

On vapor phase chromatography, a small sample of the cold pyrolysate dissolved in pentane showed two closely-spaced peaks (areas ca. 7:3) with retention times near that of dihydropentalene. When the pyrolysate was warmed to room temperature, an exothermic reaction took place, and in the v.p.c., the two peaks were now in the ratio of approximately 10:1.

The product distilled at 50–54° at 16 mm. pressure. The yield of dihydropentalene from 50.5 g. (0.382 moles) of isodicyclopentadiene was 13 g. (0.125 moles, 33%). The major fraction contained about 1% styrene. The ultraviolet spectrum in *n*-pentane has λ_{\max} 268 m μ (ϵ 4400). The n.m.r. spectrum in CCl₄ (internal TMS) has four groups of bands at 3.67, 4.2, 6.77, and 7.02 τ of integrated intensities 1.01:1.00:1.00:1.01.

Anal. Calcd. for C₈H₈: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.81.

The maleic anhydride adduct, prepared at room temperature and recrystallized from ethyl acetate, melted at 233°.

The ethylene formed in the pyrolysis was trapped by allowing the gases evolved when the traps were allowed to warm to room temperature to pass through bromine in CCl₄. Ethylene dibromide, b.p. 128°, 6.35 τ (n.m.r.), was isolated by distillation.

Pyrolysis at much higher temperatures yielded, after distillation, styrene, identified by the identity of its n.m.r. spectrum and its vapor phase chromatographic behavior with those of authentic styrene.

Hydrogenation of Dihydropentalene.—Redistilled dihydropentalene (151.6 mg., 1.46 mmoles) was added to a suspension of prereduced PtO₂ in ether (15 ml.). At room temperature (27°) and atmospheric pressure, 122 ml. of hydrogen was absorbed corresponding to 3.3 moles of hydrogen. The mixture was filtered and the ether distilled. The residue was purified by vapor-phase chromatography on a 10% silicone column. The v.p.c. retention time, the infrared spectrum (CCl₄), and the n.m.r. spectrum (CCl₄, internal TMS) were identical with those of an authentic sample of *cis*-bicyclo[3.3.0]octane.

The Pentalenyl Dianion.—A 50-ml. centrifuge tube containing a magnetic stirring bar and sealed with a serum bottle cap was evacuated (0.5 mm.) and filled with oxygen-free nitrogen. Dihydropentalene (100 mg.) and THF (1 ml.) were added. While being stirred at -70°, *n*-butyllithium in *n*-hexane (5 mole equivalents) was slowly added with a hypodermic syringe. After 10 min. the mixture was warmed to room temperature and stirred for 15 min. more. The solution was pale yellow. The product was precipitated as a white solid by the addition of *n*-pentane, centrifuged, the supernatant liquid withdrawn, and the precipitate washed further with pentane and dissolved in fresh THF. The n.m.r. spectrum of this solution (internal benzene and TMS) consisted of a triplet at 4.27 and a doublet at 5.02 τ , $J = 3.0$, relative intensity 1.01:1.98. Solutions kept at -70° for several months exhibited the same spectrum.

Recovery of *cis*-Bicyclo[3.3.0]octane from Dilithium Pentalenide.—A solution of 0.5 g. of dihydropentalene in THF (8 ml.)

was treated with 2 moles of *n*-butyllithium in *n*-hexane. Dry olefin-free *n*-pentane (20 ml.) was added and the mixture was rapidly mixed with 10 ml. of neutral phosphate buffer (50 ml. of 1.0 M KH₂PO₄ and 30 ml. of 1.0 M NaOH diluted to 100 ml.). The resulting suspension was filtered, and the yellow pentane solution was separated, dried over MgSO₄, and added to 100 mg. of prereduced PtO₂ in *n*-pentane in an atmospheric pressure hydrogenation apparatus. After hydrogen uptake had stopped, the catalyst was filtered, the solution was carefully concentrated, and the crude product was distilled on a high-vacuum manifold. Repeated injection of small samples onto a Carbowax vapor-phase chromatographic column and collection yielded 147.5 mg. (28%) of pure *cis*-bicyclo[3.3.0]octane, identified by its n.m.r. and infrared spectra.

