

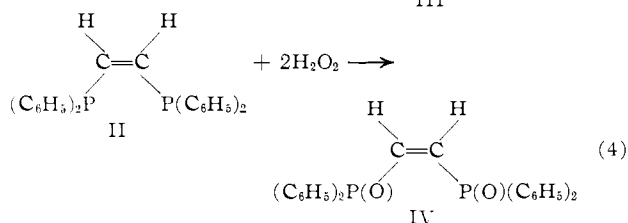
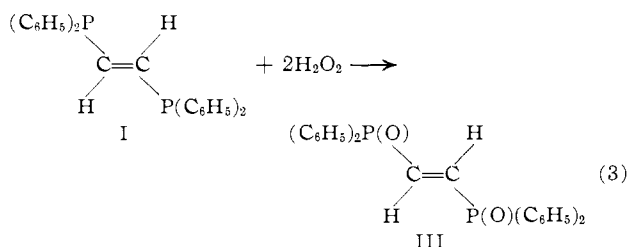
tempted hydrogenation of II under identical conditions resulted in quantitative recovery of II. This may be due to interaction between the Raney nickel and a *cis*-diphosphine.⁷

Oxidation of I and II by treatment with 3% hydrogen peroxide in hot acetone or ethanol gave III and IV, respectively.

Compound III (m.p. 310–311). *Anal.* Calcd. for $C_{26}H_{22}P_2O_2$: C, 72.89; H, 5.14; P, 14.48; mol. wt., 428. Found: C, 72.55; H, 5.23; P, 14.42; mol. wt., 458 (by osmometer method) gave an infrared spectrum which exhibited peaks at 3.28 (w), 3.35 (m), 6.3 (w), 6.7 (w), 6.95 (m), 8.4 (s), 8.55 (s), 8.9 (s), 9.1 (m), 9.3 (w), 9.8 (m), 10.0 μ (w), and four strong peaks at 13.0, 13.4, 13.85, and 14.5 μ . The n.m.r. of a glacial acetic acid solution of III showed a phenyl hydrogen complex centered at about δ 7.1 p.p.m. and two unequal-sized peaks at δ 7.5 and 7.9 p.p.m. The 7.9 peak was the smaller. Apparently the high-field peak of a triplet due to the vinyl hydrogens is hidden by the phenyl hydrogens. The coupling constant is 25 c.p.s. A trifluoroacetic acid solution of III displayed an n.m.r. spectrum showing the triplet more clearly.

Compound IV (m.p. 244–245) had the same composition and molecular weight as III but gave an infrared spectrum displaying peaks at 3.0 (w), 3.4 (w), 6.35 (w), 6.8 (w), 7.0 μ (m), a complex set between 8.2 and 8.6 μ , with the strongest peak at 8.4 μ , 9.0 (s), 9.15 (w), 9.4 (w), 9.8 (w), 10.05 (w), 12.95 (w), 13.15 (w), 13.4 (m), 13.85 (s), 14.25 (m), 14.45 (s), 14.6 (m), and 15.2 μ (w). The n.m.r. of a glacial acetic acid solution of IV showed a phenyl hydrogen complex centered at δ 6.9 p.p.m. and two equal-size peaks at δ 6.38 and 7.4 p.p.m. Perhaps the vinyl hydrogens show up as a triplet with the middle peak falling at the same point as the phenyl hydrogens. If this is the case the coupling constant is about 32 c.p.s. Use of trifluoroacetic acid as solvent gave essentially the same results. Ethylenebis(diphenylphosphine) dioxide gave an infrared spectrum which also had a weak band at 3.0 μ but had two others at 3.42 and 3.47 μ . Unlike the vinyl dioxides the saturated dioxide in deuteriochloroform exhibits a doublet at δ 2.58 p.p.m. due to the methylene hydrogens.³

On the basis of the above data compounds III and IV were assigned the structures of *trans*- and *cis*-1,2-vinylenebis(diphenylphosphine) dioxide, respectively (eq. 3 and 4).



(7) J. Chatt, F. A. Hart, and D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).

Thiolate ions have been reported to react with *cis*-1,2-dichloroethene in the presence of sodium ethoxide to give a *cis*-vinyl bridged disulfide by an elimination-addition mechanism.⁸ The *trans*-dihalide was found unreactive under similar conditions.⁸ The elimination-addition path cannot be followed by both isomers in the reaction with lithium diphenylphosphide since the same vinylenebis(diphenylphosphine) would be produced in both cases from the common intermediate, chloroacetylene.

