

# PROTONATED CYCLOPROPANES<sup>1</sup>

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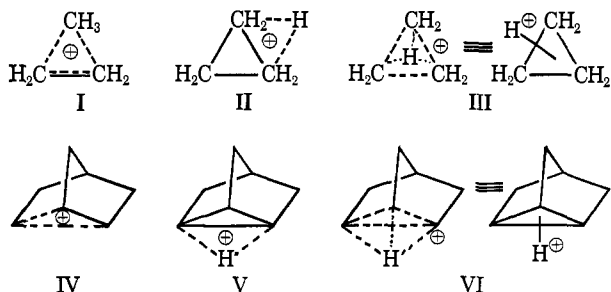
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## I. Introduction

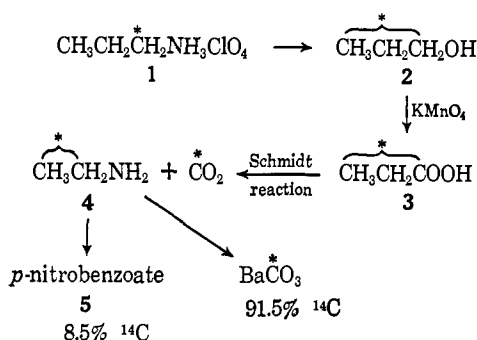
Protonated cyclopropane intermediates are of considerable importance in connection with the still unresolved question of the nonclassical norbornyl cation.<sup>2</sup> We demonstrated<sup>3</sup> that the hydride shifts which occur in remotely substituted norbornyl cations do so through discrete, sequential steps, and suggested<sup>3a</sup> that edge-protonated nortricyclenes could be useful in explaining these shifts. We also presented<sup>3a</sup> evidence against the intervention of "face-protonated" nortricyclenes.<sup>4</sup> Berson and Grubb<sup>5b</sup> had shown earlier that face-protonated intermediates were not important in a norbornyl cation in which the potential cyclopropane ring (C<sub>6</sub>, C<sub>1</sub>, or C<sub>2</sub>) contained a methyl group, thus destroying its symmetry. It was recently suggested by Olah<sup>5</sup> on the basis of Raman spectra that the nonclassical norbornyl cation might exist together with protonated nortricyclene. For these reasons I think it is worth-



while to review the evidence for the existence of such intermediates, and to decide whether they are best represented as methyl-bridged ions I, edge-protonated cyclopropanes II, or "face"-protonated cyclopropanes III. For comparison the nonclassical norbornyl cation IV and the protonated nortricyclenes V and VI are also shown. Although there are theoretical grounds for ruling out structures III and VI,<sup>6a,b</sup> it is not easy to decide between I and II or IV and V. Structures I and IV are somewhat analogous to the CH<sub>3</sub><sup>+</sup> ion,<sup>6c</sup> whereas the "bent bonds" in cyclopropane cannot be pure  $\sigma$  bonds, but must have considerable sp<sup>2</sup> character, and therefore provide a  $\pi$  cloud for interaction with a proton.<sup>6b</sup>

The methyl-bridged ion I was first proposed in 1953 by Roberts and Halmann,<sup>7</sup> who carried out the deamination of 1-aminopropane-1-<sup>14</sup>C (1) in 35% perchloric acid solution (see Chart I). Whitmore and Thorpe<sup>8</sup> had previously deami-

Chart I



nated 1-aminopropane, reporting a 7% yield of 1-propanol, 32% of 2-propanol, and 28% olefin. Roberts and Halmann subjected 1 to deaminating conditions and isolated 1-propanol-<sup>14</sup>C (2). The propionic acid (3) obtained on oxidation was degraded by the Schmidt reaction, and radioactivity assays indicated 8.5% of the original carbon-14 had gone to the 2 and 3 positions of 2. Roberts and Halmann presumed, however, that all of the carbon-14 was now in the 2 position of 2 and thus proposed that the methyl-bridged ion I was involved to the extent of 17%. In 1954 H. C. Brown pointed out to me (in a letter) that the foregoing results required an aston-

(1) Work sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) See, for example, D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967, Chapter 7; O. E. Edwards and M. Lesage (*Can. J. Chem.*, **41**, 1592 (1963)), appear to be among the first to have proposed protonated cyclopropane intermediates.

(3) (a) B. M. Benjamin, B. W. Ponder, and C. J. Collins, *J. Am. Chem. Soc.*, **88**, 1558 (1966); B. M. Benjamin and C. J. Collins, *Tetrahedron Letters*, 5477 (1966); C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **89**, 1652 (1967); (b) see also J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965).

(4) J. D. Roberts, C. C. Lee, and W. H. Saunders *ibid.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

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

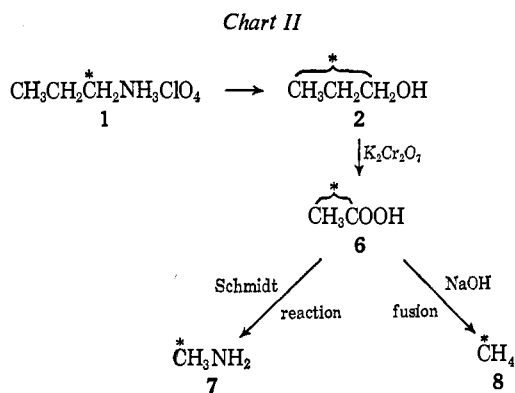
(6) (a) See, for example, A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); (b) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (c) V. L. Tal'Roze and A. K. Lyubimova, *Dokl. Akad. Nauk*, **86**, 909 (1952).

(7) J. D. Roberts and M. Halmann, *J. Am. Chem. Soc.*, **75**, 5759 (1953).

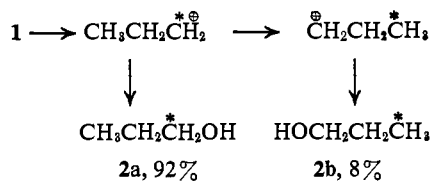
(8) F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

ishingly low phenyl/methyl migration ratio<sup>9</sup> of 3.2, and suggested that the fraction of methyl migration observed<sup>7</sup> was too high by a considerable factor.

