Tetrahedron Letters No. 30, pp. 2173-2175, 1963. Pergamon Press Ltd.
Printed in Great Britain.

BICYCLO[1. 1. 0]BUTANE[1]

By Kenneth B. Wiberg and Gary M. Lampman

Department of Chemistry, Yale University

New Haven, Conn.

(Received 2 October 1963)

The recent publication of an elegant photochemical synthesis of bicyclobutane[2] prompts us to record a simple and convenient method for its formation which is applicable to the preparation of reasonably large quantities of the compound.

The observation that cyclobutane-1, 1-dicarboxylic acid is chlorinated by sulfuryl chloride to give primarily the 3-chloro derivative[3] has been confirmed. Decarboxylation gave 3-chlorocyclobutane-1-carboxylic acid, and the latter on treatment with mercuric oxide and bromine[4] formed 1-chloro-3-bromocyclobutane. The dihalide on treat-

---

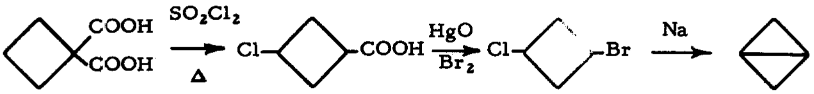
(1) This work was supported by the California Research Corporation.

(2) D. M. Lemal, F. Menger and G. W. Clark, J. Am. Chem. Soc. **85**, 2529 (1963).

(3) W. A. Nevill, D. S. Frank and R. D. Trepka, J. Org. Chem. **27**, 422 (1962).

(4) S. J. Cristol and W. C. Firth, J. Org. Chem. **26**, 280 (1961).

ment with sodium metal in dioxane gave in good yield (98%) a mixture of hydrocarbons consisting of bicyclobutane (93-96%) and cyclobutene (5-7%):



The cis- and trans- 1-chloro-3-bromocyclobutanes gave approximately the same proportions of the two products and the same yield of hydrocarbons.

The bicyclobutane was identified by its characteristic nmr spectrum[2,5] in which olefinic proton bands were absent. The compound had b. p. + 7.8 ± 0.5°C., ΔH_v = 6040 cal/mole. Its infrared spectrum showed strong C-H bands at 3030, 2950, 2920, 2882 and 2870 cm^{-1}.

In contrast to the usual synthesis of cyclopropane from 1,3-dihalides via dehalogenation, zinc in ethanol-water gave no bicyclobutane, but rather cyclobutene (23%), butadiene (69%) and 1-butene (5%). The addition of sodium ethylenediaminetetraacetate changed the proportion of products (11% cyclobutene, 41% butadiene and 47% 1-butene), but did not lead to any bicyclobutane.

Bicyclobutane reacted readily with iodine to give the 1,3-dihalide (82%) cis and 18% trans), identified by comparison with authentic samples. No direct mechanistic conclusion may be drawn from the isomer ratio since it is close to the ratio obtained in equilibration

---

(5) K. B. Wiberg and R. P. Ciula, J. Am. Chem. Soc. 81, 5261 (1959).

experiments. Bicyclobutane remains essentially unchanged on standing as a liquid at room temperature.

In the nmr spectrum, the C^{13} satellites were easily located giving $J(C^{13}\text{-}H) = 170 \pm 2$cps for the bridgehead protons and $J(C^{13}\text{-}H) = 159 \pm 2$cps for the methylene protons. The latter is close to that found for cyclopropane (161 cps),[6] but the former is considerably smaller than that observed with the bridgehead hydrogens of the bicyclobutane ring in tricyclo[4.1.0.$0^{2,7}$]heptane (200 ± 2cps).[7] This suggests that the trimethylene bridge fused across the bicyclobutane ring of the tricycloheptane has resulted in significant additional deformation of the ring and has led to increased s-character in the bridgehead orbitals.

The chemical reactions and properties of the hydrocarbon and of its 1-carboxylate[5] will be described in detail in a subsequent manuscript.

---

(6) N. Muller and D. E. Pritchard, J. Chem. Phys. **31**, 768, 1471 (1959).

(7) G. L. Closs and L. E. Closs, J. Am. Chem. Soc. **85**, 2022 (1963).