Acknowledgments.—This work was carried out under a grant from the Petroleum Research Fund of the American Chemical Society. All of the n.m.r. work was done by Mr. Gordon Boudreaux of the Spectroscopy Investigation of Cotton Physical Properties Laboratory, U. S. Southern Regional Utilization Research Center in New Orleans, Louisiana. We wish to thank Mr. Raford Holmes of the same institution for the hydrogenation of these compounds.

(8) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManis, *J. Am. Chem. Soc.*, **78**, 2743 (1956).

DEPARTMENT OF CHEMISTRY
TULANE UNIVERSITY
NEW ORLEANS 18, LOUISIANA

ADAM M. AGUIAR
DONALD DAIGLE

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Concerning the Role of Protonated Cyclopropane Intermediates in Solvolytic Reactions. II. The Deamination of 3,3,3- d_3 -1-Aminopropane

Sir:

Recently the suggestion was made¹ that a protonated cyclopropane might be the intermediate responsible for the rearranged 1-propanol obtained in the deamination of 1-aminopropane as well as for the cyclopropane obtained^{2,3} in such reactions. It was shown previously¹ that when D^+ is added to cyclopropane, extensive mixing of the added deuterium and the ring protons occurs during the lifetime of this protonated cyclopropane intermediate. If the cyclopropane formed in these deaminations is also formed *via* such an intermediate, then, by suitable choice of label, one should be able to demonstrate such mixing in the cyclopropane obtained.

A crucial test of this hypothesis is found in the deamination of 3,3,3- d_3 -1-aminopropane. In this case, formation of an intermediate such as I and subsequent mixing of H and D would lead to a mixture of cyclopropane- d_2 and cyclopropane- d_3 . The amount of cyclopropane- d_3 formed would give a measure of the extent of such mixing and of any isotope effect on deprotonation.⁴

The perchlorate of 3,3,3- d_3 -1-aminopropane was prepared from acetophenone *via* the sequence: exchange with D_2O , rearrangement,⁵ $LiAlH_4$ reduction, *p*-toluenesulfonate ester formation, $NaCN$ displacement, and reduction.⁷ The perchlorate (m.p. 167.5–

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

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

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

(4) A small amount of mixing has been observed in the "deoxidation" of 1,1- d_2 -1-propanol.⁵ However, the combination of isotope effect, method of analysis, and short ion lifetimes obtained under these conditions tends to obscure the extent of such mixing.

(5) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962 (1962).

(6) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

(7) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953).

168.2°) and all intermediates were assayed for deuterium content by n.m.r. on a Varian A-60. The isotopic purity of the CD₃ group is estimated to be 99.5 atom %.

Deamination of the 3,3,3-d₃-1-aminopropane was carried out under the conditions of Roberts.^{7,8} The gaseous products evolved were collected in a -140° trap and separated by gas chromatography.⁹ The cyclopropane fraction was analyzed by low voltage mass spectrometry¹⁰ on a Consolidated Electro Dynamics Model 21-103C mass spectrometer. The cyclopropane (after correction for normal isotopic abundances) was found to consist solely of 43 ± 1% cyclopropane-d₂ and 57 ± 1% cyclopropane-d₃.

It has previously been assumed that the rearranged 1-propanol observed in the deamination of 1-aminopropane was derived from a rearranged 1-propyl-carbonium ion.^{5,8} The 1-propylcarbonium ion was also believed to be the immediate precursor of the cyclopropane formed in "deoxidation" and deamination reactions,⁵ the rearranged ion leading to formation of some cyclopropane-d₁ on "deoxidation" of 1,1-d₂-1-propanol.⁵ Implicit in these assumptions was the assumption that the rearranged carbonium ion undergoes the same reactions as does the unrearranged ion, and it has been implied that the loss of deuterium on formation of cyclopropane in the above "deoxidation" should mirror the extent of rearrangement observed in the formation of 1-propanol in deaminations.⁵ A straightforward application of these principles to our system leads to the prediction that no more than 6% cyclopropane-d₃ should be formed if there is no isotope effect on deprotonation,⁵ and no more than 31% for k_H/k_D as large as 7. Since the observed fraction of cyclopropane-d₃ is far in excess of this amount, the above principles would not appear to be valid.

