

REACTION OF CYCLOHEPTATRIENYLIDENE WITH 1,2-DICYANOCYCLOOCTATETRAENE.¹⁾

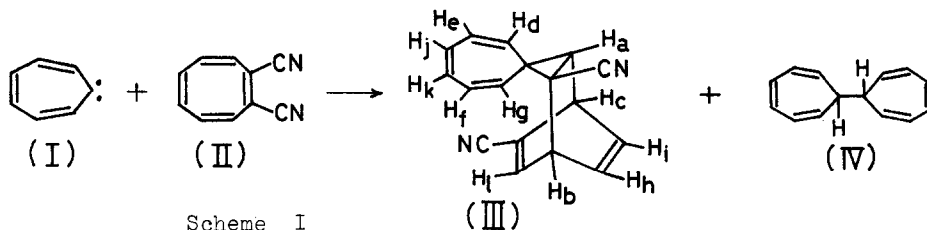
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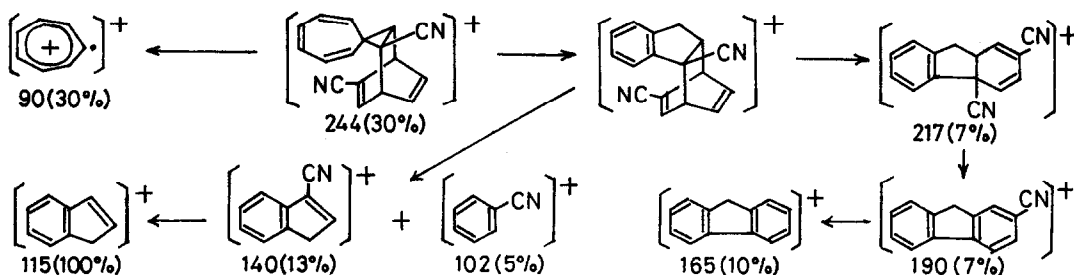
In a series of studies on the addition reactions of cycloheptatrienyliidene (I) a singlet carbene with nucleophilic property (2-5), we investigated the reaction of I with 1,2-dicyanocyclooctatetraene (II)(6), which possesses an electron poor double bond attached to two cyano groups. We wish to report here the formation of an intriguing product (III), which probably arose from the addition of I to II followed by thermal isomerization, in addition to the unexpected formation of bitropyl.

When troponetosylhydrazone sodium salt was decomposed in the presence of II by heating at 120° in diglyme, nitrogen was evolved quantitatively, and an addition product (III) and bitropyl (IV) were obtained in 3 and 12.5% yields respectively accompanied by a large amount of resinous material.

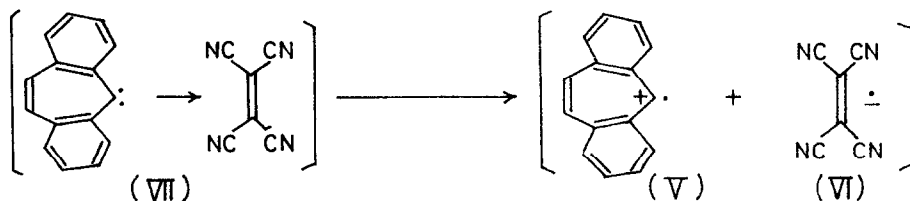


The product III is crystalline, mp 202°, and its molecular formula, C₁₇H₁₂N₂ and molecular ion (M⁺, 244, 30%) suggest that III is a 1:1 adduct of I and II. Other spectral properties are as follows: uv (in methanol) 255 nm (log ε, 3.76); ir (KBr) 2245 and 2220 cm⁻¹; nmr (100 MHz, in CDCl₃, δ ppm) 2.32 (H_a, doublet), 3.90 (H_b, quartet), 5.31 (H_c, quartet), 5.7-6.2 (H_d-H_g, 4H, multiplet), 6.3 (H_h and H_i, multiplet), 6.8 (H_j and H_k, triplet), 7.03 (H_l, doublet), coupling constants in Hz J_{ac}=6, J_{bl}=7, J_{bh}=9, J_{bi}=1, J_{ch}=0.5, J_{ci}=8, J_{hi}=ca.10. The ir

spectrum shows the existence of two kinds of cyano groups, i.e., a nonconjugated one and the other conjugated with a double bond. The former (2245 cm^{-1}) is almost the same as the cyano group of 1,2-dicyanospiro[2,6]nona-4,6,8-triene (4). In addition, the chemical shift of H_a is similar to that of the cyclopropane protons of the spiro[2,6]nonatriene system, and the shifts of H_d - H_g and H_j and H_k are similar to those of the cycloheptatriene moiety of the spiro[2,6]nonatriene system. Thus, these data suggest the existence of the 1-cyanospiro[2,6]nona-4,6,8-triene moiety. On the other hand, the chemical shifts of the other protons, H_b , H_c , H_h , H_i and H_l are nearly coincident with those of the corresponding protons of barrelene and 2,3-dihydrobarrelene derivatives (7). Furthermore, in acidic media, the uv spectrum of III exhibits a new absorption maximum around 353 nm, which seems to be ascribed to heptafulvene derivatives (9). The fragmentation pattern of the mass spectrum of III, which is shown below, would support the correctness of the proposed structure for III.

