hydrogen bromide was evolved rather slowly after about 10 minutes reaction time. If the reaction mixture was allowed to warm to room temperature, then hydrogen bromide evolution became quite rapid. Qualitatively, it was observed that there appeared to be less hydrogen bromide evolution when the reactants were carefully purified beforehand than when they were not.

Gas from the reaction of both 1-bromopropane and 2-bromopropane was trapped by being bubbled through carbon tetrachloride. Bubbles were generally formed after 10-15 minutes reaction time. The reaction time varied directly with the rate of stirring in the reaction flask. The resulting carbon tetrachloride solutions were the same, regardless of whether 1-bromopropane or 2-bromopropane was used as the initial reactant.

The infrared spectrum of this solution was identical to that of an authentic solution of 2-bromopropane in carbon tetrachloride. The 60 Mc./sec. nuclear magnetic resonance spectrum of this solution showed signals for 2-bromopropane (doublet centered at τ 8.30, multiplet centered at τ 5.78) and a complex multiplet with a sharp signlet at τ 9.09. The spectrum of this solution is shown in Figure 2. When the gases were collected in benzene, the n.m.r. spectrum again exhibited signals for 2-bromopropane; a doublet now centered at τ 8.66, and a sharp singlet of the multiplet at τ 9.13. These signals did not arise from solvent impurities. The portion of the spectrum not attributable to 2-bromopropane was found to be identical to the spectrum of an authentic solution of propane and in agreement with the published spectrum of propane (58).

A. Labeled 1-Bromopropanes

Labeled 1-bromopropanes were partially isomerized to 2-bromopropanes and converted to the alcohols by silver

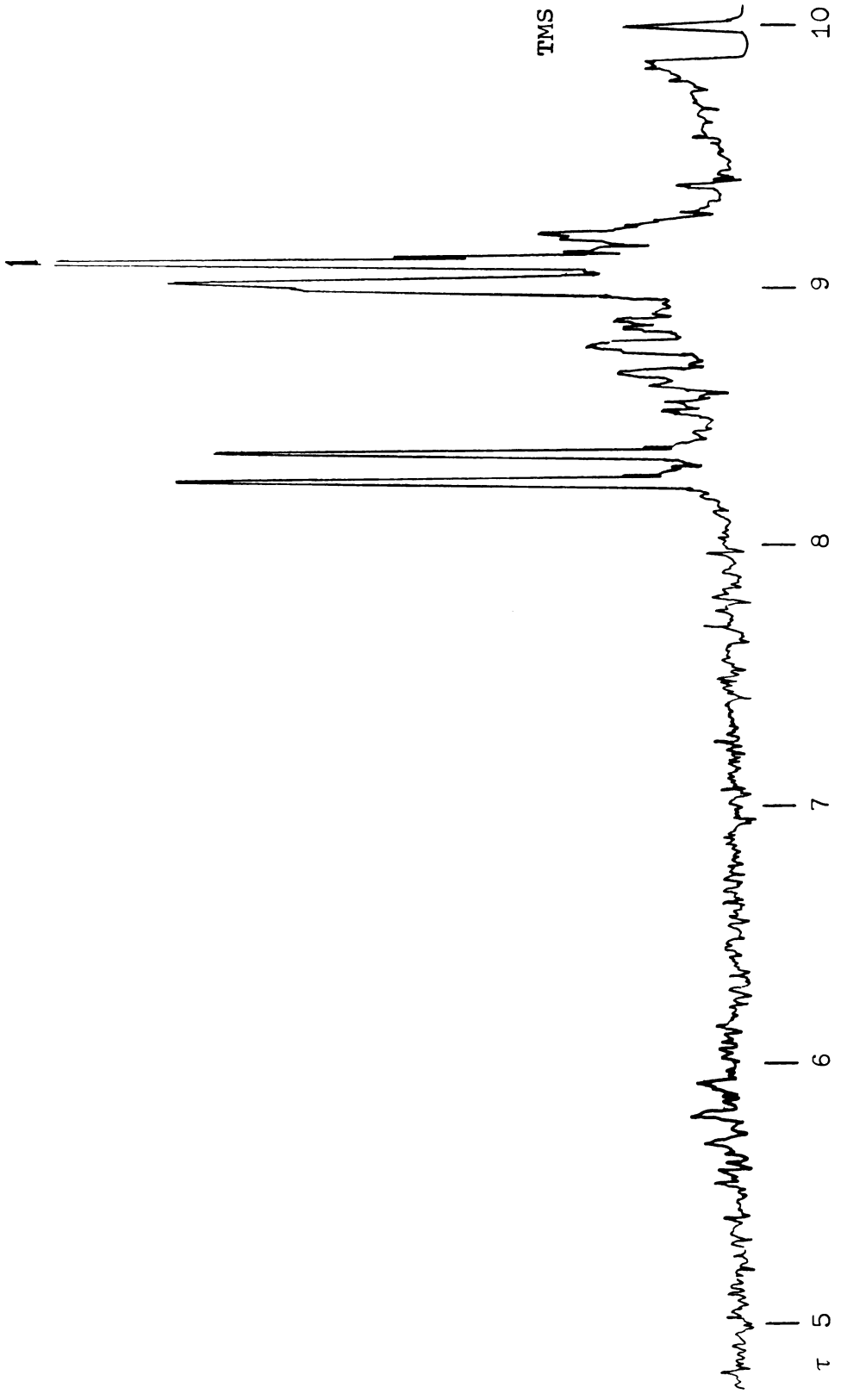


Figure 2. 60 Mc./sec. n.m.r. spectrum of gas collected in CCl_4 from the reaction of 2-bromopropane and aluminum bromide (5.7:1) at 0^0.

ion-assisted hydrolysis. Their isotopic compositions were studied by mass-spectral analysis of the trimethylsilyl ethers of the alcohols. The reaction conditions used in the various runs are summarized in Table XVIII. The mass-spectral analyses of the trimethylsilyl ethers derived from the recovered 1-bromopropane and 2-bromopropane products are summarized in Tables XIX and XX, respectively.

1. 1-Bromopropane-1,1-$\underline{d}_2$

Runs 10-14 were made with 1-bromopropane-1,1-$\underline{d}_2$ and the results of the mass-spectral analyses are given in Tables XXI-XXX. In order to facilitate interpretation of these data, it is necessary to correct for slight rearrangements occurring in the mass spectrometer and to subtract contributions from the $\underline{d}_1$ species in the reactant when discussing the isotopic composition of the 1-propyl products. The results of run 13 are used to illustrate the procedure employed.

The trimethylsilyl ether of a known sample of 1-propanol-1,1-$\underline{d}_2$ gave: $(P\text{-}Me)^+$, 99.0% $\underline{d}_2$, 1.0% $\underline{d}_1$; $(P\text{-}Et)^+$, 98.3% $\underline{d}_2$, 1.6% $\underline{d}_1$, 0.1% $\underline{d}_0$ (Table II). If it is assumed that all of the deuteria are at C-1, then rearrangement in the mass spectrometer has added an apparent increase of 0.6% to $\underline{d}_1$ and 0.1% to $\underline{d}_0$ at the expense of $\underline{d}_2$ in the parent-less-ethyl ion.

The trimethylsilyl ether of the 1-propanol derived from the recovered 1-bromopropane of run 13 gave: $(P\text{-}Me)^+$, 98.9% $\underline{d}_2$, 1.1% $\underline{d}_1$; $(P\text{-}Et)^+$, 78.2% $\underline{d}_2$, 6.4% $\underline{d}_1$, 15.4% $\underline{d}_0$ (Table XXVII).

Table XVIII. Labeled 1-bromopropane + aluminum bromide reaction at 0°.

Run	1-BrPr	1-BrPr/$AlBr_3$ (mole/mole)	Rxn. time[a] (min.)	Recovered[b] BrPr, percent	1-BrPr,[c] ± 2%	2-BrPr, ± 2%
10	$CH_3CH_2CD_2Br$	10.1[d]	6.0	97	86	14
11	$CH_3CH_2CD_2Br$	10.5	6.0	95	55	45
12	$CH_3CH_2CD_2Br$	5.6	5.0	93	21	79
13	$CH_3CH_2CD_2Br$	5.6[d]	6.0	100	20	80
14	$CH_3CH_2CD_2Br$	5.6	120.0	84	6	94
15	$CH_3CD_2CH_2Br$	5.7	5.0	78	42	58
16	$CH_3CD_2CH_2Br$	5.7	6.0	94	35	65
17	$CH_3CH_2{}^{13}CH_2Br$	5.7	4.7	94	15	85
18	$CH_3CH_2{}^{13}CH_2Br$	5.7	5.0	100	20	80

[a]Quenched with quinoline.
[b]Sum of 1-BrPr and 2-BrPr.
[c]By v.p.c. analysis.
[d]Trace of diethyl ether in starting 1-BrPr.

Table XIX. Mass spectral analysis of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane. Runs 10-16 and 18.

Run	$(P-Me)^+$	$(P-Et)^+$
10	98.8% $\underline{d}_2$, 1.2% $\underline{d}_1$	97.1% $\underline{d}_2$, 2.0% $\underline{d}_1$, 0.9% $\underline{d}_0$
11	99.0% $\underline{d}_2$, 1.0% $\underline{d}_1$	95.4% $\underline{d}_2$, 2.2% $\underline{d}_1$, 2.4% $\underline{d}_0$
12	98.7% $\underline{d}_2$, 1.3% $\underline{d}_1$	82.7% $\underline{d}_2$, 5.0% $\underline{d}_1$, 12.3% $\underline{d}_0$
13	98.9% $\underline{d}_2$, 1.1% $\underline{d}_1$	78.2% $\underline{d}_2$, 6.4% $\underline{d}_1$, 15.4% $\underline{d}_0$
14	6.1% $\underline{d}_3$, 87.0% $\underline{d}_2$, 6.5% $\underline{d}_1$, 0.4% $\underline{d}_0$	36.0% $\underline{d}_2$, 22.3% $\underline{d}_1$, 41.7% $\underline{d}_0$
15	98.1% $\underline{d}_2$, 1.9% $\underline{d}_1$	1.8% $\underline{d}_2$, 3.3% $\underline{d}_1$, 94.9% $\underline{d}_0$
16	98.0% $\underline{d}_2$, 2.0% $\underline{d}_1$	2.4% $\underline{d}_2$, 6.2% $\underline{d}_1$, 91.4% $\underline{d}_0$
18	54.6% ^{13}C, 45.4% ^{13}C	46.9% ^{13}C, 53.1% ^{12}C

Table XX. Mass spectral analysis of $(CH_3)_2$ $CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane. Runs 11-18.

Run	$(P-Me)^+$
11	84.9% $\underline{d}_2$, 1.6% $\underline{d}_1$, 13.5% $\underline{d}_0$
12	84.9% $\underline{d}_2$, 1.8% $\underline{d}_1$, 13.3% $\underline{d}_0$
13	84.6% $\underline{d}_2$, 2.1% $\underline{d}_1$, 13.3% $\underline{d}_0$
14	5.6% $\underline{d}_3$, 72.4% $\underline{d}_2$, 10.9% $\underline{d}_1$, 11.1% $\underline{d}_0$
15	80.9% $\underline{d}_2$, 18.6% $\underline{d}_1$, 0.5% $\underline{d}_0$
16	81.1% $\underline{d}_2$, 18.2% $\underline{d}_1$, 0.7% $\underline{d}_0$
17	24.1% ^{13}C, 75.9% ^{12}C
18	45.6% ^{13}C, 54.4% ^{12}C

Table XXI. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 10.

