

PROTONATED CYCLOPROPANES¹

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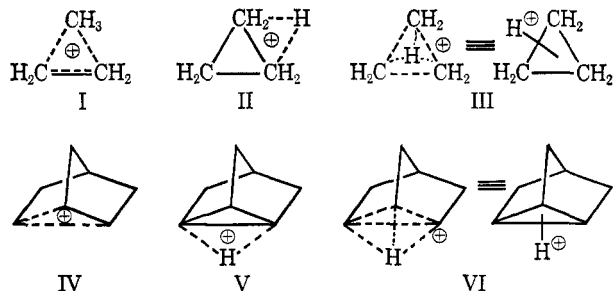
Received November 1, 1968

Contents

I. Introduction	543
II. The Search for Protonated Cyclopropane Intermediates	544
III. Reinvestigation of the Deamination of 1-Aminopropane	545
IV. Further Evidence for Protonated Cyclopropanes	548
V. Summary	550

I. Introduction

Protonated cyclopropane intermediates are of considerable importance in connection with the still unresolved question of the nonclassical norbornyl cation.² We demonstrated³ that the hydride shifts which occur in remotely substituted norbornyl cations do so through discrete, sequential steps, and suggested^{3a} that edge-protonated nortricyclenes could be useful in explaining these shifts. We also presented^{3a} evidence against the intervention of "face-protonated" nortricyclenes.⁴ Berson and Grubb^{5b} had shown earlier that face-protonated intermediates were not important in a norbornyl cation in which the potential cyclopropane ring (C₆, C₁, or C₂) contained a methyl group, thus destroying its symmetry. It was recently suggested by Olah⁵ 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-



(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).

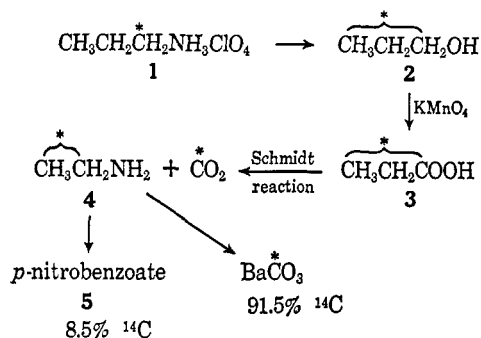
(4) J. D. Roberts, C. C. Lee, and W. H. Saunders *ibid.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).

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

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,^{6a,b} it is not easy to decide between I and II or IV and V. Structures I and IV are somewhat analogous to the CH₅⁺ ion,^{6c} whereas the "bent bonds" in cyclopropane cannot be pure σ bonds, but must have considerable sp² character, and therefore provide a π cloud for interaction with a proton.^{6b}

The methyl-bridged ion I was first proposed in 1953 by Roberts and Halmann,⁷ who carried out the deamination of 1-aminopropane-1-¹⁴C (1) in 35% perchloric acid solution (see Chart I). Whitmore and Thorpe⁸ 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-¹⁴C (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-

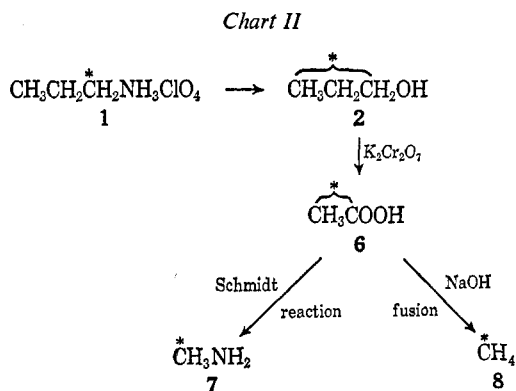
(6) (a) See, for example, A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); (b) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (c) V. L. Tal'Roze and A. K. Lyubimova, *Dokl. Akad. Nauk*, **86**, 909 (1952).