The matter rested until 1962 when Reutov and Shatkina<sup>10</sup> repeated the deamination of **1**, but carried out an additional degradation of the labeled 1-propanol (**2**) isolated (Chart II). From their results Reutov and Shatkina concluded that 8% of the original carbon-14 of **1** had found its way to the 3 position



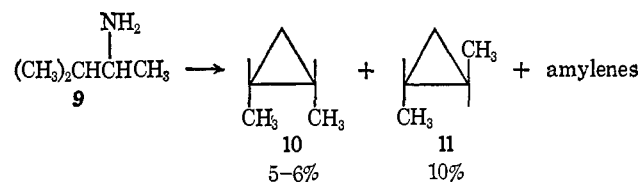
of the 1-propanol isolated (not the 2 position as proposed by Roberts and Halmann<sup>7</sup>), and thereby proposed that the carbonium ion intermediate undergoes a 1,3 shift of hydrogen. The data of Reutov and Shatkina<sup>10</sup> were apparently confirmed



in 1962, when Karabatsos and Orzech<sup>11</sup> subjected 1-amino-propane-1,1,2,2-*d*<sub>4</sub> to the deaminating conditions used by the previous investigators<sup>7,10</sup> and stated that the 1-propanol isolated—on the basis of nmr evidence—had undergone 12% 1,3-hydride shift. Karabatsos summed up the situation as follows: "The 1-propyl cation... undergoes a 1,3-hydride shift; protonated cyclopropanes are not intermediates in the formation of the propanols; methyl migration does not occur." As we shall see later, the results of Roberts,<sup>7</sup> Reutov,<sup>10</sup> and Karabatsos,<sup>11</sup> in one of the most astonishing coincidences of modern mechanistic chemistry, all indicated three to four times more rearrangement on deamination of 1-aminopropane than really occurs. Further, the 1,3 shift of hydrogen through the *n*-propyl cation<sup>10,11</sup> will be shown to have no basis in experimental fact.

It was already clear, in fact, that the question of the role of protonated cyclopropanes in the deamination of 1-aminopropanes was far from solved. In 1959–1962, Skell and Starer<sup>12</sup>

published their results on the deoxidation reaction, and noted its similarity to the deamination of aliphatic amines. Briefly, a series of alkoxides, when dissolved in the corresponding alcohol plus bromoform, yielded carbon monoxide plus the olefins. In the case of 1-propanol the product consisted of 90% propylene and 10% cyclopropane. The cyclopropane was not formed by an intramolecular carbene insertion reaction, since at least 94% of the cyclopropane formed on deoxidation of 1-propanol-1,1-*d*<sub>2</sub> was dideuterated on a single carbon, whereas the carbene insertion mechanism should have led to monodeuterated cyclopropane. Thus it is highly likely that a protonated cyclopropane was involved in the reaction. It was also pointed out<sup>12</sup> that the intermediates formed on deoxidation [RO—C<sup>+</sup>: ↔ RO<sup>+</sup>=C:] and on deamination [R—N<sup>+</sup>≡N: ↔ R $\ddot{\text{N}}$ =N<sup>+</sup>] are isosteres and should produce the same carbonium ion upon loss of CO or N<sub>2</sub>, respectively. Thus a series of alcohol deoxidations was carried out, and the results were compared with the corresponding deaminations. In the 1-propyl cases, both reactions yielded 90% propylene and 10% cyclopropane in the hydrocarbon fraction. Additional evidence for protonated cyclopropane intermediates was adduced by Silver,<sup>13</sup> who deaminated 2-amino-3-methylbutane (**9**) in acetic acid–sodium acetate and isolated, in addition to the three possible amylenes, both *cis*- (**10**) and *trans*-dimethylcyclopropane (**11**).



## II. The Search for Protonated Cyclopropane Intermediates

All evidence<sup>12,13</sup> thus far quoted for protonated cyclopropane intermediates depends upon the formation of cyclopropane or its derivatives from linear reactants. Although such evidence is indicative, it is not really compelling, for it is possible that a primary 1-propyl cation can close to a three-carbon ring with simultaneous loss of a proton. In 1963 the first clear evidence for the intermediate was reported by Baird and Aboderin,<sup>14</sup> who cycled cyclopropane through D<sub>2</sub>SO<sub>4</sub> for 17 hr and found that 21% of the hydrogen in C<sub>3</sub>H<sub>6</sub> had been replaced with deuterium. Later<sup>15</sup> these same investigators repeated the experiment, but allowed the cyclopropane to go through 8.43 M D<sub>2</sub>SO<sub>4</sub> (at 25.0°) so rapidly that only one deuterium atom per mole of product was taken up. Upon cautious neutralization of the D<sub>2</sub>SO<sub>4</sub> solution, 1-propanol was isolated as the only important product (plus 0.27% 2-propanol and a trace of di-*n*-propyl ether). Analysis by nmr of the *p*-toluate ester of the 1-propanol produced showed the following deuterium distribution: C<sub>1</sub>, 0.38 D; C<sub>2</sub>, 0.17 D; C<sub>3</sub>, 0.46 D. It was also shown that 1,1-dideuteriopropyl alcohol is stable under the conditions of the reaction. These results cannot be explained through the usual carbonium ion reactions of a 1-propyl cation, nor are they explicable through 1,3-hydride (or deuteride) shifts of the type suggested by Reutov<sup>10</sup> and by Karabatsos.<sup>11</sup> Given in Chart III is a partial

(9) J. D. Roberts and C. D. Regan, *J. Am. Chem. Soc.*, **75**, 2069 (1953), found, upon deamination of PhCH<sub>2</sub>C\*H<sub>2</sub>NH<sub>2</sub>, that 27% of the carbon-14 rearranged to the 2 position of β-phenylethanol. Thus we calculate the phenyl/methyl migration ratio for deamination by dividing 27 by 8.5 ≈ 3.2. The phenyl/alkyl migration ratio in the deamination of 1-amino-2-phenyl-2-propanol [M. Tiffeneau and H. Cahnman, *Bull. Soc. Chim. Fr.*, 1876 (1953)] must be very much larger than 3.2, however, since no evidence of methyl migration could be found in the reaction product, despite a strong attempt to isolate the semicarbazone of phenyl *n*-propyl ketone.

(10) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).

