

Photochemical Isomerization of 9-Cyano-9-azabicyclo[4,2,1]nona-2,4,7-triene

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CURRENT concern with photochemical isomerizations of bicyclic π -systems¹ prompts us to record some preliminary observations on the photochemical reorganization of the title compound, (I)

Irradiation of a dilute solution of (I)² in pentane (0.016% w/v) at *ca.* 10° with a high-pressure 450W mercury arc leads to 9-cyano-9-azabicyclo[6,1,0]nona-2,4,6-triene, (II). The isomerization occurs rapidly in quartz and slowly in Pyrex. For example, irradiation through quartz for 5 min. produces a clean mixture consisting of 54% (I) and 46% (II) whereas irradiation through a Pyrex filter for 1 hr. leads to an 83:17 mixture of (I) to (II), respectively.† Short reaction times are necessary when the irradiation is carried in quartz as (II) is itself labile to light. Thus, irradiation through quartz for a period of 20 min. produces a complex mixture in which neither (I) nor (II) can be detected. Because of thermal instability, (II) was not isolated but was positively identified by direct comparison of the n.m.r. spectrum of the two-component mixture with that of a similar

mixture prepared from reaction of cyanonitrene with cyclo-octatetraene.^{2,3}

In contrast to its pronounced photochemical instability (I) is quite stable thermally. For example, it undergoes no detectable (n.m.r., i.r.) decomposition when heated at 180° for 45 min. either as a melt or in nitrobenzene.

Although a definitive comment on the mechanism of the transformation would be premature at this stage, the virtually complete absence of by-products is suggestive of a concerted sigmatropic reorganization.‡§ As such, the isomerization deserves brief description in terms of orbital symmetry requirements.⁴

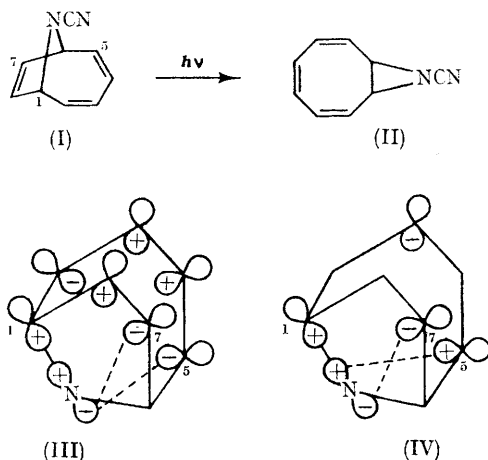
In principle, the rearrangement described here can occur either by a 1,3(C-1 to C-7) or 1,5(C-1 to C-5) migration of the NCN bridge. In turn, either shift may occur in one of two distinct ways depending on whether in the transition state the originally bonding or antibonding lobe of the ring nitrogen is interacting with the migration terminus. The orbital symmetries describing the observed

† The composition of the mixtures was determined by n.m.r. In each case the reaction mixture accounts for *ca.* 95% of the reactant.

‡ Involvement of the ring-nitrogen lone-pair of electrons in the rearrangement appears unlikely in view of the presence of the cyano-function. This, for obvious reasons, reduces the availability of the electron pair on the ring nitrogen in both the ground state and the excited state ($n-\pi^*$ charge transfer state) of the NCN chromophore.

§ An alternative mechanism involving fragmentation of (I) to NCN and cyclooctatetraene followed by recombination of the two fragments in a 1,2 fashion to produce (II) is very unlikely in view of the complete absence of any NCN-solvent insertion products. Both singlet and triplet NCN "insert" fairly efficiently into C-H bonds of saturated hydrocarbons; A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1966, **88**, 2322.

photorearrangement and an analogous, hypothetical, thermal rearrangement are depicted in (III) and (IV), respectively.[¶] It can be readily seen that within this orbital picture (III) can lead to (II) only by way of backside bonding irrespective of whether a 1,3 or a 1,5 shift is involved,



i.e., a concerted photorearrangement of (I) to (II) must occur through backside bonding to the migration terminus. The situation in the hypothetical thermal isomerization is less straightforward since here the orbital symmetry arrangement (IV) requires a 1,3 shift to occur through back-side bonding and a 1,5 shift to occur by way of front-side bonding to the migration centre. In short, the symmetry requirements in (III) and (IV) are similar for a 1,3 shift but opposite for a 1,5 migration. This, coupled with the thermal stability of (I) suggests a distinct preference for the 1,5 process over the 1,3 process. Such preference is in keeping with the notion⁵ that, if given a choice, a sigmatropic change will follow the path of maximum conjugation. The possible non-equivalence of migration termini C-5 and C-7 is currently examined by means of appropriately labelled compound (I).

A complete study of the photoisomerization of (II) is currently under way.

We gratefully acknowledge financial support by the National Science Foundation and by the Chemistry Department of Syracuse University.

(Received, June 22nd, 1967; Com. 640.)

[¶] The orbital arrangements in (III) and (IV), are respectively those of ψ_5 and ψ_4 of the heptatrienyl system.

¹ See, for example, W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, 1966, **88**, 2078; W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 1967, 349; J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, 1967, **89**, 2778.

² A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1965, **87**, 5512.

³ A. G. Anastassiou, unpublished results.

⁴ R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.