# Novel Products in the Reaction of 6-Cyanotricyclo[5.5.0.0$^{2,5}$]dodeca-3,6,9,12-tetraene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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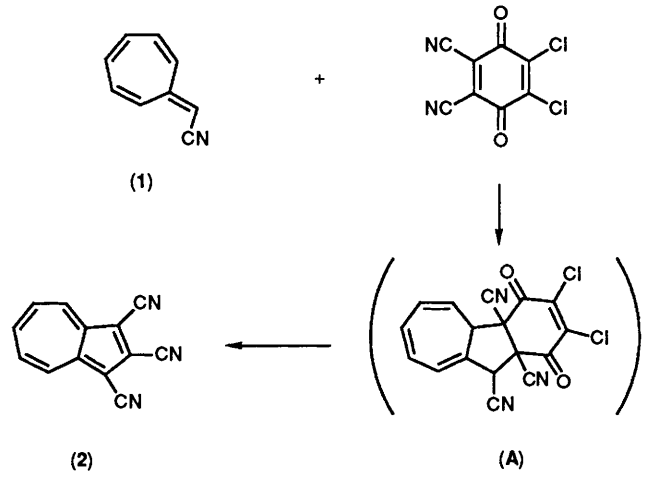
It has been established that the two minor products obtained from the reaction of 6-cyanotricyclo[5.5.0.0$^{2,5}$]dodeca-3,6,9,12-tetraene (**3**) with DDQ are 6-cyano-Dewar aceheptylene (**5**) and 5-cyanobenz[*a*]azulene (**6**), the formation of which show a new mode for the reaction of a substituted 8-cyanoheptafulvene with DDQ.

Because of the frontier orbitals lying close to the nonbonding level, the pericyclic reactions of nonalternant hydrocarbons play important roles in the construction of novel conjugated compounds.[1] 8-Cyanoheptafulvene (**1**)[2] prepared as a tractable derivative of heptafulvene efficiently undergoes various [8 + 2]-cycloadditions with electron deficient double bonds.[2,3] An intriguing example is the reaction of (**1**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) from which 1,2,3-tricyanazulene (**2**) was prepared in a moderate yield through the cycloaddition followed by the fragmentation.[3]

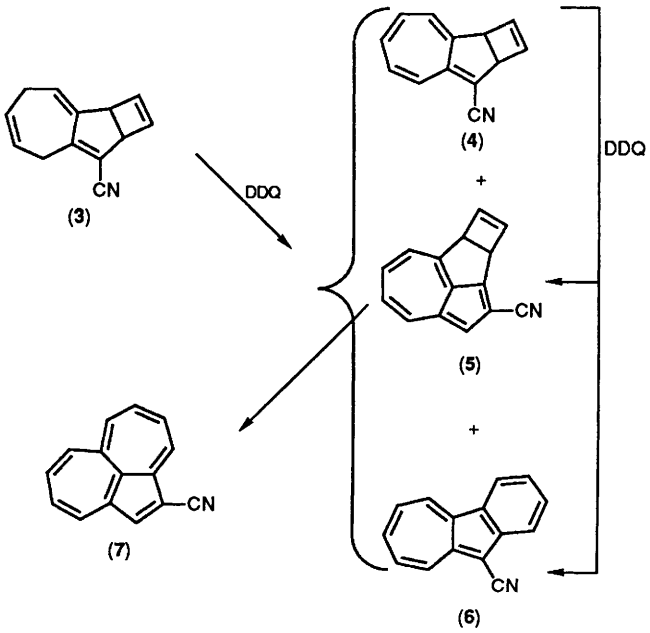
It has been observed recently that the controlled dehydrogenation of 6-cyanotricyclo[5.5.0.0$^{2,5}$]dodeca-3,6,9,12-tetraene (**3**) with DDQ proceeds with formation of the expected 6-cyanotricyclo[5.5.0.0$^{2,5}$]dodeca-3,6,8,10,12-pentaene (**4**)[4] together with coloured by-products. Here we report the structures of minor by-products obtained in low, formation of which displays novel types of reaction of the 8-cyanoheptafulvene chromophore with DDQ.

In addition to (**4**), a less polar blue eluate was obtained from the above-mentioned reaction through alumina column chromatography. The eluate could further be separated into two fractions by means of preparative HPLC. Concentration of the first ($t_R$ = 27 min) and the second fractions ($t_R$ = 37 min) afforded blue crystals (**5**), m.p. 132–133 °C (0.6%) and yellowish green crystals (**6**), m.p. 148–150 °C (0.3%), respectively. The identity of (**5**) was established as 6-cyano-6b,8a-dihydrocyclobuta[*a*]cyclopent[*c*,*d*]azulene, based on the evidence of spectral data and the results of thermal isomerisation. Thus, the UV spectrum of (**5**) shows distinctive features due to azulene chromophore. The absorption maximum of the first band is not markedly shifted as compared with that of the parent azulene suggesting the substituent site of the cyano group. In its $^1$H NMR spectrum, signals at δ 8.37, 7.32, 7.76, and 7.42 with relatively large vicinal coupling constants are assigned to alkenic hydrogens arranged in series on the seven-membered ring of the azulene nucleus. A singlet signal at δ 7.70 is compatible with that of hydrogen at the *peri* position of the five-membered ring. A set of four characteristic signals at δ 6.48, 6.42, 4.99, and 4.63 with small vicinal coupling constants can reasonably be assigned to the fused cyclobutene protons. Further support for the fused cyclobutene is furnished by the thermal valence isomerisation. Thus, when heated in [$^2H_8$]-tolulene at 150 °C for 215 min, compound (**5**) was cleanly converted into its isomer (**7**), m.p. 113–116 °C.