The Ultraviolet Spectrum of the Pentalenyl Dianion.—An improved procedure for preparing dilithium pentalenide was used in the determination of its ultraviolet spectrum. A 25-ml. centrifuge tube containing a magnetic stirring bar was sealed with a serum bottle cap and kept filled with a nitrogen atmosphere. Dihydropentalene (400 mg., 3.8 mmoles) was injected, stirred at -70° with THF (10 ml.), and treated with excess *n*-butyllithium in *n*-hexane (10 ml., 1.6 M, from the Foote Mineral Co., Exton, Pa.). After stirring at -70° for 15 min., the mixture was allowed to warm to room temperature. The white solid, which precipitated upon cooling to -70°, was separated by centrifugation and by withdrawal of the supernatant liquid with a syringe. The precipitate was washed twice with 15-ml. portions of DME. Then 20 ml. of DME, in which the salt is not very soluble, was added, the mixture was stirred, and the precipitate centrifuged. An aliquot of the solution was transferred to a 0.105-mm. path length quartz ultraviolet cell sealed with a serum bottle cap pierced by a nitrogen inlet; another aliquot was diluted with water, and the total base titrated. The ultraviolet spectrum was determined on the Cary Model 14 spectrophotometer. The precipitate was treated with fresh DME, and the solution examined as above. This was repeated. Finally, the salt was dissolved in THF (8 ml.), and an aliquot diluted and analyzed as above.

A base-line correction was made for the absorption of the cell filled with pure solvent. Found for the dilithium pentalenide solutions were, in DME, λ_{\max} 295 m μ ($\log \epsilon$ 3.8), and in THF, λ_{\max} 296 m μ ($\log \epsilon$ 3.7). The extinction coefficients were based on the assumption that the concentration of the pentalenyl dianion was equal to the total base titer.

Addition of a small amount of water yielded a spectrum with λ_{\max} 283 and 405 m μ .

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Concerning the Role of Protonated Cyclopropane Intermediates in Solvolytic Reactions. I. The Solvolysis of Cyclopropane in Deuteriosulfuric Acid¹

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The solvolysis of cyclopropane in 8.4 M sulfuric acid solutions leads to 1-propanol (and its acid-sulfate) as the only important products. In deuteriosulfuric acid, deuterium is incorporated into all three positions of the 1-propanol carbon skeleton, although control experiments indicate that no scrambling of deuterium occurs either before or after solvolysis of the cyclopropane. The implications of this observation are discussed and a mechanism involving protonated cyclopropane intermediates is proposed to account for it.

Introduction

The role of protonated cyclopropane intermediates in aliphatic systems has recently been the subject of considerable controversy. The existence of methyl-bridged intermediate I was seriously questioned by Reutov's observation³ that the supposed methyl migration *via* ion I in the deamination of 1-propylamine⁴ did not, in fact, occur. Subsequently, other

workers^{5,6} verified Reutov's supposition that a 1,3-hydride shift had occurred, and an intermediate of structure II was proposed.⁵

In addition to the above observations, the observation was made that cyclopropanes were formed in the deamination of alkylamines^{7,8} and in the "deoxidation" of 1-propanol.⁸ Accordingly, protonated cyclopropanes of structure IIIa were suggested as possible intermediates in both the above and in Wagner-Meerwein rearrangements.⁸ This hypothesis has since

(1) We wish to acknowledge partial support of this work by a grant from Research Corporation.

(2) National Science Foundation Undergraduate Fellow, 1962 to the present.