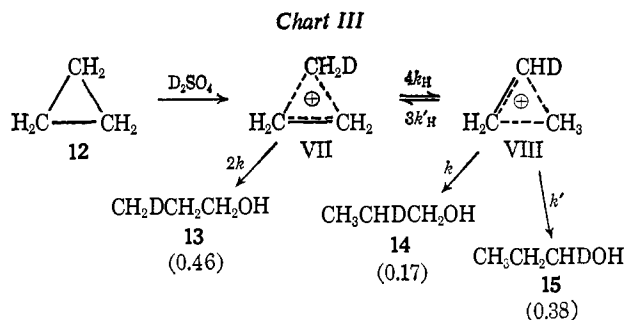
(11) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

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

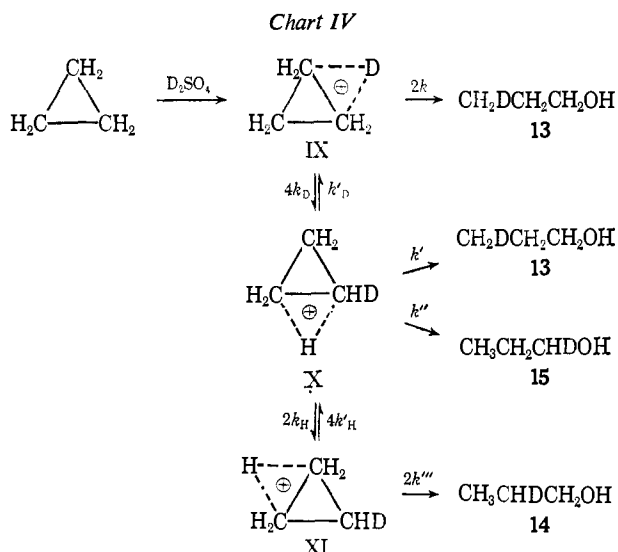
(13) M. S. Silver, *ibid.*, **82**, 2971 (1960).

(14) R. L. Baird and A. A. Aboderin, *Tetrahedron Letters*, 235 (1963).

(15) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).



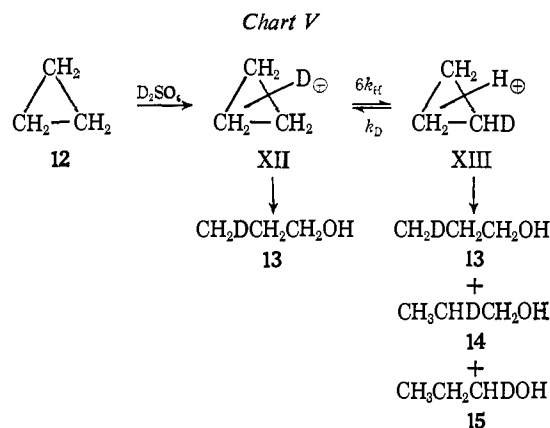
explanation for the results (the mole fractions of each product are shown in parentheses). Structures VII and VIII are the only monodeuterated methyl-bridged ions possible here, and the mechanism of Chart III requires that at equilibrium the ratio 13:14:15 be 3:2:2. Before equilibrium between VII and VIII is attained, however, the ratio 14:15 should also be 1, except for a small, secondary isotope effect. The ratio  $k'/k = 0.38/0.17 = 2.2$ , however, is clearly too large to be ascribed to a secondary deuterium isotope effect, and thus Baird and Aboderin favored cyclopropane intermediates which were "edge"-protonated or deuterated. In Chart IV such a mechanism is constructed. Clearly, if we presume the intermediates IX, X, and XI have achieved equilibrium conditions then, except for a small secondary isotope effect,  $k''/k'''$  should be equal to the ratio 15:14 which should be one. Since  $15:14 = 0.38:0.17 = 2.2$ , however, the isotope effect once again is much too large and we are thus unable to distinguish between the methyl-bridged ion (Chart III) and the edge-protonated species (Chart IV). If we assume that the experiments of Baird and Aboderin<sup>14,15</sup> with 8.43 M D<sub>2</sub>SO<sub>4</sub> do not allow the intermediates to come to equilibrium, then the edge-protonated intermediates of Chart IV allow



more 1-propanol-1-*d* (15) than 1-propanol-2-*d* (14), and are also consistent with the fraction (0.46) of deuterium in the 3 position (1-propanol-3-*d* (13)). Very recently Deno<sup>16</sup> and coworkers repeated the Baird and Aboderin<sup>14,15</sup> experiments using D<sub>2</sub>SO<sub>4</sub> of higher molarity, and found the monodeuterio-propanol isolated therefrom possesses the statistical 3:2:2

distribution of deuterium in the 3, 2, and 1 positions, respectively. Both Deno<sup>16</sup> and Lee and Gruber<sup>17</sup> confirmed Baird's original data<sup>14,15</sup> under nonequilibrium conditions.

In Chart V a mechanism is written including the face-protonated structures XII and XIII. In the absence of an isotope effect (that is, if  $k_H = k_D$ ), then at equilibrium the distribution of deuterium at C<sub>3</sub>, C<sub>2</sub>, and C<sub>1</sub> must be 3:2:2. Before equilibrium, however, and even under the condition of a large isotope effect, these intermediates require (as do methyl-bridged cations, Chart III) that the deuterium contents of C<sub>2</sub> (14) and C<sub>1</sub> (15) are identical.



Thus the presence of edge-protonated cyclopropane intermediates in the reaction of cyclopropane with sulfuric acid seems to rest on firm ground, with Deno's demonstration<sup>16</sup> that in higher concentrations of deuteriosulfuric acid cyclopropane is, in fact, converted to monodeuterated 1-propanols which are formed in statistical yields.

### III. Reinvestigation of the Deamination of 1-Aminopropane

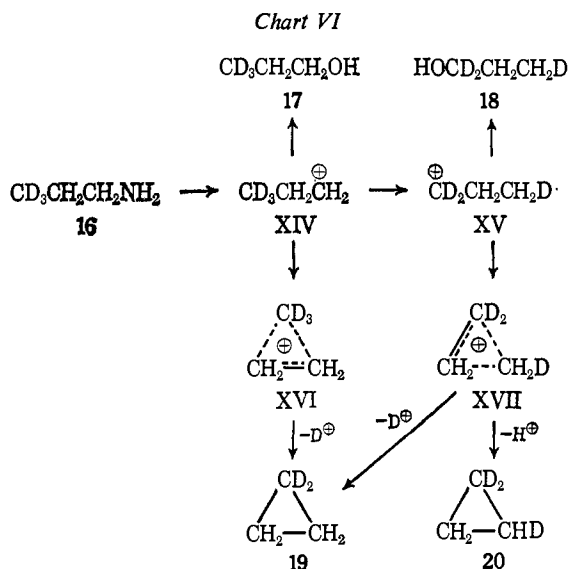
In 1964 Baird<sup>18</sup> examined the cyclopropane fraction formed on deamination of 3,3,3-trideuterio-1-aminopropane (16), and found that  $57 \pm 1\%$  of its molecules still contained three deuterium atoms per molecule, whereas the rest ( $43 \pm 1\%$ ) contained only two. This result seems to demand the presence of protonated cyclopropanes which are rapidly undergoing shifts of hydrogen and deuterium. Consider first the mechanism of Reutov<sup>10</sup> and Karabatsos<sup>11</sup> which is modified in Chart VI to include the formation of cyclopropane. Since the ratio of 17:18 was believed<sup>11</sup> to be 88:12, then the sequence XIV  $\rightarrow$  XVI  $\rightarrow$  19 (Chart VI) would be expected to produce 88% of cyclopropane-*d*<sub>2</sub> (19), whereas XV  $\rightarrow$  XVII  $\rightarrow$  19 should provide an additional 3–6%. Thus the mechanism in Chart VI can never account for  $53 \pm 1\%$  of cyclopropane-*d*<sub>3</sub> (20).

