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[4π+2π]Cycloaddition Reactions of *o*-Benzoquinones with Symmetrical 6,6-Dialkyl and Cycloalkylfulvenes: Formation of Bicyclo[2.2.2]Octene Diones and Cyclopenta[*b*][1,4]Benzodioxins. Some Novel Observations [#1]

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Abstract: 3,5-Di-*tert*-butyl-*o*-benzoquinone on reaction with 6,6-dimethylfulvene furnished the bicyclo [2.2.2] adduct **5** whereas the 6,6-tetramethylenefulvene afforded a novel product **11** which arises by the hetero Diels-Alder reaction of the quinone with the isomerized fulvene. Analogous reaction of 6,6-pentamethylenefulvene gave rise to the benzodioxin **14** and the bicycloadduct **15**; 6,6-Hexamethylenefulvene afforded only the bicyclo[2.2.2] adduct **16**. Similar reactivity is observed in the case of 4-*tert*-butyl-*o*-benzoquinone.

The chemistry of *o*-quinones has invoked considerable interest and the cycloaddition reactions of these versatile compounds have been the subject of a number of investigations.[2-11] In spite of these efforts, surprisingly, very little information has been available on the cycloaddition profile of *o*-quinones with electron rich dienes and trienes. We have recently shown that *o*-benzoquinones undergo hetero Diels-Alder reaction with electron rich acyclic dienes and 2,5-dimethylpyrrole.[12-14]

As a part of our quest to gain insight into the reactivity of *o*-quinones towards dienes and trienes an investigation of the cycloaddition of selected *o*-quinones with fulvenes appeared particularly interesting since, in addition to the [4π+2π] mode, these systems offer the prospect of higher order cycloadditions. Fulvenes are highly reactive dienes and much theoretical as well as experimental work has been done on their Diels-Alder reactions leading to a clear understanding of the transition state for these reactions.[15] Remote substituent effects in the reactivity and stereoselectivity in Diels-Alder reactions of *p*-substituted 6-phenyl-6-methyl fulvenes have been reported recently.[16] The current interest on the use of fulvenes as synthons for substituted cyclopropanones[17]and the synthesis of vinyl fulvenes is also noteworthy.[18]

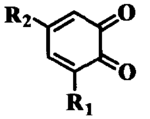
There is vast literature available on the cycloaddition involving fulvenes with maleic anhydride and assorted dienophiles.[19] The cycloaddition of *o*-quinones to fulvenes, however, has received only limited attention. The information available in this area rests solely on Friedrichsen's work on the reaction of 2,3,4,5-tetraarylfulvenes and 6,6-dimethylfulvene with *o*-chloranil[20,21] and the reaction of 6,6-diarylfulvenes with methyl substituted *o*-quinones.[22,23]

[#] *This paper is dedicated with respect and affection to Professor Gilbert Stork in celebration of his path-breaking contributions to the art and science of organic synthesis during the past fifty years.*

We have recently demonstrated that 6-arylfulvenes undergo facile cycloaddition to substituted *o*-benzoquinones leading to an efficient synthesis of bicyclo[2.2.2]octene diones.[24,25] In continuation of this work we have investigated the cycloaddition of selected *o*-benzoquinones with symmetrical 6,6-dialkyl and cycloalkylfulvenes. Our results which reveal some unprecedented reactivity differences in these systems are reported here.[26]

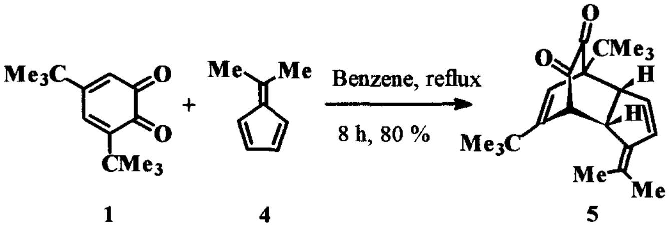
RESULTS AND DISCUSSION

The present work is focussed on the cycloaddition of the *o*-benzoquinones (**1**, **2** and **3**) with the 6,6-substituted fulvenes (**4**, **6**, **8**, **10a**, **10b** and **10c**). The quinones were prepared by the routine oxidation of the corresponding catechols and the fulvenes were obtained by the condensation of cyclopentadiene with the appropriate carbonyl compound in the presence of pyrrolidine.[27,28]

