Addition of Cycloheptatrienylidene to 2,3-Dicyanobicyclo[2,2,2]octatriene

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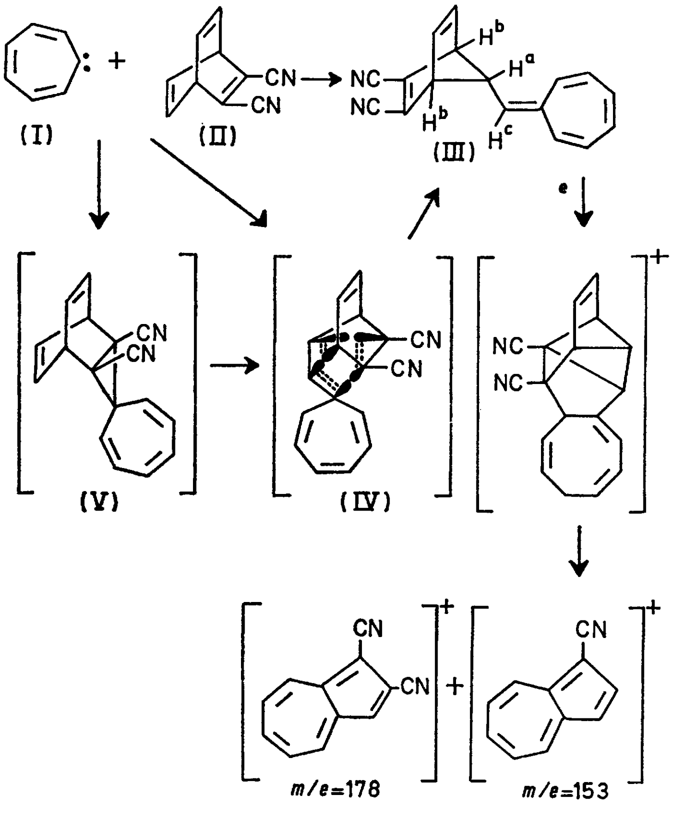
Summary Reaction of cycloheptatrienylidene (I) with 2,3-dicyanobicyclo[2,2,2]octatriene (II) afforded an unexpected product (III), presumably formed *via* a carbene addition mechanism.

SEVERAL recent reports have described the addition of cycloheptatrienylidene (I) to olefins having electron withdrawing groups.[1] We report here that the carbene (I) reacts with 2,3-dicyanobarrelene (II) to give, unexpectedly, compound (III).

When tropone tosylhydrazone sodium salt was heated at 120 °C in diglyme in the presence of compound (II), nitrogen was evolved quantitatively, and a red oily product (III)† (8%) was obtained together with heptafulvalene (6%) and bitropyl (3%). Assignment of structure (III) was based on spectral and chemical evidence: λ_{max} (MeOH) 244 and 359 nm (log ϵ, 4·16 and 3·95); ν_{max} (neat), 2192 cm^{-1}; δ (100 MHz; CDCl$_3$)‡ 1·98 (H^a), 5·48 (H^b), and 6·4—6·8 (remaining 9H), J_{ab} 7, J_{ac} 5·5 Hz; *m/e* 244 (3%, M^+), 178 (30), 153 (12) and 128 [100, $C_6H_4(CN)_2$]. The spectral data suggest that the CN groups are conjugated with a double bond (i.r.), and a heptafulvene (u.v.)[2] and a bicyclo-[2,2,1]hepta-2,5-diene fragment (n.m.r. and mass). The mass spectrum can be explained by the fragmentation pattern in the Scheme. When compound (III) was heated at 250 °C in the presence of Pd–C in xylene, 1-cyanoazulene, m.p. 55°,[3] was obtained (25%).

We suggest that compound (III) is formed *via* a mechanism involving the adduct (IV), which is formed by the homo-1,4-addition of (I) to (II) or by a thermal homo-1,3-carbon shift of the adduct (V) which is formed first.

Thermal rearrangement of (IV) to (III) is considered to be a [$_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$] process and likely to occur, because of the good overlap of the three σ-bonds, and the relief of strain in the three- and four-membered rings.



SCHEME

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† Elemental analysis was satisfactory.

‡ All chemical shifts and coupling constants were confirmed by double and triple resonance experiments.

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