Given in Chart VII is a scheme by which 3,3,3-trideuterio-1-aminopropane (16) can proceed to cyclopropane-*d*<sub>2</sub> and cyclopropane-*d*<sub>3</sub> by means of protonated or deuterated cyclopropane intermediates which can interconvert as shown. Edge-protonated as well as face-protonated species could also be used, but since they are not demanded by the data, the point will be made with the less complicated, methyl-bridged

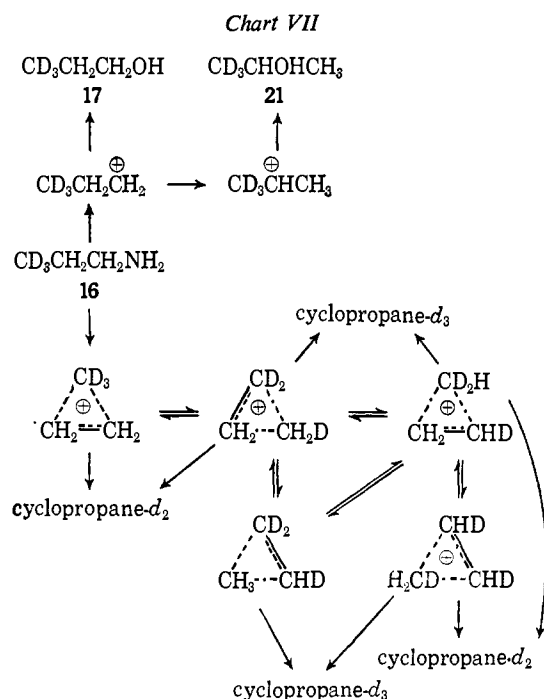
(16) Private communication during the 21st Mechanisms Conference, Brandeis University, Waltham, Mass., June 19–22, 1968; N. C. Deno, D. LaViertes, J. Mockus, and P. C. Scholl, *J. Am. Chem. Soc.*, **90**, 6457 (1968).

(17) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968), passed cyclopropane through tritiated sulfuric acid and found the following tritium distribution at C<sub>3</sub>, C<sub>2</sub>, and C<sub>1</sub>: 36.9, 26.1, and 37.0%; see also C. C. Lee, W. K. Y. Chwang, and K. M. Wan, *ibid.*, **90**, 3778 (1968), who treated cyclopropane with Lucas' reagent and determined a corresponding distribution of 43% (C<sub>3</sub>), 19% (C<sub>2</sub>), and 38% (C<sub>1</sub>).

(18) A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).



intermediates. It is clear that this mechanism is compatible with Baird's<sup>18</sup> result of 57% cyclopropane-*d*<sub>3</sub> and 43% cyclopropane-*d*<sub>2</sub>. If there were no *d*<sub>3</sub> product found, then a protonated cyclopropane intermediate would not really be required since the sequence XIV → XVI → 19 (Chart VI)



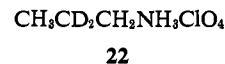
need not involve intermediate XVI at all. That is, it could occur by means of a simultaneous ring closure and deuteron ejection by XIV to give cyclopropane-1,1-*d*<sub>2</sub> (19) directly. Thus Baird's determination that 57% of the cyclopropane formed on deamination of 16 was trideuterated must be taken as very good evidence that protonated cyclopropane intermediates are formed in the deamination of *n*-propylamine—at least as precursors of cyclopropane itself.

In 1965 Lee and coworkers, in a remarkable series of experiments,<sup>19,20</sup> studied the deaminations of the perchlorates

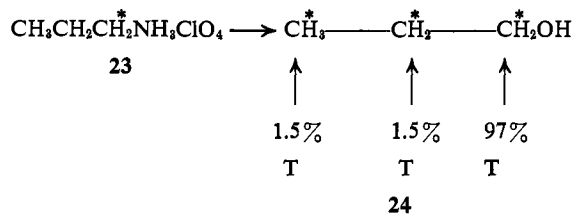
(19) C. C. Lee, J. E. Kruger, and E. W. C. Wong, *J. Am. Chem. Soc.*, **87**, 3985 (1965).

(20) C. C. Lee and J. E. Kruger, *ibid.*, **87**, 3986 (1965).

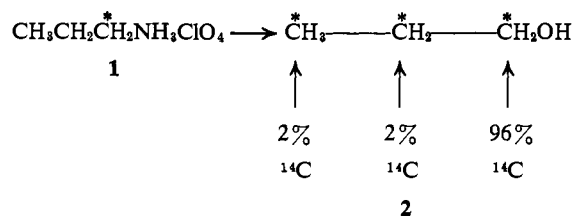
of 2,2-dideuterio-1-aminopropane (22),<sup>19</sup> 1-tritio-1-aminopropane (23),<sup>19</sup> and 1-aminopropane-1-<sup>14</sup>C (1),<sup>20</sup> and examined the variously labeled 1-propanol fractions obtained. Lee, *et al.*, noticed that the nmr spectrum of 2,2-dideuterio-1-propanol obtained on deamination of 22 exhibited a little stronger signal at  $\tau$  8.45 than they observed in the nmr



spectrum of 22 itself. This signal represented 1–2% protium in the 2 position of 2,2-dideuterio-1-propanol where there should have been more than 99.5% deuterium. As a check, 23 (asterisk denotes tritium) was deaminated under identical conditions with the results shown under structure 24.

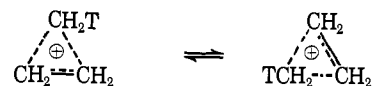


As a final illustration that radioactivity was, in fact, leaking from the 1 to the 2 and 3 positions, Lee repeated the deamination of 1 → 2 with the results shown under structure 2.