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

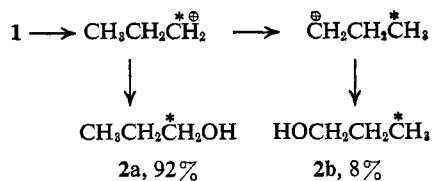
(8) F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

ishingly low phenyl/methyl migration ratio⁹ of 3.2, and suggested that the fraction of methyl migration observed⁷ was too high by a considerable factor.

The matter rested until 1962 when Reutov and Shatkina¹⁰ 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



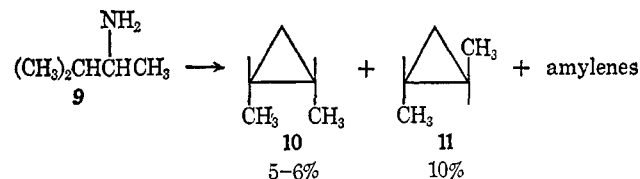
of the 1-propanol isolated (not the 2 position as proposed by Roberts and Halmann⁷), and thereby proposed that the carbonium ion intermediate undergoes a 1,3 shift of hydrogen. The data of Reutov and Shatkina¹⁰ were apparently confirmed



in 1962, when Karabatsos and Orzech¹¹ subjected 1-amino-propane-1,1,2,2-*d*₄ to the deaminating conditions used by the previous investigators^{7,10} 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,⁷ Reutov,¹⁰ and Karabatsos,¹¹ 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^{10,11} 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 Starer¹²

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*₂ 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 out¹² that the intermediates formed on deoxidation [RO—C⁺: ↔ RO⁺=C:] and on deamination [R—N⁺≡N: ↔ R⁺N=N:] are isosteres and should produce the same carbonium ion upon loss of CO or N₂, 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,¹³ 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^{12,13} 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,¹⁴ who cycled cyclopropane through D₂SO₄ for 17 hr and found that 21% of the hydrogen in C₃H₆ had been replaced with deuterium. Later¹⁵ these same investigators repeated the experiment, but allowed the cyclopropane to go through 8.43 M D₂SO₄ (at 25.0°) so rapidly that only one deuterium atom per mole of product was taken up. Upon cautious neutralization of the D₂SO₄ 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: C₁, 0.38 D; C₂, 0.17 D; C₃, 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 Reutov¹⁰ and by Karabatsos.¹¹ 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 PhCH₂C*H₂NH₂, 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).

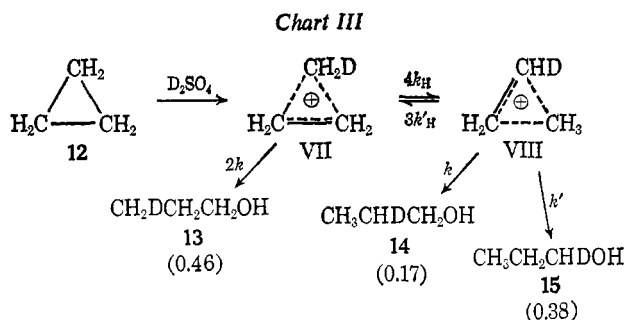
(11) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

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

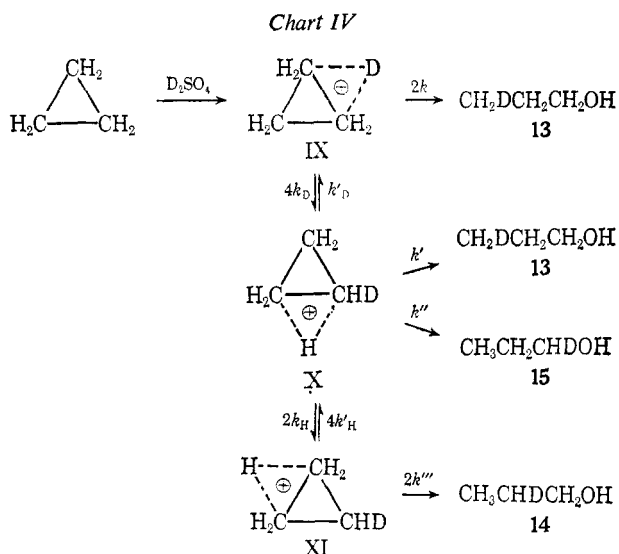
(13) M. S. Silver, *ibid.*, **82**, 2971 (1960).

