[4π+2π]Cycloadditions of *o*-Quinones and Symmetrical 6,6-Dialkyl and Cycloalkylfulvenes[1]

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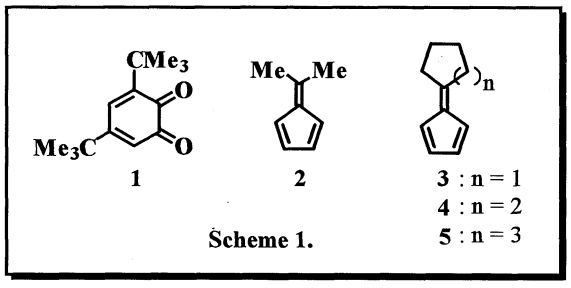
3,5-Di-*tert*-butyl-*o*-benzoquinone on reaction with 6,6-dimethylfulvene furnished the bicyclo[2.2.2]adduct **9** whereas the 6,6-tetramethylenefulvene afforded a novel product **10**, which presumably arises by the hetero Diels-Alder reaction of the quinone with the isomerized fulvene. The structure of **10** was confirmed by X-ray crystallography.

Diels-Alder reactions of *o*-quinones have received considerable attention due to the propensity of these compounds to function as carbodienes, heterodienes and dienophiles.[2-15] Recently we have shown that 3,5-di-*tert*-butyl-*o*-benzoquinone reacts as 1,4-dioxabutadiene with electron rich dienes.[16] Our interest in the cycloaddition of *o*-quinones to fulvenes stems from the intriguing possibility that in such systems either the quinone or the fulvene can participate as the 4π or 2π component.[17] Additionally such systems offer the prospect of higher order cycloaddition.[18] The scant information available in this area is mainly derived from the reaction of 2,3,4,5-tetraarylfulvene and 6,6-dimethylfulvene with *o*-chloranil.[9] In these cases the quinone participates as a heterodiene. Isolated examples of the cycloaddition of 6,6-diarylfulvenes to methyl substituted *o*-quinones in which the latter function as carbodienes have also been reported.[19]

We report here the preliminary results of our investigations on the cycloaddition of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** with symmetrical 6,6-dialkyl and cycloalkyl fulvenes, **2-5** (Scheme 1)[20] which reveal some remarkable reactivity differences.



Scheme 1.

3,5-Di-*tert*-butyl-*o*-benzoquinone undergoes cycloaddition to 6,6-dimethylfulvene **2** to afford the bicyclo[2.2.2]octene-7,8-dione adduct **9** in 80% yield. The structure of **9** was ascertained from its IR, ^{1}H and ^{13}C NMR and mass spectral data. The IR spectrum of **9** shows a strong absorption at 1738 cm^{-1}, indicating α-diketone. The *cis* stereochemistry is discerned from the coupling constant (J = 9.5, 1.74 Hz) of the ring junction protons. This is in agreement with the calculated J values (J = 9.61, 1.77 Hz MMX method).

The cycloaddition of **1** with 6,6-tetramethylenefulvene **3** takes an entirely different course leading to **10**. The IR spectrum of **10** does not show any characteristic carbonyl absorption. In the ^{1}H NMR spectrum the signals appearing at δ 4.72 and 5.01 are due to the protons at C_3 and C_2 respectively. The corresponding carbon signals appeared at δ 75.3 and 79.8 respectively. The proton connectivity has been established by 2D COSY experiments. Final confirmation of the structure assigned for **10** was determined by X-ray crystallography (Figure 1).[21]

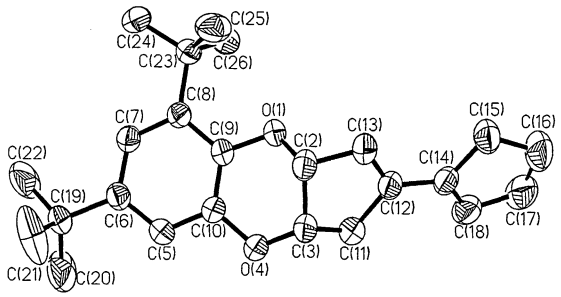
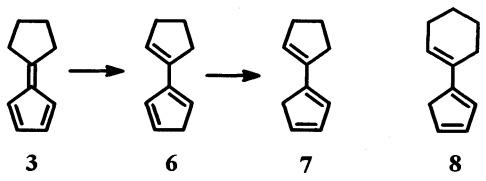


Figure 1. Molecular structure of **10**.

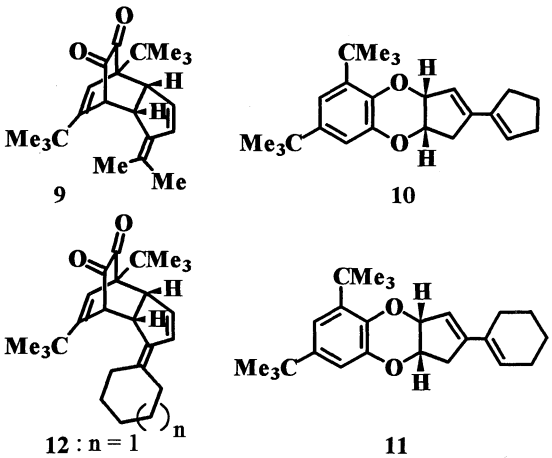
While the mechanistic pathway leading to **10** remains obscure, it may be speculated that the fulvene **3** suffers a slow isomerization to the cyclopent-1-enyl cyclopentadiene **7** which then undergoes cycloaddition to the quinone to afford **10** (Scheme 2). However a stepwise addition mechanism also cannot be ruled out.