M/e	Pk.Ht.	Mono.		$(P\text{-}Me)^+$	
				Mono.	Dist'n.
122	4.7	0.2			
121	84.5	0.02			
120	229.8	0.1			
119	2136.0	2132.8	99.3% of	2132.8	98.8% d_2
118	28.2	27.3	Σ = 2158.7	25.9	1.2% d_1
117	6.6	5.8		2158.7	
116	7.1	7.0			
115	1.0	1.0			
		Σ 2173.9			
108	0.6	0.6			
107	16.0	0.2			
106	39.7	0.1			
105	410.0	408.2	91.2% of	408.2	97.1% d_2
104	11.2	8.4	Σ = 420.2	8.4	2.0% d_1
103	27.6	26.9		3.6	0.9% d_0
102	5.9	5.3		420.2	
101	5.0	4.4			
100	5.3	5.1			
99	1.7	1.6			
98	0.8	0.8			
		Σ 460.7			
147	3.0				

$(P\text{-}Et)^+$

Table XXII. Mass spectrum of $CH_3CH_2CD_2OSi(CH_3)_3$ from precursor for 1-bromopropane-1,1-$\underline{d}_2$ used in runs 11, 12, and 14.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.2	0.2			
122	5.2	0.02			
121	97.5	0.2			
120	261.0	-3.5			
119	2460.0	2456.6	99.3% of	2456.6	99.0% $\underline{d}_2$
118	30.9	30.2	Σ = 2481.2	24.6	1.0% $\underline{d}_1$
117	4.1	3.2		2481.2	
116	8.0	7.9			
115	0.8	0.8			
		Σ 2498.7			
108	0.9	0.1			
107	18.3	0.2			
106	45.3	-.1			
105	471.0	469.1	91.2% of	469.1	98.2% $\underline{d}_2$
104	10.8	7.8	Σ = 477.7	7.8	1.6% $\underline{d}_1$
103	29.3	28.5		0.8	0.2% $\underline{d}_0$
102	6.5	5.8		477.7	
101	5.7	5.1			
100	6.0	5.8			
99	1.7	1.7			
		Σ 523.8			
147	3.9	Conc. HMDS = 0.08 vol. percent			

Table XXIII. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 11.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.2	0.2			
122	5.0	-.2			
121	96.1	-1.5			
120	260.1	-4.4			
119	2460.0	2456.8	99.3% of	2456.8	99.0% d_2
118	29.6	28.9	Σ = 2480.6	23.8	1.0% d_1
117	4.6	3.7		2480.6	
116	8.0	7.9			
115	0.8	0.8			
		Σ 2498.1			
108	1.0	0.2			
107	17.6	0.04			
106	43.2	-1.0			
105	457.0	454.5	91.2% of	454.5	95.4% d_2
104	14.6	10.6	Σ = 476.4	10.6	2.2% d_1
103	40.0	39.3		11.3	2.4% d_0
102	6.3	5.6		476.4	
101	5.4	4.8			
100	6.1	5.9			
99	1.7	1.7			
		Σ 522.4			
147	1.0	Conc. HMDS = 0.02 vol. percent			

Table XXIV. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 11.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	3.8	0.1			
121	68.6	-1.8			
120	188.1	-3.6			
119	1791.0	1775.5	99.1% of	1775.5	84.9% $\underline{d}_2$
118	66.4	34.5	Σ = 2091.1	34.5	1.6% $\underline{d}_1$
117	297.0	296.6		281.1	13.5% $\underline{d}_0$
116	3.2	3.2		2091.1	
115	0.3	0.3			
		Σ 2110.1			
105	1.7				
104	3.3				
103	18.3				
102	8.3				
101	9.1				
100	1.0				
99	1.0				
147	6.1	Conc. HMDS = 0.12 vol. percent			

Table XXV. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 12.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.2	0.2			
122	5.2	0.1			
121	95.7	-.7			
120	258.9	-3.6			
119	2439.0	2434.8	99.3% of	2434.8	98.7% $\underline{d}_2$
118	38.1	37.2	Σ = 2467.6	32.8	1.3% $\underline{d}_1$
117	6.2	5.4		2467.6	
116	7.1	7.0			
115	0.6	0.6			
		Σ 2485.0			
108	0.8	0.1			
107	14.8	-.1			
106	37.6	-.5			
105	391.0	385.5	91.2% of	385.5	82.7% $\underline{d}_2$
104	31.4	23.1	Σ = 466.1	23.1	5.0% $\underline{d}_1$
103	84.6	83.8		57.5	12.3% $\underline{d}_0$
102	6.9	6.2		466.1	
101	5.9	5.3			
100	5.7	5.5			
99	1.7	1.7			
		Σ 511.1			
147	2.7	Conc. HMDS = 0.05 vol. percent			

Table XXVI. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 12.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	$(P\text{-}Me)^+$ Dist'n.
122	3.9	0.1			
121	70.3	-1.6			
120	194.1	-2.5			
119	1830.0	1813.9	99.1% of	1813.9	84.9% d_2
118	71.8	39.5	Σ = 2137.7	39.5	1.8% d_1
117	300.0	299.6		284.3	13.3% d_0
116	3.7	3.6		2137.7	
115	0.8	0.7			
		Σ 2157.2			
106	0.2				
105	2.0				
104	3.7				
103	19.3				
102	8.4				
101	9.3				
100	1.1				
99	1.2				
147	10.9	Conc. HMDS = 0.21 vol. percent			

Table XXVII. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 13.

M/e	Pk. Ht.	Mono.[a]		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.2	0.2			
122	4.7	0.3			
121	82.3	-.1			
120	224.1	0.5			
119	2082.0	2077.1	99.3% of	2077.1	98.8% $\underline{d}_2$
118	26.1	23.3	Σ = 2102.4	23.2	1.1% $\underline{d}_1$
117	11.6	9.3		2.0	0.1% $\underline{d}_0$ (?)
116	6.3	6.2		2102.4	
115	1.3	1.3			
		Σ 2117.2			
107	12.3	0.1		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
106	31.4	0.2			
105	320.0	313.3	91.2% of	313.3	78.2% $\underline{d}_2$
104	34.7	25.5	Σ = 400.8	25.5	6.4% $\underline{d}_1$
103	85.6	82.9		62.0	15.4% $\underline{d}_0$
102	6.3	5.6		400.8	
101	5.7	5.2			
100	4.8	4.6			
99	1.7	1.6			
98	0.8	0.8			
		Σ 439.5			
147	10.0				
207	20.3				

[a]Corrected for silicone grease impurity (from m/e 207).

Table XXVIII. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 13.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.2	0.2			
122	3.9	0.2			
121	69.2	-.8			
120	192.0	0.05			
119	1785.0	1768.8	99.1% of	1768.8	84.6% $\underline{d}_2$
118	74.9	43.4	Σ = 2090.2	43.4	2.1% $\underline{d}_1$
117	293.0	292.2		278.0	13.3% $\underline{d}_0$
116	4.3	4.1		2090.2	
115	0.9	0.7			
		Σ 2109.2			
106	0.3				
105	2.7				
104	4.0				
103	23.7				
102	8.7				
101	9.5				
100	1.1				
99	1.1				
147	27.3	Conc. HMDS = 0.54 vol. percent			

Table XXIX. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane[a] of run 14.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	10.1	0.1			
121	96.0	0.6			
120	366.0	143.2	99.3% of	143.2	6.1% $\underline{d}_3$
119	2040.0	2022.6	Σ = 2325.3	2022.6	87.0% $\underline{d}_2$
118	153.0	150.5		150.5	6.5% $\underline{d}_1$
117	21.0	18.0		9.0	0.4% $\underline{d}_0$
116	7.0	6.3		2325.3	
115	2.2	0.7			
114	0.1	0.1			
113	0.9	0.3			
		Σ 2341.7			

M/e	Pk. Ht.	Mono.		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
107	6.1	0.0			
106	19.0	0.1			
105	171.3	152.9	91.0% of	152.9	36.0% $\underline{d}_2$
104	114.3	94.5	Σ = 424.1	94.5	22.3% $\underline{d}_1$
103	202.2	199.3		176.7	41.7% $\underline{d}_0$
102	10.0	7.7		424.1	
101	8.3	6.3			
100	5.0	3.5			
99	1.8	1.8			
		Σ 466.0			

147	184.2	Conc. HMDS = 3.7 vol. percent

[a]Parent ion analysis of this bromide gave an isotopic distribution of 7.6% $\underline{d}_3$, 83.7% $\underline{d}_2$, 8.1% $\underline{d}_1$, and 0.6% $\underline{d}_0$.

Table XXX. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane[a] of run 14.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	7.3	0.2			
121	66.0	-.4			
120	262.5	106.8	99.1% of	106.8	5.6% $\underline{d}_3$
119	1407.0	1375.9	Σ = 1899.7	1375.9	72.4% $\underline{d}_2$
118	231.3	207.3		207.3	10.9% $\underline{d}_1$
117	223.5	222.8		209.7	11.1% $\underline{d}_0$
116	3.6	3.4		1899.7	
115	1.0	0.8			
		Σ 1917.0			
106	0.4				
105	2.4				
104	6.9				
103	16.9				
102	10.0				
101	7.9				
100	1.1				
99	1.1				
147	22.2	Conc. HMDS = 0.44 vol. percent			

[a]Parent ion analysis of this bromide gave an isotopic distribution of 6.0% $\underline{d}_3$, 82.2% $\underline{d}_2$, 10.6% $\underline{d}_1$, and 1.2% $\underline{d}_0$.

After correction for rearrangement in the mass spectrometer, the composition of the α-methylene group of the 1-propanol derived from recovered 1-bromopropane becomes 78.9% $\underline{d}_2$, 5.8% $\underline{d}_1$, and 15.3% $\underline{d}_0$. Since about 80% (78.9/98.9) of the 1-propyl product is unrearranged, the original 1-bromopropane-1-$\underline{d}_1$ (1.1%) contributes 0.9% $\underline{d}_1$ and 0.2% $\underline{d}_0$ to $(P\text{-}Et)^+$ of the ether of the product. The contribution to the α-methylene group of the product which results solely from 1-bromopropane-1,1-$\underline{d}_2$ (98.9%) is, therefore, 78.9% $\underline{d}_2$, 4.9% $\underline{d}_1$, and 15.1% $\underline{d}_0$. Normalization then gives the following results for run 13:

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

100%	79.8%	5.0%	15.2%

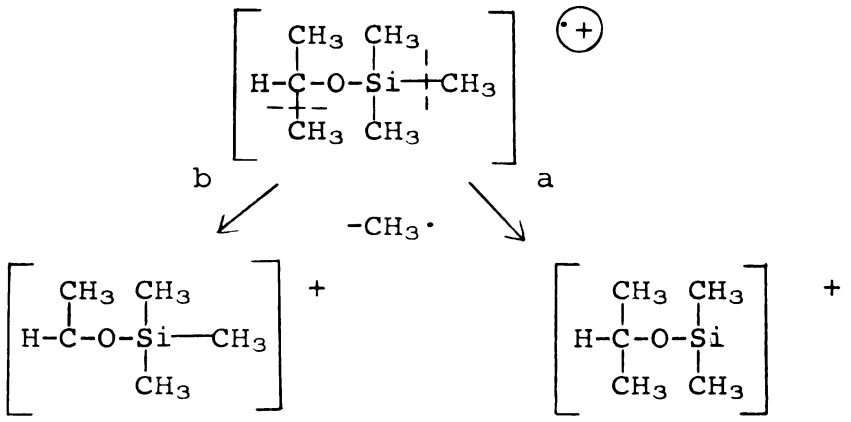
Similar treatment of the data from runs 10-12 yields the distributions which are shown below. The presence of $\underline{d}_3$ species in the product of run 14 precludes this treatment.

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

	100%		
Run			
10	99.0%	0.2%	0.8%
11	97.1%	0.6%	2.3%
12	84.5%	3.3%	12.2%

Interpretation of the data from analysis of the isopropyltrimethylsilyl ethers derived from the 2-bromopropane products is more difficult, for these ethers can produce a parent-less-methyl-ion either by fission of a carbon-silicon

bond (path a) or of a carbon-carbon bond (path b).



Mass-spectral analysis of the trimethylsilyl ether of 2-propanol-1-^{13}C (19.7% ^{13}C and 80.3% ^{12}C by parent ion analysis of its benzoate ester) gave a parent-less-methyl ion distribution of 17.0% ^{13}C and 83.0% ^{12}C, indicating that 27% of these ions were formed from path b and 73% from path a (55). Analysis of the trimethylsilyl ether of 2-propanol-1,1,1,3,3,3-$\underline{d}_6$ (Table XXXI, 96.4% $\underline{d}_6$ and 3.6% $\underline{d}_5$ by parent ion analysis of its benzoate ester) gave a parent-less-methyl ion distribution of 72.1% $\underline{d}_6$, 2.4% $\underline{d}_5$, 0.1% $\underline{d}_4$, and 25.4% $\underline{d}_3$, indicating that 25.2% of these ions were formed by path b and 74.8% by path a. It is apparent that a slight isotope effect favors cracking by path a for the highly deuterated species.

From Tables XIX and XX, it may be seen that, although the isotopic compositions of the trimethylsilyl ethers derived from the recovered 1-bromopropanes vary considerably, those from the 2-bromopropane products are practically the same (for runs 11-13). If the 2-bromopropane product were

Table XXXI. Mass spectrum of $(CD_3)_2CHOSi(CH_3)_3$ from 2-propanol-1,1,1,3,3,3-$\underline{d}_6$.[a]

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	$(P\text{-}Me)^+$ Dist'n.
126	1.8	0.1			
125	31.2	1.5			
124	80.9	-.4			
123	753.0	749.8	99.1% of	749.8	72.1% $\underline{d}_6$
122	35.1	24.4	Σ = 1039.4	24.4	2.4% $\underline{d}_5$
121	30.4	1.5		1.5	0.1% $\underline{d}_4$
120	267.9	267.3		263.7	25.4% $\underline{d}_3$
119	5.2	5.1		1039.4	
118	0.3	0.2			
117	0.5	0.5			
		Σ 1048.8			
108	0.6				
107	3.6				
106	3.6				
105	2.0				
104	4.0				
103	6.3				
102	0.3				
101	0.6				
147	1.1	Conc. HMDS = 0.03 vol. percent			

[a]Parent ion analysis of the benzoate ester of this alcohol gave 96.4% $\underline{d}_6$ and 3.6% $\underline{d}_5$.

formed from 1-bromopropane-1,1-$\underline{d}_2$ by a simple 1,2-hydride shift, then it would have been exclusively 2-bromopropane-1,1-$\underline{d}_2$.

The trimethylsilyl ether of a known sample of 2-propanol-1,1-$\underline{d}_2$ (98.5% $\underline{d}_2$ and 1.5% $\underline{d}_1$, Table XXXII) gave a parent-less-methyl ion distribution of 84.5% $\underline{d}_2$, 1.8% $\underline{d}_1$, and 13.7% $\underline{d}_0$. Assuming that the 2-bromopropane products have the same gross isotopic compositions as their 1-bromopropane precursors, it is calculated that the 2-bromopropane-$\underline{d}_2$ products from runs 11-13 must be composed of at least 97% (run 13) 2-bromopropane-1,1-$\underline{d}_2$.