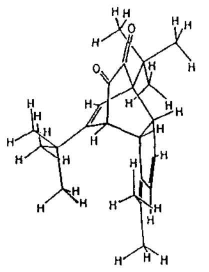


1: $R_1 = R_2 = CMe_3$
2: $R_1 = H, R_2 = CMe_3$
3: $R_1 = OMe, R_2 = H$

6,6-Dimethylfulvene (**4**), one of the simplest members of the fulvene family, undergoes cycloaddition with 3,5-di-*tert*-butyl-*o*-benzoquinone in refluxing benzene solution to furnish the bicyclo[2.2.2]octene dione adduct **5** in 80% yield. The reaction can be represented as follows.

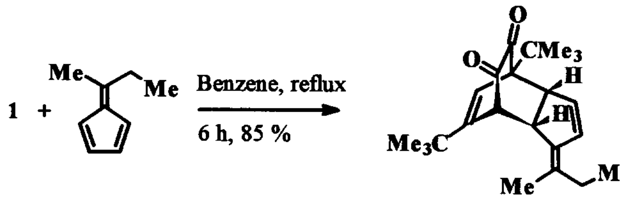


The IR spectrum of **5** showed a strong absorption at 1738 cm^{-1} indicating the presence of an α-diketone. The ^{1}H and ^{13}C NMR spectra are in accordance with the assigned structure. Examination of the ^{1}H NMR spectrum of **5** showed the presence of three proton signals other than those of methyl groups. These signals appeared at δ 3.25 (d, 1H) and 3.64 (m, 2H). The *cis* stereochemistry is discerned from the coupling constants (J=9.5, 1.7 Hz) of the ring junction protons. This is in agreement with the calculated J values (J=9.6, 1.7 Hz; MMX method). The three olefinic signals appeared at δ 5.73, 5.86 and 6.40. The *endo* stereochemistry of the representative adduct has been confirmed by single crystal X-ray analysis.[24] The energy minimized structure of **5** has been determined by MMX method and is given below.

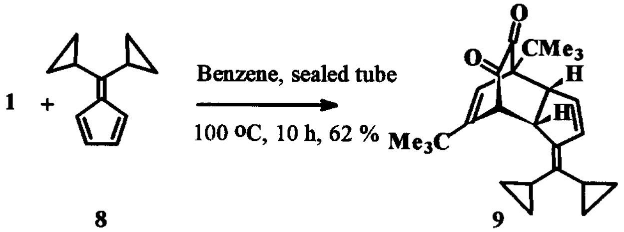


Energy minimized conformation of 5 *(MMX method)*

Similar adducts 7 and 9 were isolated from the reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone respectively with 6-ethyl-6-methyl and 6,6-dicyclopropylfulvene.



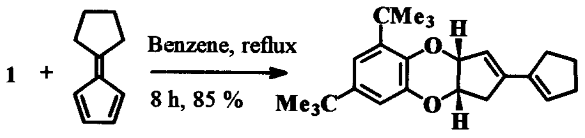
6 7 (mixture of isomers)



8 9

In the adduct 9 the cyclopropyl proton signals appeared at 0.25, 0.4, 0.7-0.85 and 1.45 ppm downfield from TMS. The corresponding carbon signals appeared at 5.0, 5.5, 6.0, 7.0, 12.0 and 16.0 ppm.

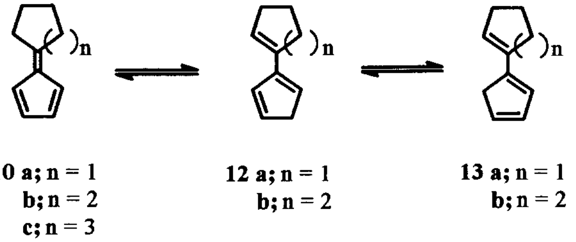
After having studied the cycloaddition reactions of the fulvenes derived from acyclic ketones, we turned our attention to those derived from cyclic ketones. First we examined the cycloaddition reaction of 6,6-tetramethylenefulvene with 3,5-di-*tert*-butyl-*o*-benzoquinone. The reaction took a surprisingly different course leading to 11 presumably resulting from the rearranged fulvene, with the quinone now serving as a 1,4-dioxabutadiene.