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

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

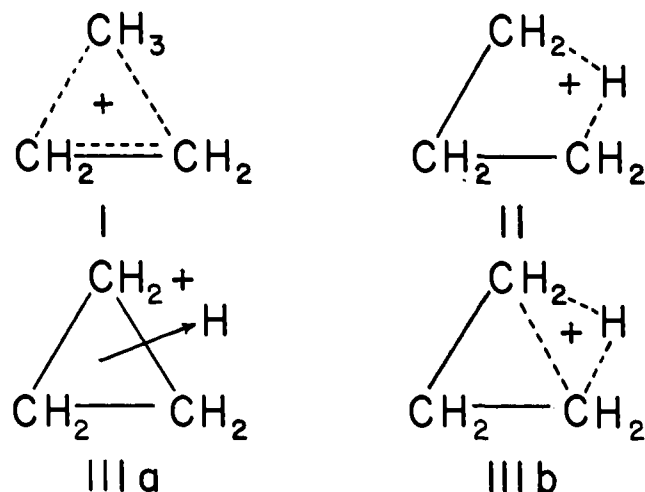
(5) C. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962).

(6) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

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

(8) P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960).

been found invalid in rearrangements of neopentyl derivatives^{9,10} and has been "excluded" in the 1-propyl



system under conditions of "deoxidation".⁶ More recently, however, we have reported evidence which indicates that protonated cyclopropanes may still be involved in the 1-propyl system,¹¹ since an intermediate of type I or III could be involved if it lost a proton in preference to solvolytic ring opening.

We now wish to present evidence derived from a study of the products of solvolytic ring opening of cyclopropane which we believe can best be interpreted by way of protonated cyclopropane intermediates.

Experimental

The cyclopropane used was Matheson 99%, which was purified by passage through a gas train consisting of two bromine-water and one 50% sodium hydroxide gas-wash bottles, followed by a calcium sulfate drying tower and an ice-cooled trap. Samples were removed from the gas train with a gas syringe and assayed for propylene by gas chromatography on a GE SF-96 silicone oil column at 25°. By this method the propylene content could be reduced to below 0.05%, which was about the limit of detection under the conditions used.

The D₂SO₄ used was prepared by distillation of Baker and Adamson Sulfan B into sufficient 99.8% D₂O (purchased from the Chemistry Department, Harvard University) to give ca. 98% D₂SO₄. More dilute solutions were made up by the cautious dilution of weighed portions of this acid with 99.8% D₂O. The molarities of these solutions were obtained by determination of the densities of the solutions and titration of weighed samples with standard sodium hydroxide. (The very high viscosities of these solutions made ordinary volumetric manipulations impractical.) The 8.43 M D₂SO₄ solution, prepared in this way, assayed for 99.65% D by n.m.r. analysis.^{12,13}

Solutions of H₂SO₄ were prepared from du Pont reagent grade sulfuric acid by dilution and were standardized as above.

Solvolytic of Cyclopropane.—For kinetic determinations the solvolyses were performed in a Clauson-Kaas and Limborg modification¹⁴ of the Breitschneider and Burger microhydrogenation apparatus, further modified so as to permit larger volumes of gas to be absorbed. The acid solutions used were degassed *in vacuo* before addition of the cyclopropane. The effect of stirring was such that essentially no cyclopropane was absorbed by an unstirred solution, but above a certain stirring rate the rate of solvolysis was completely independent of stirring rate. All solvolysis (and product) runs were carried out at stirring rates well above this minimum value. The solvolysis rates (measured by disappearance of cyclopropane) were cleanly (pseudo) zero-order. At 25.0° and 1 atm. pressure the rates were 1.38×10^{-5} mmole of cyclopropane/ml. of acid/sec. in 8.43 M D₂SO₄ and 2.08×10^{-5} mmole/ml./sec. in 8.41 M H₂SO₄.

The initial solubility of cyclopropane in both solvents was estimated by extrapolation of the cyclopropane uptake to zero time (the time stirring was commenced). In the D₂SO₄ solution it

was found to be 0.11 ± 0.02 ml./ml. of acid and in H₂SO₄, 0.10 ± 0.02 ml./ml. of acid.

Small samples of gas were taken from time to time and analyzed for propylene content. In no case was more than 0.05% propylene detected.

Product Isolation Experiments.—For the product determination experiments the conditions of stirring, temperature, and pressure were the same as above, but purified cyclopropane was continuously passed through the apparatus at a rate of ca. 0.7 ml. of cyclopropane/ml. of acid/min. The net amount of cyclopropane absorbed was never greater than 1.5–2% (by weight) of the acid solution used.