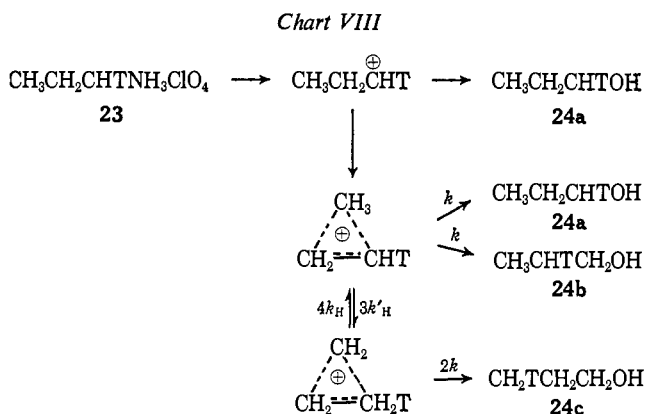


Thus 3–4% of the isotope originally in the 1 position of 1-aminopropane had leaked to the 2 and 3 positions and not 8% to the 2 position as stated by Roberts,<sup>7</sup> or 8 or 12% to the 3 position as indicated by Reutov<sup>10</sup> or by Karabatsos,<sup>11</sup> respectively.<sup>21</sup> Thus Lee, *et al.*, showed that a small fraction of the protonated cyclopropanes (which Baird had demonstrated<sup>18</sup> were cyclopropane precursors in the deamination of 1-aminopropane) also decomposed to give *n*-propyl alcohol. It would be redundant to show all possible intermediates from the three different isotope position isomers 1, 22, and 23. It will be sufficient to make the point with just one example and to state that Lee's results<sup>19,20</sup> demand that a very small fraction of the 1-propanol formed on deamination of 1-aminopropane comes from protonated cyclopropane precursors. Consider, for example, the mechanism shown in Chart VIII through which 23 might be converted to the tritiated 1-propanols 24a–c. Here we see that at equilibrium, the proportions of 24c:24b:24a from the cyclopropane intermediates should be in the ratio 3:2:2; but before equilibrium is established the ratio 24c:24b can be less than 1. The situation

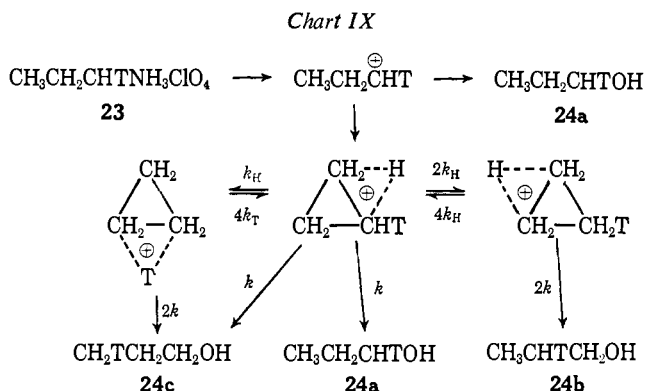
(21) The point should perhaps be emphasized that a monotrity methyl-bridged cyclopropyl cation would not be expected to exhibit an observable *primary* isotope effect during hydride or tritide shift, because when tritium migrates as shown



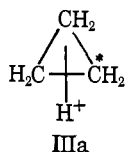
it produces a structure isotopically indistinguishable from its parent; see C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).



for the edge-protonated species (Chart IX), however, is considerably different. Although it is clear that after all intermediates have reached equilibrium the proportions of **24c**:**24a** formed from the protonated cyclopropanes will once again be in the ratio 3:2:2, before equilibrium has been established.



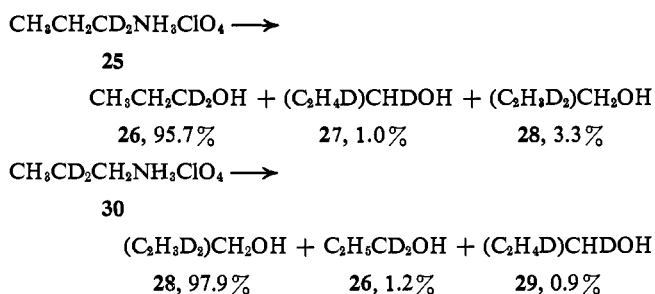
lished the fraction of **24c** must exceed that of **24b**; that is, there should be more tritium in the 3 position than in the 2 position. It can also be shown (see Charts XI and XII, later in the discussion) that on deamination of **1**, methyl-bridged ions will never allow more carbon-14 in  $\text{C}_3$  than  $\text{C}_2$  of the product, whereas the edge-protonated species require that the label in  $\text{C}_3$  be greater than  $\text{C}_2$ . Face-protonated intermediates like IIIa require the same amounts of carbon-14 in all three carbons of the 1-propanol- $^{14}\text{C}$  derived therefrom. Thus in Lee's case<sup>20</sup> if the deamination of **1** proceeds through IIIa, then the fractions of carbon-14 at  $\text{C}_2$  and  $\text{C}_3$  should be the



same. Of course, the small differences reported<sup>19,20</sup> by Lee between  $\text{C}_2$  and  $\text{C}_3$  are not significant. It is interesting, however, that in principle, the isotopic distribution in the 1-propanol obtained on deamination of 1-aminopropane-1-*t* or -1- $^{14}\text{C}$  can be used to distinguish methyl-bridged, edge-protonated, and face-protonated intermediates.

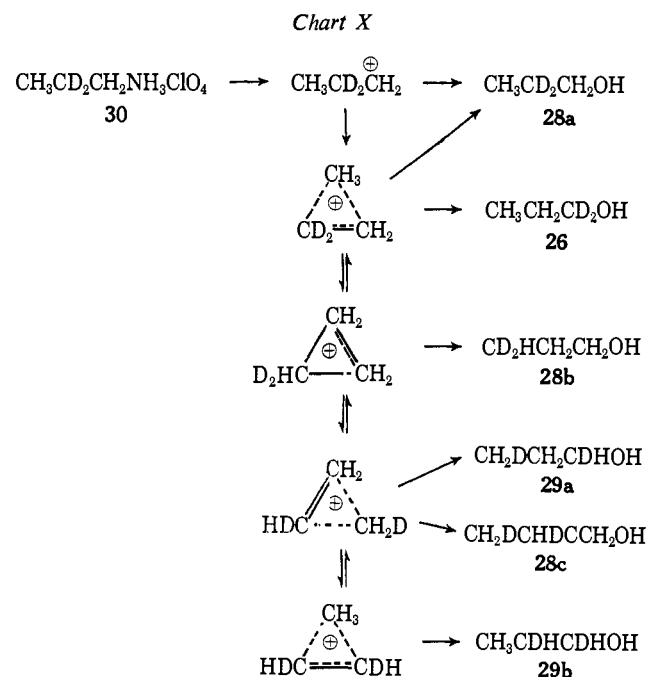
Also in 1965, Karabatsos and coworkers<sup>22</sup> deaminated both 1,1-dideuterio-1-aminopropane perchlorate (**25**) and 2,2-dideuterio-1-aminopropane perchlorate (**30**), and by mass

spectrographic measurements determined partial deuterium distributions in the 1-propanol fractions (**26**–**29**) produced.



