Tetrahedron Letters No.3, pp. 341-343, 1968. Pergamon Press. Printed in Great Britain.

THE SELECTIVE DEUTERATION OF THE VINYLIC PROTONS OF CYCLOPROPENE

E. A. Dorko and R. W. Mitchell

U. S. Army Missile Command, Redstone Arsenal, Alabama 35809

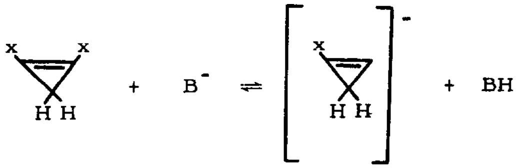
(Received in USA 14 August 1967)

Recently a sample of 1,2-dideuterocyclopropene was required for an analysis of the vibrational spectrum of cyclopropene. This necessitated the selective deuteration of the vinylic protons. Previous deuteration procedures had produced random distribution of the deuterium in the molecule (1). We have now succeeded in selectively deuterating the vinyl position of cyclopropene by taking advantage of the acidity of the vinylic protons (2-4). The procedure employed consisted of bubbling a sample of cyclopropene in a gas stream through a 10% solution of potassium t-butoxide in t-butyl alcohol-d.

Cyclopropene was prepared as reported by Closs and Krantz (5). A 1-g. portion of this material was allowed to pass through a U-tube filled with 40 g. of a 10% solution of potassium t-butoxide in t-butyl alcohol-d. The gas stream on emerging from the base solution was passed through a U-tube maintained at 0°, to condense out the alcohol, and through a U-tube maintained at -196°, to condense out the dideuterocyclopropene. After nine passes through the base solution, a 30% recovery of product was obtained in which 84% of the vinylic protons had been replaced by deuterium. The NMR spectrum obtained at -67° showed two singlets at τ 2.87 and τ 9.05 (6) in the ratio of 1.8 to 9.1. The mass spectral cracking pattern of the product showed the incorporation of no more than two deuteriums. The parent peak occurred at m/e 42. The solid phase infrared spectrum of the deuterated product (7) shows that the absorption bands due to methylenic C-H stretch at 2983 cm^{-1} and 2997 cm^{-1} occur at the same frequency as for undeuterated material, and no new bands attributable to methylenic C-D stretch are present. But the bands at 3158 cm^{-1} and 3124 cm^{-1} due to the vinylic C-H stretch have shifted to 2391 cm^{-1} and 2450 cm^{-1}. This data indicates that the deuteration process was selective for the vinyl position.

The t-butyl alcohol-d used for the deuteration was prepared by a simplified procedure. Potassium t-butoxide (Research Corporation, Callery, Pennsylvania, 44.8 g., 0.4 mol) was added in small portions to 24.0 g. (1.2 mol) of D_2O. The reaction mixture was stirred vigorously during the addition which was accomplished in a nitrogen atmosphere. The resulting mixture was distilled. The fraction boiling at 82° was dried over barium oxide to remove final traces of D_2O. This procedure gave 29.0 g. (97%) of the deuterated alcohol. Mass spectral analysis showed it to be free of D_2O. NMR and infrared analysis showed that the hydroxyl position was 98% deuterated.

While it has been postulated that the vinylic protons of cyclopropene are substantially more acidic than normal vinyl protons (2) and while this property has been used in the preparation of cyclopropene derivatives (3, 4, 9), there has been no direct evidence to indicate that the equilibrium shown in Eq. (1) can be established.



(1)

Ia x = H

Ib x = D

The recovery and characterization of 1,2-dideuterocyclopropene is direct evidence which establishes that this equilibrium does exist.

REFERENCES

1. K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.* **82**, 6375 (1960)
2. G. L. Closs, *Proc. Chem. Soc.*, 1962, 152.
3. G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.* **83**, 1003 (1961).
4. K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Am. Chem. Soc.* **79**, 4994 (1957)

5. G. L. Closs and K. D. Krantz, *J. Org. Chem.* **31**, 638 (1965).
6. G. L. Closs, Advances in Alicyclic Chemistry, Vol. I, p. 76, Academic Press, Inc., New York (1966).
7. The complete infrared spectrum of both protonated and dideuterated material is being published elsewhere.
8. The spectrum was taken with a Consolidated Engineering Corporation Type 21-60 spectrograph operating at 100 v. I. P. The source temperature was maintained at 150°C.
9. G. Schröder, *Ber.* **96**, 3178 (1963)