After passage of cyclopropane for periods of about 10 hr., the acid solutions were either (a) cooled to 0° and cautiously neutralized with the calculated amount of 25% NaOH solution, or (b) heated at 50.0° for about 36.5 hr. and then cooled and neutralized as in a. After neutralization the (slightly alkaline) solutions were distilled at atmospheric pressure, the first 2.5–4% of the distillate being found to contain essentially all of the volatile organic products.

The products were separated from the aqueous distillate by preparative gas chromatography on a 2-m. THEED (15% on Anakrom ABS) column at 100°. The material balances ranged from 25–40% in the solutions isolated by procedure a to 79% in that isolated *via* procedure b. In both cases these material balances are believed to correspond to the amount of free alcohol present in the respective solutions (*vide infra*). In all of the runs carried out *via* procedure a the only alcoholic product obtained was 1-propanol. Solutions to which 2-propanol and 2-propen-1-ol were added and which were then treated by procedure a, gave back these alcohols in undiminished proportions. The solution isolated by procedure b contained 2-propanol amounting to 0.27% of the 1-propanol isolated. In all cases the only volatile organic product observed was a trace of di-*n*-propyl ether.

Deuterium Analyses.—The alcohol as isolated was found unsatisfactory for deuterium analyses because of the presence of small amounts of water which made n.m.r. integration of these (small) samples unreliable. Mass spectral analyses were not attempted because of the complicated cracking patterns of 1-propanol, even at low voltages. Consequently, the 1-propanol was converted to its *p*-toluate ester by treatment of the chromatographed product with a slight excess of *p*-toluyl chloride in pyridine. After heating for 30 min. at 50° the cooled pyridine solutions were diluted with water and ether, and successively washed with water (twice), 5% HCl (twice), water, 10% NaHCO₃ (twice), saturated NaCl solution, and were dried with sodium sulfate. The ether was allowed to evaporate at ca. 60° and the solutions were diluted with a small amount of hexane to precipitate any *p*-toluic anhydride which had survived the above treatment. The samples were then purified by preparative gas chromatography on a 1.25-m. Carbowax 20M (20% on Anakrom ABS) column at 175°.

Deuterium analyses were performed by integration of the n.m.r. spectra¹³ of solutions of the above ester in carbon tetrachloride solution. The methyl group of the *p*-toluyl moiety at $\tau = 7.65$ p.p.m. was used as an internal standard of 3.00 protons. A sample of unlabeled 1-propyl *p*-toluate integrated by this method gave values for the O-CH₂-C, C-CH₂-C, and C-CH₃ protons of the *n*-propyl moiety in the regions $\tau = 5.8, 8.3,$ and 9.0 p.p.m., of 1.95, 1.99, and 3.00 protons, respectively. The values obtained for the ester from the product runs in 8.43 M D₂SO₄ in the same regions were $1.62 \pm 0.03, 1.83 \pm 0.04,$ and 2.56 ± 0.03 protons, respectively, both in runs isolated by method a and that by method b. This corresponds to a deuterium distribution for the 1-propanol in the O-CH₂-C, C-CH₂-C, and C-CH₃ groups of $0.38 \pm 0.03, 0.17 \pm 0.04,$ and 0.46 ± 0.03 atom of deuterium. The net uptake of deuterium in the carbon skeleton of the 1-propanol was 1.01 ± 0.05 atoms of deuterium per molecule of 1-propanol.

Control Experiments on the Solvolysis Products.—The preparation of 1,1-dideuterio-1-propanol was accomplished by the reduction of 15.0 g. of phenyl propionate (m.p. 19.0–20.5°), diluted with 15 ml. of triethylene glycol dimethyl ether, with 2.14 g. of LiAlD₄ (Metal Hydrides, Inc., 98%) dissolved in 60 ml. of triethylene glycol dimethyl ether (purified by vacuum distillation from LiAlH₄). The product was isolated by the addition of 17.8 g. of redistilled benzyl alcohol and distillation of the product *in vacuo*. The 1-propanol obtained was further purified by simple distillation and by preparative gas chromatography on a 2-m. THEED column. The n.m.r.¹³ of this alcohol (neat) revealed less than 0.02 ± 0.01 hydrogen in the $\tau = 6.45$ p.p.m. region (O-CH₂-C), and no peaks not directly attributable to the C-CH₂-CH₃ and OH functions.