10 a 11

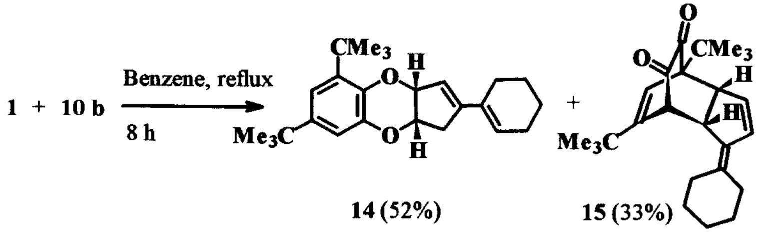
IR spectrum of 11 does not show any characteristic carbonyl absorption. The peak at 1421 cm^{-1} in the IR spectrum is due to the -C-O- vibration in the dioxin ring. Examination of the ^{1}H NMR spectrum of 11 indicated the presence of two sp3 C-H signals at δ 4.70 (q, 1H, J=4.9 Hz) and 5.00 (d, 1H, J=4.7 Hz) and these have been assigned to the ring junction protons adjacent to the two oxygen atoms in the benzodioxin ring. The proton spectrum of 11 exhibited one doublet at δ 2.84 (J=4.7Hz, 2H) and has been assigned to the proton at C11 (for numbering, see the crystal structure).[29] The hydrogens at position 15 and 17 appeared at δ 2.5 (4H) as a multiplet. The multiplet at δ 1.9 (2H) has been assigned to the proton at position 16. In the ^{13}C NMR spectrum the signal at δ 23.30 has been assigned to the carbon atom at position 16. The carbon atoms at position 15 and 17 appeared at δ 32.39 and 33.25. The C11 carbon resonated at δ 38.45. The two carbon atoms on the benzodioxin ring appeared at δ 75.16 and 79.57. The downfield signal (δ 79.57) has been assigned to the carbon at position 2. The assignments of carbon signals have been confirmed by QUART, DEPT and APT measurements. DEPT study on 11 showed the presence of four -CH$_2$- carbons and these appeared at δ 23.29, 32.39, 33.25 and 38.44. The proton connectivity has been established by 2D COSY experiments. From the 2D spectrum of 11 it has been found that the signals at δ 1.95 are coupled with signals at δ 2.50 which in turn are coupled with the olefinic signal at δ 5.67. Again the signal at δ 4.70 is coupled with the signal at δ 2.84. These clearly indicate the connectivity between various protons in **11**. Final proof of the structure was obtained by single crystal X-ray analysis.[29]

While the mechanistic pathway leading to **11** remains obscure, it may be suggested that the 6,6-tetramethylenefulvene **10a** suffers slow isomerization to the cyclopent-1-enyl cyclopentadiene **13a** which then undergoes cycloaddition to the quinone to afford **11**. Analysis of the interrupted reaction mixture has revealed the presence of **11** along with the unchanged starting materials suggesting that the Diels-Alder addition of the quinone to the cyclopent-1-enyl cyclopentadiene is faster than the isomerization of the fulvene. It is noteworthy that the isomerization of the fulvene invoked here, as far as we know, is unprecedented. So far our attempts to obtain direct evidence for the isomerization of fulvene have met with only limited success.[30] This may be attributed to the fact that the equilibrium heavily favours the more stable fulvene **10a**. The isomerization of **10a** can be represented as follows.



The MMX calculations showed that there is a difference in the heat of formation between **10a** and **13a** which is of the order of 4.9 kcal/mol. The energy difference between **10b** and **13b** is 4.0 kcal/mol. The heat of formation as well as the MMX energy are higher for the unisomerized fulvenes. Although it is not very clear why the quinone serves as a heterodiene towards **13a**, it may be recalled that a similar reactivity pattern was observed with an acyclic triene, *trans*, *trans*-2,6-dimethyl-2,4,6-octatriene.[12] Although we favour the mechanistic rationale given above, a stepwise mechanism also cannot be ruled out.

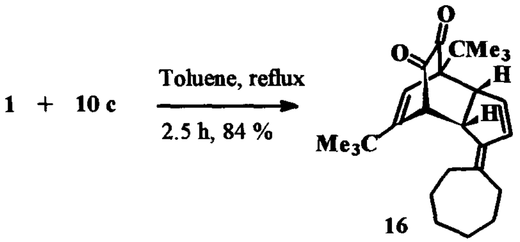
With 6,6-pentamethylenefulvene (**10b**), a mixture of the adducts **14** and **15** were obtained. The two products result from the cyclohex-1-enyl cyclopentadiene **13b** and the fulvene **10b** respectively. The reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with the fulvene can be illustrated as follows.