Thus five different isotopic experiments now confirm a total of 2–4% rearrangement during the deamination of 1-aminopropane, quite in contrast to the 8–12% originally<sup>7,10,11</sup> reported.

The results for the deamination of **25** are consistent either with the original Reutov<sup>10</sup>–Karabatsos<sup>11</sup> mechanism involving 1,3 shifts of hydrogen, or with all three kinds of protonated cyclopropane intermediates, since they tell us very little about the deuterium distribution in the 2 and 3 positions of the product. The data for the deamination of **30**, however, are most revealing, for they rule out a series of 1,3 shifts as the sole mechanism of rearrangement, since 1,3 shifts would never put a deuterium atom at carbon no. 1. Further, the higher proportion of  $\text{C}_2\text{H}_5\text{CD}_2\text{OH}$  (**26**) over  $(\text{C}_2\text{H}_4\text{D})\text{CHDOH}$  (**29**) [1.2:0.9%] cannot be explained through a series of 1,2 shifts. Thus we are left with protonated cyclopropanes of some type as the only reasonable explanation for the results. Given in Chart X is a mechanism involving equilibrating methyl-bridged ions, which illustrates how protonated cyclopropanes of some sort are required to explain the deamination of **30**. It should be noted that this mechanism requires that the fraction of **26** exceed that of **29** as, in fact, was observed.<sup>22</sup>



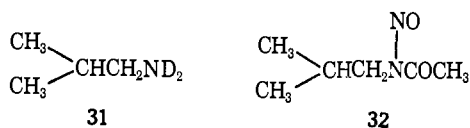
Mechanisms involving face- or edge-protonated intermediates will also explain the results and also require that **26** > **29**, so we are unable to distinguish the kinds of cations. Since the latter mechanisms are considerably more complicated than

(22) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *J. Am. Chem. Soc.*, **87**, 4394 (1965).

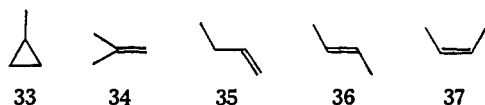
the mechanism of Chart VIII, they have not been reproduced here.<sup>23</sup>

Karabatsos, *et al.*,<sup>22</sup> then reinvestigated the product<sup>11</sup> of deamination of 1,1,2,2-tetradeuterio-1-aminopropane. According to nmr evidence the amine contained 97.5% deuterium and 2.5% hydrogen in the 1 and 2 positions; mass spectral analysis<sup>22</sup> of the deuterated 1-propanol produced on deamination, however, revealed that only 85% of the molecules contained four deuteriums, 12% three deuteriums, and 3% two deuteriums. Thus there was more hydrogen at C-1 than their later<sup>22</sup> results indicate, but there was also much less of the tetradeuterated 1-propanol. Thus there were two possibilities for error: (1) the nmr evidence could have been wrong, and the original 1-aminopropane might actually have contained only 85% (instead of 95%) tetradeuterated molecules; or (2) H<sup>+</sup> and D<sup>+</sup> exchange during the reaction.

In connection with the latter possibility, there is an interesting paper by Bayless and Friedman<sup>24</sup> who carried out an aprotic diazotization-deamination of isobutylamine-N-d<sub>2</sub> (31), as well as the thermal decomposition of its N-nitrosoacetyl derivative 32. Compound 31 was deaminated in refluxing benzene containing octyl nitrite and 1 equiv of CH<sub>3</sub>COOD,



whereas 32 was thermally decomposed in refluxing benzene containing 1 equiv of deuterium oxide or hexanol-*d*. Both reactions gave nearly identical yields of the five products 33–37.



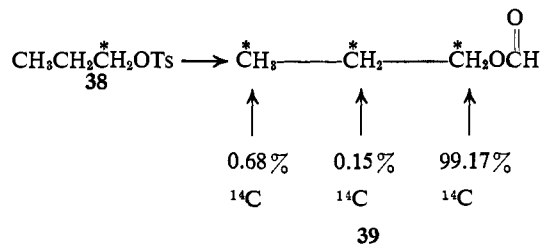
In a typical experiment 32 afforded these products in yields of 14, 73, 6, 5, and 2%, respectively. Indiscriminate mass spectrographic examination of the products indicated 51% undeuterated, 36% monodeuterated, and 12% dideuterated material. This incorporation of deuterium was drastically reduced as the solvents for the reaction became more polar (D<sub>2</sub>O–DOAc, D<sub>2</sub>O–DCl); nonetheless, in DOAc both 31 and 32 led to products which had taken up 4–6% deuterium (monodeuteration). Thus the possibility cannot be discounted that Karabatsos and Orzech<sup>11</sup> encountered hydrogen-deuterium exchange during their deamination of 1,1,2,2-tetradeuterio-1-aminopropane.<sup>25</sup> But how can we explain the anomalous results of Roberts<sup>7</sup> and Reutov?<sup>10</sup> On examination of the experimental sections of these papers,<sup>7,10</sup> one finds that in the sequence testing the degradative procedure, Roberts and Halmann<sup>7</sup> used a sample of 1-propanol-1-<sup>14</sup>C more radioactive by 80-fold than the sample in which they detected 8% rearrangement by “methyl participation.” The presence of a highly radioactive contaminant in the final degradation product is likely. The same is true of Reutov’s experiment.<sup>10</sup> Here a 60-fold dilution of radioactive inter-

mediates with their nonradioactive partners is revealed. Thus if we assume the radioactive impurities were 80 and 60 times more radioactive, respectively, than the final labeled 1-propanol samples obtained on deamination, then the presence of 0.05 and 0.07% of these impurities would be sufficient to account for the spurious radioactivity in excess of the per cent rearrangement later<sup>19,20,22</sup> demonstrated.

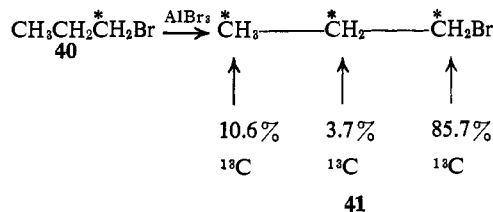
#### IV. Further Evidence for Protonated Cyclopropanes

The results of Baird and Aboderin<sup>14,15</sup> on the reaction between cyclopropane and D<sub>2</sub>SO<sub>4</sub> require protonated (and deuterated) cyclopropane intermediates. Deno’s demonstration<sup>16</sup> that Baird’s<sup>14,15</sup> experiments were not carried out under strict equilibrium conditions provides strong evidence that the intermediates are not methyl-bridged ions I nor face-protonated species III, but rather edge-protonated ions II. The data compiled by Lee,<sup>19,20</sup> Baird,<sup>18</sup> and Karabatsos<sup>22</sup> and their coworkers for the deamination of various isotope position isomers of 1-aminopropane require protonated cyclopropanes, but the differences in radioactivity content between C<sub>2</sub> and C<sub>3</sub> in the products are within experimental error, and thus do not allow us to decide whether the active intermediate is I, II, or III. Deaminations are notoriously different from other carbonium ion reactions,<sup>26</sup> and it would be interesting to pursue this question further.