2. 1-Bromopropane-2,2-$\underline{d}_2$

In runs 15 and 16, 1-bromopropane-2,2-$\underline{d}_2$ (96.1% $\underline{d}_2$ and 3.9% $\underline{d}_1$ by parent ion analysis) was used as the reactant. The results of the mass-spectral analyses are given in Tables XXXIII-XXXVII.

The isotopic compositions of the trimethylsilyl ethers derived from the recovered 1-bromopropanes were corrected for rearrangements occurring in the mass spectrometer (0.3% $\underline{d}_2$ and 0.3% $\underline{d}_1$ subtracted from $(P\text{-}Et)^+$) and contributions from $\underline{d}_1$ species in the starting material, as was done in runs 10-13. The results, normalized to 100% isotopic purity, are shown below.

$$CH_3CD_2CH_2Br \longrightarrow C_2H_5\text{-}CD_2Br + C_2H_4D\text{-}CHDBr + C_2H_3D_2\text{-}CH_2Br$$

100%

Run			
15	1.5%	3.0%	95.5%
16	2.1%	5.8%	92.1%

Table XXXII. Mass spectrum of $CH_3CH[OSi(CH_3)_3]CHD_2$ from 2-propanol-1,1-$\underline{d}_2$.[a]

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	2.7	2.3			
121	43.8	3.4			
120	111.3	1.4			
119	1026.0	1016.8	99.1% of	1016.8	84.5% $\underline{d}_2$
118	40.3	21.7	Σ = 1202.9	21.7	1.8% $\underline{d}_1$
117	173.1	172.9		164.4	13.7% $\underline{d}_0$
116	2.2	2.2		1202.9	
115	0.2	0.2			
		Σ 1213.8			
106	0.2				
105	2.0				
104	5.0				
103	43.6				
102	4.8				
101	5.8				
100	0.9				
99	0.9				
147	2.8	Conc. HMDS = 0.07 vol. percent			

[a]Parent ion analysis of the benzoate ester of this alcohol gave 96.9% $\underline{d}_2$ and 3.1% $\underline{d}_1$. However, in view of the fact that other products prepared from the same source of lithium aluminum deuteride have been at least 98.7% $\underline{d}_2$ species, it would seem that this value is too low for percent $\underline{d}_2$. A reasonable lower limit for the isotopic purity of this alcohol is 98.5% $\underline{d}_2$ and 1.5% $\underline{d}_1$.

Table XXXIII. Mass spectrum of $CH_3CD_2CH_2OSi(CH_3)_3$ from precursor for 1-bromopropane-2,2-$\underline{d}_2$ used in runs 15 and 16.

M/e	Pk. Ht.	Mono.			
123	0.3	0.1			
122	5.7	0.3			
121	97.8	4.4		$(P\text{-}Me)^+$	
120	252.0	-3.8		Mono.	Dist'n.
119	2364.0	2354.7	99.3% of	2354.7	96.7% $\underline{d}_2$
118	85.1	84.2	Σ = 2435.8	81.1	3.3% $\underline{d}_1$
117	6.9	6.1		2435.8	
116	7.3	7.2			
115	0.8	0.8			
		Σ 2453.0			
				$(P\text{-}Et)^+$	
106	0.9	0.0		Mono.	Dist'n.
105	18.3	1.8	91.2% of	1.8	0.4% $\underline{d}_2$
104	41.6	0.5	Σ = 408.4	0.5	0.2% $\underline{d}_1$
103	426.0	425.1		406.1	99.5% $\underline{d}_0$
102	8.2	7.4		408.4	
101	6.7	6.1			
100	5.8	5.7			
99	1.2	1.2			
		Σ 447.8			
147	0.7	Conc. HMDS = 0.01 vol. percent			

Table XXXIV. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 15.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	5.2	0.1			
121	94.8	-1.3			
120	257.1	-4.8			
119	2430.1	2424.2	99.3% of	2424.2	98.1% d_2
118	52.5	51.6	Σ = 2472.2	48.0	1.9% d_1
117	6.3	5.5		2472.2	
116	7.7	7.6			
115	0.7	0.7			
		Σ 2489.6			

				$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
107	0.3	0.3			
106	2.1	0.1			
105	24.7	7.4	91.2% of	7.4	1.8% d_2
104	54.0	13.9	Σ = 416.1	13.9	3.3% d_1
103	415.0	414.0		394.8	94.9% d_0
102	8.3	7.5		416.1	
101	6.8	6.2			
100	6.2	6.1			
99	1.2	1.2			
		Σ 456.3			

147 2.0 Conc. HMDS = 0.04 vol. percent

Table XXXV. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 15.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	Dist'n.
122	3.9	0.3			
121	68.4	-1.2			
120	197.7	-4.1			
119	1779.0	1735.4	99.1% of	1735.4	80.9% d_2
118	401.0	398.2	Σ = 2145.2	398.2	18.6% d_1
117	24.3	23.5		11.6	0.5% d_0
116	6.6	6.4		2145.2	
115	1.3	1.2			
		Σ 2164.7			
106	0.1				
105	2.0				
104	4.7				
103	16.8				
102	17.0				
101	3.8				
100	1.3				
99	0.8				
147	16.6	Conc. HMDS = 0.32 vol. percent			

Table XXXVI. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 16.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
123	0.1	0.1			
122	4.8	0.02			
121	88.8	-1.4			
120	241.5	-4.2			
119	2280.0	2274.7	99.3% of	2274.7	97.9% d_2
118	47.0	45.5	Σ = 2322.8	45.5	2.0% d_1
117	12.2	11.4		2.6	0.1% d_0(?)
116	6.9	6.8		2322.8	
115	0.8	0.8			
		Σ 2339.2			

				$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
107	0.2	-.2			
106	2.7	0.2			
105	26.3	9.3	91.2% of	9.3	2.4% d_2
104	61.3	24.6	Σ = 394.6	24.6	6.2% d_1
103	380.0	379.1		360.7	91.4% d_0
102	8.0	7.2		394.6	
101	6.3	5.7			
100	5.7	5.6			
99	1.2	1.2			
		Σ 432.7			

147 2.9 Conc. HMDS = 0.06 vol. percent

Table XXXVII. Mass spectrum of $(CH_3)_3CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 16.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	3.7	0.2			
121	64.8	-1.8			
120	189.9	-3.2			
119	1704.0	1662.9	99.1% of	1662.9	81.1% $\underline{d}_2$
118	377.0	374.0	Σ = 2051.5	374.0	18.2% $\underline{d}_1$
117	26.8	26.0		14.6	0.7% $\underline{d}_0$
116	6.3	6.2		2051.5	
115	1.0	1.0			
		Σ 2070.1			
106	0.1				
105	1.3				
104	3.8				
103	15.6				
102	16.6				
101	3.2				
100	1.3				
99	0.8				
147	5.9	Conc. HMDS = 0.12 vol. percent			

The 1-propanol derived from the recovered 1-bromopropane of run 16 was examined by n.m.r. (Figure 3). Integration showed that the deuterium distribution of this alcohol (not corrected for $\underline{d}_1$ 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. This distribution agrees with the mass-spectral analysis (0.10 deuterium atom at C-1).

The isotopic distributions for the trimethylsilyl ethers derived from the 2-bromopropane products of runs 15 and 16 are somewhat anomalous. If the 2-bromopropane-$\underline{d}_2$ was formed from the 1-bromopropane-2,2-$\underline{d}_2$ by a simple 1,2-hydride (deuteride) shift, then it would have been exclusively 2-bromopropane-1,2-$\underline{d}_2$. The isotopic distribution of the parent-less-methyl ion of the trimethylsilyl ethers derived from runs 15 and 16 would thus be predicted to be, roughly, 84.8% $\underline{d}_2$, 14.7% $\underline{d}_1$, and 0.5% $\underline{d}_0$. Inspection of Tables XXXV and XXXVII shows that the actual distribution is different by $\underline{d}_1$ being about 3.5% higher than predicted.

In order to resolve this anomaly, the n.m.r. spectrum of the 2-propanol derived from the 2-bromopropane product of run 16 was obtained. This spectrum is shown in Figure 4. From the lack of any C-2 proton signals, or C-1 proton splitting, it must be concluded that the 2-bromopropane formed from 1-bromopropane-2,2-$\underline{d}_2$ in runs 15 and 16 is primarily, if not exclusively, 2-bromopropane-1,2-$\underline{d}_2$, $\underline{i}.\underline{e}.$, the result of a simple 1,2-hydride (deuteride) shift. The anomalous mass-spectral distributions may arise partially from an unexpected

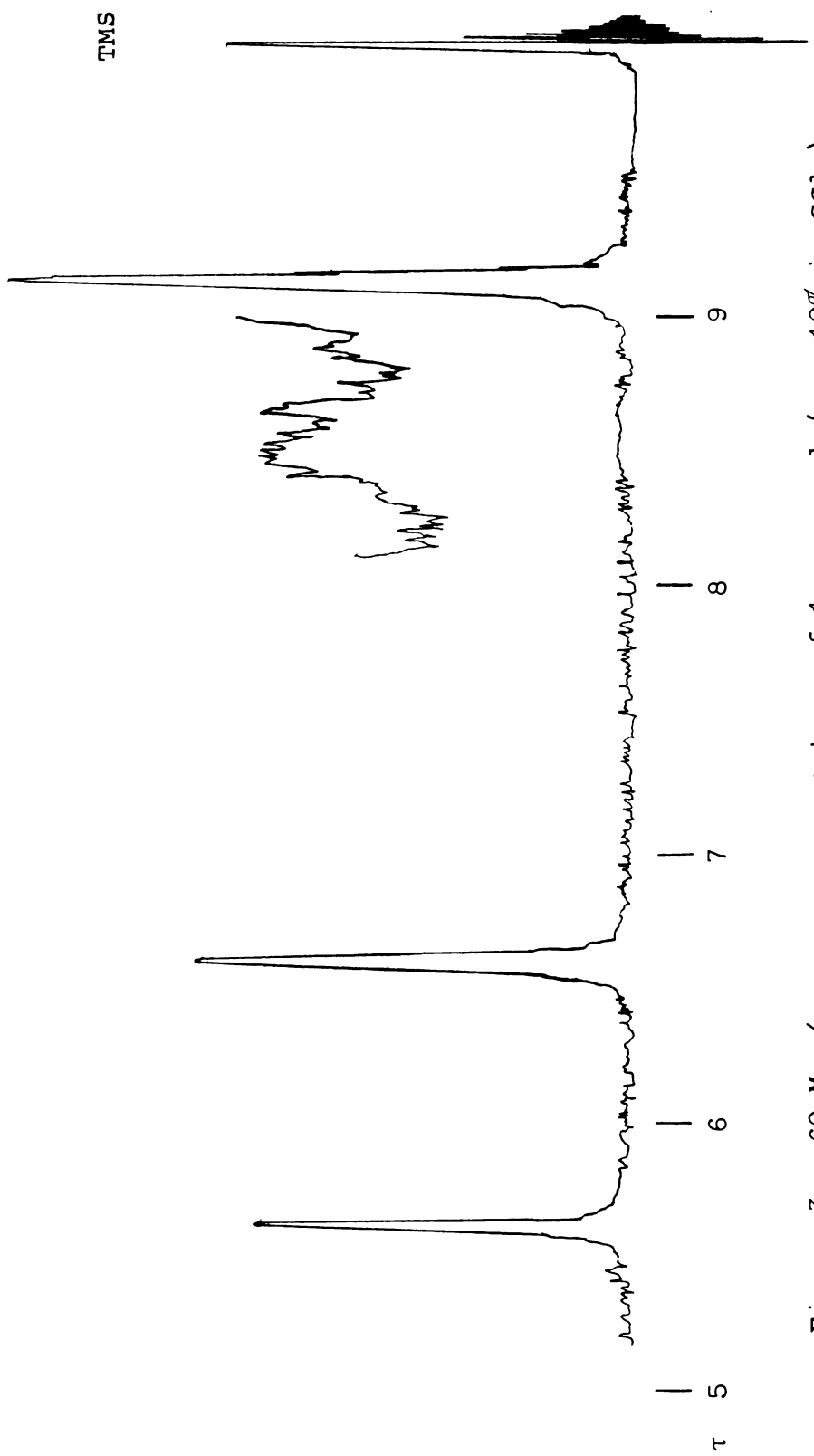


Figure 3. 60 Mc./sec. n.m.r. spectrum of 1-propanol (ca. 10% in CCl_4) derived from recovered 1-bromopropane of run 16.