(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).



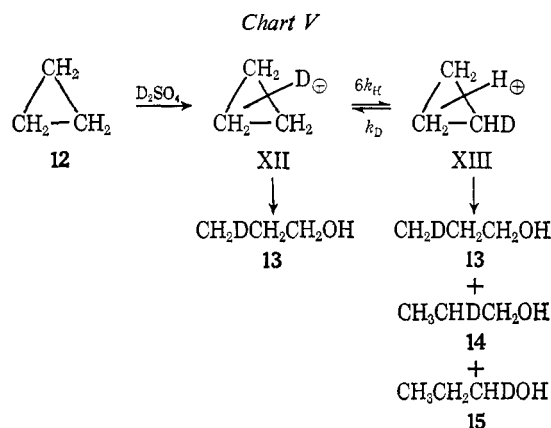
explanation for the results (the mole fractions of each product are shown in parentheses). Structures VII and VIII are the only monodeuterated methyl-bridged ions possible here, and the mechanism of Chart III requires that at equilibrium the ratio 13:14:15 be 3:2:2. Before equilibrium between VII and 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^{14,15} with 8.43 M D₂SO₄ 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 Deno¹⁶ and coworkers repeated the Baird and Aboderin^{14,15} experiments using D₂SO₄ 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 Deno¹⁶ and Lee and Gruber¹⁷ confirmed Baird's original data^{14,15} 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 C₃, C₂, and C₁ 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 C₂ (14) and C₁ (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 demonstration¹⁶ 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

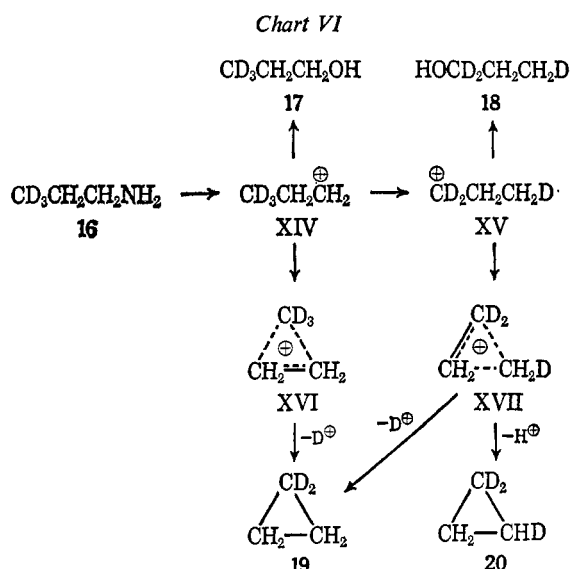
In 1964 Baird¹⁸ examined the cyclopropane fraction formed on deamination of 3,3,3-trideuterio-1-aminopropane (16), and found that $57 \pm 1\%$ of its molecules still contained three deuterium atoms per molecule, whereas the rest ($43 \pm 1\%$) contained only two. This result seems to demand the presence of protonated cyclopropanes which are rapidly undergoing shifts of hydrogen and deuterium. Consider first the mechanism of Reutov¹⁰ and Karabatsos¹¹ which is modified in Chart VI to include the formation of cyclopropane. Since the ratio of 17:18 was believed¹¹ to be 88:12, then the sequence XIV \rightarrow XVI \rightarrow 19 (Chart VI) would be expected to produce 88% of cyclopropane-*d*₂ (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*₃ (20).