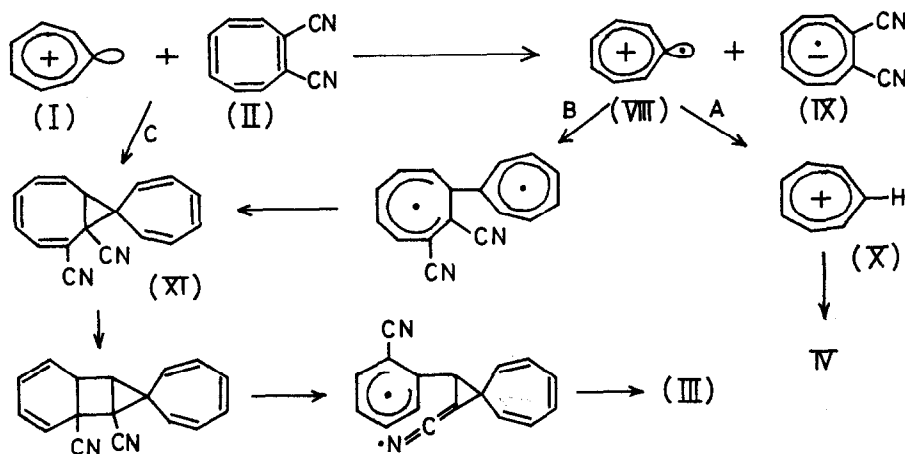


Since the formation of bitropyl (IV) has not been reported in the reaction of I (3), the consideration of the reaction mechanism would be of interest. The controlled experiments showed that both I and II were needed for the formation of IV. Recently, Moritani, Yamamoto and Murahashi reported that in the reaction of dibenzocycloheptatrienyliene with tetracyanoethylene, radical cation (V) and radical anion (VI) were formed via the C-T complex (VII) (10).



1,2-Dicyanocyclooctatetraene (II) can also be stabilized as an anion, so it seems reasonable that an electron is transferred from I to II affording radical cation (VIII) and radical anion (IX). Then, the resulting radical cation (VIII) abstracts a hydrogen from surrounding solvent (path A in Scheme III), and affords tropylium cation (X), which in turn is transformed into bitropyl (IV) as is known in the literature (11).

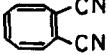
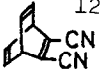
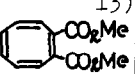

To account for the formation of III, it is considered that an adduct (XI) of VIII and IX rearranges thermally into III via valence isomerization followed by 1,3-carbon migration as shown in path B in the following Scheme. However, the possibility that XI was afforded directly from I and II (path C in the Scheme III) could not be ruled out.



Scheme III

On the basis of these considerations, it is expected that the more electron acceptable the substrate is, the more easily the electron transfer from I takes place. Thus, we synthesized dimethylcyclooctatetraene-1,2-dicarboxylate and 2,3-dicyanobarrelene and investigated the reaction of I with them. As expected, it was found that the formation of IV was closely related to the electron affinity of the substrates. For instance, the yield of IV increased when the polarographic reduction potential of the substrates became larger, as shown in the Table. Thus, this result seems to support our interpretation that electron transfer between I and II resulted in the formation of bitropyl (IV).

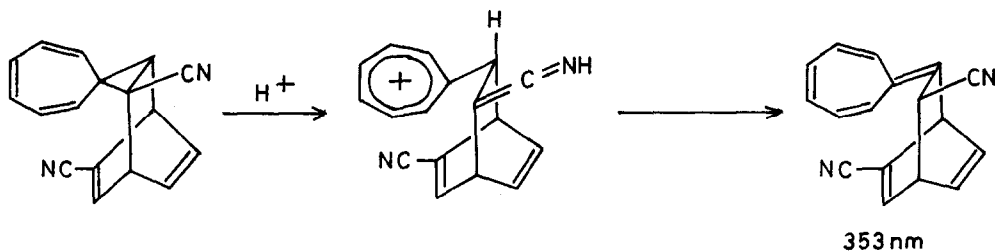
Table The relationship between yield of III and reduction potential of the substrates

| |  |  |  |  |
|---------------------|---|---|--|---|
| reduction potential | -0.93 V | -1.47 V | -1.48 V | -1.79 V |
| yield of III (%) | 12.5 | 3 | 2.5 | 0.9 |

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9. This absorption maximum is quite reasonable for a heptafulvene derivative (2,3,8). Although the heptafulvene derivative was not isolated because of the unstability of the system without an electron withdrawing group, its formation is explained by the following reaction path.



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