When a solution of the above alcohol was heated for a week at 50° in 8.43 M D₂SO₄, no protons were observed in the O-CH₂-C region in the n.m.r. spectrum.

A solution of 132 μ l. of the 1,1-dideuterio-1-propanol, dissolved in 4.85 ml. of 8.43 M D₂SO₄, was heated for 92.5 hr. at 50.0°.

(9) P. S. Skell, I. Starer, and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960).

(10) G. J. Karabatsos and J. D. Graham, *ibid.*, **82**, 5250 (1960).

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

(12) Varian Associates, *Chem. Eng. News*, **41**, No. 20, 27 (1963).

(13) The n.m.r. spectra were obtained on a Varian Model A-60 n.m.r. spectrometer. We wish to acknowledge the assistance of NSF Grant No. G22689 in obtaining this instrument for our department.

(14) N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 854 (1947).

The products were then isolated as in the cyclopropane solvolysis experiments. A 78% material balance was obtained, the major product being 1-propanol. The only impurities observed were 0.30% 2-propanol and a trace of di-*n*-propyl ether. The 1-propanol isolated was converted to its *p*-toluate ester and the n.m.r. spectrum obtained as described above. Integration of this indicated that no hydrogen had been introduced into the O-CH₂-C region ($\tau = 5.8$ p.p.m.) and no hydrogen had been lost from (deuterium introduced into) the C-CH₂-C and C-CH₃ regions ($\tau = 8.3$ and 9.0 p.p.m.).

Study of the Alcohol-Acid Sulfate Equilibrium.—When solutions of 1-propanol in 8.41 *M* H₂SO₄ or 8.43 *M* D₂SO₄ were heated for a short time at 100° for several hours at 50° or several days at 25°, the low-field triplet in the n.m.r. spectrum attributable to the O-CH₂-C group diminished in intensity (relative to the other protons in the molecule) and a new triplet, centered 0.29 p.p.m. downfield, commenced to increase. We attribute this new triplet to the acid sulfate, since it is formed at the expense of the alcohol, and since no other peaks appear in the spectrum, except for slight splitting of the C-CH₂-C and C-CH₃ peaks. Neither triplet is observed in solutions of 1,1-dideuterio-1-propanol, although the same changes in the C-CH₂-C and C-CH₃ groups occur. With 1-propanol in D₂SO₄ at 25°, the reaction proceeds to an equilibrium in which 76% of the (protonated)¹⁵ alcohol and 24% of the acid sulfate are present. At 50.0°, the percentages are 74 and 26%, respectively.

When cyclopropane solvolyzes in these acid solutions, the same two triplets are observed, but with the low-field one initially predominating.¹⁶ On standing for several days at 25° or on heating for 13 hr. at 50° the same equilibrium values as observed above are obtained. In 8.43 *M* D₂SO₄ the rate constants for approach to equilibrium (*i.e.*, the sums of the forward and reverse rate constants) are 6.2×10^{-6} sec.⁻¹ at 25°, and 1.5×10^{-4} sec.⁻¹ at 50°. In 8.41 *M* H₂SO₄, the half-lives for the formation of alcohol from acid sulfate and formation of acid sulfate from alcohol at 25° are 108 and 302 hr., respectively. Both of these values compare with the half-life for oxygen-18 exchange in 8.41 *M* H₂SO₄ (interpolated) of 86.4 hr., found by Kennedy.¹⁸

Because of the predominant initial formation of acid sulfate on solvolysis of cyclopropane, the control experiment with added 1,1-dideuterio-1-propanol was subjected to conditions much more vigorous than necessary for the simple attainment of equilibrium, so that essentially all of the alcohol had been through the acid sulfate stage. The low material balances obtained in the product runs isolated by procedure a appear to reflect incomplete hydrolysis of the acid sulfate, since the sodium salt of the acid sulfate is essentially stable to the isolation conditions.¹⁹ Thus, the high material balances obtained by procedure b appear to reflect the equilibrium values and indicate essentially quantitative isolation of the available alcohol. It is significant in this context that both methods a and b gave 1-propanol of identical isotopic distribution.