Both the characteristic electronic absorption extending up to 1 200 nm and the highfield $^1$H NMR chemical shifts of (**7**) are fully consistent with the structure of 1-cyanoaceheptylene (**7**).[5] On the other hand, (**6**) was identified as 5-cyanobenz[*a*]azulene by comparison of its spectral data with those of an authentic sample.[6a,b]




Scheme 1.




Scheme 2.

Treatment of (**4**) with DDQ gave compounds (**5**) and (**6**). Therefore, the formation of (**5**) seems reasonably to be explained by assuming the intermediate similar to (**A**), in which the

moieties involved in [8 + 2]cycloaddition between (**4**) and DDQ likewise construct the azulene skeleton in (**5**), although the mechanism is not entirely comparable to the formation of (**2**) from (**1**). Unfortunately, we have at present no explanation for the mechanism accounting for the unusual formation of (**6**).

Recently, theoretical attention has been focussed on the isomerisation of Dewar aceheptylene in the ground and excited states.[7] Since (**5**) is one of the least substituted Dewar aceheptylenes known to date,[5c] the reaction described in this paper will open a way to examine the detailed, properties of Dewar aceheptylene, provided the yield is improved.

## Experimental

*6-Cyano-6b,8a-dihydrocyclobuta*[a]*cyclopent*[c,d]*azulene* (**5**) *and 5-Cyanobenz*[a]*azulene* (**6**).—6-Cyanotricyclo[5.5.0.0$^{2,5}$]-dodeca-3,6,9,12-tetraene (**3**) was treated with DDQ and the reaction mixture was separated as described in an earlier paper.[4b] In addition to compound (**4**), a blue eluate was obtained. After several runs, the combined eluates were further separated into two fractions by means of preparative HPLC (ODS-10 μm, MeOH–$H_2O$ (1 : 1, v/v; 5 ml/min). Concentration of the first ($t_R$ 27 min) and the second fractions ($t_R$ 37 min) afforded blue crystals (**5**) (9 mg, 0.6%), m.p. 132–133 °C and yellowish green crystals (**6**) (4.5 mg, 0.3%), respectively.

Compound (**5**) ($M^+$, 203.0734. $C_{15}H_9N$ requires $M^+$, 203.0735); $\lambda_{max}$(cyclohexane) 212 (17 900), 245 (19 400), 297 (24 400), 309 (28 200), 359 (5 100), 378 (6 400), 572 (400), 599 (390), 608 (370), 626 (450), 661 (220), 675 (170), and 694 nm (230); $\nu_{max}$(KBr) 2 200 cm$^{-1}$ (CN); δ([$^2H_2$]dichloromethane) 4.63 (1 H, d, *J* 2.1 Hz, 6b-H or 8a-H), 4.99 (1 H, d, *J* 2.1 Hz, 6b-H or 8a-H), 6.42 (1 H, dd, *J* 2.4, 0.9 Hz, 7-H or 8-H), 6.48 (1 H, d, *J* 2.4 Hz, 7-H or 8-H), 7.32 (1 H, t, *J* 9.8 Hz, 3-H), 7.42 (1 H, d, *J* 9.8 Hz, 1-H), 7.70 (1 H, s, 5-H), 7.76 (1 H, t, *J* 9.8 Hz, 2-H), and 8.37 (1 H, d, *J* 9.8 Hz, 4-H).

*1-Cyanoaceheptylene* (**7**).—6-Cyano-6b,8a-dihydrocyclobuta[*a*]cyclopent[*c,d*]azulene (**5**) (4.1 mg) was dissolved in toluene (0.2 ml). The solution was degassed, sealed in an NMR tube and heated at 150 °C. After 215 min, the solvent was removed *in vacuo* to give crystals, which were passed through deactivated silica gel (10% $H_2O$; 1.5 g) with benzene and recrystallised from hexane to give reddish brown needles (4.0 mg, 97%), m.p. 113–116 °C ($M^+$, 203.0754. $C_{15}H_9N$ requires $M^+$ 203.0735); $\lambda_{max}$(cyclohexane) 253, 259, 283, 300sh, 370sh, 390, 418, 437, 747, 823, and 1 200 nm; $\nu_{max}$ 2 205 cm$^{-1}$ (CN); δ([$^2H_1$]chloroform) 5.32 (1 H, dd, *J* 10.7, 8.2 Hz, 4-H), 5.48 (1 H, d, *J* 11.9 Hz, 6-H), 5.67 (1 H, d, *J* 11.9 Hz, 7-H), 5.69 (1 H, dd, *J* 10.7, 8.5 Hz, 9-H), 5.87 (1 H, ddd, *J* 11.9, 8.2, 1.2 Hz, 5-H), 6.16 (1 H, ddd, *J* 11.9, 8.5, 1.2 Hz, 8-H), 6.62 (1 H, d, *J* 10.7 Hz, 3-H), 7.15 (1 H, d, *J* 10.7 Hz, 10-H), and 7.15 (1 H, s, 2-H).

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