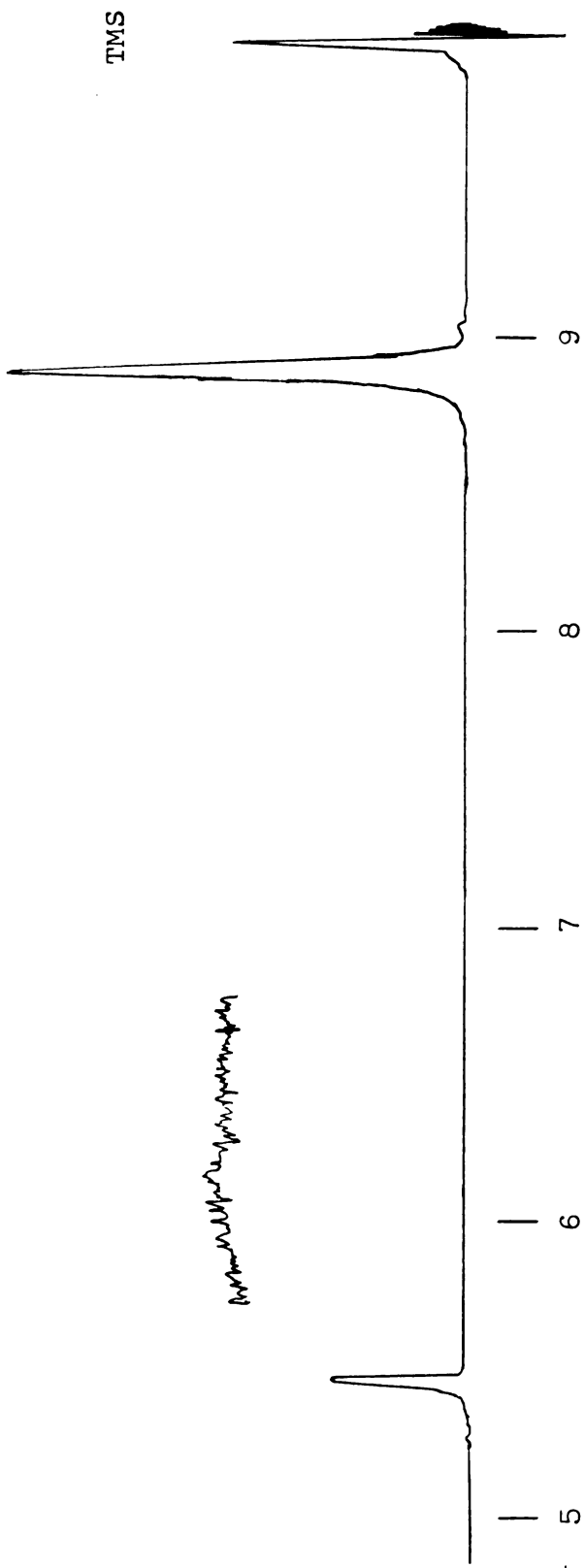


Figure 4. 60 Mc./sec. n.m.r. spectrum of 2-propanol (ca. 20% in CCl_4) derived from 2-bromopropane product of run 16.

fragmentation in the mass spectrometer for this particular species. It is likely that the 2-propyl products contain a larger percentage of $\underline{d_1}$ species than the reactants or recovered 1-bromopropanes because of preferential hydride shift in $\underline{d_1}$ species in the reactants.

3. <u>1-Bromopropane-1-^{13}C</u>

Run 17 was conducted by using 1-bromopropane-1-^{13}C which was 28.8% ^{13}C and 71.2% ^{12}C (Table XXXVIII). The recovered 1-bromopropane was examined by n.m.r. at 100 Mc./sec. Careful integration of the lower field carbon-13-proton satellite from ^{13}C-1 and the upper field satellite from ^{13}C-3 gave a ^{13}C-3/^{13}C-1 value of 0.206 ± 0.002. C-1 was 23.3 ± 0.3% ^{13}C by direct integration. The amount of carbon-13 at C-2 was found by difference. After correction for the natural abundance of carbon-13 was made, normalization to 100% isotopic purity gave the following distribution:

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

100% 80.2 ± 1.1% 6.5 ± 1.8% 13.3 ± 0.4%

The n.m.r. spectrum of the 2-bromopropane-^{13}C product showed no evidence for any carbon-13 at C-2. From the mass spectrum of the trimethylsilyl ether (Table XXXIX) derived from this product, it was calculated that the ^{13}C species were exclusively 2-bromopropane-1-^{13}C.

1-Bromopropane-1-^{13}C which was 54.6% ^{13}C and 45.4% ^{12}C (Table XL) was used as the reactant in run 18. From the

Table XXXVIII. Mass spectrum of $CH_3CH_2{}^{13}CH_2OSi(CH_3)_3$ from precursor for 1-bromopropane-1-^{13}C used in run 17.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
121	1.0	0.2			
120	20.0	0.5			
119	87.1	-.1			
118	560.0	452.0	99.3% of	452.0	28.8% ^{13}C
117	1119.0	1118.4	Σ = 1569.8	1117.8	71.2% ^{12}C
116	4.1	3.4		1569.8	
115	6.9	6.9			
114	0.2	0.2			
		Σ 1580.9			

M/e	Pk. Ht.	Mono.		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
106	3.9	0.0			
105	17.2	0.3			
104	114.0	93.9	91.2% of	93.9	28.8% ^{13}C
103	234.0	232.8	Σ = 325.9	232.0	71.2% ^{12}C
102	8.4	7.0		325.9	
101	16.0	15.6			
100	3.0	2.5			
99	5.6	5.6			
		Σ 357.4			

147 1.6 Conc. HMDS = 0.04 vol. percent

Table XXXIX. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 17.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
121	0.8	0.1			
120	17.4	-0.3			
119	86.1	-1.4			
118	520.0	398.7	99.1% of	398.7	24.1% ^{13}C
117	1257.0	1255.8	Σ = 1652.9	1254.2	75.9% ^{12}C
116	7.2	6.4		1652.9	
115	7.1	7.0			
		Σ 1667.9			
105	0.3				
104	0.6				
103	2.1				
102	8.2				
101	21.0				
100	1.0				
99	2.2				
147	16.3	Conc. HMDS = 0.42 vol. percent			

Table XL. Mass spectrum of $CH_3CH_2{}^{13}CH_2OSi(CH_3)_3$ from precursor for 1-bromopropane-1-^{13}C used in run 18.

M/e	Pk. Ht.	Mono.			
122	0.3	0.1			
121	2.9	0.4			
120	50.9	5.0		$(P-Me)^+$	
119	147.3	1.9		Mono.	Dist'n.
118	1221.0	1130.9	99.3% of	1130.9	54.9% ^{13}C
117	933.0	932.0	Σ = 2061.4	930.5	45.1% ^{12}C
116	7.8	7.3		2061.4	
115	5.7	5.6			
114	0.1	0.1			
		Σ 2075.9			
107	0.6	0.1			
106	10.1	0.9		$(P-Et)^+$	
105	28.6	1.4		Mono.	Dist'n.
104	248.4	231.3	91.3% of	231.3	54.6% ^{13}C
103	195.0	193.1	Σ = 423.8	192.5	45.4% ^{12}C
102	16.7	15.2		423.8	
101	14.1	13.3			
100	6.7	6.2			
99	5.1	5.1			
		Σ 464.2			
147	7.1	Conc. HMDS = 0.15 vol. percent			

60 Mc./sec. n.m.r. spectrum of the recovered 1-bromopropane (Figure 5), a ^{13}C-3/^{13}C-1 value of 0.145 ± 0.007 was obtained. The amount of carbon-13 at C-1 was found to be 46.9% ^{13}C by mass-spectral analysis of the trimethylsilyl ether derivative (Table XLI). The following distribution was calculated for run 18 after correction for carbon-13 natural abundance and normalization to 100% isotopic purity:

$$\underset{100\%}{CH_3CH_2{}^{13}CH_2Br} \longrightarrow \underset{85.7\pm0.2\%}{CH_3CH_2{}^{13}CH_2Br} + \underset{3.7\pm0.9\%}{CH_3{}^{13}CH_2CH_2Br} + \underset{10.6\pm0.6\%}{{}^{13}CH_3CH_2CH_2Br}$$

In addition to being more precise, these results should be more accurate than those of run 17, since the amount of carbon-13 at C-1 was determined by mass spectrometry rather than by n.m.r. integration.

Both the n.m.r. spectrum (Figure 6) of the recovered 2-bromopropane-^{13}C and the mass spectrum of the trimethylsilyl ether derived from it (Table XLII) showed that the ^{13}C species were exclusively 2-bromopropane-1-^{13}C.

B. Labeled 2-Bromopropanes

Isotopically labeled 2-bromopropanes were partially isomerized to 1-bromopropanes and the isotopic compositions studied by mass-spectral analysis as previously described for the 1-bromopropanes. The reaction conditions used in the various runs are summarized in Table XLIII.

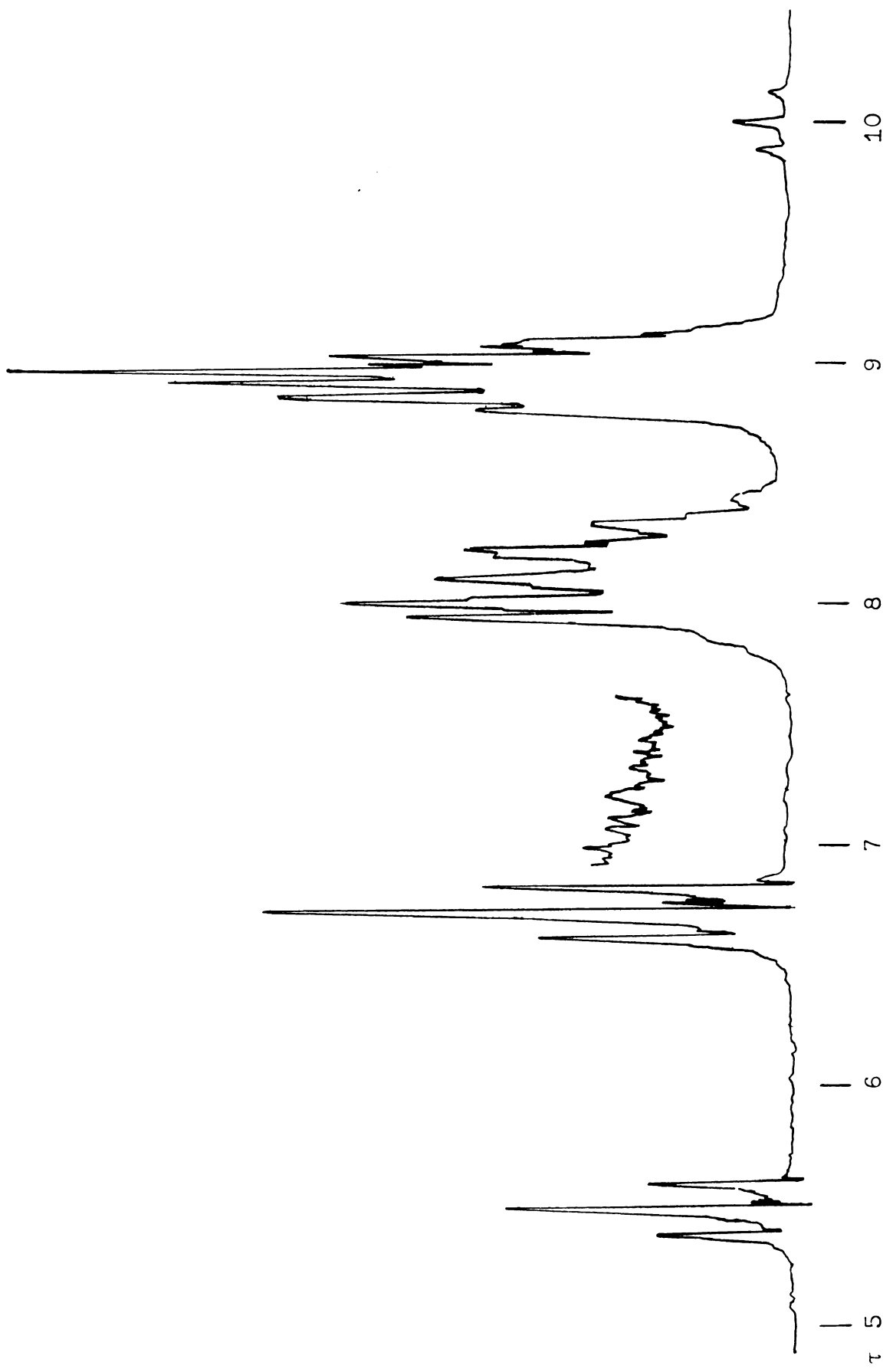


Figure 5. 60 Mc./sec. n.m.r. spectrum of recovered 1-bromopropane-^{13}C from run 18.

