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THE ACID-CATALYZED PROTON EXCHANGE OF CYCLOPROPANE

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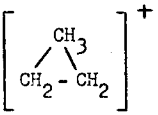
IT has recently been reported that cyclopropane is formed in the "deoxideation" of *n*-propyl alcohol,[2] and in the deamination of *n*-propylamine,[2] reactions which are believed to proceed via the *n*-propylcarbonium ion.[3] Since this reaction can be formulated as involving a bridged species such as (I), it is of considerable interest



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that Reutov[4] has been able to demonstrate that (I) cannot be involved in the rearrangement observed on deamination of *n*-propylamine-1-C^{14}. One can conclude from these results that if (I) is involved in the formation of cyclopropane, it must lose a proton faster than it opens to give rearranged product. This conclusion suggested to us the possibility that cyclopropane itself might protonate reversibly, in competition with solvolysis. If equilibration of the added proton with

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[1] National Science Foundation Undergraduate Fellow, 1962.

[2] P. S. Skell and I. Starer, *J. Am. Chem. Soc.* **82**, 2971 (1960).

[3] P. S. Skell and I. Starer, *ibid.* **84**, 3962 (1962).

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

those on the ring occcurred, it should be possible to observe acid-catalyzed deuterium exchange.

We now wish to report that exchange of deuterium for hydrogen does occur with cyclopropane. Treatment of cyclopropane with D_2SO_4 for varying lengths of time resulted in mixtures of cyclopropane and monodeuteriocyclopropane plus small amounts of dideuteriocyclopropane.

In one experiment a sample of 62 ml. of cyclopropane (Matheson 99.5%--which was shown to contain less than 0.1% of propylene by gas chromatography) was stirred at atmospheric pressure with 5 ml. of 7.52 M D_2SO_4 (prepared by distillation of Baker and Adamson "Sulfan B" into 99.8% D_2O) in 99.8 D_2O in a micro-hydrogenation apparatus thermostated at 25.0°C. Small gas samples were taken at intervals and purified by gas chromatography on a 3 meter column of G.E. "SF 96 (300)" silicone oil on "Chromosorb W". The crude gas samples were found to consist almost entirely of cyclopropane, no more than 0.1% propylene being observed as the only organic impurity. The deuterium content of the cyclopropane was determined by low voltage mass spectrometry[5] on a Bendix time of flight mass spectrometer. Exchange was found to have occurred to the extent of 3.6 ± 0.8%, 8 ± 2%, and 21 ± 2% (calculated as gram atoms of deuterium per mole of cyclopropane remaining) after 3.5, 7.25, and 17 hours, respectively.

Solvolysis of cyclopropane occurred concurrently with the exchange, the rate of solvolysis being about twice that of exchange in the above experiment. In another experiment under slightly different conditions, exchange occurred to the extent of 24 ± 3% in 20 hours, but the solvolysis rate was not measured. We are currently investigating these reactions

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[5] K. Biemann, "Mass Spectrometry", McGraw Hill Book Co., Inc., New York, 1962, Chapter 5.

under a variety of conditions in an effort to elucidate the mechanism of these transformations.

On the basis of evidence presently available, the observation of exchange can be accommodated by a variety of mechanisms in addition to that involving the reversible formation of an intermediate such as (I). Among the possibilities are reversible opening to the n-propylcarbonium ion and reversible formation of a cyclopropane-D^+-π-complex which rearranges to a deuteriocyclopropane-H^+-π-complex. Although preliminary evidence indicates that it is unlikely, an ionic chain mechanism involving the cyclopropylcarbonium ion cannot be completely excluded at this time.