Scheme 2.

Although it is not clear why the quinone serves as a heterodiene[22] towards **7**[23], it may be pointed out that a similar reactivity pattern was observed with an acyclic triene, *trans,trans*-2,6-dimethyl-2,4,6-octatriene.[16]

With 6,6-pentamethylenefulvene **4** a mixture of the adducts **11** and **12** were obtained.[24] The two products result from the cyclohex-1-enyl cyclopentadiene **8** and the fulvene **4** respectively. With 6,6-hexamethylenefulvene **5**, only the bridged adduct **13** was formed. The results are summarized in Scheme 3 and Table 1. Preliminary results obtained with 4-*tert*-butyl-*o*-benzoquinone are similar and it may be surmised that the phenomenon is general.



Scheme 3.

Table 1.

Entry	Fulvene	Condition	Product(s)	Yield %[a]
1	2	Benzene reflux, 8 h	9	80
2	3	"	10	85
3	4	"	11 and 12	52 and 33
4	5	Toluene reflux, 2.5 h	13	84

[a] Isolated yield.

The speculation that **9, 12** and **13** might be products of kinetic control could not be substantiated as attempts to transform these compounds to benzodioxins by thermal isomerization were unsuccessfull. Other experiments also failed to establish temperature dependence on product distribution. Further work is in progress to determine the scope of this reaction and to gain insight into its theoretical underpinnings.

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References and Notes

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20 For the preparation of fulvenes, see, a) K. J. Stone and R. D. Little, *J. Org. Chem.*, **49**, 1849 (1984); b) M. S. Erickson, J.M. Cronen, J.G. Garcia, and M.L. McLaughlin, *J. Org. Chem.*, **57**, 2504 (1992).
21 Crystallographic data for **10**: Triclinic, P1, a = 5.7600(10)A°, b = 9.708 (2) A°, c = 19.032 (4) A°, α = 75.87 (3)°, β = 87.65 (3)°, γ = 85.82 (3)°, V = 1029 (4) Å^3, Z = 2, density = 1.138 Mg/m^3, Temp = 298 K, R = 0.0545, Rw = 0.0568. Formula weight : 352.50, No. of unique reflections = 3624. Radiation source: MoKα (λ=0.71073°A).
22 For an excellent review on Hetero Diels-Alder reactions,see. D. L. Boger and S. M. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis", Academic Press, (1978).
23 Our attempts to obtain direct evidence for the isomerization have been unsuccessful. This may be attributed to the fact that the equilibrium heavily favors the more stable fulvene **3**.
24 Physical and Spectroscopic data for **10:** mp 114-116 °C. IR, KBr, cm^{-1}: 2960, 2930, 2872, 1587, 1484, 1421, 1362, 1313, 1289, 1237, 1077. ^{1}H NMR($CDCl_3$) : δ 6.86 (d, 1H, aromatic), 6.79 (d, 1H, aromatic), 5.81 (s, 1H), 5.67 (s, 1H), 5.008 (d, 1H, *J* = 4.7 Hz), 4.073 (q, 1H, *J* = 4.9 Hz), 2.84 (d, 2H, *J* = 4.7 Hz), 2.5 (m, 4H), 1.95 (m, 2H), 1.388 (s, 9H) 1.266 (s, 9H): ^{13}C NMR ($CDCl_3$):δ 144.22, 143.25, 142.04, 140.72, 139.56, 137.93, 131.18, 123.30, 115.80, 112.25, 79.57, 75.16, 38.45, 34.90, 34.40, 33.25, 32.39, 31.55, 29.92, 23.30: HRMS : 352.2413 ; Calcd for $C_{24}H_{32}O_2$: 352.2402.

11: IR, film, cm^{-1} : 2960, 2870, 1590, 1485, 1363, 1036. ^{1}H NMR ($CDCl_3$) : δ 6.45 (d, 1H), 6.4 (d, 1H), 5.6-5.4 (m, 2H), 4.7 (m, 1H), 4.35 (q, 1H), 2.55 (m, 2H), 2.0 (m, 4H), 1.4 (m, 4H), 1.25 (s, 9H), 1.1 (s, 9H). ^{13}C NMR ($CDCl_3$) : δ 146.5, 144.3, 143.0, 141.0, 138.0, 133.5, 128.5, 120.5, 116.0, 112.5, 79.5, 75.0, 37.5, 35.0, 34.0, 31.5, 30.0, 26.0, 25.5, 22.5, 22.0; HRMS : 366.2560; Calcd for $C_{25}H_{34}O_2$: 366.2559.