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PHOTOLYTIC AND THERMAL DECOMPOSITIONS OF EXO-6,7-DIAZATRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE. EVIDENCE FOR UNIMPORTANCE OF CYCLOPROPYL PARTICIPATION IN THE FORMER DECOMPOSITION

Hiroshi Tanida and Shuji Teratake

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan

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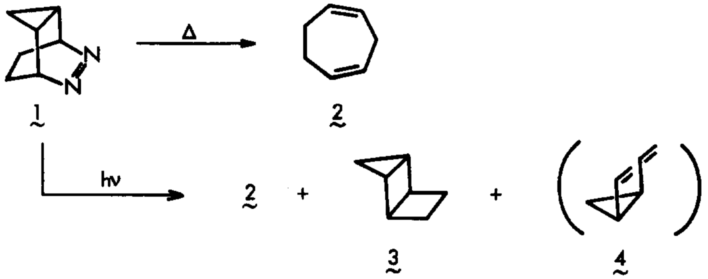
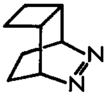
We recently reported that, whereas the thermal elimination of molecular nitrogen from anti-6,7-diazatricyclo[3.2.2.$0^{2,4}$] non-6-ene (1) proceeds with the formation of only one compound, cyclohepta-1,4-diene (2), photolytic elimination results in a product mixture consisting of 2, anti-tricyclo[4.1.0.$0^{2,5}$] heptane (3), and conceivably, cis-1,2-divinylcyclopropane (4) (1,2). We interpreted this difference between products



in terms of participation of the cyclopropane moiety in the transition state of the thermal decomposition, but not in that of the photolytic decomposition. Although participation of a neighboring cyclopropyl ring in the thermal decomposition of polycyclic azo compounds has been recently suggested by several workers and evidence is rapidly being accumulated (3-5), our results provided one of the best pieces of evidence for demonstration of unimportance of such participation in photolytic decomposition. The product difference between the photolytic and the thermal decompositions of anti-7,8-diazatricyclo[4.2.2.$0^{2,5}$] dec-7-ene (5) (6) is not inconsistent with this view. The thermolysis of exo-6,7-diazatricyclo[3.2.1.$0^{2,4}$] oct-6-ene (6) has been well established to give only 1,4-cyclohexadiene in more than 99% yield (5a). We have therefore undertaken the photolytic decomposition of 6 and compared products between the two kinds of nitrogen



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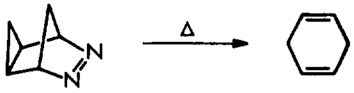

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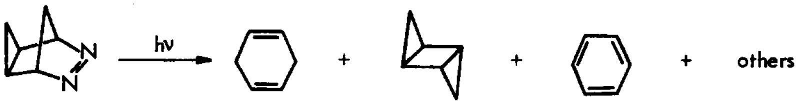
elimination, in order to get further information about the role of a neighboring cyclopropane ring in the transition state of such reactions.

The CuCl complex of 6 was prepared as reported (5a). The free 6 was isolated by shaking suspensions of the complex in deuterochloroform with concentrated ammonia solution below -35°. The deuterochloroform solution was washed several times with the ammonia at this temperature until the color of copper ion disappeared and was then shown by nmr to be free of fragmentation products (7).

This solution was irradiated at -30±5° using a 450-W high pressure mercury lamp equipped with a Pyrex-filter. The decomposition of the azo compound was monitored by its nmr spectrum and took 4.5 hr. No change in the nmr was observed for an unirradiated solution under otherwise identical conditions. Capillary vpc analysis of the reaction mixture (column: Ucon oil LB-550X 0.25mm x 45 m) revealed five products in the area ratios of 92, 6, 1, 1, and 0.3. The major, 92, and minor, 0.3, products were identified as 1,4-cyclohexadiene and benzene, respectively. A mixture of the 6, 1, and 1 products was



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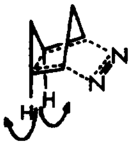
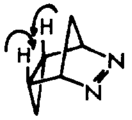


(thermally, but not photochemically)



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isolated from the other products by washing the reaction solution at 0° with a saturated aqueous silver nitrate solution and then, by passing the solution at 0° through an $AgNO_3$ (20%)—alumina column. The nmr spectrum thereafter showed no peaks in the vinyl region and the major signals were identical with those reported for trans-tricyclo[3.1.0.0^{2,4}]hexane (7) (8). Such inversion of configuration as observed on the transformation into 7 is generally favored in the decomposition of polycyclic azo compounds (1,6,9).

Consequently, it is concluded that the thermolysis of **6** produces only one compound, while photolysis gives several compounds. This strengthens the view that participation of a neighboring cyclopropyl ring as suggested in thermolysis is unimportant in photolysis.

It would be of particular interest to look at decompositions of the endo counterpart of **6** (**8**), not yet synthesized. We consider that the cyclopropane in the thermolysis of **6** opens with outward disrotation of the hydrogens at C_2 and C_4, and therefore predict that **8** should be thermally more stable than **6**, since **8** cannot undergo ring opening without inward flailing of its hydrogens; such would not, however, be the case with photochemical decomposition.

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