The above experimental result can readily be accommodated by our mechanism,¹ which involves equilibration of the initially formed I with isomeric methyl-bridged ions. By invoking an isotope effect for proton loss of from *ca.* 2.7 to 3.0¹¹ one can arrive at the observed ratios of cyclopropane-d₂ and -d₃.¹²

A variation of our mechanism has recently been suggested to us,¹³ however, which we feel is important enough to merit separate discussion. This mechanism involves the equilibration of hydrogen-bridged ions, I, II, III, etc., by a process which can be viewed as the (hindered) rotation of quasi-methyl groups. If the lifetimes of the bridged ions are sufficiently long, the deuterium and hydrogen will be statistically distributed among the five positions involved. Loss of the bridging hydrogen or deuterium would lead to cyclopropane-d₃ or -d₂,¹⁴ respectively, and solvolytic opening to (rearranged) 1-propanols.¹⁵ With longer

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

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

(10) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

(11) In view of the observed isotope effect ($k_H/k_D = 1.5$) on the protonation of cyclopropane,¹ it is not unreasonable to expect an isotope effect of this magnitude on the reverse reaction.

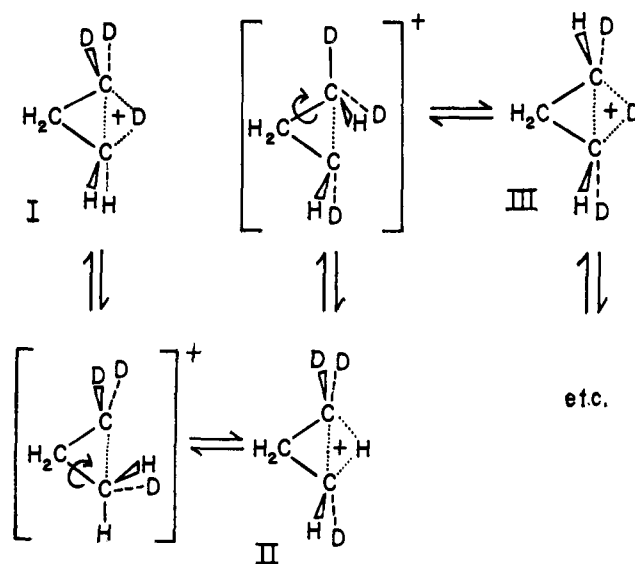
(12) The lower isotope effect is for proton transfers involving the methyl-bridged ions and the higher one for those involving the hydrogen-bridged ions.

(13) Private communication from Professor K. B. Wiberg.

(14) In this case an isotope effect for deprotonation of $k_H/k_D = 2.0$ would account for the product ratio.

(15) This mechanism also affords an explanation for the different extents of rearrangement observed in the 1-propanol obtained on deamination of labeled 1-aminopropane,^{7,8} since one would expect more mixing of hydrogens than of carbons in an intermediate analogous to I.

lifetimes, subsequent rearrangement to involve the remaining two hydrogens can occur *via* a transition state resembling our methyl-bridged ion.



The Wiberg mechanism may be considered to involve equilibration of hydrogen-bridged ions *via* methyl-bridged ions which differ from those postulated by us in that they have a "memory" (provided by a barrier to internal rotation) as to which side the hydrogen was originally bridged on. Although one would expect some differences between the two, most of these are small enough that experimental differentiation is not possible at present.¹⁶

Irrespective of the intimate details of the above mechanisms, it would appear that 1,3-rearrangements in the 1-propyl system are more readily interpreted as occurring *via* protonated cyclopropane intermediates than *via* equilibration of primary carbonium ions, but that great care must be exercised in extrapolation of these results to related systems (and *vice versa*).¹⁷

Acknowledgment.—We wish to acknowledge the assistance of National Science Foundation Grants G22689 and GP1442 for the purchase of an A-60 n.m.r. and a mass spectrometer for our department.

(16) For example, one can also rationalize the different extents of rearrangement of 1-propanol¹⁵ within the observed experimental error *via* our mechanism.

(17) See, for example, G. J. Karabatsos and J. D. Gramh, *J. Am. Chem. Soc.*, **82**, 5250 (1960).

(18) National Science Foundation Undergraduate Fellow.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

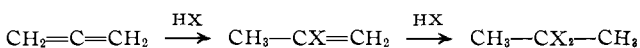
AKINTOLA A. ABODERIN¹⁸
RICHARD L. BAIRD

RECEIVED APRIL 6, 1964

Cyclobutane Compounds. I. Formation of a Four-Membered Ring during the Electrophilic Addition of Hydrogen Bromide to Allene

Sir:

Electrophilic additions of HX compounds to allene are generally considered to occur according to Markovnikov's rule^{1,2} leading to 2-substituted propenes and/or 2,2-disubstituted propenes.



(1) A. A. Petrov and A. V. Fedorova, *Uspekhi Khim.*, **33**, 1, 3 (1964).

(2) T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).