Lee and Kruger<sup>27</sup> formolyzed 1-propyl-1-<sup>14</sup>C tosylate (38), isolated the formate (39) produced, and determined the radioactivity contents of carbons no. 1, 2, and 3. The results are



shown under structure 39. Here, C<sub>3</sub> clearly contains *more* radioactivity than C<sub>2</sub>. Similarly, Karabatsos, *et al.*,<sup>28</sup> treated 1-bromopropane-1-<sup>13</sup>C (40) with aluminum bromide, reisolated the partially rearranged 1-bromopropane-<sup>13</sup>C (41),



and determined the isotopic distribution. The results are shown under structure 41. In the formolysis of 38 and in the isomerization of 40, therefore, C<sub>3</sub> of the product contains more of the isotope than does C<sub>2</sub>. These results cannot be rationalized with methyl-bridged cations (Chart XI), for it is clear that the concentration of XIX can never be greater than one-half the concentration of XVIII. Therefore the fraction of the

(23) For related work, see G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 5469 (1966); G. J. Karabatsos, R. A. Mount, D. O. Rickett, and S. Meyerson, *ibid.*, **88**, 5651 (1966).

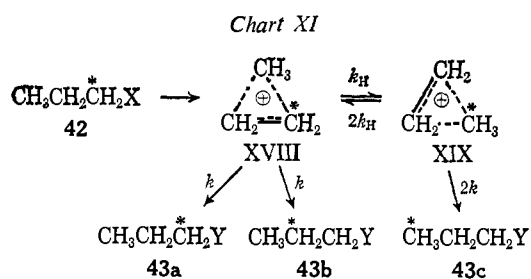
(24) J. H. Bayless and L. Friedman, *ibid.*, **89**, 147 (1967).

(25) A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967), employed the same technique used by Skell and Starer<sup>12</sup> to rule out a carbene insertion mechanism.

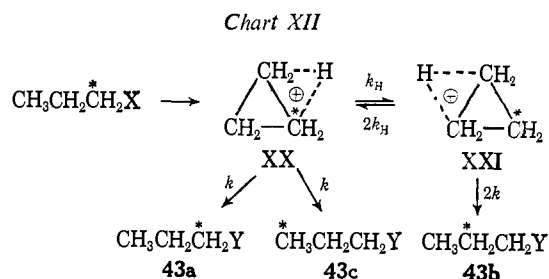
(26) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

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

(28) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Letters*, **38**, 3735 (1967).

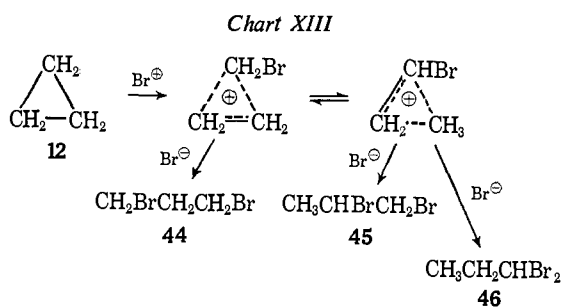


label at C<sub>3</sub> could never exceed that in C<sub>2</sub> (43b). For reasons discussed earlier in connection with the deamination<sup>20</sup> of 1-amino-1-<sup>14</sup>C-propane (see structure IIIa), the data are likewise incompatible with face-protonated cations, since the latter require the fractions of isotope in C<sub>3</sub> and C<sub>2</sub> of the product to be the same (that is, 43b and 43c would have to be formed in identical yields). The edge-protonated species XX and XXI (Chart XII), however, are compatible with and



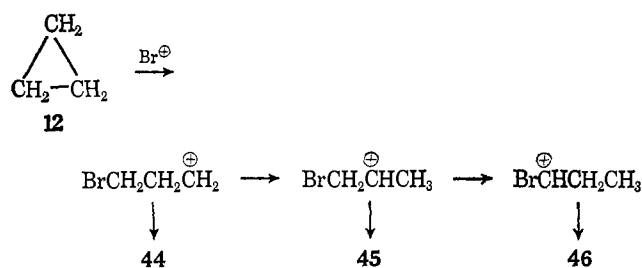
nicely explain the data.<sup>27, 28</sup>

Several other experiments<sup>29-31</sup> have been interpreted with protonated cyclopropane intermediates. Deno and Lincoln<sup>29</sup> treated cyclopropane with bromine in the presence of ferric bromide and, in separate experiments, in the presence of aluminum bromide and aluminum chloride. In each case all of the isomeric (1,1-, 1,2-, and 1,3-) dibromopropanes were produced (Chart XIII). In the absence of information con-

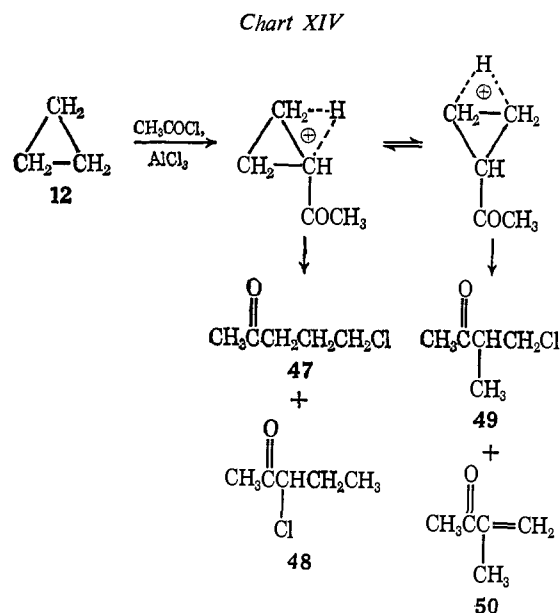


cerning the modes of hydride shift during the reaction, an alternate mechanism such as the following cannot be excluded.

