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BICYCLO[1.1.1] PENTANE FROM MERCURY SENSITIZED AND UNSENSITIZED GAS PHASE PHOTOLYSES OF BICYCLO[2.1.1] HEXAN-2-ONE*

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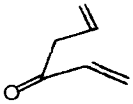
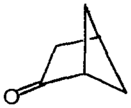
The impact of photochemical techniques on the synthesis of small ring compounds would be difficult to overestimate. As examples, the syntheses of bicyclo[2.2.0] hexane,[1] the bicyclo[2.1.1] hexanes,[2] bicyclo[1.1.0] butane,[3] tricyclo[2.1.0.$0^{2,5}$] pentane[4] and tricyclo[2.2.0.$0^{2,6}$] hexane[5] all owe their success to at least one photochemical step.

The recently described, convenient photocyclization of 1,5-hexadien-3-one (1)[6] to give bicyclo[2.1.1] hexan-2-one (2) prompted us to investigate its gas phase photolysis as a possible route to bicyclo[1.1.1] pentane (3).



(1)



(2)

(3)

Gas phase decarbonylations[7] of bicyclic ketones such as bicyclo[3.2.0] heptan-3-one,[1] camphor,[8] and norcamphor[9] have provided good analogy for the usefulness of this method of ring contraction for the preparation of highly strained products. Thus, in the mercury sensitized decomposition of norcamphor, Srinivasan[9] has reported the formation of bicyclo[2.1.1] hexane in 10% yield, accompanied by 1,5-hexadiene, allyl cyclopropane and bicyclo[2.2.0] hexane.

Mercury sensitized. gas phase photolysis of 2, using a 2537 Å light source, was found to give a mixture of volatile products,[10] the infrared spectrum of which (3080 and 1650 cm^{-1}) gave clear indication for the presence of olefins. Low temperature glpc analysis of this mixture

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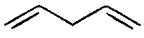
showed four well-resolved components, considered to be bicyclo[1.1.1] pentane (3) (32%), 1,4-pentadiene (4) (57%), bicyclo[2.1.0] pentane[11] (5) (1%), and vinyl cyclopropane (6) (11%) on the basis of direct glpc comparisons with authentic samples.[12]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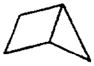
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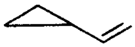
(6)

These structural assignments were further supported by the nmr spectrum of the mixture. The bicyclo[1.1.1] pentane was characterized by peaks at 7.55 and 8.16τ (lit.[13]: 7.55 and 8.16τ) with a 1:3 area ratio; 1,4-pentadiene and vinylcyclopropane had vinyl protons appearing as a broad multiplet from 3.8 to 5.3τ, the latter also showed cyclopropyl protons as a multiplet centered at 9.5τ. The nmr spectra of authentic samples of 1,4-pentadiene and vinylcyclopropane were exactly superimposable on the spectrum of the photolysate mixture. The ratio of hydrocarbons 3 to 4 to 6, as determined from the nmr spectrum, was 3:5:1.

The over-all conversion of bicyclo[2.1.1] hexan-2-one to bicyclo[1.1.1] pentane by this technique was 13%. While this route to bicyclo[1.1.1] pentane offers certain advantages over that previously described,[13] a further improvement could be effected by a non-sensitized photolysis of 2. Vapor phase irradiation of 2 with a 200-watt Hanovia high-pressure mercury lamp through a Vycor filter afforded, in 40-50% conversion, a 40:60 mixture of compounds 3 and 4.[14] The unchanged ketone could be recovered easily. The only limitation of this method at present is that after a few hours the quartz immersion well becomes coated with polymer and, consequently, the transmission of useful light is greatly diminished, making large scale runs inefficient.

It is significant to note that while vinylcyclopropane is formed in the sensitized reaction, it is not found in the unsensitized one. A likely explanation is that vinylcyclopropane as well as 5 are not primary photochemical products derived from the ketone itself, but arise from the mercury sensitized photolysis of 1,4-pentadiene. Recent investigations[15] have shown that 5 and 6 are, indeed, products of the mercury sensitized photolysis of 4.

References and Footnotes

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6. F. T. Bond, H. L. Jones and L. Scerbo, *Tetrahedron Letters*, 4685 (1965).
7. (a) J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, John Wiley and Sons, Inc., New York, N. Y., 1966, pp. 389-427; (b) R. Srinivasan in *Advances in Photochemistry*, Vol. I, eds. W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y., 1963, p. 105.
8. R. Srinivasan, *J. Am. Chem. Soc.*, 83, 2590 (1961).
9. R. Srinivasan, *ibid.*, 83, 4923 (1961).
10. The apparatus employed was a commercial unit consisting of 16 8-watt germicidal lamps arranged in a circle around a two-liter Vycor flask, fitted at the top with a nitrogen inlet valve and a water condenser. To the condenser was attached two Dry-Ice traps and a vacuum pump. After first purging with nitrogen, the Vycor flask was heated with a sand bath at 120° and a pressure of 110-120 mm. was maintained. With the lamps on, the enclosed air around the flask reached 70-80°. Products which formed were distilled into a collecting coil cooled to -80°.
11. While this component had a retention time corresponding to that of authentic bicyclo[2.1.0]-pentane, it was not rigorously identified because of the very small amount produced.
12. Using a tricyanoethoxypropane column, typical retention times at 10° were: bicyclo[1.1.1]-pentane, 4.6 min.; 1,4-pentadiene, 5.5 min.; bicyclo[2.1.0]pentane, 8.5 min.; and vinylcyclopropane, 12.5 min.
13. K. B. Wiberg and D. S. Connor, *J. Am. Chem. Soc.*, 88, 4437 (1966).
14. The ketone was vaporized into a foil-wrapped reaction vessel, fitted with a quartz immersion well (housing the lamp), a water-cooled condenser, and a side arm to allow the condensed ketone to return to a heated round-bottom flask. Attached to the top of the condenser were a series of Dry-Ice traps to collect the volatile products, a nitrogen inlet valve, and a vacuum pump. The quartz well was kept hot by passing 80° water through its water jacket in order to prevent the ketone from condensing on the well.
15. G. W. Smith, Doctoral Dissertation, Cornell University, 1966; R. Srinivasan, private communication.