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PHOTOCHEMICAL DECOMPOSITION OF anti-7,8-DIAZATRICYCLO[4.2.2.0^{2,5}]DEC-7-ENE

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

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

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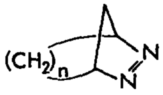
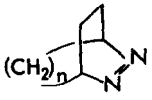
The stereochemistry involved in the decompositions of monocyclic and polycyclic 1-pyrazoline (1) and 3,4,5,6-tetrahydropyridazine (2) derivatives is currently a subject of considerable interest.[1-8] As the first observation that ring formation by the decomposition of a bicyclic 1-pyrazoline prefers inversion, Roth and Martin reported that the thermolysis in a gas phase of exo-5,6-dideutero-2,3-diazabicyclo[2.2.1]hept-2-ene (3) gave a 75 : 25 mixture of trans- and cis-dideuterobicyclo[2.1.0]pentanes (4 and 5), and that the photolysis in a gas phase, though resulting in the same products, gave decreased selectivity of products.[3a] These authors attributed the inversion to concerted elimination of nitrogen with accompanying back-side p-orbital overlap;[3a] however, Allred and Smith have proposed an alternative mechanism, in which molecular nitrogen is extruded to give 1,3-diradical-like intermediates which then form products.[4a] The existence of such intermediates in the thermodecomposition of monocyclic 1-pyrazolines has been well established by the elegant works of Crawford and coworkers.[1,2] We wish to report the first example (to the best of our knowledge) of stereospecific inversion in ring formation observed in the photodecomposition of a polycyclic tetrahydropyridazine, anti-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-7-ene (6).[9]



1



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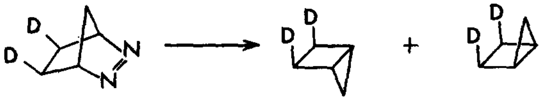

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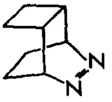

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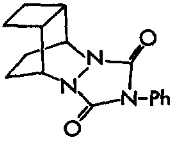
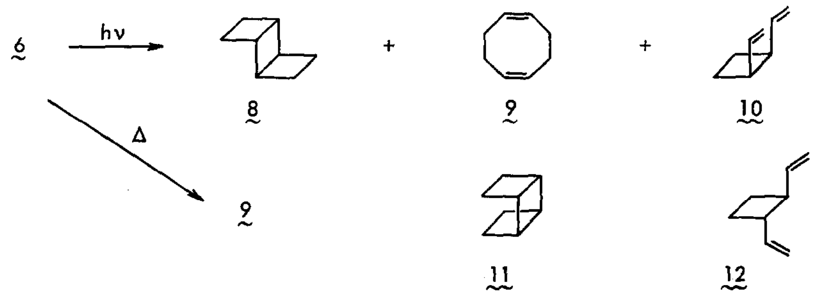


7

The Diels-Alderadduct of cyclooctatetraene and 4-phenyl-1,2,4-triazoline-3,5-dione was hydrogenated to give 7.[10] The orientation of the cyclobutane ring is established as *anti* to the triazo ring by the works of Masamune[11] and Berson.[8] Treatment of a dimethylsulfoxide solution of 7 with sodium methoxide under nitrogen atmosphere, followed by neutralization with dilute hydrochloric acid and then addition of aq. cupric chloride, afforded the CuCl complex of 6 in a sufficiently pure state for use in the next steps. The complex was decomposed with aq. sodium hydroxide to give 6, mp 142-143°; UV max (ether) 284 mμ. *Anal*. Calcd for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.67; H, 8.89; N, 20.82.