Tab

M

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Table XLI. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from recovered 1-bromopropane of run 18.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$	
				Mono.	Dist'n.
121	1.9	0.0			
120	44.8	-1.3			
119	144.9	-2.1			
118	1233.0	1141.1	99.3% of	1141.1	54.6% ^{13}C
117	951.0	949.9	Σ = 2089.6	948.5	45.4% ^{12}C
116	8.0	7.5		2089.6	
115	5.6	5.5			
114	0.1	0.1			
113	0.2	0.2			
		Σ 2104.3			
106	8.1	0.1		$(P-Et)^+$	
105	26.2	0.1		Mono.	Dist'n.
104	222.3	202.1	91.3% of	202.1	46.9% ^{13}C
103	231.9	229.8	Σ = 431.2	229.1	53.1% ^{12}C
102	17.1	15.6		431.2	
101	14.9	14.1			
100	6.1	5.6			
99	5.1	5.1			
		Σ 472.3			
147	17.2	Conc. HMDS = 0.37 vol. percent			

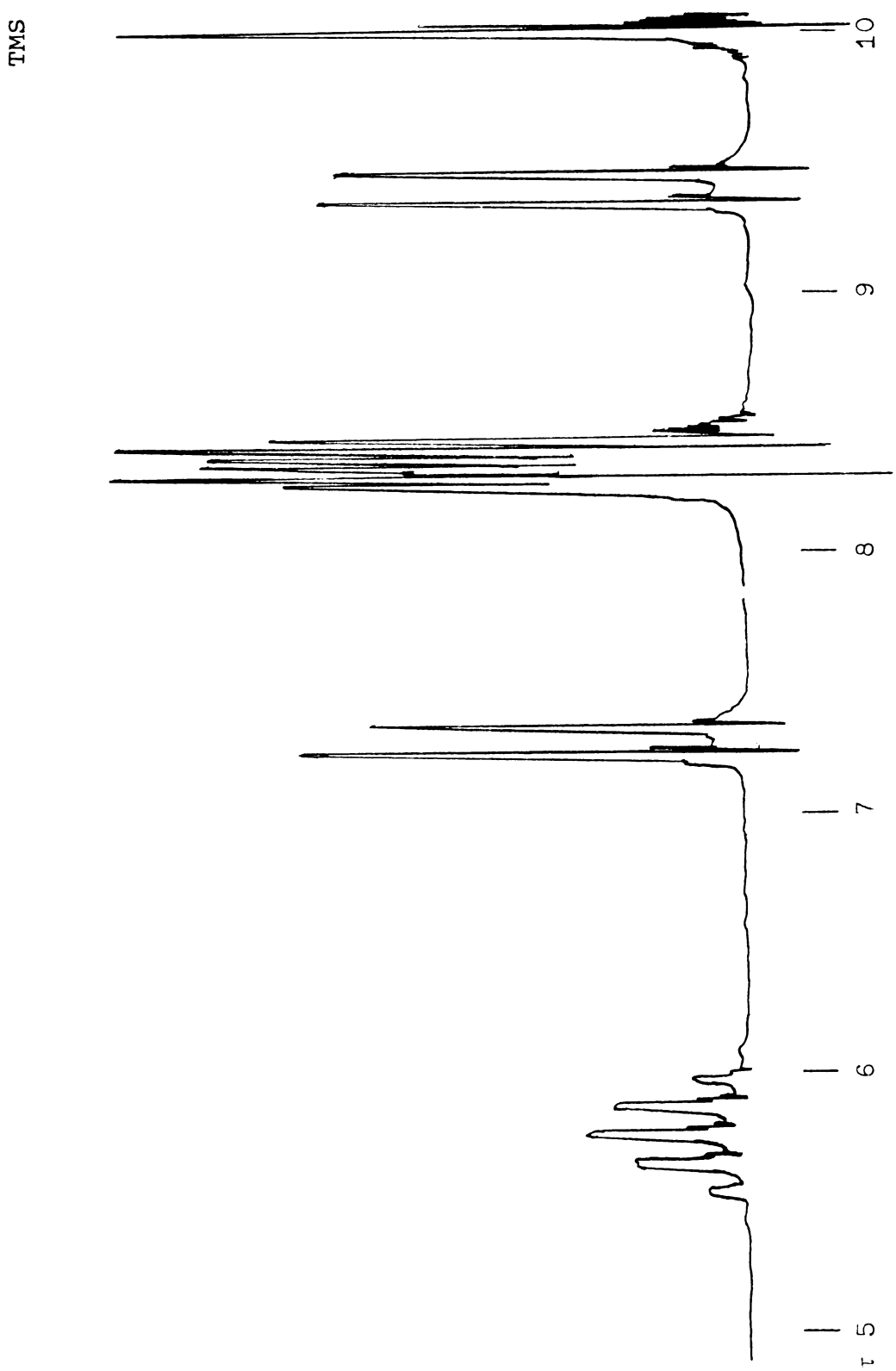


Figure 6. 60 Mc./sec. n.m.r. spectrum of 2-bromopropane-^{13}C product from run 18.

Table XLII. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from 2-bromopropane of run 18.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
121	1.7	0.2			
120	35.0	-0.9			
119	123.0	-2.0			
118	975.0	873.8	99.1%	873.8	45.6% ^{13}C
117	1047.0	1045.8	Σ = 1916.2	1042.4	54.4% ^{12}C
116	9.4	8.9		1916.2	
115	5.3	5.2			
		Σ 1933.7			
105	0.2				
104	0.9				
103	4.0				
102	14.0				
101	18.2				
100	1.3				
99	2.0				
147	6.7	Conc. HMDS = 0.15 vol. percent			

Table XLIII. Labeled 2-bromopropane + aluminum bromide reaction at 0°.

Run	2-BrPr	2-BrPr/$AlBr_3$ (mole/mole)	Rxn. time[a] (min.)	Recovered[b] BrPr, percent	1-BrPr,[c] ± 1 %	2-BrPr, ± 1%
19	$CH_3CDBrCH_3$	5.8	120.0	54	6	94
20	$CH_3CDBrCH_3$	6.3	120.0	52	7	93
21	$CH_3CDBrCH_3$	5.7	6.0	74	4	96
22	$CD_3CHBrCD_3$	5.7	10.0	100	3	97
23	$CD_3CHBrCD_3$[d] and $CH_3CDBrCH_3$	5.7	10.0	100	4.6±0.5	95.4±0.5

[a] Quenched with quinoline.
[b] Sum of 1-BrPr and 2-BrPr.
[c] By v.p.c. analysis.
[d] Mixture 2-BrPr-$\underline{d}_6$ and 2-BrPr-$\underline{d}_1$ in molar ratio of 49.8/50.2 (by weight).

1. 2-Bromopropane-2-d

2-Bromopropane-2-d (99.0% d_1 and 1.0% d_0 by parent ion analysis) was used in runs 19-21. The mass spectrum of the trimethylsilyl ether of the 2-propanol-2-d from which this bromide was prepared is given in Table XII.

In runs 19 and 20, the 2-bromopropane was in contact with aluminum bromide for 2 hours. The mass spectrum of the extensively isotope-position scrambled trimethylsilyl ether derived from 2-bromopropane recovered from run 19 is shown in Table XLIV. The bromides obtained from run 20 were purified and their isotopic compositions determined by parent ion analysis. The composition of the 1-bromopropane was 4.0% d_2, 78.7% d_1, and 17.3% d_0. That of the 2-bromopropane was 2.8% d_2, 77.4% d_1, and 19.8% d_0.

In run 21, the 2-bromopropane was in contact with aluminum bromide for only 6 minutes. Parent ion analysis of the products yielded an isotopic composition of 0.6% d_2, 95.5% d_1, and 3.9% d_0 for the 1-bromopropane and 94.5% d_1, and 5.5% d_0 for the 2-bromopropane. Verification of the composition of the recovered 2-bromopropane was shown by parent-less-methyl ion analysis, 94.7% d_1 and 5.3% d_0 (Table XLV), of the trimethylsilyl ether derived from it.

2. 2-Bromopropane-1,1,1,3,3,3-d_6

2-Bromopropane-1,1,1,3,3,3-d_6 was used in run 22. The mass spectrum of the trimethylsilyl ether of the 2-propanol

Table XLIV. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from recovered 2-bromopropane of run 19.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	0.3	0.1			
121	6.1	0.1			
120	63.0	1.2			
119	233.4	68.3	99.1% of	68.3	3.7% d_2
118	1392.0	1344.1	Σ = 1827.5	1344.1	73.6% d_1
117	440.0	422.0		415.1	22.7% d_0
116	9.1	4.2		1827.5	
115	16.0	5.1			
114	0.8	0.1			
113	4.7	0.3			
		Σ 1844.1			
107	1.1				
106	2.0				
105	13.6				
104	15.2				
103	22.0				
102	28.7				
101	22.9				
100	2.0				
99	2.3				
147	1380.0	Conc. HMDS = 27.4 vol. percent			

Table XLV. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from recovered 2-bromopropane[a] of run 21.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
122	0.3	0.3			
121	4.3	-0.04			
120	81.1	-0.9			
119	224.4	-2.1			
118	2079.0	2065.4	99.1% of	2065.4	94.7% $\underline{d}_1$
117	126.0	124.6	Σ = 2181.5	116.1	5.3% $\underline{d}_0$
116	3.9	2.8		2181.5	
115	8.8	8.3			
114	0.2	0.2			
		Σ 2201.3			
106	1.0				
105	2.0				
104	8.9				
103	8.5				
102	26.4				
101	10.5				
100	2.1				
99	1.3				
147	63.8	Conc. HMDS = 1.2 vol. percent			

[a]Parent ion analysis of this bromide gave an isotopic distribution of 94.5% $\underline{d}_1$ and 5.5% $\underline{d}_0$.

from which it was made is given in Table XLVI. The mass spectrum of the trimethylsilyl ether derived from the 1-bromopropane product is shown in Table XLVII, while that derived from the recovered 2-bromopropane is given in Table XLVIII.

3. Mixture of 2-Bromopropane-2-d and -1,1,1,3,3,3-d_6

A mixture of 2-bromopropane-2-d and 2-bromopropane-1,1,1,3,3,3-d_6 (same as used in run 22) was prepared in a 50.2:49.8 molar ratio by weight. A portion of this mixture was converted to the alcohols by silver ion-assisted hydrolysis. The mass spectrum of the trimethylsilyl ether from this mixture is shown in Table LXIX. The bromide mixture was isomerized under the same conditions as used in run 22. The mass spectra of the trimethylsilyl ethers derived from the 1-bromopropane and 2-bromopropane products recovered from this isomerization (run 23) are shown in Tables L and LI, respectively.

Table XLVI. Mass spectrum of $(CD_3)_2CHOSi(CH_3)_3$ from precursor[a] for 2-bromopropane-1,1,1,3,3,3-$\underline{d}_6$ used in run 22.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
126	3.0	-0.1			
125	58.5	1.7			
124	152.7	-2.7			
123	1437.0	1430.2	99.1% of	1430.2	72.0% $\underline{d}_6$
122	72.4	51.9	Σ = 1986.4	51.9	2.6% $\underline{d}_5$
121	58.1	3.1		3.1	0.2% $\underline{d}_4$
120	510.0	508.9		501.2	25.2% $\underline{d}_3$
119	10.0	10.0		1986.4	
118	0.3	0.3			
117	0.1	0.0			
		Σ 2004.4			
109	0.6				
108	1.2				
107	6.8				
106	6.8				
105	4.0				
104	7.6				
103	11.0				
102	0.7				
101	1.0				
147	11.4	Conc. HMDS = 0.24 vol. percent			

[a]Parent ion analysis of the benzoate ester of this alcohol gave 96.0% $\underline{d}_6$ and 4.0% $\underline{d}_5$.

Table XLVII. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from 1-bromopropane of run 22.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
126	4.5	0.2			
125	80.9	-0.1			
124	221.1	-1.9			
123	2052.0	2040.4	99.3% of	2040.4	94.1% $\underline{d}_6$
122	107.7	106.3	Σ = 2167.1	106.3	4.9% $\underline{d}_5$
121	6.6	3.6		3.6	0.2% $\underline{d}_4$
120	27.0	26.5		16.8	0.8% $\underline{d}_3$
119	4.7	4.4		2167.1	
118	0.3	0.0			
117	2.2	1.0			
116	0.3	0.0			
115	0.9	0.2			
		Σ 2182.4			

M/e	Pk. Ht.	Mono.		$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
109	0.7	0.4			
108	1.4	-0.3			
107	19.0	6.9	91.0% of	6.9	2.3% $\underline{d}_4$[a]
106	39.0	10.8	Σ = 298.7	10.8	3.6% $\underline{d}_3$[a]
105	289.0	286.5		281.0	94.1% $\underline{d}_2$
104	16.2	15.4		298.7	
103	7.2	6.0			
102	3.4	2.6			
101	1.0	0.2			
		Σ 328.2			

147	93.6	Conc. HMDS = 1.99 vol. percent

[a]These values have no real meaning and must have arisen through rearrangements in the mass spectrometer.

TABLE XLVIII. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from recovered 2-bromopropane of run 22.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
126	2.8	0.0			
125	54.1	-0.8			
124	150.0	-0.9			
123	1392.0	1383.4	99.1% of	1383.4	71.1% d_6
122	87.0	66.3	Σ = 1946.0	66.3	3.4% d_5
121	65.0	12.3		12.3	0.6% d_4
120	489.0	487.6		484.0	24.9% d_3
119	13.1	13.0		1946.0	
118	0.8	0.8			
117	0.4	0.3			
		Σ 1963.7			
109	0.2				
108	1.1				
107	6.5				
106	7.0				
105	4.1				
104	8.7				
103	21.1				
102	0.9				
101	1.0				
147	6.0	Conc. HMDS = 0.13 vol. percent			

Table XLIX. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ derived from the 2-bromopropane-2-$\underline{d}$ and -1,1,1,3,3,3-$\underline{d}_6$ mixture used as reactant in run 23.