Given in Chart VII is a scheme by which 3,3,3-trideuterio-1-aminopropane (16) can proceed to cyclopropane-*d*₂ and cyclopropane-*d*₃ 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

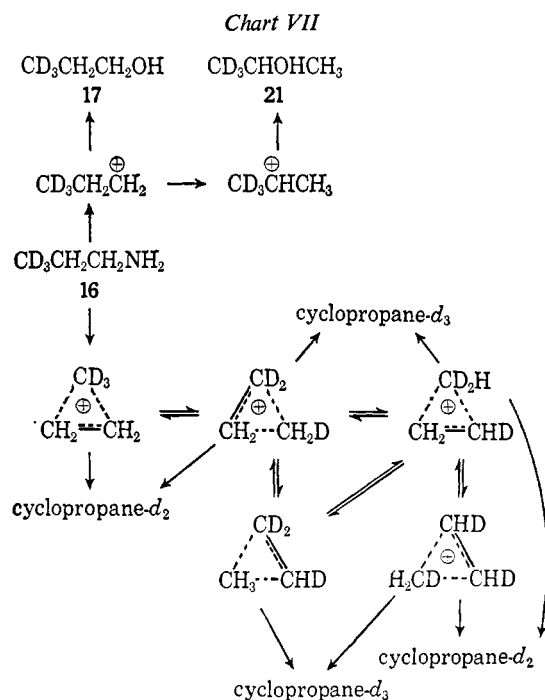
(16) Private communication during the 21st Mechanisms Conference, Brandeis University, Waltham, Mass., June 19–22, 1968; N. C. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *J. Am. Chem. Soc.*, **90**, 6457 (1968).

(17) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968), passed cyclopropane through tritiated sulfuric acid and found the following tritium distribution at C₃, C₂, and C₁: 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% (C₃), 19% (C₂), and 38% (C₁).

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



intermediates. It is clear that this mechanism is compatible with Baird's¹⁸ result of 57% cyclopropane-*d*₃ and 43% cyclopropane-*d*₂. If there were no *d*₃ product found, then a protonated cyclopropane intermediate would not really be required since the sequence XIV → XVI → 19 (Chart VI)



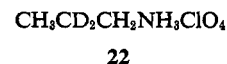
need not involve intermediate XVI at all. That is, it could occur by means of a simultaneous ring closure and deuteron ejection by XIV to give cyclopropane-1,1-*d*₂ (19) directly. Thus Baird's determination that 57% of the cyclopropane formed on deamination of 16 was trideuterated must be taken as very 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,^{19,20} studied the deaminations of the perchlorates

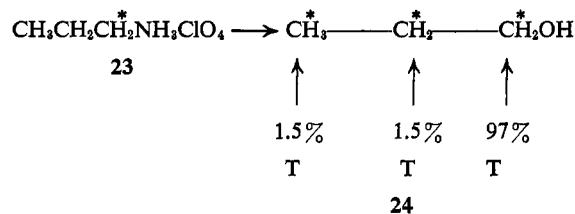
(19) C. C. Lee, J. E. Kruger, and E. W. C. Wong, *J. Am. Chem. Soc.*, **87**, 3985 (1965).

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

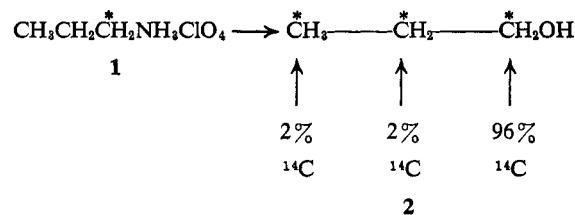
of 2,2-dideuterio-1-aminopropane (22),¹⁹ 1-tritio-1-aminopropane (23),¹⁹ and 1-aminopropane-1-¹⁴C (1),²⁰ and examined the variously labeled 1-propanol fractions obtained. Lee, *et al.*, noticed that the nmr spectrum of 2,2-dideuterio-1-propanol obtained on deamination of 22 exhibited a little stronger signal at τ 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.

