

Thermal Dimerization of (Cyanomethylene)cycloheptatriene (8-Cyanoheptafulvene); Synthesis of a Dihydrobenzo[1,2:4,5]dicycloheptene

By MASAJI ODA, YASUTAKA KAYAMA, and YOSHIO KITAHARA*

(Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan)

Summary Thermal dimerization of 8-cyanoheptafulvene (II) gave a dimer, the benzodicycloheptene (III), which may be formed *via* an 8 + 8-type dimer (VII).

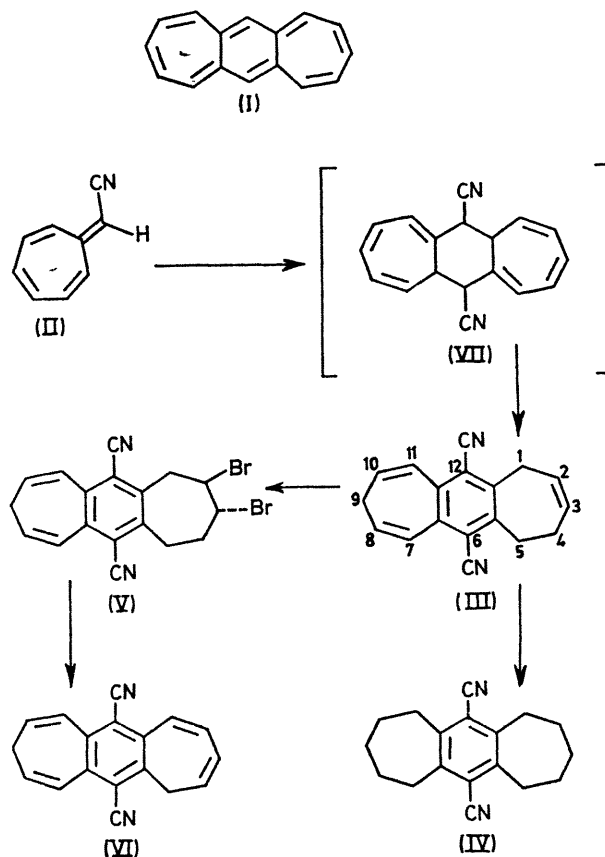
8 + 8-DIMERS of heptafulvenes might be potential intermediates in the synthesis of the new cyclic conjugated system (I). Although the attempted photochemical 8 + 8-dimerization of 8-cyanoheptafulvene (II)^{1,2} has failed so far, it appears that the polar character of (II) makes the 8 + 8-type dimerization thermally probable. We report here our results for this system.

Heating of (II) under reflux with mesitylene for 21 h gave the dimer (III) as prisms, m.p. 172–173 °C, (20–28%); mass spectrum, *m/e* 258 (*M*⁺, 100%), 243(95), 229(46), 204(36), 182(36), 154(73), and 149(31). The i.r. spectrum showed ν_{\max} (KBr) 3010w, 2950w, 2880w, 2220m, 1658w, 1632w, 1430s, 760s, and 735s cm⁻¹, indicating the presence of a conjugated cyano-group and two types of double bond. The u.v. spectrum (EtOH) showed maxima at 225sh (log ϵ 4.42), 233 (4.45), 247(4.44), 257(4.41), and 348 nm (3.66). The n.m.r. spectrum (100 MHz; CDCl₃; Me₄Si) exhibited signals at τ 3.10 (1H, d, *J* 10.3 Hz, 7- or 11-H), 3.12 (1H, d, *J* 10.3 Hz, 11- or 7-H), 3.87 (2H, dt, *J* 10.3 and 6.5 Hz, 8- and 10-H), 4.26 (1H, dtt, *J* 11.2, 5.2, and 2.0 Hz, 2-H), 4.48 (1H, dtt, *J* 11.2, 3.0, and 0.6, 3-H), 6.19 (2H, dtd, *J* 5.2, 2.0, and 0.6 Hz, 1a- and 1b-H), 6.61 (2H, dd, *J*, 7.5 and 5.5 Hz, 5a- and 5b-H), 7.55 (2H, m, 4a- and 4b-H), and 7.57 (2H, t, *J* 10.3 Hz, 9a- and 9b-H). On irradiation at τ 7.55, the signals at τ 3.87 changed into a doublet (*J* 10.3 Hz), that at 4.26 to dt (*J* 11.2 and 5.2), that at 4.48 to dt (*J* 11.2 and 1.0), that at 6.19 to dd (*J* 5.2 and 0.6), and that at 6.61 to a singlet. On irradiation at τ 6.19, the signals at τ 4.26 changed to dt (*J* 11.2 and 2.0), and that at 4.48 to dt (*J* 11.2 and 0.6). These results are consistent with the dimer having the structure (III), 6,12-dicyano-1,4,5,9-tetrahydrobenzo[1,2:4,5]dicycloheptene as shown.