Hart and Schlosberg<sup>30</sup> treated cyclopropane with acetyl chloride-aluminum chloride in chloroform and in dichloromethane—among other solvents. Shown in Chart XIV are the structures (47-50) of the products observed, together with the edge-protonated cationic intermediates these authors propose. As evidence they cite: (1) addition of acetyl chloride-aluminum chloride solution to the cyclopropane solution

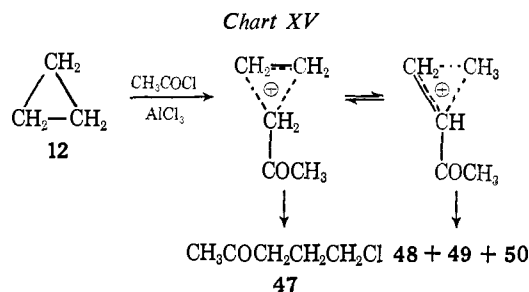


reduces the concentration of the nucleophile below what it is during reverse addition, and this should allow more time for the intermediates to equilibrate (Chart XIV), thus increasing the yields of 49 and 50—as observed—at the expense of 47



and 48; (2) changing solvent polarity should affect the equilibrium between the ions, the more polar solvents—as observed—also increasing the yields of 49 and 50 at the expense of the other two products; and (3) acetylcyclopropane itself was shown not to be an intermediate in the reaction.

The edge-protonated intermediates are not really demanded by Hart and Schlosberg's data, for the results can equally well be accommodated by the methyl- and acetylmethyl-bridged ions shown in Chart XV. Here one would expect longer



lifetimes of the intermediates to increase the proportions of 48, 49, and 50 at the expense of 47, and this is also observed. Unfortunately, the yield of 48 is low and relatively insensitive to changes in solvent polarity and to nucleophilicity of the medium, so it is impossible to tell whether it has the same ionic precursor as 47 (Chart XIV) or 49 and 50 (Chart XV). Nor can the face-protonated intermediates be excluded. The loss

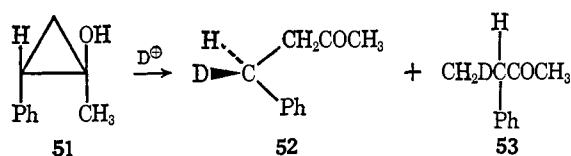
(29) N. C. Deno and D. N. Lincoln, *J. Am. Chem. Soc.*, **88**, 5357 (1966).

(30) H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966); **90**, 5189 (1968).

(31) C. H. De Puy, F. W. Breitbeil, and K. R. De Bruin, *ibid.*, **88**, 3347 (1966).

of threefold symmetry as cyclopropane is converted to acetyl-cyclopropane rules out an intermediate in which the proton to carbon distance to all three ring carbons is the same. Changes in solvent polarity would affect charge distribution in an unsymmetrically face-protonated cation, however, and we cannot say what effect this would have on product ratio. The data of Hart and Schlosberg<sup>30</sup> do seem to rule out classical, open ions, for to invoke these cations it is necessary for secondary carbonium ions to rearrange to primary ions by hydride shift.

It has been proposed<sup>32</sup> that a "reasonable mechanistic picture" for the acid-catalyzed ring opening<sup>31</sup> of *trans*-2-phenyl-1-methylcyclopropanol (**51**) with DCl is an edge-protonated structure, with D<sup>+</sup> partially bonded to C<sub>1</sub> and C<sub>2</sub> to yield **52**, and to C<sub>2</sub> and C<sub>3</sub> to yield **53**.



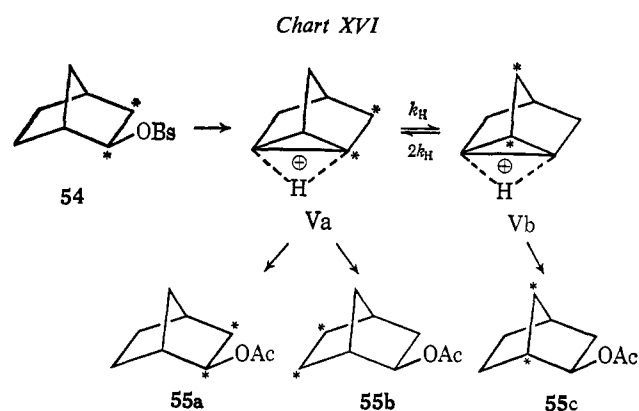
A very recent series of papers by Friedman and coworkers<sup>33</sup> on aprotic and protic deamination of aliphatic amines is pertinent to the present discussion. Both *n*-propyl-3,3-*d*<sub>3</sub>-amine (**16**) and *n*-propyl-2,2-*d*<sub>2</sub>-amine (**30**) were deaminated in solvents of widely varying acidity. The results are nicely consistent with and, in fact, lend strong support to the intermediacy of protonated cyclopropanes (see Charts VII and X).

## V. Summary

The existence of protonated cyclopropane intermediates now rests on firm experimental ground. Many of the results dis-

cussed in this review can be explained by any one of the three structures I, II, or III. However, none of the data demand either the methyl-bridged ion I or face-protonated structure III, whereas several experiments<sup>14-16, 27, 28</sup> require the edge-protonated intermediate II.

This brings us to the question of the nonclassical norbornyl cation. Can it be the edge-protonated nortricyclene V or the nonclassical structure IV, or is it a rapidly equilibrating pair of classical ions? The face-protonated structure of type VI has been excluded as an intermediate by our previous experiments<sup>3</sup> with deuterium-labeled, substituted norbornyl tosylates. If cations of type V do become involved in solvolytic reactions of 2-*exo*-norbornyl brosylate (**54**), they cannot be the sole intermediates, for the original carbon-14 labeling data of Roberts, *et al.*,<sup>4</sup> excludes them. This can be shown very easily by reference to Chart XVI. At equilibrium the concentration of ion



Va will be double that of Vb, and the distribution of radioactivity would then be C<sub>23</sub> (**55a**), 33.3%; C<sub>56</sub> (**55b**), 33.3%; and C<sub>1,7</sub> (**55c**), 33.3%. Before equilibrium is established, however, the fractions of **55a** (C<sub>23</sub>) and **55b** (C<sub>56</sub>) must always be the same. Since Roberts, *et al.*, showed the acetolysis product to consist of 40% **55a** (C<sub>23</sub>) and 15% **55b** (C<sub>56</sub>), then the edge-protonated intermediates Va and Vb are excluded, at least as the sole cations involved in promoting hydride shift.

(32) C. H. DePuy, *Accounts Chem. Res.*, **1**, 36 (1968).

(33) (a) L. Friedman and J. H. Bayless, *J. Am. Chem. Soc.*, **91**, 1790 (1969); (b) L. Friedman, A. T. Jurewicz, and J. H. Bayless, *ibid.*, **91**, 1745 (1969); (c) L. Friedman and A. Jurewicz, *ibid.*, **91**, 1800, 1803, 1808 (1969).