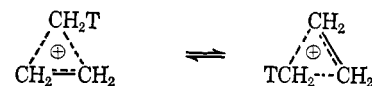


As a final illustration that radioactivity was, in fact, leaking from the 1 to the 2 and 3 positions, Lee repeated the deamination of 1 → 2 with the results shown under structure 2.



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,⁷ or 8 or 12% to the 3 position as indicated by Reutov¹⁰ or by Karabatsos,¹¹ respectively.²¹ Thus Lee, *et al.*, showed that a small fraction of the protonated cyclopropanes (which Baird had demonstrated¹⁸ 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^{19,20} 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 monotritio 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

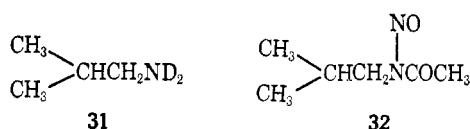


it produces a structure isotopically indistinguishable from its parent; see C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).

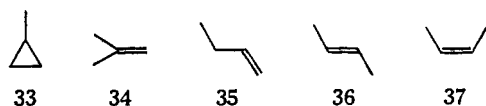
the mechanism of Chart VIII, they have not been reproduced here.²³

Karabatsos, *et al.*,²² then reinvestigated the product¹¹ 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 analysis²² 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 later²² 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⁺ and D⁺ exchange during the reaction.

In connection with the latter possibility, there is an interesting paper by Bayless and Friedman²⁴ who carried out an aprotic diazotization-deamination of isobutylamine-N-d₂ (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 CH₃COOD,



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.



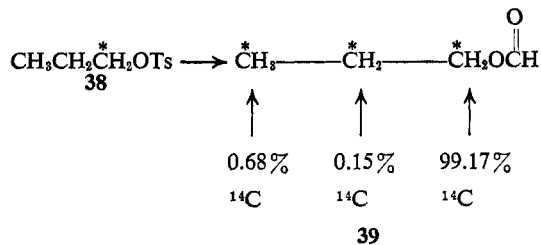
In a typical experiment 32 afforded these products in yields of 14, 73, 6, 5, and 2%, respectively. Indiscriminate mass spectrographic examination of the products indicated 51% undeuterated, 36% monodeuterated, and 12% dideuterated material. This incorporation of deuterium was drastically reduced as the solvents for the reaction became more polar (D₂O-DOAc, D₂O-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 Orzech¹¹ encountered hydrogen-deuterium exchange during their deamination of 1,1,2,2-tetradeuterio-1-aminopropane.²⁵ But how can we explain the anomalous results of Roberts⁷ and Reutov?¹⁰ On examination of the experimental sections of these papers,^{7,10} one finds that in the sequence testing the degradative procedure, Roberts and Halmann⁷ used a sample of 1-propanol-1-¹⁴C 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.¹⁰ 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^{10, 20, 22} demonstrated.

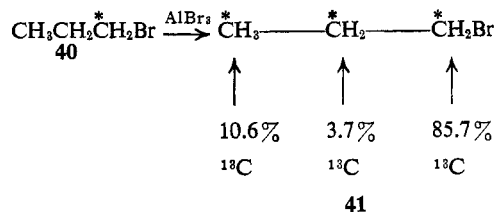
IV. Further Evidence for Protonated Cyclopropanes

The results of Baird and Aboderin^{14,15} on the reaction between cyclopropane and D₂SO₄ require protonated (and deuterated) cyclopropane intermediates. Deno's demonstration¹⁶ that Baird's^{14,15} 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,^{19,20} Baird,¹⁸ and Karabatsos²² and their coworkers for the deamination of various isotope position isomers of 1-aminopropane require protonated cyclopropanes, but the differences in radioactivity content between C₂ and C₃ 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,²⁶ and it would be interesting to pursue this question further.