When irradiated in an ether solution at -20° using a 450-w high-pressure mercury lamp equipped with a Pyrex-filter, 6 produced four compounds (by Ucon-R 15 m capillary vpc) plus a major nonvolatile material.[12] Among the four, three important compounds were identified as *anti*-tricyclo[4.2.0.$0^{2,5}$]octane (8, 18% yield), cycloocta-1,5-diene (9, 7%), and *cis*-1,2-divinylcyclobutane (10, 5%). For identifications, authentic samples of 8 and 10 were prepared by the methods of Nenitzescu, *et al*.[13] and Hammond, *et al*.,[14] respectively. An authentic sample of 9 is commercially available. The *syn* isomer of 8 (11)[13] and the *trans* isomer of 10 (12)[14a] was demonstrated to be absent, or at least not present in amounts greater than 0.1% (by comparison of retention times on capillary vpc with authentic samples). All the products, as well as 11 and 12, were found to be stable under the reaction conditions. Therefore, once formed, 11 and 12 should be detectable.



When 6 was thermally decomposed at 160° for 1 hr, only 9 was formed, in more than 90% yield.[15] It was found however that, even if 8 and 10 are primary products, the reaction conditions convert them into 9.[16,17]

The fact that the yield of 9 is not so different from that of 10 does not favor an importance of participation of the cyclobutyl bonding electrons of 6 in the products-forming transition state. Although it is not definite at the present stage of our investigation whether all or any of the products are produced with loss of nitrogen concertedly or with collapse of an initially-formed intermediate 1,4-diradical(s), the assumption of such a diradical(s) seems to accommodate best all the present results. In any case the completely stereospecific inversion on ring formation in 8 is very noteworthy.

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REFERENCES

1. R. J. Crawford, et al., J. Amer. Chem. Soc. 87, 3023, 3768 (1965); 88, 2589, 3963 (1966); 89, 3907, 3908 (1967); Can. J. Chem. 45, 691 (1967).
2. A. Mishra and R. J. Crawford, Can. J. Chem. 47, 4515 (1969).
3. W. R. Roth and M. Martin, (a) Ann. Chem. 702, 1 (1967); (b) Tetrahedron Lett. 3865 (1967); (c) ibid. 4695 (1967); (d) M. Martin and W. R. Roth, Chem. Ber. 102, 811 (1969).
4. (a) E. L. Allred and R. L. Smith, J. Amer. Chem. Soc. 89, 7133 (1967); (b) E. L. Allred and J. C. Hinshaw, ibid. 90, 6885 (1968); (c) J. C. Hinshaw and E. L. Allred, Chem. Commun. 72 (1969); (d) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, J. Amer. Chem. Soc. 91, 3382 (1969); (e) E. L. Allred and J. C. Hinshaw, Chem. Commun. 1021 (1969).
5. (a) P. D. Bartlett and P. S. Engel, J. Amer. Chem. Soc. 90, 2960 (1968); (b) P. D. Bartlett and N. A. Porter, ibid. 90, 5317 (1968).
6. T. Sanjiki, H. Kato, and M. Ohta, Chem. Commun. 496 (1968).
7. A. B. Evnin and D. R. Arnold, J. Amer. Chem. Soc. 90, 5330 (1968).
8. J. A. Berson and S. S. Olin, J. Amer. Chem. Soc. 91, 777 (1969).
9. The thermolysis of 6 in a gas phase was very recently reported by an independent group. See reference 4e.
10. R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, J. Chem. Soc., C 1905 (1967).
11. S. Masamune, H. Cuts, and M. G. Hogben, Tetrahedron Lett. 1017 (1966).
12. A monochromatic light (380 ± 10 mμ) with a JASCO CRM-FA Irradiation spectrometer gave identical results.
13. M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, Chem. Ber. 97, 382 (1964).
14. (a) G. S. Hammond, N. J. Turro, and R. S. H. Liu, J. Org. Chem. 28, 3297 (1963); (b) G. S. Hammond and C. D. DeBoer, J. Amer. Chem. Soc. 86, 889 (1964).
15. This result confirms the data independently obtained by Allred and Hinshaw.[4e]
16. The first-order rate constants of isomerization of 8 and 11 to 9 were determined: for 8, 4.98×10^{-5} sec^{-1} at 131.6° and 3.14×10^{-4} at 151.2°; for the syn, 3.18×10^{-4} sec^{-1} at 131.6° and 1.96×10^{-3} at 151.2°.
17. For rates and products of the isomerizations (Cope rearrangements) of 10 and 12, see reference 14b.