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Cycloadditions of 8,8-dicyanoheptafulvene to styrenes: manifestation of dual reactivity modes

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Abstract—A facile cycloaddition reaction of 8,8-dicyanoheptafulvene with styrenes leading to the corresponding [8+2] and [4+2] adducts in excellent yields is described.

The recognition of cycloheptafulvenes as 8π cross-conjugated systems, analogous to tropone, with the carbonyl oxygen being replaced by a methylene, has invoked interest in these species from the vantage point of their potential participation in higher order cycloadditions.[1] Investigations by different groups have shown that alkoxy and alkyl substituted cycloheptafulvenes enter into cycloadditions mainly as 8π components.[2] The picture is less clear in the case of 'electron deficient' heptafulvenes, exemplified by 8,8-dicyanoheptafulvene **1**. Available information reveals that they can elicit all possible modes of reactivity,[3] but the parameters controlling such multiple reactivity profiles have not been defined. In particular, the cycloadditions of **1** with styrenes have not been investigated. In view of this, and in the context of our interest in the cycloadditions of fulvenes,[4] especially cycloheptafulvenes,[5] we have studied the reaction of **1** with styrenes. Our preliminary results are presented here.

In the first instance, **1** was treated with styrene **2a** at 110 °C in benzene under sealed tube conditions. The reaction was essentially complete in 48 h and two adducts **3a** and **4a** were obtained in 85% combined yield (1:1) in chromatographically pure form. The reaction was found to be general with respect to the styrene component as is evident from Scheme 1.[6]

The products were characterized by spectroscopic techniques. In the IR spectrum of **3b** the cyano absorption was visible at 2241 cm^{-1}. This was further supported by the presence of the cyano carbons at δ 113.1 and δ 114.5 in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum was also in accordance with the proposed structure [the methylene protons appeared as a multiplet at δ 2.57–2.73, the sp^3 C–H on the cycloheptatriene ring appeared as a multiplet at δ 2.87–2.89, and the benzylic proton was visible as a doublet of doublets at δ 3.79 (J_1 = 6.0 Hz, J_2 = 13.1 Hz)].

In the IR spectrum of **4b** the α,β-unsaturated cyano absorption was visible at 2220 cm^{-1}. The ^{13}C NMR spectrum exhibited the cyano carbons at δ 111.8 and δ 112.5, respectively. The ^{1}H NMR spectrum was also in agreement with the proposed structure. Unambiguous evidence for the structures and stereochemistries assigned for **3b** and **4b** was obtained by single crystal X-ray analysis (Fig. 1).

In conclusion, we have shown that 8,8-dicyanoheptafulvene exhibits dual reactivity modes in its cycloaddition reaction with styrenes resulting in the [8+2] and [4+2] adducts in approximately 1:1 ratio. The excellent overall yields obtained are noteworthy. Further studies aimed at gaining insight in to the reactivity of 8,8-dicyanoheptafulvene and related systems will be pursued.

Keywords: Higher order cycloadditions; Dicyanoheptafulvene; Styrenes; Diels–Alder reaction.

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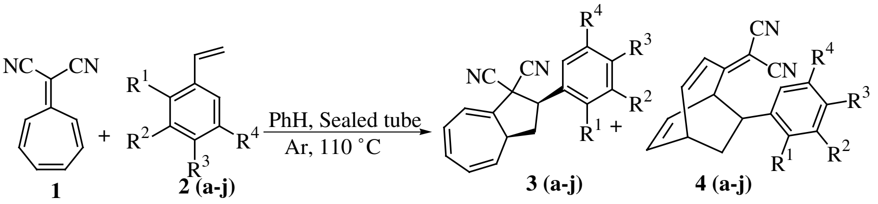
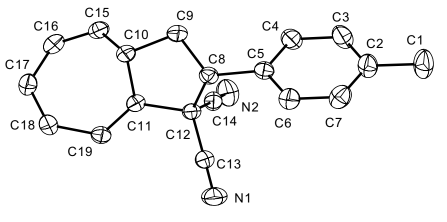