Results

Our observation that the (average) deuterium distribution in the 1-, 2-, and 3-positions of the 1-propanol, obtained from the solvolysis of cyclopropane in D₂SO₄, is 0.38, 0.17, and 0.46 deuterium atom, respectively, suggests that something more complex than a simple concerted ring opening has occurred.

The possibility that this distribution in the 1-propanol results from equilibration prior to solvolysis¹¹ can be ruled out under the conditions used (rapid stirring and continuous cyclopropane passage), because the deuterated cyclopropane, once formed, has essentially no probability of solvolyzing. This conclusion is confirmed by the uptake of only one deuterium atom on the carbon skeleton of the 1-propanol. Moreover, our observation that the rates of solvolysis of cyclopropane in 8.43 *M* D₂SO₄ and 8.41 *M* H₂SO₄ are in the ratio of 0.66:1 strongly suggests that the cyclopropane is protonated slowly relative to its subsequent reactions.

The possibility of scrambling of the deuterium occurring after formation of the acid sulfate or alcoholic

(15) E. M. Arnett and J. N. Anderson, *J. Am. Chem. Soc.*, **85**, 1542 (1963).

(16) This observation requires some comment, since the molar ratio of water to sulfuric acid in 8.4 *M* H₂SO₄ (or D₂SO₄) is approximately 4.15:1. In view of the fact that essentially all of the water appears to be involved in the first hydration shell of the hydronium ion,¹⁷ however, it does not seem unreasonable that the negatively charged bisulfate ion should compete successfully for the (positively charged) protonated cyclopropane.

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(18) T. C. Hoering and J. W. Kennedy, *J. Am. Chem. Soc.*, **79**, 56 (1957).

(19) G. H. Green and J. Kenyon, *J. Chem. Soc.*, 1389 (1950).

products can be eliminated as a result of the observation that 1,1-dideuterio-1-propanol is not affected by conditions considerably more severe than those used in the ordinary isolation procedure. The similarity of the rates of formation and hydrolysis of the acid sulfate to those observed in the oxygen-18 exchange of sulfuric acid,¹⁸ the difficulty with which primary alcohols undergo oxygen exchange with solvent,²⁰ the stereochemical results obtained in acid sulfate hydrolyses,²¹ and the absence of rearranged products in our experiments make it seem quite likely that sulfur-oxygen and not carbon-oxygen bond cleavage is involved in these reactions of the acid sulfate.

Discussion

The above results make it very unlikely that a mechanism involving methyl-bridged ions such as I, alone or in equilibrium with isomeric methyl-bridged ions, can account for the isotopic distribution. The deuterium content of the 1- and 2-positions of the 1-propanol would necessarily be identical in such a mechanism. Correspondingly, a system of equilibrating primary carbonium ions or an intermediate such as II alone^{6, 22} would not be expected to lead to 2-deuterio-1-propanol.

The observed isotopic distribution could formally be accounted for by a system of equilibrating primary carbonium ions, accompanied by some Wagner-Meerwein rearrangement of the methyl group. A mechanism involving primary carbonium ions, however, seems difficult to reconcile with the observed lack of isomeric products in this system. Thus, in the deamination of 1-propylamine,²³ where the 1-propyl-carbonium ion is believed to be involved,^{8, 22} the products, propylene, 2-propanol, and 1-propanol, are found in the approximate ratio 4:4.6:1, respectively. In the present system, the maximum values are 0.0005:0.0027:1, and the actual values are probably considerably lower.²⁴

One can also account for the experimental results by way of intermediates corresponding to IIIa and IIIb, that is, by π -complex, and by hydrogen-bridged^{25a} intermediates. However, in view of the association of π -complex intermediates with rapid and reversible proton exchange with solvent,^{25b} we prefer to utilize a bridged-ion formulation.

