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A PHOTOCHEMICAL SYNTHESIS OF BICYCLO [2.2.0]-HEXANE[1]

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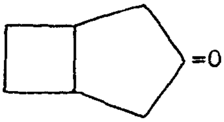
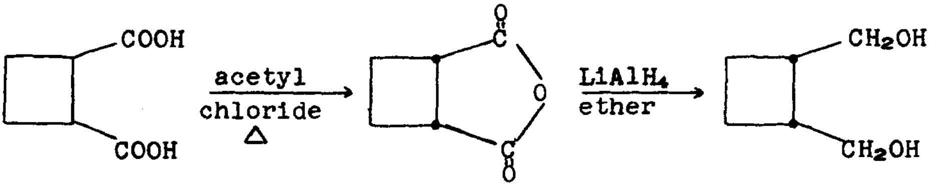
One of three methods by which a cyclobutane ring may be synthesized photochemically is the vapor phase photolysis of a substituted cyclopentanone. Photolysis of cyclopentanone itself gives rise to cyclobutane and carbon monoxide among other products.[2] One may expect that the photolysis of bicyclo [3.2.0]-heptanone-3 (I) would lead to bicyclo [2.2.0]-hexane by an analogous process.


I

I was synthesized from cyclobutane-1,2-dicarboxylic acid by the following steps:



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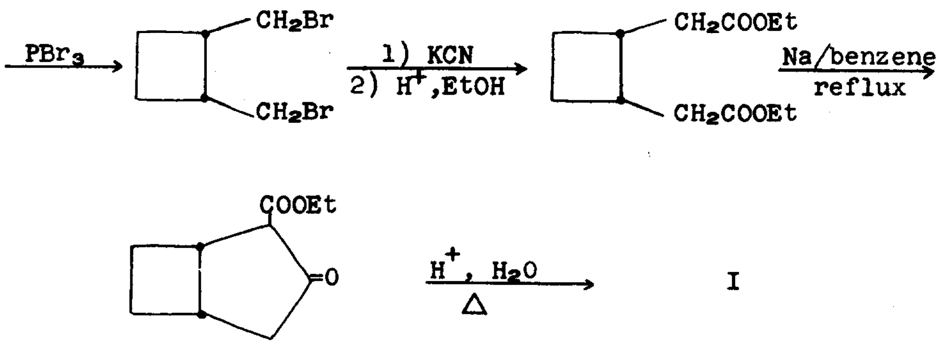
[1] The authors wish to thank the National Science Foundation for a grant to the Department of Chemistry, University of Rochester, in support of this work.

[2] S. W. Benson and G. B. Kistiakowsky, J. Am. Chem. Soc. 64, 80 (1942).



The first four steps have been described before.[3] The fifth and sixth steps were adapted from similar processes in the literature.[3,4]

I (b.p. 107.5° at 113 mm; Found: C, 76.36; H, 9.15. Calc. for $C_7H_{10}O$: C, 76.32; H, 9.15%) had an infrared spectrum which strongly resembled that of cyclopentanone. The nuclear magnetic resonance spectrum was consistent with the bicyclic formulation. I gave rise to a semicarbazone derivative (m.p. 197-200° dec. Found: N, 25.20. Calc. for $C_8H_{13}ON_3$: N, 25.13%). The intermediate carbethoxy derivative of I (b.p. 66-67° at 0.4 mm. $n_D^{25} = 1.4855$. Found: C, 65.70; H, 7.63. Calc. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%).

Photolyses of I were carried out in a 2 liter Pyrex bulb heated to 80°. The ketone (15 mm) and carbon dioxide (150 mm) were admitted through a conventional vacuum line. Two Hanovia medium pressure mercury arcs were used as light

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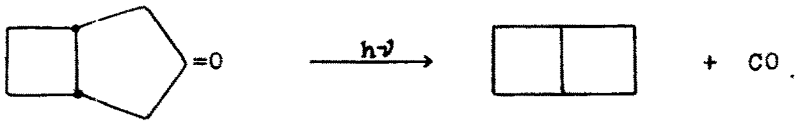
[3] N. L. Allinger, M. Nakazaki, and V. Zalkow, <u>ibid.</u> **81**, 4074 (1959).

[4] R. P. Linstead and E. M. Meade, <u>J. Chem. Soc.</u> 935 (1934).

sources.

In addition to carbon monoxide and 1,5-hexadiene, which were the major products, a third product (II) was formed to a small extent. It was separated by gas chromatography and characterized by physical methods. The molecular weight as determined by mass spectrometry was 82 (C_6H_{10}). The vapor pressure at 26.5° was 100 mm. By a micro method,[5] the b.p. at atmospheric pressure was estimated to be about 90°. The infra-red spectrum (solvent: CCl_4) showed strong absorption at 3.46 and 3.52 (shoulder) µ and weak ones at 6.98 and 11.0 µ. There was no evidence of unsaturation. The nuclear magnetic resonance spectrum (solvent: CCl_4; chloroform as internal standard) confirmed the absence of unsaturation and indicated that the resonances of all the protons occurred within a broad (1.26τ wide) band centered at 7.66 τ. A solution of the product in CCl_4 was sealed in a glass bulb and heated to 230° for 20 mins. The infrared spectrum of the solution then indicated the presence of vinyl group(s) and no other strong absorption. Gas chromatography showed that a product with the same retention time as 1,5-hexadiene had been formed. These facts may be interpreted to mean that II is bicyclo [2.2.0]-hexane which is formed as follows:



II

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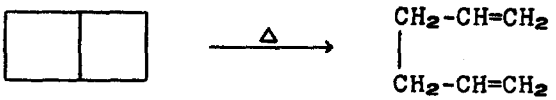
[5] S. W. Benson, Ind. Eng. Chem. Anal. Ed. 14, 189 (1942).

On heating, a reaction



analogous to the thermal decomposition of cyclobutane to ethylene may have taken place. The alternative formulation of II as bicyclo [2.1.1]-hexane is not excluded by the evidence given here. But it is known from the photolysis of cyclopentanone-1,1,2,2-d_4 that a skeletal rearrangement does not accompany the photodecomposition to give cyclobutane-d_4.[6] Hence II is most probably bicyclo[2.2.0]-hexane.

It was further observed that the photochemical formation of 1,5-hexadiene and II from I was sensitive to changes in wavelength and total pressure. An increase in the wavelength or pressure favored the formation of II.
This effect is entirely similar to the influence of wavelength and pressure on the formation of cyclobutane and ethylene from cyclopentanone.[7,8] However, even under the most favorable conditions II was produced from the decomposition of I in only 5% yield. Hence this method cannot be recommended for the preparation of II in quantity.

Acknowledgement: The authors wish to thank Professors W. Albert Noyes, Jr. and D. S. Tarbell for their advice and encouragement.

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6. R. Srinivasan, J. Am. Chem. Soc. 81, 1546 (1959).
7. F. E. Blacet and A. Miller, ibid. 79, 4327 (1957).
8. R. Srinivasan, Unpublished Results.