The products **14** and **15** were characterized by elaborate spectral analysis. Adduct **14** showed ^{1}H and ^{13}C NMR signals similar to those of **11**. IR spectrum does not show any carbonyl absorption. The -CH$_2$- group of cyclopentene moiety exhibited a broad doublet at δ 2.55. The protons adjacent to oxygen atom of the dioxin ring appeared at δ 4.35 and 4.70 as multiplets. The corresponding carbon signals appeared at δ 75.0 and 79.5 respectively in the ^{13}C NMR spectrum. The high resolution mass spectrum showing peak at 366.2560 is also in accordance with the proposed structure.

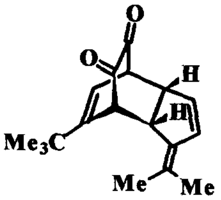
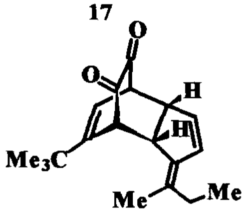
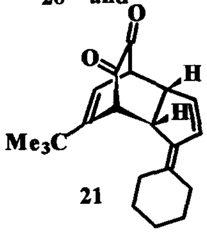
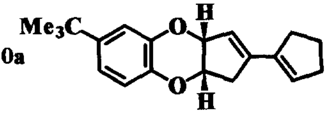
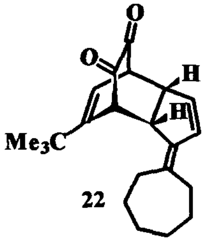
The adduct **15** showed a strong absorption at 1747 cm^{-1} in the IR spectrum indicating the presence of α-diketone. The ^{1}H and ^{13}C NMR spectra are in agreement with the proposed structure. The bridgehead and ring junction protons resonated at δ 3.31 (1H), 3.57 (1H) and 3.67 (1H). The signals at δ 3.31 and 3.67 appeared as two doublets with a *J* value of 9.9 Hz, which is diagnostic for a *cis* ring junction. High resolution mass spectrum with molecular ion peak at 366.2544 is also in accordance with the proposed structure.

Interestingly with 6,6-hexamethylenefulvene (10c), only the bicyclo[2.2.2] adduct 16 was formed; evidently no isomerization of 6,6-hexamethylenefulvene occurred under the conditions of cycloaddition.



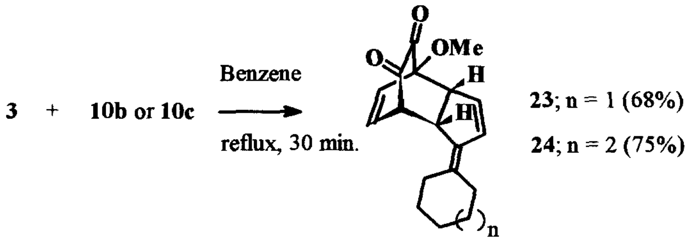
Similar results were obtained with 4-*tert*-butyl-*o*-benzoquinone and the results are summarized in the following Table 1.

Table 1 Cycloaddition reactions of 2 with fulvenes

Entry	Fulvene	Product(s)	Yield(%)[1]	Entry	Fulvene	Product(s)	Yield(%)[1]
1	4	 17	80	4	10b	 20 and	10
2	6	 18	78			 21	75
3	10a	 19	84	5	10c	 22	75

[1] Isolated yield. Benzodioxin adducts are nearly colourless, whereas the bicyclo[2.2.2]octene diones are yellow. **Conditions**: For entries 1and 2: Benzene, rt, 8 h; For entries 3 and 4: Benzene, rt, 4h; For entry 5: Benzene, reflux, 8h

Subsequently we studied the Diels-Alder reactions of 3-methoxy-*o*-benzoquinone (**3**) with the fulvenes. Reactions of **3** with **4**, **6**, and **10a** afforded intractable mixtures under a variety of conditions. Reactions of **3** with **10b** and **10c** afforded the adducts **23** and **24** respectively in good yields and the latter were characterized by their spectral and analytical data. Interestingly no benzodioxin adducts were obtained in these cases.