M/e	Pk. Ht.	Mono.		$(P\text{-}Me)^+$ Mono.	$(P\text{-}Me)^+$ Dist'n.
126	2.0	0.0			
125	38.0	-0.6			
124	102.9	-3.2			
123	978.0	972.1	99.1% of	972.1	33.4% $\underline{d}_6$
122	61.2	47.1	Σ = 2907.8	47.1	1.6% $\underline{d}_5$
121	43.6	2.8		2.8	0.1% $\underline{d}_4$
120	410.0	348.7		348.7	12.0% $\underline{d}_3$
119	171.0	6.2		6.2	0.2% $\underline{d}_2$
118	1533.0	1530.9		1530.9	52.7% $\underline{d}_1$
117	19.1	18.4		2907.8	
116	2.6	2.5			
115	5.7	5.6			
		Σ 2934.2			
109	0.5				
108	1.1				
107	4.3				
106	5.0				
105	3.3				
104	7.0				
103	13.2				
102	19.1				
101	7.0				
147	15.9	Conc. HMDS = 0.34 vol. percent			

Table L. Mass spectrum of $CH_3CH_2CH_2OSi(CH_3)_3$ from 1-propanol obtained from 1-bromopropane of run 23.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
126	1.2	0.0			
125	22.1	0.3			
124	60.2	0.2			
123	552.0	548.9	99.3% of	548.9	33.2% $\underline{d}_6$
122	29.0	28.7	Σ = 1652.3	28.7	1.7% $\underline{d}_5$
121	4.0	1.3		1.3	0.1% $\underline{d}_4$
120	46.7	4.6		4.6	0.3% $\underline{d}_3$
119	114.9	0.7		0.7	0.1% $\underline{d}_2$
118	1062.0	1060.5		1060.5	64.2% $\underline{d}_1$
117	15.1	13.9		7.6	0.4% $\underline{d}_0$
116	4.1	3.9		1652.3	
115	2.1	1.5			
		Σ 1664.0			
				$(P-Et)^+$ Mono.	$(P-Et)^+$ Dist'n.
108	0.7	0.3			
107	5.1	1.7	91.0% of	1.7	0.6% $\underline{d}_4$[a]
106	11.7	3.5	Σ = 279.9	3.5	1.3% $\underline{d}_3$[a]
105	87.5	78.5		78.5	28.0% $\underline{d}_2$
104	28.0	8.8		8.8	3.1% $\underline{d}_1$
103	195.9	193.6		187.4	67.0% $\underline{d}_0$
102	15.4	14.4		279.9	
101	3.1	2.0			
100	3.7	3.1			
99	2.0	2.0			
		Σ 307.6			
147	78.7	Conc. HMDS = 1.68 vol. percent			

[a]These values have no real meaning and must have arisen through rearrangements in the mass spectrometer.

Table LI. Mass spectrum of $(CH_3)_2CHOSi(CH_3)_3$ from 2-propanol obtained from recovered 2-bromopropane of run 23.

M/e	Pk. Ht.	Mono.		$(P-Me)^+$ Mono.	$(P-Me)^+$ Dist'n.
126	1.2	-0.3			
125	27.2	-0.7			
124	77.4	0.9			
123	705.0	700.6	99.1% of	700.6	35.8% $\underline{d}_6$
122	44.1	33.6	Σ = 1958.0	33.6	1.7% $\underline{d}_5$
121	35.1	6.3		6.3	0.3% $\underline{d}_4$
120	286.0	247.4		247.4	12.7% $\underline{d}_3$
119	109.5	6.0		6.0	0.3% $\underline{d}_2$
118	960.0	957.8		957.8	48.9% $\underline{d}_1$
117	20.0	19.6		6.3	0.3% $\underline{d}_0$
116	1.8	1.5		1958.0	
115	3.1	3.0			
		Σ 1975.8			
109	0.3				
108	0.5				
107	3.2				
106	3.4				
105	2.3				
104	5.0				
103	10.0				
102	12.0				
101	4.3				
100	1.0				
147	6.9	Conc. HMDS = 0.15 vol. percent			

DISCUSSION

I. Formic Acid Solvolysis of 1-Propyl Tosylates

Comparison of the data of Tables III and IV with those of Table II shows that the 1-propyl product of run 2 is isotope-position unrearranged and that of run 1 not more than 0.4% rearranged. Comparison of the data of Table VIII with those of Table VII shows that the 1-propyl product of run 3 is similarly unrearranged.

The analyses of the trimethylsilyl ethers derived from the 2-propanols are uncertain. The spectrum of the derivative from run 2 (Table VI) is less than one-tenth as intense as that normally observed in these analyses; the ether from run 3 was contaminated (Table IX).

In view of the small amount of 2-propyl products obtained, it is highly probable that little "free" propyl cation is formed under these conditions. Rather, it would seem likely that most of the 1-propyl product arises from an S_N2-like attack on the tosylate or on an incipient tight-ion pair. The 2-propyl product is probably formed by a 1,2-hydride shift occurring in a tight-ion pair.

Shortly after this work was completed, Lee and Kruger reported (59) on a study of the anhydrous acetic and formic acid solvolyses of 1-propyl-1-^{14}C tosylate. Solvolysis in

acetic acid at 115° gave, in addition to a small amount of 2-propyl acetate (ca. 1%), 1-propyl acetate which had undergone no isotope-position rearrangement. Solvolysis in refluxing anhydrous formic acid produced 1-propyl formate which had 0.15% of the carbon-14 label at C-2 and 0.68% at C-3, plus some 2-propyl formate (1-2%). These data were explained by assuming that a small portion of the reaction proceeded through a pathway involving edge-protonated cyclopropanes whose lifetimes were too short to permit complete equilibration of the carbon atoms, while most of the product was produced from an S_N2 attack on the tosylate or on a "covalently solvated carbonium ion."

A study of the solvolyses of isotopically labeled cyclohexyl tosylates in acetic acid of varying water content has indicated that a rather striking difference exists for the optimum solvent composition which promotes 1,2-hydride shifts vs. 1,3-hydride shifts in this system (30). Whereas the amount of 1,2-hydride shift varied inversely with the water content in the solvent range of 94-100% acetic acid, the amount of 1,3-hydride shift went through a maximum that occurred at 97-98% acetic acid.

While one is on admittedly tenuous grounds in extending these results to include the formolysis of propyl tosylate, nevertheless, it is conceivable that the discrepancy between the two studies might be due to differences in the water content of the solvent.

II. Bromopropane Hydrolyses

From the identity of the mass spectra of the trimethylsilyl ether derivatives of the starting alcohols and the product alcohols (compare Table II with Table X, VII with XI, and XII with XIII), it is apparent that isotope-position labeled 1-propanols and 2-propanols may be successfully converted to 1-bromopropanes and 2-bromopropanes by treatment with phosphorous tribromide and then converted back to their respective alcohols by hydrolysis in 15% aqueous silver nitrate with overall integrity of the isotope-position label being maintained.

Since 1-bromopropane yielded no 2-propanol upon hydrolysis, it is reasonable to assume that this reaction proceeds through nucleophilic attack by water on the side opposite that of the partially ionized carbon-bromine bond.

$$CH_3CH_2CH_2Br \xrightarrow{Ag^+} CH_3CH_2CH_2\overset{\delta^+}{\text{----}}Br\overset{\delta^+}{\text{----}}Ag \xrightarrow{H_2O} CH_3CH_2CH_2OH + H^+ + AgBr$$

Comparison of the data of Table II with those of Table XIV and of the data of Table XII with those of Table XV shows that the hydrolysis of isotope-position labeled 1-bromopropanes to 1-propanols is accomplished in 10% aqueous sodium hydroxide with no isotope-position rearrangements. These observations are in agreement with the report that 1-bromopropane-1,1-$\underline{d}_2$ is hydrolyzed to 1-propanol-1,1-$\underline{d}_2$ with no

isotope-position rearrangement by treatment with 10% aqueous potassium carbonate at 140° (60). The data are in accord with an S_N2 type displacement of bromide by hydroxide.

III. Aluminum Bromide Catalyzed Isomerizations of Bromopropanes

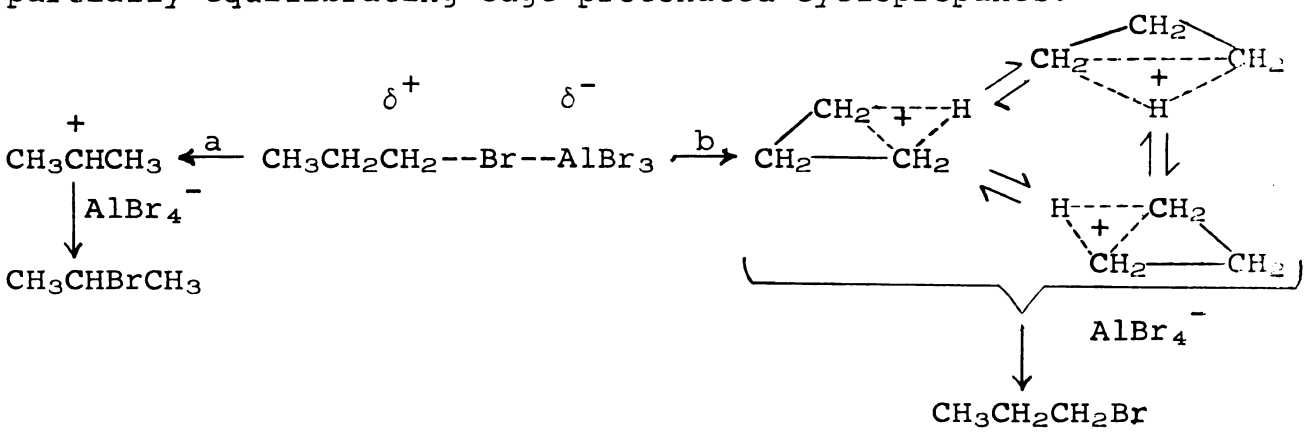
For the reaction of 1-bromopropane with aluminum bromide for less than 6 minutes, the results of runs 10-13 and 15-18 have several things in common. First, the recovered 1-bromopropanes show extensive rearrangement of the protons (deuteria) and the carbon skeleton. Second, the 2-bromopropanes are, within the limits of measurement, formed from 1-bromopropane by a 1,2-hydride shift and exhibit no carbon skeletal rearrangements.

Although several possible mechanisms can be devised to account for these observations, it is possible to discount most of these at the outset. The absence of any $\underline{d}_3$ species in the products from deuterium labeled starting materials (runs 10-13 and 15-16) rules out the importance of any intermolecular hydride transfers, bimolecular reactions, or elimination-addition reactions for short reaction times under these conditions. The results of runs 15 and 16 also rule out either 1,2-methyl shifts or 1,3-hydride shifts by themselves as the exclusive cause of rearrangement in the products. A combination of rapid 1,3-hydride shifts and classical 1,2-methyl shifts might be used as an explanation. However, there is no reason to believe that 1,2-hydride shifts should not be

competitive under such circumstances. Such 1,2-hydride shifts would have led to extensively isotope-position scrambled 2-bromopropane product. That was not the case.

The contribution to the scrambling observed in the recovered 1-bromopropane by multiple 1,2-hydride shifts proceeding through the 2-propyl cation cannot be very important. Such a mechanism fails to account for the carbon skeleton scrambling and predicts a measurable amount of deuterium scrambling in the 2-bromopropane product. In addition, in order for C_2H_5-CD_2Br species to be formed from $CH_3CD_2CH_2Br$ exclusively through multiple 1,2-hydride shifts, it is necessary that 10 times as many C_2H_4D-CHDBr species be formed. The actual ratio obtained was 1:2.0-2.8 (runs 15 and 16).

The combined data are most readily accommodated by a mechanism in which the incipient carbonium ion from the 1-bromopropane-aluminum bromide complex may take one of the two separate and distinct paths; path a, in which a single 1,2-hydride shift leads to 2-bromopropane, or path b, which leads to isotope-position rearranged 1-bromopropane through partially equilibrating edge-protonated cyclopropanes.



The results of runs 17 and 18 indicate that a methyl-bridged ion can not be the first species formed in path b, for if it were, then the carbon-13 label should be distributed either equally between C-2 and C-3, or unequally with more at C-2. Incomplete equilibration of the edge-protonated species, however, predicts more label at C-3 than at C-2. Experimentally more label was found at C-3. It is difficult to speculate on how "free" the protonated cyclopropane of path b is from its gegenion. It is reasonable to assume that its degree of freedom is somewhere between that of the intermediate formed from the deamination of aminopropane or deoxidation of 1-propanol on the one hand, and that of the intermediate formed in the reaction of zinc chloride and hydrochloric acid with 1-chloropropane on the other.

The presence of $\underline{d}_3$ species in the products of run 14 (Tables XXIX and XXX) indicates that some form of an intermolecular hydride transfer or elimination-addition reaction assumes some importance at a reaction time of 2 hours. If the deuteria were statistically scrambled in the 1-bromopropane recovered from this reaction, the parent-less-ethyl ion distribution for its trimethylsilyl ether derivative should be, roughly, 5.1% $\underline{d}_2$, 46.8% $\underline{d}_1$, and 48.1% $\underline{d}_0$ (calculated from $(P\text{-}Me)^+$ distribution). The actual distribution of 32.2% $\underline{d}_2$, 22.3% $\underline{d}_1$, and 41.7% $\underline{d}_0$ (Table XXIX) indicates that the aluminum bromide catalyst may become deactivated at long reaction times.

The results of runs 19 and 20 show that after 2 hours of reaction, 2-bromopropane-2-d has also undergone rather extensive amounts of either intermolecular hydride transfers or elimination-addition reactions, or some combination of the two. The net effect, however, has been a loss of deuterium with replacement by hydrogen for the 2-bromopropane, and, to a lesser extent, for the 1-bromopropane product.

