Specific Photodimerization of 9-Cyano-9-azabicyclo[4,2,1]nona-2,4,7-triene. Synthesis of a Novel Dimer of Cyclo-octatetraene

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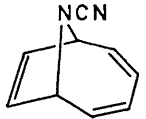
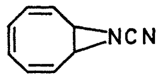
Summary Sensitized irradiation of 9-cyano-9-azabicyclo-[4,2,1]nona-2,4,7-triene produces a single dimeric product, characterized through its conversion into a novel dimer of cyclo-octatetraene.

RECENTLY, we indicated[1] that (I) undergoes rapid valence isomerization to (II) when subjected to direct irradiation. We now report that sensitized excitation of (I) leads, exclusively and specifically, to cyclodimerization. Thus, illumination (through Pyrex) of a dilute, degassed, benzene solution of (I) and benzophenone with a 450 w "Hanovia" light source at ambient temperature generates a single $C_{18}H_{16}N_4$† substance in 70% yield. The dimer, m.p. 220—221°, displays the following spectral characteristics: {ν_{max} (KBr) 2200 cm^{-1}; λ_{max} (MeOH) 203 nm (ϵ 4300 at 220 nm); n.m.r. τ [$(CD_3)_2SO$] 4·0—4·4 (8H multiplet), 5·2—5·5 (4H multiplet), and 6·5—7·1 (4H multiplet)}. The spectral information readily eliminates a number of possible structures. In the first place, the occurrence of only end-absorption in the u.v. spectrum requires that the dimer contain only isolated olefinic functions. Consequently, one can safely dismiss any "tail-to-tail" or "head-to-tail" structures.‡ Secondly, the n.m.r. spectrum appears to be much too simple for a "4 + 2" "head-to-head" structure and far too complex for a "4 + 4" "head-to-head" arrangement. Hence, of all possible dimeric structures only the two "2 + 2" "head-to-head" arrangements (V) and (VI) are fully consistent with the available spectral information.



(I)



(II)

Clearly, structures (V) and (VI) are not readily distinguishable. Mechanistic considerations do, however, provide a reasonably safe provisional choice between the two. There exists, for example, a large body of compelling experimental evidence that photosensitized dimerization of butadiene occurs in such a fashion as to generate the most stable diradical intermediate.[2] Close analogy thus points to (III) as the preferred intermediate which should in turn produce (V) but not (VI). Significantly, bonding interaction eventually leading to (III) is also favoured on the basis of the magnitude of the product of appropriate frontier-orbital atomic coefficients,§ a criterion which, unlike radical stability, predicts the course of reactions

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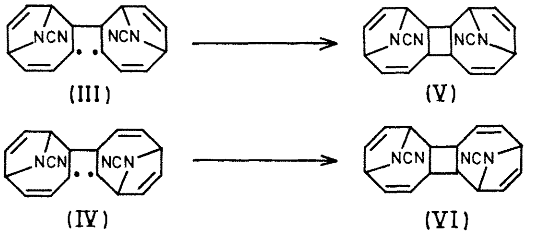
† Satisfactory elemental analyses and molecular weights were obtained for all new compounds described.

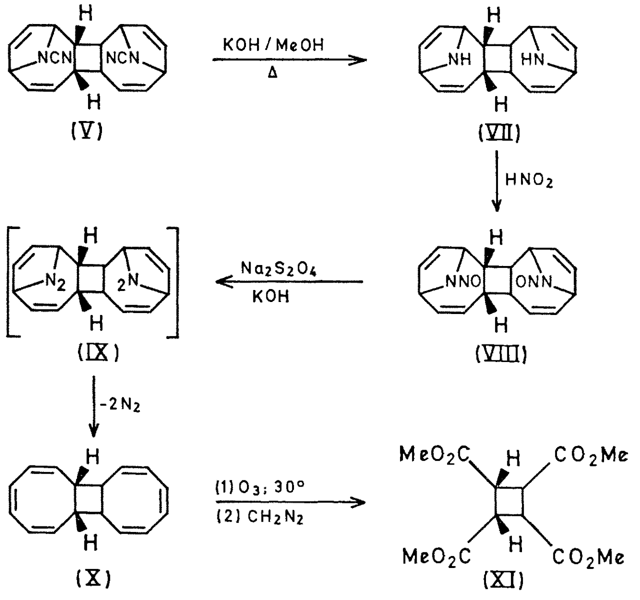
‡ The terms head and tail refer, respectively, to the butadiene and ethylene segments of (I).