Hydrogenation of (III) (Pd-C) gave the decahydro-product (IV), m.p. 212–213 °C (100%); ν_{\max} (KBr) 2925, 2850, 2230, 1456, 1426, 1190, and 960 cm⁻¹; λ_{\max} (EtOH) 213 (log ϵ 4.72), 220sh (4.56), 248 (4.24), 256 (4.28), 310 (3.64), and 321 nm (3.72); τ (60 MHz; CDCl₃; Me₄Si) 6.86 br and 8.25br with integrated area in the ratio 2:3. These data are consistent with the proposed structure.

Bromination of (III) with bromine (1 mol equiv.) in methylene dichloride, gave a dibromide (V)†, m.p. 214–215 °C (decomp.) (33% after 2 recrystallizations from CH₂Cl₂-MeOH). The i.r. absorption at 1658 cm⁻¹ (isolated double bond) observed for (III) had disappeared. The n.m.r. spectrum (60 MHz; CDCl₃; Me₄Si) showed signals at τ 2.93 (2H, d, *J* 10.2 Hz), 3.69 (2H, dt, *J* 10.2 and 6.5 Hz), 5.08 (2H, m), 5.74 (1H, dd, *J* 15.0 and *ca.* 1.0 Hz), 6.00–6.74 (3H, m), 7.48 (2H, t, *J* 6.5 Hz), and 7.57 (2H, m), indicating the presence of the 3,4-benzocycloheptatriene fragment

and no isolated double bond. The stereochemistry of the bromine substituent is not certain; however, it may be *trans*. The greater inertness of the diene system may be mainly due to the large electron-withdrawing nature of the



cyano-groups. Dehydrobromination of the crude dibromide with dimethylformamide-LiCl (90 °C) gave the dihydro-compound (VI)†, m.p. 184–185 °C (84%); ν_{\max} (KBr) 2220, 1626, 1576, 868, 777, and 758 cm⁻¹; λ_{\max} (EtOH) 227 (log ϵ 4.25), 250 (4.32), 269 (4.33), 315 (3.86), and 368 nm (3.72); τ (60 MHz; CDCl₃; Me₄Si) 2.49 (1H, d, *J* 12.0 Hz, 1-H), 3.01 (2H, d, *J* 10.0 Hz, 7- and 11-H), 3.16 br (1H, dd, *J* 12.0 and 6.3 Hz), 3.53–4.22 (4H, complex m), 6.62 (2H, d, *J* 6.3 Hz, 5a- and 5b-H), and 7.51 (2H, t, *J* 6.5 Hz, 9a- and 9b-H). These results indicate that compound (VI) has the asymmetric structure‡ as shown.

The dimer (III) presumably arises from the initially

† Satisfactory elemental analyses were obtained.

‡ A symmetrical dicyanodihydrobenzo[1,2:4,5]dicycloheptene, an isomer of (VI), has been obtained in one step by the reaction of 8-cyano-8-cycloheptatrienylheptafulvenylium fluoroborate³ with malononitrile as a minor product; to be reported.

expected 8+8-type dimer (VII) by a thermal 1,5-hydrogen shift in the cycloheptatriene fragment and subsequent aromatization of the six-membered ring under the reaction

conditions Attempts to obtain (VII) under milder conditions have failed so far.

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¹ M Oda, and Y. Kitahara, *Chem Comm*, 1969, 352

² M. Oda, and Y Kitahara, *Angew Chem*, 1969, **81**, 702 (*Internat Edn*, 1969, **8**, 673).

³ T. Otomo, M Oda, and Y Kitahara, *Chem Comm*, 1971, 114