At a reaction time of 6 minutes, the recovered 2-bromopropane had completely lost about 5% of its deuterium. The 1-bromopropane product retained slightly more of its isotopic purity.

It is tempting to suggest that a set of reactions such as those represented by equations 1-4 may contribute to a

$$CH_3CDBrCH_3 + CH_3\overset{+}{C}DCH_3 \longrightarrow CH_3CD_2CH_3 + CH_3\overset{+}{C}BrCH_3 \qquad \text{(eq. 1)}$$

$$CH_3\overset{+}{C}BrCH_3 + CH_3CDBrCH_3 \longrightarrow CH_3CDBrCH_3 + CH_3\overset{+}{C}BrCH_3 \qquad \text{(eq. 2)}$$

$$CH_3\overset{+}{C}BrCH_3 + CH_3CDBrCH_3 \longrightarrow CH_3CHBrCH_3 + CH_3C\overset{+}{D}\!\!-\!\!-\!\!-CH_2 \quad (Br) \qquad \text{(eq. 3)}$$

$$CH_3C\overset{+}{D}\!\!-\!\!-\!\!-CH_2 \quad (Br) + CH_3CDBrCH_3 \longrightarrow CH_3CD_2CH_2Br + CH_3\overset{+}{C}BrCH_3 \qquad \text{(eq. 4)}$$

small extent to the rearrangements in this system, since these reactions explain the formation of propane, and the greater net loss of deuterium from the recovered 2-bromopropane than from the 1-bromopropane product. Presumably, the 2-bromo-2-propyl cation could also lose a proton and polymerize. Such

a path would explain the deactivation of the catalyst and the formation of hydrogen bromide at longer reaction times.

By analogy with the results of run 21, one might expect the formation of some 2-bromopropane-$\underline{d}_7$ from 2-bromopropane-1,1,1,3,3,3-$\underline{d}_6$ when similarly treated. No $\underline{d}_7$ species were formed after 10 minutes reaction time in run 22. Unfavorable isotope effects prevailing in this system, however, might prevent detectable formation of species from bimolecular reactions. This is especially true if equation 3 is the rate determining step.

Taken collectively, the results of runs 19-23 suggest that the main path by which 2-bromopropane is converted to 1-bromopropane is by an intramolecular 1,2-hydride shift. The results of run 23 indicate that the less highly deuterated $\underline{d}_1$ species is isomerized more rapidly than the $\underline{d}_6$ species, and that at short reaction times no appreciable amount of hydride or deuteride transfer between the two species need occur for this conversion. Relatively slow intermolecular hydride transfers do become important, however, at long reaction times. The results suggest, but neither prove nor disprove, the possibility that reactions such as those represented by equations 1-4 may intervene to a small extent in this system.

IV. Summary

The following points have been made salient by the work described in this thesis:

1-Propyl tosylate is hydrolyzed to 1-propanol in 99% formic acid at 75° without undergoing isotope-position rearrangements.

1-Bromopropane prepared from isotope-position labeled 1-propanol may be converted back to 1-propanol with overall maintenance of isotope-position integrity by hydrolysis either in 15% aqueous silver nitrate at room temperature or in 10% aqueous sodium hydroxide at steam bath temperature. Isotope-position labeled 2-bromopropane may also be hydrolyzed in silver nitrate solution without undergoing isotope-position rearrangements.

When 1-bromopropanes are partially isomerized to 2-bromopropanes by the action of aluminum bromide, the recovered 1-bromopropanes are extensively isotope-position rearranged, while the 2-bromopropanes are the result of a 1,2-hydride shift and are not extensively scrambled. The data are most easily interpreted by assuming that the isotope-position scrambled 1-bromopropanes arise from a reaction path involving equilibrating edge-protonated cyclopropanes.

The major pathway for the conversion of 2-bromopropane into 1-bromopropane is an intramolecular 1,2-hydride shift.

At longer reaction times, intermolecular hydride transfers can become important. The exact mechanism for these transfers has not been unambiguously established.

EXPERIMENTAL

Vapor Phase Chromatography (V.P.C.)

V.p.c. analyses were performed using an Aerograph A-90-P, equipped with a thermal conductivity detector and employing helium as the carrier gas. Relative peak areas were determined either by planimetry, or by multiplication of peak height times the width at half height, depending on the resolution and shape of the peaks. In a few cases the peaks were cut out and weighed.

Infrared Spectra (I.R.)

I.r. spectra were determined, in most cases, on a Perkin-Elmer 237B double beam grating spectrophotometer and, in a few instances, on a Beckman IR-5 instrument. Samples were run either as 5-10% solutions in carbon tetrachloride in 0.1 mm. cavity cells or as thin films between sodium chloride plates.

Nuclear Magnetic Resonance Spectra (N.M.R.)

N.m.r. analyses, unless otherwise stated, were performed on a Varian Associates A-60 Analytical NMR Spectrometer with a probe temperature of ca. 38° or on a JEOLCO C-6QH at room temperature. Signal areas were integrated electronically.

Preparation of Trimethylsilyl Ether and Benzoate Ester Derivatives of 1- and 2-Propanol

Trimethylsilyl ether derivatives were prepared by adding a small drop of trimethylchlorosilane (Stauffer) to a 2:1 molar mixture of the alcohol and hexamethyldisilazane (Metallomer Laboratories) in a small flask fitted with a water-cooled reflux condenser topped with a "Drierite" drying tube and warming the mixture overnight over a steam bath. The ethers were purified by vapor phase chromatography (v.p.c.) from a 20' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W column at 60-80°, 30 p.s.i.g. He.

Benzoate esters were prepared by overnight refluxing of an equimolar mixture of alcohol and benzoyl chloride (Baker Analyzed Reagent) over a steam bath. The esters were purified by v.p.c. from a 6' x 1/4" 20% Apiezon L on 60/80 Chromosorb W column at 155-165°, 30 p.s.i.g. He.

Preparation of 1-Propanol-1,1-d_2

A slurry of 5.00 g. (0.119 mole) of lithium aluminum deuteride (Metal Hydrides) in 100 ml. of anhydrous diethyl ether, freshly distilled from lithium aluminum hydride, was prepared in a 300 ml. 3-necked flask equipped with a "Drierite" drying tube fitted to a water-cooled reflux condenser, a "Teflon"-bladed Tru-bore stirrer, and a 50 ml. addition funnel with equalizing tube. A solution of 12.7 ml. (12.8 g., 0.098 mole) of distilled propionic anhydride

(Matheson, Coleman and Bell, b.p. 58-9°/11 mm.) in 25 ml. of anhydrous diethyl ether was slowly dripped into the rapidly stirred slurry at a rate sufficient to cause gentle refluxing. After addition was completed, the pale gray slurry was stirred for an additional 20 hr. and then hydrolyzed at 0° by careful addition of first 10 ml. of water and then 10 ml. of 5% aqueous sodium hydroxide solution. The mixture was stirred for 17 hr. at room temperature and the clear ether supernatant decanted off. The white precipitate was rinsed six times with 15 ml. of ether and the ether portions combined and dried over anhydrous magnesium sulfate. Distillation of the ether solution through a 4" glass spiral packed column yielded 9.98 g. of product boiling above 90° (thermometer reading fluctuated a great deal). Analysis by vapor phase chromatography (6' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W, 75°, 30 p.s.i.g. He) showed this product to be pure 1-propanol. Vacuum distillation of the residue yielded an additional 0.53 g. of product which v.p.c. analysis showed to be 1-propanol containing a trace of unidentified higher boiling impurity. The yield of 1-propanol-1,1-$\underline{d}_2$ was 87%, based on propionic anhydride used. A trimethylsilyl ether derivative was prepared and purified in the usual manner for mass-spectral analysis.

Preparation of 1-Propyl-1,1-$\underline{d}_2$ $\underline{p}$-Toluenesulfonate

The method used was that of Tipson (61). Distilled $\underline{p}$-toluenesulfonyl chloride, 21.00 g. (0.110 mole), in 40 ml.

of pyridine (Matheson, Coleman and Bell, dried over barium oxide) was slowly added to 5.91 g. (0.0952 mole) of 1-propanol-1,1-$\underline{d}_2$ in 20 ml. of pyridine at -5° and then allowed to stand overnight in a refrigerator freezer. Seventy ml. of water was then added to the reaction mixture at 0°, the first 10 ml. being added slowly and in very small portions. The mixture, consisting of an upper aqueous layer and a lower, pink organic layer, was extracted with 155 ml. of diethyl ether in three portions. The combined ether extracts were then washed four times with 50 ml. portions of cold 10% hydrochloric acid, once with 50 ml. of water, and twice with 50 ml. of saturated aqueous sodium bicarbonate solution. After drying over anhydrous magnesium sulfate, the ether was stripped off in a rotary evaporator at 40° with maximum water aspirator vacuum and the resulting crude tosylate distilled at reduced pressure. The first distillation yielded 18.51 g. of slightly yellow product, b.p. 128.5-130°/0.7-0.8 mm. Redistillation yielded 18.31 g. of colorless 1-propyl tosylate, b.p. 115-6°/0.4 mm., which was pure by n.m.r. analysis. The yield was 90%, based on 1-propanol-1,1-$\underline{d}_2$ used.

Preparation of 1-Propyl-2,2-d_2 p-Toluenesulfonate

p-Toluenesulfonyl chloride, 14.22 g. (0.0747 mole), in 40 ml. of dry pyridine was reacted with 4.00 g. (0.0642 mole) of 1-propanol-2,2-$\underline{d}_2$ (supplied by C. E. Orzech, Jr., prepared by repeated exchange of methylmalonic acid with deuterium oxide,

followed by decarboxylation to propionic acid and lithium aluminum hydride reduction to 1-propanol) in 20 ml. of pyridine and worked-up as described for 1-propyl-1,1-$\underline{d}_2$ p-toluenesulfonate. The reaction yielded 11.20 g. of 1-propyl-2,2-$\underline{d}_2$ p-toluenesulfonate, b.p. 108-108.5°/0.1 mm., which was pure by n.m.r. analysis. The yield was 81%, based on 1-propanol-2,2-$\underline{d}_2$ used.

Hydrolysis of 1-Propyl p-Toluenesulfonates in Aqueous Formic Acid

Anhydrous formic acid was prepared by the method of Winstein and Marshall (62). Two kg. of 98% formic acid (Matheson, Coleman and Bell) was placed in a still pot and distillation begun through a 20" Vigreaux column until a distillation temperature of 98.5° was reached. The remaining acid was then allowed to stand over 330 g. of boric anhydride for 5 days and decanted into a still pot containing 85 g. of boric anhydride. The anhydrous acid was then distilled off under vacuum as needed. The boiling point was 29.5-30.0°/51 mm. Anhydrous acid was added to water to bring the water concentration to 0.556 molar (ca. 0.86% by weight). This mixture was used in the 1-propyl tosylate solvolyses.

In a typical experiment, 4.52 g. (0.021 mole) of 1-propyl-1,1-$\underline{d}_2$ 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 separated, and the aqueous layer 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 anhydrous magnesium sulfate. Distillation produced 0.47 g. of product boiling above 36°. Vapor phase chromatographic analysis (6'x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W, 75°, 30 p.s.i.g. He) showed it to be composed of 6% 2-propanol and 94% 1-propanol, with a trace of diethyl ether. The trimethylsilyl ether derivatives of the alcohols were prepared and purified for mass-spectral analysis.

The hydrolysis of 1-propyl-2,2-$\underline{d}_2$ $\underline{p}$-toluenesulfonate was performed in the same manner.

Preparation of 1-Bromopropane-1,1-$\underline{d}_2$

To 5.00 g. (0.081 mole) of 1-propanol-1,1-$\underline{d}_2$ 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 was slowly added with moderate stirring at 0° 3.3 ml. (9.4 g., 0.035 mole) of phosphorous tribromide. Stirring was continued for 23 hr. at room temperature, during which time HBr was evolved, and then 10 ml. of water was added at 0°. The upper aqueous layer was extracted twice with 8 ml. of distilled 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 anhydrous magnesium sulfate. Distillation through a 4" glass spiral packed column yielded 5.56 g. of 1-bromopropane, b.p. 69-70°, which was shown by vapor phase chromatographic analysis (6' x 1/4" 20% Carbowax 20M on 69/80 Chromosorb W, 75°, 30 p.s.i.g. He) to be pure except for a trace of pentane. N.m.r. analysis revealed no trace of α-protons. The yield of 1-bromopropane-1,1-$\underline{d}_2$ was 56%, based on 1-propanol-1,1-$\underline{d}_2$ used.

Preparation of 1-Bromopropane-2,2-$\underline{d}_2$

The reaction of 10.19 g. (0.167 mole) of 1-propanol-2,2-$\underline{d}_2$ (supplied by C. E. Orzech, Jr.) with 6.5 ml. (18.5 g., 0.068 mole) of phosphorous tribromide yielded 11.22 g. of 1-bromopropane, b.p. 68.5-70.0°, which was pure by v.p.c. analysis (6' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W, 75°, 30 p.s.i.g. He). The yield of 1-bromopropane-2,2-$\underline{d}_2$ was 57%, based on 1-propanol-2,2-$\underline{d}_2$ used.

