PHOTOCHEMISTRY OF BRIDGED CYCLOHEPTADIENES.¹ MULTIPLICITY DEPENDENT PERICYCLIC REARRANGEMENTS OF EXCITED BICYCLO[4.2.1]NONA-2,4-DIENE-7,7,8,8-TETRACARBONITRILE

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Summary: Bicyclo[4.2.1]nona-2,4-diene-7,7,8,8-tetracarbonitrile rearranges selectively under direct irradiation in acetonitrile to tricyclo[$3.2.2.0^{2,4}$]non-6-ene-8,8,9,9-tetracarbonitrile, and upon acetone sensitization to bicyclo[3.2.2]nona-2,6-diene-8,8,9,9-tetracarbonitrile. Both products are derived from sigma bond cleavage, in contrast to the parent unsubstituted diene where only the m-bonds react.

The periselectivity of photochemical rearrangements if often reported to be extremely sensitive to the nature of substituents.² In this context, the introduction of two cyano groups on a saturated carbon is of special interest. While the malononitrile group itself is only weakly chromophoric, it can stabilize both diradical and zwitterionic intermediates derived from excitation of adjacent chromophores. This explains the observed cleavage of the dicyano-substituted sigma bond in photochemical rearrangements of di- π -methane^{3,4} and cyclo-propylketone⁵ systems containing the malononitrile group.

It has been previously reported that bicyclo[4.2.1] nona - 2,4-diene (I, R=H) and its vinyl-substituted chloro derivatives, undergo a selective photoelectrocyclic reaction to give cyclobutenes (II).⁶ A mixture of the exo and endo isomers was obtained, though in different ratios, from both the singlet and triplet excited states (eq. 1). Likewise, the 7-cyano derivative (III), upon either direct or sensitized irradiation, afforded only a mixture of dimeric 2+2 cycloadducts (eq. 2).⁷ Obviously, in both cases only π -components participated in the reaction.



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We wish to report herein that the photochemistry of bicyclo[4.2.1]nona-2,4-diene-7,7,8,8-tetracarbonitrile (V),⁸ the formal 6+2 adduct of cycloheptatriene and tetracyano-ethylene (TCNE), takes a completely different course, favoring rearrangements involving cleavage of the allylic sigma bonds.

Direct irradiation of (V) (254nm, quartz NMR tubes, 30mM, CD_3CN) afforded a single product which was identified from its ¹H NMR spectrum as tricyclo[3.2.2.0^{2,4}]non-6-ene-8,8,9,9-tetracarbonitrile (VI)⁹. On the other hand, the sensitized irradiation of (V) (310nm, pyrex, 20mM, in $(CD_3)_2CO$) provided a different isomeric product, identified as bicyclo[3.2.2]nona-2,6-diene-8,8,9,9-tetracarbonitrile (VII)^{8,10} (eq. 3).¹¹ In none of the experiments could any other isomeric products be detected. Interestingly, (VII) was unreactive in both excited states, even though related bicyclic hydrocarbons usually undergo the di- π -methane rearrangement upon either direct or sensitized photolysis.¹² We also note that no rearrangement of (VII) to (VI) occurred under the conditions in which (V) rearranged to (VI).



The mechanism of the photorearrangements of (V) clearly involves cleavage of allylic sigma bonds. A reasonable pathway for the triplet reaction includes a suprafacial 1,3-sigmatropic carbon migration, often observed in the photosensitization of activated allylic sigma bonds.¹³ However, it is more difficult to envision the singlet reaction as an intramolecular process. Furthermore, realizing that (VI) is the product of the thermal reaction of cycloheptatriene with TCNE,⁹ we suspected that the mechanism of the singlet reaction might involve more than one step. In order to test this hypothesis, (V) was irradiated in the presence of an excess of cyclohexadiene. The reaction mixture contained cycloheptatriene and a single adduct (VIII), which is derived from the thermal 4+2 reaction of cyclohexadiene and TCNE¹⁴ (eq. 4). This clearly indicates that the singlet reaction of (V) proceeds in two consecutive steps. Initially, an unusual photochemically allowed 6+2 cycloreversion¹⁵ occurs to give cycloheptatriene and TCNE. This is followed by a thermal Diels-Alder cycloaddition of the products,⁹ affording (VI) (eq. 5).



The observed periselectivity of (V) toward sigma bond cleavage may be attributed to the substantial weakening of its allylic sigma bonds by the dicyano groups. If we assume that a homolytic bond clevage follows the excitation of the butadiene function, then the incipient triplet diradical derived from (V) is estimated to be more stable than the corresponding diradical obtained from (I) by ca. 28 kcal/mole.^{16,17} This, together with the steric congestion expected to develop by ring closure to cyclobutene, makes the 1,3-migration and the cycloreversion more favorable than the electrocyclic reaction.

Finally, the multiplicity dependence observed in the photochemistry of (V) indicates that the singlet and triplet excited states do not decay along a common pathway, but rather via two different electronic states. Since, however, both excited states are those of butadiene, it is perhaps the differences in polarity of the electronic states 1^{7} which are responsible for the different chemical consequences.

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(Received in UK 29 June 1987)