Lee and Kruger²⁷ formolyzed 1-propyl-1-¹⁴C 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, C₃ clearly contains *more* radioactivity than C₂. Similarly, Karabatsos, *et al.*,²⁸ treated 1-bromopropane-1-¹³C (40) with aluminum bromide, reisolated the partially rearranged 1-bromopropane-¹³C (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, C₃ of the product contains more of the isotope than does C₂. 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).

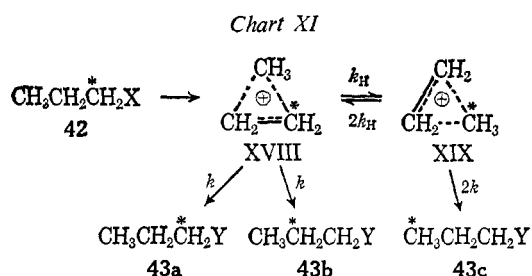
(24) J. H. Bayless and L. Friedman, *ibid.*, **89**, 147 (1967).

(25) A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967), employed the same technique used by Skell and Starer¹² to rule out a carbene insertion mechanism.

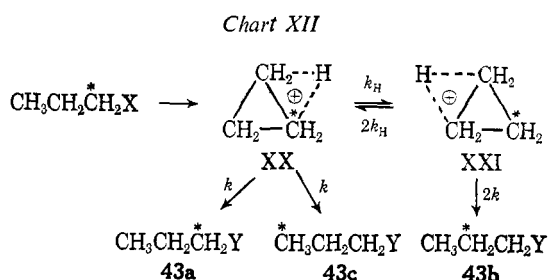
(26) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

(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).

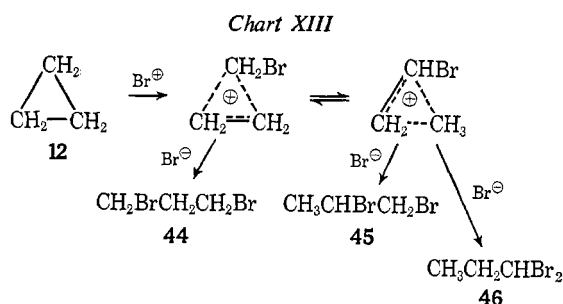


label at C₃ could never exceed that in C₂ (43b). For reasons discussed earlier in connection with the deamination²⁰ of 1-amino-1-¹⁴C-propane (see structure IIIa), the data are likewise incompatible with face-protonated cations, since the latter require the fractions of isotope in C₃ and C₂ of the product 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



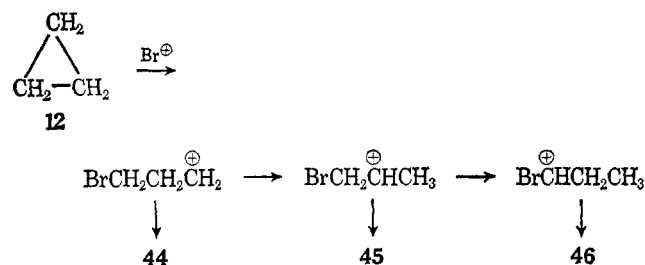
nically explain the data.^{27, 28}

Several other experiments²⁹⁻³¹ have been interpreted with protonated cyclopropane intermediates. Deno and Lincoln²⁹ 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-

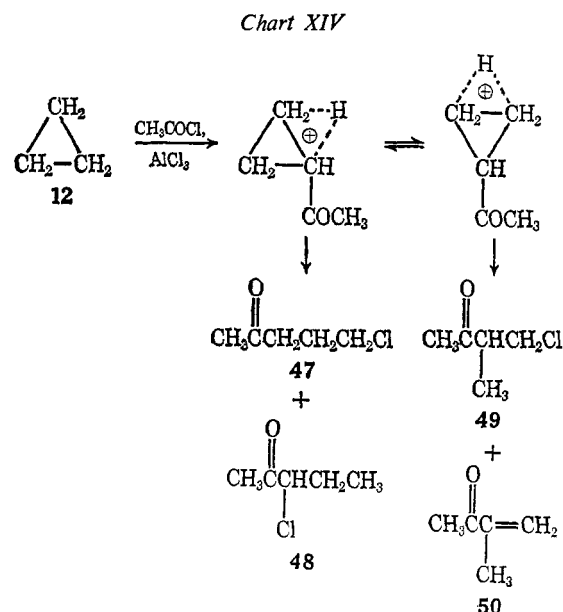


cerning the modes of hydride shift during the reaction, an alternate mechanism such as the following cannot be excluded.