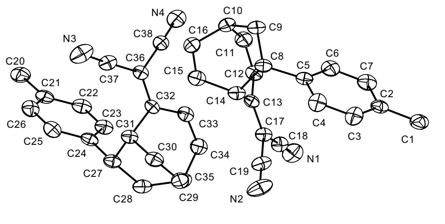
1 **2 (a-j)** **3 (a-j)** **4 (a-j)**

Entry	Styrene	Products with yield (%)
1	**2a**, R^1 = R^2 = R^3 = R^4 = H	**3a** (43), **4a** (42)
2	**2b**, R^1 = R^2 = R^4 = H, R^3 = CH$_3$	**3b** (42), **4b** (45)
3	**2c**, R^1 = R^4 = CH$_3$, R^2 = R^3 = H	**3c** (49), **4c** (32)
4	**2d**, R^1 = R^3 = CH$_3$, R^2 = R^4 = H	**3d** (47), **4d** (36)
5	**2e**, R^1 = R^3 = R^4 = H, R^2 = CH$_3$	**3e** (36), **4e** (46)
6	**2f**, R^1 = R^2 = R^4 = H, R^3 = OCH$_3$	**3f** (43), **4f** (48)
7	**2g**, R^1 = R^3 = OCH$_3$, R^2 = R^4 = H	**3g** (46), **4g** (45)
8	**2h**, R^1 = H, R^2 = R^3 = R^4 = OCH$_3$	**3h** (43), **4h** (46)
9	**2i**, R^1 = R^3 = R^4 = H, R^2 = Cl	**3i** (40), **4i** (24)
10	**2j**, R^1 = R^2 = R^4 = H, R^3 = Cl	**3j** (46), **4j** (27)

Scheme 1. Cycloaddition products and yields.



3b



4b

Figure 1. Single crystal X-ray structures of compounds **3b** and **4b**.

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6. General procedure: 8,8-Dicyanoheptafulvene was prepared following a literature procedure.[7] Typical experimental procedure and data for compounds **3b** and **4b**: Heptafulvene **1** (1 mmol) and styrene **2b** (3 mmol) were taken in 2 mL dry benzene in a glass tube. The tube was evacuated and sealed under an argon atmosphere. It was then heated at 110 °C for 48 h. The solvent was removed and the residue, after column chromatography on silica gel using hexane/ethyl acetate (95:5), afforded the adducts **3b** (42%) and **4b** (45%).
   Compound **3b**: Colorless crystalline solid, recrystallized from dichloromethane/hexane mixture, mp 175–177 °C; IR (KBr) $\nu_{\max}$: 3027, 2970, 2924, 2241, 1620, 1517, 1460, 1385, 1320, 1191, 1015, 870, 819, 716 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.39 (s, 3H), 2.57–2.73 (m, 2H), 2.87–2.89 (m, 1H), 3.79–3.82 (dd, 1H, J_1 = 6.0 Hz, J_2 = 13.1 Hz), 5.26–5.31 (dd, 1H, J_1 = 3.8 Hz, J_2 = 9.5 Hz), 6.12–6.18 (m, 1H), 6.49–6.70 (m, 3H), 7.24 (d, 2H, J = 7.8 Hz), 7.41 (d, 2H, J = 8.0 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.2, 35.2, 40.7, 45.8, 56.1, 113.1, 114.5, 123.6, 126.6, 128.0, 129.0, 129.4, 129.8, 130.7, 133.9, 134.1, 139.1. Anal. Calcd for C$_{19}$H$_{16}$N$_2$: C, 83.79; H, 5.92; N, 10.29%. Found: C, 83.73; H, 6.08; N, 10.26%. X-ray data for compound **3b**: C$_{19}$H$_{16}$N$_2$, M = 272.34, monoclinic, space group = P 21/a, a = 14.005(3), b = 7.3107(10), c = 14.479(3) Å, β = 95.45(3)°, V = 1475.8(5) Å^3, Z = 4, D_{calcd} = 1.226 Mg/m^3, λ =

0.71073 Å, μ = 0.073 mm^{-1}, $F(000)$ = 576, T = 180(2) K, crystal dimensions: 0.72 × 0.60 × 0.40 mm. CCDC 258899 contains the supplementary crystallographic data for this compound.

Compound **4b**: Colorless crystalline solid, recrystallized from dichloromethane/hexane mixture, mp 109–111 °C; IR (KBr) ν_{max}: 3019, 2952, 2220, 1598, 1527, 1403, 1351, 1209, 1151, 1030, 930, 807, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.22–2.40 (m, 5H), 3.42–3.49 (m, 1H), 3.54–3.61 (m, 1H), 4.09–4.12 (m, 1H), 6.24–6.29 (m, 1H, J_1 = 7.4 Hz, J_2 = 8.2 Hz),6.55–6.60 (m, 2H), 7.01 (d, 1H, J = 8.1 Hz), 7.10–7.18 (m, 3H). ^{13}C NMR (75 MHz $CDCl_3$) δ 21.0, 34.0, 37.4, 44.6, 51.3, 111.8, 112.5, 126.2, 126.9, 127.7, 129.1, 129.5, 129.7, 137.0, 137.9, 153.4, 169.1. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29%. Found: C, 83.66; H, 5.90; N, 10.42%. X-ray data for compound **4b**: $C_{19}H_{16}N_2$, M = 272.34, triclinic, space group = P 2-1, a = 9.298(3), b = 13.567(4), c = 13.826(4) Å, α = 64.99(3)°, β = 95.45(3)°, γ = 82.21(3)°, V = 1506.2(7) Å^3, Z = 4, D_{calcd} = 1.201 Mg/m^3, λ = 0.71073 Å, μ = 0.071 mm^{-1}, $F(000)$ = 576, T = 180(2) K, crystal dimensions: 0.96 × 0.80 × 0.80 mm. CCDC 258898 contains the supplementary crystallographic data for this compound.

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