In considering such a hydrogen-bridged-ion formulation, one may assume that cyclopropane adds D⁺ either by route 1 to give ion IV or by route 2 to give ion VIII, as indicated in Fig. 1. In order to fit the experimental results one must next assume that *sololytic ring opening occurs primarily with the hydrogen-bridged ions V, VII, and VIII, rather than with the carbon-bridged ions IV and VI.*

As indicated in Fig. 1, ion V would lead to 1- and 3-deuterio-1-propanol, ion VIII to 3-deuterio-1-propanol, and ion VII to 2-deuterio-1-propanol. Since ion VII is formed only *via* ion V, it might be anticipated that 2-deuterio-1-propanol would be formed in appreciable quantities only in systems where the rate of rearrangement is large relative to the rate of solvolysis.²⁶

(20) I. Dostrovsky and F. S. Klein, *ibid.*, 4401 (1955).

(21) (a) J. S. Brimacombe, A. B. Foster, and M. Stacey, *Chem. Ind. (London)*, 262 (1959); (b) H. K. Gardner and H. J. Lucas, *J. Am. Chem. Soc.*, **72**, 5497 (1950).

(22) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

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

(24) The 2-propanol observed may be formed from the products, since it is also observed in the control experiments.

(25) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); (b) L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956).

(26) The stationary-state treatment of such a system depends on the mode of D⁺ addition and on the degree of equivalence assumed for the hydrogens in the methyl-bridged species, but it appears that self-consistent rate

The attractiveness of the above scheme stems in large part from the possibility of its involvement in a variety of reactions of the 1-propyl system. It is tempting to postulate that the rearranged 1-propanol observed in the deamination of labeled 1-aminopropane, ^{3,5} the rearranged 1-chloropropane obtained on treatment of labeled 1-chloropropane with zinc chloride,²⁷ and the cyclopropane obtained in deamination,⁸ "deoxidation,"⁸ and exchange¹¹ reactions are formed *via* a reaction sequence of the type shown in Fig. 1 rather than directly from the 1-propylcarbonium ion.

We would tentatively suggest that the 1-propylcarbonium ion (or its immediate precursor) may either lose a proton, add solvent, rearrange to the 2-propylcarbonium ion, or cyclize to form the hydrogen-bridged ion IIIb²⁸ (or its isotopically-labeled counterpart). Direct formation of the hydrogen-bridged ion IIIb (which is effectively the reverse of the solvolytic opening of this ion) circumvents the objections posed to the direct formation of carbon-bridged ion I,^{3,5} since predictions based on solvolytic opening of ion IIIb lead to the same results as those based on ion II. In systems (such as the one reported in this work) where the lifetime of the ions involved is fairly long, ion IIIb, unlike ion II, can rearrange (as depicted for the analogous deuterium-substituted ions in Fig. 1), so as to account for the greater scrambling of deuterium. In deamination of 1-aminopropane the total amount of reaction proceeding *via* bridged ions would be small, as evidenced by the small amount of rearranged 1-propanol obtained.^{4,5} The hydrogen-bridged ions IX and X which would be formed initially in the systems studied by Reutov^{3,27} and by Karabatsos,⁵ respectively, by analogy with ion V in our system, would have to rearrange to isomeric hydrogen-bridged ions (analogous to ion VII) in order to lead to 1-propanol labeled (with carbon-14 and hydrogen, respectively) in the 2-position. Since other reactions such as solvolysis compete at each step, the total amount of 2-labeled material obtained in deaminations would be expected to be extremely small, as is observed.^{3,5,27}

The formation of cyclopropanes in the above reactions would also appear to fit into the proposed scheme. The formation of cyclopropanes from the bridged-ions depicted in Fig. 1 would occur most reasonably *via* reversal of the protonation step. Thus, depending on the mode of protonation involved (route 1 or 2 in Fig. 1), the loss of a proton from ions IV and VI or from ions V and VII, would lead to deuterium-labeled cyclopropane.¹¹ The observation that the "deoxidation" of 1,1-dideuterio-1-propanol leads to a mixture of $94 \pm 2\%$ dideuteriocyclopropane and 5-6% monodeuteriocyclopropane⁶ can most readily be accommodated in the above scheme by assuming that proton loss occurs primarily from the initially formed hydrogen-bridged ion XI rather than from the (rearranged) methyl-bridged ions XII and XIII. This, however, may not necessarily preclude proton loss from methyl-

constant ratios can be obtained if isotope effects are invoked in the reactions of VIII.

