

PHOTOCHEMICAL AND THERMAL DECOMPOSITIONS OF

anti-6,7-DIAZATRICYCLO[3.2.2.0<sup>2,4</sup>]NON-6-ENE

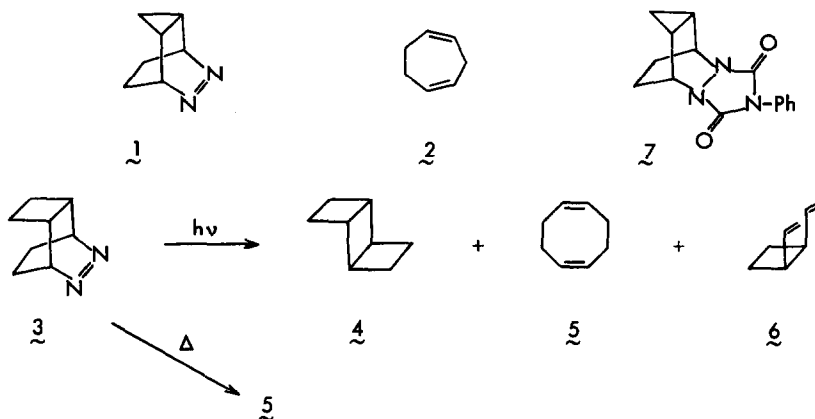
EVIDENCE FOR MECHANISTIC DIFFERENCE BETWEEN THE REACTIONS

Hiroshi Tanida, Shuji Teratake, Yoshiteru Hata, and Masamichi Watanabe

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

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Martin and Roth recently reported that the photochemical decomposition of anti-6,7-diazatricyclo-[3.2.2.0<sup>2,4</sup>]non-6-ene (1) in ether at -60°,<sup>1</sup> as well as the thermal decomposition<sup>1,2</sup> at a room temperature, produced only cyclohepta-1,4-diene (2) with elimination of molecular nitrogen. In the

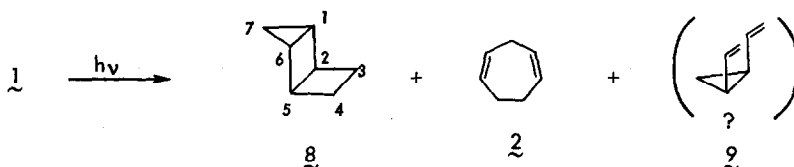


preceding communication,<sup>3</sup> we found that the photochemical decomposition of anti-7,8-diazatricyclo-[4.2.2.0<sup>2,5</sup>]dec-7-ene (3) (a 3,4,5,6-tetrahydropyridazine derivative) proceeded forming one saturated anti-tricyclo[4.2.0.0<sup>2,5</sup>]octane (4) and two unsaturated cycloocta-1,5-diene (5) and cis-1,2-divinylcyclobutane (6), while the thermal decomposition yielded only 5. We were interested in the fact that whereas 1 gave the identical product in photolysis and thermolysis, 3 gave the different products. Does either the cyclopropyl ring in 1 or the cyclobutyl ring in 3 have a major effect on the reaction? To solve this question we undertook reinvestigation of decompositions of 1.

The adduct of cycloheptatriene with 1-phenyl-1,2,4-triazoline-3,5-dione<sup>4</sup> was reduced over Pd-

charcoal to give 7. Hydrolysis-decarboxylation with sodium methoxide in dimethylsulfoxide converted 7 into a hydrazine, which was oxidized with cupric chloride leading to the CuCl complex of 1, mp 120° (decomp). Anal. Calcd for C<sub>7</sub>H<sub>10</sub>N<sub>2</sub> CuCl: C, 38.01; H, 4.56. Found: C, 38.23; H, 4.57. The complex was decomposed with aq sodium hydroxide to give 1, which was accommodated into cold ether and immediately used in the next step, because of its instability at room temperature.

The photolytic decomposition of 1 in ether at -20° with 300-w high-pressure mercury lamp, equipped with a Pyrex-filter, produced anti-tricyclo[4.1.0.0<sup>2,5</sup>]heptane (8) in 20% yield and 2 in 60% yield.

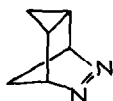
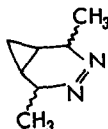


Variation of the reaction temperature from -70° to 0° did not affect the product composition. The structure of 8, bp 80° (760 mm), was indicated by both elementary analysis and spectral data. Anal. Calcd for C<sub>7</sub>H<sub>10</sub>: C, 89.29; H, 10.71. Found: C, 88.99; H, 10.64. The mass spectrum (70 eV) showed the M<sup>+</sup> ion at m/e 94, the tropylium ion at m/e 91, and the M<sup>+</sup>-(CH<sub>2</sub>-CH<sub>2</sub>) ion at m/e 66. The nmr spectrum in CCl<sub>4</sub> shows peaks at τ 7.68 (4H at C<sub>3</sub> and C<sub>4</sub>, multiplet), 7.95 (2H at C<sub>1</sub> and C<sub>6</sub>, multiplet), 8.41 (2H at C<sub>2</sub> and C<sub>5</sub>, doublet of triplets) 9.35 (exo-H at C<sub>7</sub>, quartet), 9.77 (endo-H at C<sub>7</sub>, doublet of triplets). The anti form of 8 was assigned by the fact that long-range coupling is absent in the quartet due to the exo-hydrogen at C<sub>7</sub>.<sup>5</sup> Also, the nmr did not indicate the presence of appreciable amounts of the syn-isomer of 8. When heated at 175° for 10 min, 8 was converted into a 10 : 1 mixture of two compounds, the major of which was identified as 2.<sup>7</sup> However, 8 is stable under the conditions of the thermolysis reaction, which Martin and Roth<sup>1</sup> and Allred and Hinshaw<sup>2</sup> carried out on 1. On the other hand, cis-1,2-divinylcyclopropane (9), which corresponds to 6 obtained in the photolysis of 3, does not survive the thermolysis conditions as well as the photolysis conditions.<sup>8</sup> By analogy with the results from 3, it is conceivable on photolysis that 9 is formed as a primary product from 1.

We confirmed the reported results in the thermolysis of 1. Our run gave only 2 in a yield of >98%.

As a consequence, it becomes definite that the thermolysis and photolysis of 1 produce different compounds. This is a strong indication for the existence of different mechanisms between thermolysis and

photolysis of azo compounds. It has been suggested<sup>1,2,9,10</sup> that participation by cyclopropane rings in the transition state occurs in the thermolyses of some bridged and non-bridged cyclic azo compounds. As pertinent evidence for this may be given; the high reactivities of anti-6,7-diazatricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene (10)<sup>10</sup> and 1,<sup>2</sup> and a stereochemical study of the thermolysis of the 3,4-diazabicyclo[4.1.0]heptyl

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A  
thermally, but  
(not photochemically)

system (11) by Berson and Olin.<sup>9</sup> However, the composition of the products in the present photolysis does not indicate the importance of such participation. In view of the orbital symmetry rule<sup>11</sup> we consider that participation by the cyclopropane ring is thermally, but not photochemically an allowed process (Picture A). In this regard we are currently investigating the relative reactivities of several types of azo compounds, fused with cyclopropane rings, upon thermolysis and photolysis.

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