Hart and Schlosberg³⁰ 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

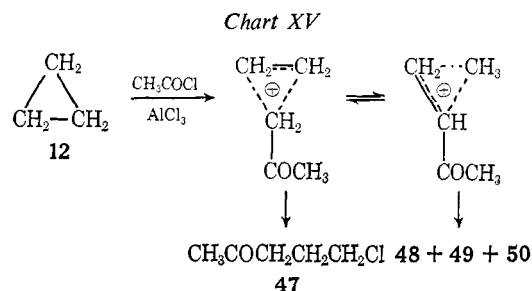


reduces the concentration of the nucleophile below what it is during reverse addition, and this should allow more time for the intermediates to equilibrate (Chart XIV), thus increasing the yields of 49 and 50—as observed—at the expense of 47



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

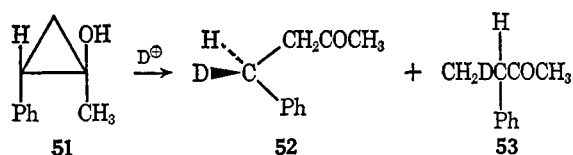
(29) N. C. Deno and D. N. Lincoln, *J. Am. Chem. Soc.*, **88**, 5357 (1966).

(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 Schlosberg³⁰ 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 proposed³² that a "reasonable mechanistic picture" for the acid-catalyzed ring opening³¹ of *trans*-2-phenyl-1-methylcyclopropanol (**51**) with DCl is an edge-protonated structure, with D⁺ partially bonded to C₁ and C₂ to yield **52**, and to C₂ and C₃ to yield **53**.



A very recent series of papers by Friedman and coworkers³³ on aprotic and protic deamination of aliphatic amines is pertinent to the present discussion. Both *n*-propyl-3,3-*d*₃-amine (**16**) and *n*-propyl-2,2-*d*₂-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

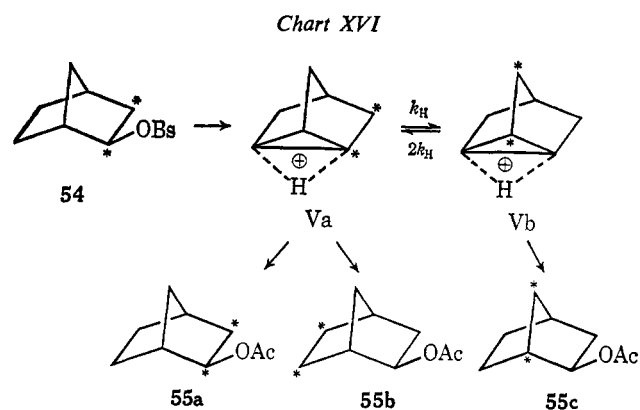
The existence of protonated cyclopropane intermediates now rests on firm experimental ground. Many of the results dis-

(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).

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^{14-16, 27, 28} 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 experiments³ 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.*,⁴ 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 C₂₃ (**55a**), 33.3%; C₆₆ (**55b**), 33.3%; and C_{1,7} (**55c**), 33.3%. Before equilibrium is established, however, the fractions of **55a** (C₂₃) and **55b** (C₆₆) must always be the same. Since Roberts, *et al.*, showed the acetolysis product to consist of 40% **55a** (C₂₃) and 15% **55b** (C₆₆), then the edge-protonated intermediates Va and Vb are excluded, at least as the sole cations involved in promoting hydride shift.