§ ψ_3 of butadiene is the frontier molecular orbital of choice for either interacting monomeric unit. In this $c_1 = c_4 = 0{\cdot}6$ and $c_2 = c_3 = 0{\cdot}37$. Hence, $c_1^2 > c_1c_2$.

involving "early" transition states. We therefore conclude that mechanism favours structure (V) over (VI) irrespective of whether the transition state for dimerization materializes early or late along the reaction co-ordinate.

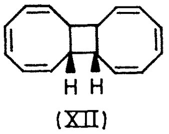


The photoproduct was characterised as an *anti* "2 + 2" dimer as in the Scheme. Prolonged treatment of the dimer with hot, concentrated, methanolic hydroxide produced a diamine (VII) m.p. 100—101° in 65% yield. This compound, shown to be formed without rearrangement, through its ready conversion into the photodimer on treatment with cyanogen bromide, is characterized by the following spectral data: ν_{max} (KBr) 3250 cm^{-1}; λ_{max} (C_6H_{12}) $<$ 210 nm (ϵ 7100 at 220 nm); n.m.r. τ [$(CD_3)_2CO$], 3·9—4·8 (8H multiplet), 5·8 (2H broad doublet, *J ca.* 6 Hz), 6·1 (2H broad singlet), 6·9—7·2 (4H multiplet), and 7·4 (2H sharp, exchangeable, singlet). The diamine (VII) was then treated with an excess of sodium nitrite in dilute mineral acid to produce, cleanly and quantitatively, a bis-nitroso-derivative (VIII) m.p. 203—204° [ν_{max} (KBr) 1420, 1320, and 1220 cm^{-1}; λ_{max} (CH_3CN) 358 nm (ϵ 158) and 238 nm (ϵ 11,300); n.m.r. τ ($CDCl_3$) 3·9—4·7 (12H multiplet) and 6·9—7·5 (4H multiplet)], which was readily re-converted into its diamine progenitor (VII) on treatment with tin(II) chloride in mineral acid. Treatment of (VIII) with sodium hydrosulphite¶ in warm alkali led to rapid gas evolution and the formation, in 65% yield, of a crystalline $(CH)_{16}$ hydrocarbon, m.p. 98—99°, [ν_{max} (KBr) 2920, 2820, 792, and 708 cm^{-1}; λ_{max} (C_6H_{12}) 248 nm (ϵ 4580) and 213 nm (ϵ 30,000); n.m.r. τ ($CDCl_3$) 4·2 (12H unsymmetrical doublet) and 7·0 (4H sharp singlet)]. The spectral characteristics of this compound are entirely as expected for a "2 + 2" dimer of cyclo-octatetraene, but its m.p. differs greatly from that of the known *syn* "2 + 2" dimer (m.p. 53°).[4] Definitive chemical proof that the $C_{16}H_{16}$ substrate is indeed the previously unknown *anti* "2 + 2" dimer of cyclo-octatetraene (X) was obtained through exhaustive ozonolysis (oxidative work-up) followed by treatment with diazomethane. This sequence produced *cis,trans,cis*-1,2,3,4-tetrakismethoxycarbonylcyclobutane (XI) entirely identical (mixed m.p.; i.r.) with an authentic sample.**



SCHEME

We are studying the thermal and photochemical behaviour of hydrocarbon (X).



(XII)

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¶ We chose this reagent for overall extrusion of two moles of N_2O from (VIII) strictly on the basis of orbital symmetry. The bisdiazine (IX), believed to be a fleeting intermediate[3] in such a process, is ideally suited for ready extrusion of two moles of nitrogen; *i.e.*, the relative signs of key atomic coefficients c_1 and c_4 in ψ_3 (HOMO) of hexa-1,3,5-triene are such as to allow for disrotatory (sigmasymmetric) extrusion of molecular nitrogen.

** We note that the available information concerning hydrocarbon (X) does not serve to eliminate the alternative "chair" arrangement shown in (XII). Nevertheless, we believe this arrangement to be sterically impossible within the original dimer (V) on account of the stringent conformational requirements imposed by the two nitrogen bridges.

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