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MERCURY PHOTOSENSITIZED REACTION OF CYCLOHEPTENE. MECHANISM OF NORCARANE FORMATION

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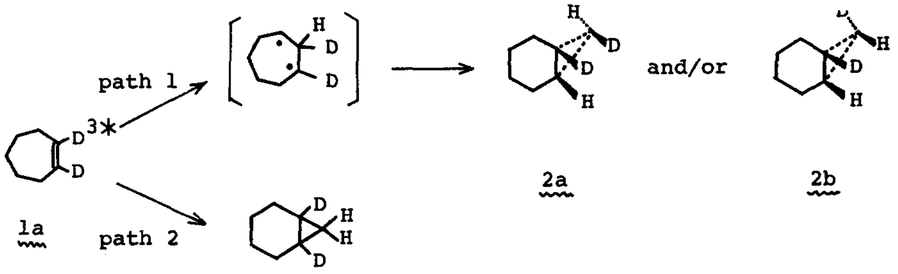
Previously we reported that α,ω-diene and bicycloalkanes are formed in the mercury photosensitized reaction of cyclooctene vapor.[1] The formation of bicycloalkanes, however, has not been reported in the mercury photosensitized reactions of cyclopentene[2] and cyclohexene[3] vapor. Therefore, we have been interested in the effects of ring size on the photochemical behaviors of cycloalkenes, and also in the mechanism of bicycloalkane formation.

In the present communication, we wish to report a mechanistic investigation of the mercury photosensitized reaction of cycloheptene vapor. Cycloheptene(1, 99.9% by vpc) vapor was irradiated with a low pressure mercury lamp in the presence of mercury vapor at room temperature. The photolysis products were mainly norcarane(2, $\Phi = 0.088$), vinylcyclopentane(3, 0.054), and 1,6-heptadiene (4, 0.025); hydrogen, ethylene, and 1,4-pentadiene were also observed as minor products. The formation of 3 and 4 were also observed in the pyrolysis of 1.[4] Norcarane, however, is peculiar to the photochemical reaction and its formation mechanism is of interest. The mercury photosensitized cyclization of olefin to cyclopropane derivative has been observed in some cases.[5] There, however, are some mechanistic uncertainties with the formation of cyclopropane derivatives, since the following alternative paths may be considered; 1) a 1,2-migration of an allylic hydrogen atom (simultaneous or stepwise path), 2) a $(2\pi+2\sigma)$ intramolecular cycloaddition reaction well-known in the photocyclization of cycloalkenones in solution.[6] Although the mechanism of photocyclization of the olefins may differ in each cases, it is worthwhile to reveal the formation mechanism of 2. To the purpose, cycloheptene-1,2-d_2(isotopic purity of 98%

by nmr) was synthesized and photolyzed using a preparative irradiation apparatus of 5 l. volume.



Then **2**-d_2 was separated gas-chromatographically from the photolyzate.[7] The nmr spectrum in $CDCl_3$ showed the signals of the bridge-head proton at ca. 0.9 δ (m), 7-exo-proton at ca. 0.5 δ (m), and 7-endo-proton at -0.02 δ (br. s) with their ratio of 2:1:1. This indicates that the resulting **2** consists of **2a** and **2b** in the ratio of 1:1. Therefore, it is concluded that **2** is formed *via* the stepwise path composed of 1,2-hydrogen-shift followed by 1,3-closure of the resulting biradical(stepwise path 1).

The whole mechanism of the photolysis of cycloheptene, which includes the formation processes of **3**, **4** and the degradation products, is still under investigation.

REFERENCES AND FOOTNOTES

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