Preparation of 1-Bromopropane-1-^{13}C

1-Bromopropane-1-^{13}C was prepared by $^{13}CO_2$ carboxylation of ethylmagnesium bromide to form propionic acid-1-^{13}C, followed by lithium aluminum hydride reduction of the acid to 1-propanol-1-^{13}C, and treatment of the alcohol with phosphorous tribromide.

A solution of ethylmagnesium bromide in 800 ml. of anhydrous ether was prepared from 7.32 g. (0.301 g. at.) of magnesium turnings and 23.0 ml. (33.4 g., 0.307 mole) of ethyl bromide (Matheson, Coleman and Bell) in a 2 l. 3-necked flask equipped with a 250 ml. addition funnel, a "Teflon"-bladed Trubore stirrer and a water-cooled reflux condenser. A tube leading to a calcium chloride drying tube and then to two gas scrubbers containing 25% aqueous barium chloride solution was fitted to the top of the condenser. The addition funnel was then replaced by a 12 mm. o.d. glass tube which extended below the surface of the ether solution and was connected to two sulfuric acid gas scrubbers and then to a 300 ml. 3-necked flask fitted with a "Teflon" covered magnetic stirring bar, a stopper, and an addition funnel, the top of which served as an inlet for a source of dry nitrogen. Aqueous perchloric acid, 35%, was placed in the addition funnel and 40.00 g. (0.20 mole) of barium carbonate-^{13}C (Merck, Sharp and Dohme of Canada, 56.5 atom percent ^{13}C) placed in the flask. After all tubing connections were tightly wired and glass tapers were held in place with heavy rubber bands, the entire system was swept with dry nitrogen for 15 minutes and the ethyl-

magnesium bromide solution was cooled to 0°. Carbon dioxide was then bubbled into the rapidly stirred solution by slowly dripping dilute acid onto the barium carbonate.

After 3 hr. (ca. 75 ml. of acid used), the barium carbonate was consumed and the system was swept with dry nitrogen for 20 minutes. The bubbler tube was then replaced by an addition funnel and the intermediate complex was decomposed by addition of 100 ml. of 10% aqueous hydrochloric acid and stirred for 1.5 hr. To this was added 25 ml. of 37% aqueous hydrochloric acid, the lower aqueous layer was saturated with sodium chloride and the mixture was stirred overnight. The aqueous layer was then extracted three times with 50 ml. of ether and the ether portions combined and dried over anhydrous magnesium sulfate. Distillation produced two cuts boiling above 36°. The first cut, b.p. 86-127°, 1.94 g., was shown by vapor phase chromatographic analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 135°, 30 p.s.i.g. He) to be a mixture of ca. 75% 3-pentanone and 25% propionic acid, with a trace of diethyl ether. The second cut, b.p. 138-141°, 12.51 g., was shown to be propionic acid containing traces of 3-pentanone and diethyl ether. Infrared spectra of these fractions confirmed the product assignments. The yields were 87% for propionic acid and 8% for 3-pentanone, based on barium carbonate used. No barium carbonate was recovered.

To a slurry of 6.50 g. (0.171 mole) of lithium aluminum hydride (Metal Hydrides) in 200 ml. of ether, was added 12.5 g. (0.167 mole) of the propionic acid-1-^{13}C in 50 ml. of anhydrous diethyl ether and the product was worked-up in the

usual way. Distillation produced 8.68 g. of 1-propanol which was pure except for traces of diethyl ether and ethanol (v.p.c., 6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 65°, 30 p.s.i.g. He). Vacuum distillation of the residue yielded an additional 0.80 g. of 1-propanol which contained ca. 5% of a higher boiling impurity. The yield of 1-propanol-1-^{13}C was 93%, based on propionic acid-1-^{13}C used. A trimethylsilyl ether derivative was prepared and purified in the usual manner for mass-spectral analysis.

The reaction of 5.13 g. (0.0845 mole) of 1-propanol-1-^{13}C with 3.2 ml. (9.1 g., 0.034 mole) of phosphorous tribromide, as previously described for the preparation of 1-bromopropane-1,1-d_2, yielded 6.45 g. of 1-bromopropane (b.p. 69-71°) containing a trace of pentane, and an additional 0.78 g. of 1-bromopropane containing a trace of higher boiling impurity. The later portion was purified by vapor phase chromatography (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He). The yield of 1-bromopropane-1-^{13}C was 69%, based on 1-propanol-1-^{13}C used.

Preparation of 2-Propanol-2-d

Ten g. (0.173 mole) of acetone (Baker Analyzed Reagent, dried over anhydrous magnesium sulfate) was reduced with 2.18 g. (0.0518 mole) of lithium aluminum deuteride (Alpha Inorganics) to obtain 7.01 g. of 2-propanol, b.p. 79.5-80.5°, which was pure by v.p.c. analysis (6' x 1/4" 15% FFAP on 60/80

Chromosorb W, 55°, 30 p.s.i.g. He). Infrared analysis confirmed the absence of carbonyl impurities. Vacuum distillation of the residue yielded an additional 1.14 g. of 2-propanol which contained traces of diethyl ether and acetone. The yield of 2-propanol-2-d was 77%, based on acetone used.

Preparation of 2-Bromopropane-2-d

2-Propanol-2-d, 5.15 g. (0.0843 mole), was reacted with 3.3 ml. (9.4 g., 0.035 mole) of phosphorous tribromide (Eastman), as previously described for the preparation of 1-bromopropane-1,1-d_2, to yield 5.94 g. of 2-bromopropane, b.p. 57.5-58.5°, which was pure by v.p.c. analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He). The yield of 2-bromopropane-2-d was 57%, based on 2-propanol-2-d used.

Preparation of 2-Propanol-1,1,1,3,3,3-d_6

The reduction of 10.33 g. (0.161 mole) of acetone-d_6 (Merck, Sharp and Dohme of Canada, > 99.5 atom percent D) with 2.00 g. (0.053 mole) of lithium aluminum hydride (Metal Hydrides) yielded 9.00 g. of 2-propanol, b.p. 79.5-81.0°, which was pure by v.p.c. analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He). Infrared analysis confirmed the absence of carbonyl impurities. The yield of 2-propanol-1,1,1,3,3,3-d_6 was 85%, based on acetone-d_6 used.

Trimethylsilyl ether and benzoate ester derivatives were prepared and purified in the usual way for mass-spectral analysis.

Preparation of 2-Bromopropane-1,1,1,3,3,3-$\underline{d}_6$

2-Propanol-1,1,1,3,3,3-$\underline{d}_6$, 5.16 g. (0.078 mole), was reacted with 3.0 ml. (8.3 g., 0.030 mole) of phosphorous tribromide (Eastman), as previously described for the preparation of 1-bromopropane-1,1-$\underline{d}_2$, to yield 5.8 g. of 2-bromopropane, b.p. 56.5-58.0^{6}, which was pure by v.p.c. analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He). Vacuum distillation of the reaction residue yielded another 0.3 g. of product consisting of 2-bromopropane and a trace of unidentified higher boiling impurity. The yield of 2-bromopropane-1,1,1,3,3,3-$\underline{d}_6$ was 61%, based on 2-propanol-1,1,1,3,3,3-$\underline{d}_6$ used.

Silver Ion-Assisted Hydrolysis of Bromopropanes

In a typical experiment, 4.89 g. (0.0392 mole) of 1-bromopropane-1,1-$\underline{d}_2$, 8.69 g. (0.0511 mole) of silver nitrate (Baker and Adamson Reagent), 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 mole)

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 anhydrous magnesium sulfate and distilled to yield 1.63 g. of product, boiling above 80°, which was found by v.p.c. analysis (6' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb W, 75°, 30 p.s.i.g. He) to be 1-propanol with a trace of diethyl ether.

1-Bromopropane-2,2-$\underline{d}_2$ and 2-bromopropane-2-$\underline{d}$ were also solvolyzed to their respective alcohols in this way, as were the propyl bromide products of various isomerization reactions described elsewhere in this thesis. Trimethylsilyl ether derivatives of the alcohols were prepared and purified in the usual way for mass-spectral analysis.

Basic Hydrolysis of Bromopropanes

In a typical experiment, 4.14 g. (0.0331 mole) of 1-bromopropane-1,1-$\underline{d}_2$, 5.00 g. (0.125 mole) 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 solution was extracted with 50 ml. of diethyl ether in three portions. The combined ether extracts were dried over anhydrous magnesium sulfate and distilled to yield 0.74 g. of product, boiling above 70°, which was shown by v.p.c. analysis (6' x 1/4" 20% Carbowax 20M on 60/80 Chromosorb

W, 75°, 30 p.s.i.g. He) to be 1-propanol containing a trace of diethyl ether.

1-Bromopropane-2,2-$\underline{d}_2$ was also hydrolyzed to its respective alcohol by this technique. The trimethylsilyl ether derivatives of the alcohols were prepared and purified in the usual way for mass-spectral analysis.

Aluminum Bromide Catalyzed Isomerizations of Bromopropanes

Both 1- and 2-bromopropanes were reacted 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 with a weighed amount of aluminum bromide (Fisher anhydrous), and a small "Teflon" coated magnetic stirring bar in a dry nitrogen-filled dry bag 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 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 begun 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 vapor phase chromatography, and then converted to their respective alcohols by hydrolysis in 15% aqueous silver nitrate. The trimethylsilyl ether derivatives were prepared and subjected to mass-spectral analysis.

Preparation of 2-Propanol-1,1-$\underline{d}_2$

2-Propanol-1,1-$\underline{d}_2$ was prepared by lithium aluminum deuteride reduction of $\underline{n}$-octylformate to methanol-$\underline{d}_2$, conversion of the methanol to methyl-$\underline{d}_2$ iodide by treatment with red phosphorous and iodine, formation of methyl-$\underline{d}_2$-magnesium iodide, and addition of acetaldehyde to it.

A solution of 33.67 g. (0.213 mole) of $\underline{n}$-octyl formate (K & K, redistilled, b.p. 62.5-63.5°/2.5 mm.) in 35 ml. of di-$\underline{n}$-butyl ether (Matheson, Coleman and Bell, redistilled from lithium aluminum hydride, b.p. 64-5°/50 mm.) was reduced by addition to a slurry of 5.02 g. (0.120 mole) of lithium aluminum deuteride (Metal Hydrides) in 160 ml. of butyl ether. After being stirred for 17 hr., the mixture was hydrolyzed with 10 ml. of water and 10 ml. of 5% aqueous sodium hydroxide and stirred another 12 hr. Work-up in the usual manner yielded 4.73 g. (65%) of product, b.p. 64-5°, which was shown by vapor phase chromatographic analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He) to be methanol containing $\underline{ca}$. 5% of butyl ether. This reduction was not run in diethyl ether, because the azeotrope of methanol and diethyl ether makes purification extremely difficult.

Methanol-$\underline{d}_2$, 4.55 g. (0.134 mole), was slurried with 2.06 g. (0.0166 mole P_4) of purified (63) red phosphorous in a 50 ml. round-bottomed flask containing a small "Teflon" covered magnetic stirring bar and fitted with a water-cooled reflux condenser. Iodine (Baker and Adamson, resublimed, U.S.P.), 22.80 g. (0.09 mole I_2), was then slowly added through the condenser over 1.5 hr. at 0° and the resulting blood-red mixture was stirred overnight at room temperature. The condenser was replaced by a still head and 16.5 g. of crude methyl-$\underline{d}_2$ iodide, b.p. 40-3°, was distilled off. This was dissolved in 22 ml. of dry butyl ether to facilitate handling and washed once with 17 ml. of cold 10% aqueous sodium carbonate solution and once with 20 ml. of ice water. After drying over anhydrous magnesium sulfate, the solution was distilled, yielding 11.23 g. (58%) of methyl iodide, b.p. 42-3°, which was pure by v.p.c. analysis (6' x 1/4" 15% FFAP on 60/80 Chromosorb W, 55°, 30 p.s.i.g. He).

A solution of methyl-$\underline{d}_2$-magnesium iodide in 25 ml. of anhydrous diethyl ether was prepared from 1.57 g. (0.0654 g. at.) of magnesium turnings and 5.15 g. (0.0358 mole) of methyl-$\underline{d}_2$ iodide in a 100 ml. 3-necked flask equipped with a calcium chloride drying tube fitted to a water-cooled reflux condenser, a "Teflon"-bladed Tru-bore stirrer, and an ice water-jacketed addition funnel with equalizing tube. A 2.25 ml. (1.8 g., 0.041 mole) portion of freshly distilled acetaldehyde (Matheson, Coleman and Bell), dissolved in 4 ml. of

ether, was slowly added to the Grignard solution at 0°. The solution was stirred for 3 hr. at room temperature and 45 min. at reflux. The addition of 3.5 ml. of saturated aqueous ammonium chloride solution to the mixture at 0° immediately caused a hard, yellow mass to precipitate. After standing overnight, the ether layer was decanted off and the salts were washed several times with ether. The ether portions were combined and dried over anhydrous magnesium sulfate. Distillation yielded 0.56 g. of product boiling above 36° which was shown by v.p.c. analysis (6' x 1/4" 15% **FFAP** on 60/80 Chromosorb **W**, 55°, 30 p.s.i.g. He) to consist of ca. 80% 2-propanol (20% yield) and 20% diethyl ether. The trimethylsilyl ether and benzoate ester derivatives were prepared and purified in the usual manner for mass-spectral analysis.

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