(27) O. A. Reutov and T. N. Shatkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 195 (1963); *Chem. Abstr.*, **58**, 10063c (1963).

(28) In the case of the zinc chloride treatment of 1-chloropropane, the zinc chloride-alkyl halide complex may be converted directly to the hydrogen-bridged ion.²⁷

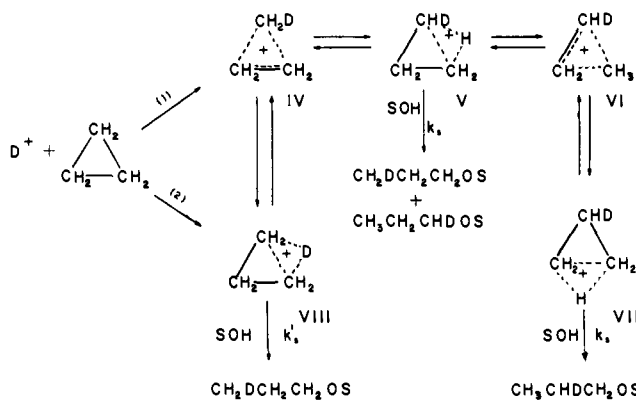
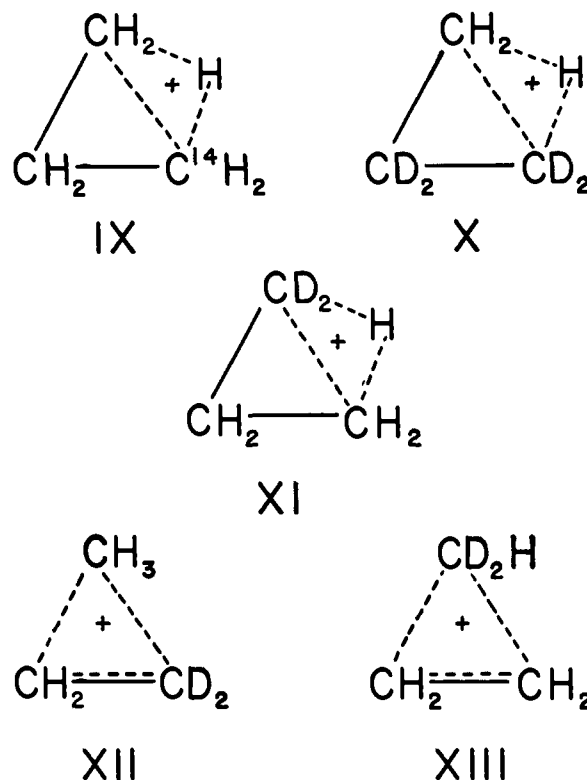


Figure 1.

bridged ions under conditions different from the strongly alkaline conditions of "deoxidation."



We would suggest that the importance of such hydrogen-bridged ions as IIIb is greatest in systems where the classical or the carbon-bridged ions would be the least stable, that is, in systems like the above, where the classical carbonium ion structures would be primary (or otherwise destabilized).²⁹ In other systems, Wagner-Meerwein rearrangements,^{9,10} classical carbonium ions,³⁰ or carbon-bridged ions^{31,32} would appear to be favored over hydrogen-bridged ions.

(29) (a) O. E. Edwards and M. Lesage, *Chem. Ind. (London)*, 1107 (1960). (b) NOTE ADDED IN PROOF.—Edwards and Lesage have recently suggested a hydrogen-bridged intermediate similar to IIIb to explain their results: O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963).

(30) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.*, **81**, 466 (1959).

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

(32) S. Winstein, *Experientia Suppl.*, **11**, 137 (1955).