In conclusion, our investigations have revealed that the reactions of *o*-benzoquinones with 6,6-dialkyl- and cycloalkylfulvenes proceed *via* remarkably different pathways. To account for the formation of the benzodioxin adducts from cycloalkyl fulvenes a slow isomerization of the latter to cycloalkenyl cyclopentadienes prior to cycloaddition is invoked. Such an isomerization of fulvenes is unprecedented. It is noteworthy that the products of cycloaddition reported herein, especially the bicyclo[2.2.2] adducts can potentially undergo a number of synthetically useful transformations. Further work along these line is in progress.

EXPERIMENTAL DETAILS

All reactions were carried out in oven dried glassware (120 °C) under an atmosphere of nitrogen. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100-200 mesh). Mixtures of ethyl acetate and petroleum ether (60-80 °C) were used as eluents. MPLC was done on Buchi 688 system. Melting points are uncorrected. The IR spectra were recorded on a Perkin-Elmer model 882 infrared spectrophotometer using potassium bromide pellets. NMR spectra were recorded on Hitachi-60, Jeol EX-90, Bruker-300, Nicolet GE-300 spectrometer using chloroform-*d* as solvent. The chemical shifts are given in the δ-scale with tetramethylsilane as internal standard. The mass spectra were recorded on a Finnigan MAT Model 8430 and Fisons GC 8000-MD 800. The purity of the adducts has been checked by HPLC (Shimadzu LC-10AS).

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(dimethyl)methylene]-4,7-ethanoindene-8,9-dione (5)

3,5-Di-*tert*-butyl-*o*-benzoquinone (2.0 g, 9.0 mmol) and 6,6-dimethylfulvene (1.0 g, 9.4 mmol) were dissolved in dry benzene (20 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the residue was subjected to chromatography on a silica gel column (petroleum ether/ethyl acetate) to afford **5** (2.37 g, 80%) as yellow crystals, m p. 145-147 °C.

IR , KBr : 2966, 2913, 1738, 1591, 1466, 1367, 1239 cm^{-1}.
^{1}H NMR : δ 6.42 (dd, 1H), 5.86 (d, 1H), 5.73 (d, 1H), 3.64 (t, 2H), 3.25 (d, 2H), 1.78 (s, 3H), 1.71 (s, 3H), 1.20 (s, 9H), 0.977 (s, 9H).
^{13}C NMR : δ 192.34, 190.20, 150.00, 138.95, 135.55, 132.58, 123.96, 120.74, 61.10, 51.53, 50.02, 41.43, 35.10, 33.88, 27.87, 21.07, 20.86.
HRMS calcd for $C_{22}H_{30}O_2$: 326.459 , found : 326.4360

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(methylethyl)methylene]-4,7-ethanoindene-8,9-dione (7)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0. 1g, 0.45 mmol) and 6-methyl-6-ethyl fulvene (0.4 g, 3.3 mmol,) were dissolved in dry benzene (10 mL) and refluxed under nitrogen for 6 h. The solvent was removed *in vacuo* and the residue was subjected to chromatography on silica gel (pet.ether/EtOAc) to afford 7 (0.131 g, 85%) as viscous yellow oil.

IR, film : 2968, 2878, 1733, 1624, 1468, 1369, 1236, 1165, 1107, cm^{-1}.
^{1}H NMR : δ 6.6 (m, 1H), 6.0 (m, 2H), 3.7 (m, 2H), 3.4 (d, 2H), 2.2 (q, 2H), 1.85 (s, 3H), 1.35 (s, 9H), 1.25 (t, 3H), 1.1 (s, 9H).
^{13}C NMR : δ 192.3, 190.0, 150.0, 138.5, 135.0, 132.5, 130.0, 120.5, 61.0, 51.0, 50.0, 41.5, 35.0, 34.0, 28.0, 27.5, 27.0, 18.5, 12.5.
MS *m/z* : 340 (M$^+$), 314, 197, 152, 113.
Anal. Calcd for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47. Found: C, 81.0; H, 9.93.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(dicyclopropyl)methylene]-4,7-ethanoindene-8,9-dione (9)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.125 g, 0.56 mmol) and 6,6-dicyclopropylfulvene (0.09 g, 0.56 mmol) were dissolved in dry benzene (1 mL) in a glass tube and it was sealed under nitrogen and heated at 100 °C for 10 h. The solvent was removed *in vacuo* and the product subjected to chromatography on silica gel using petroleum ether/ ethyl acetate mixture as eluent to yield the cycloadduct 9 (0.133 g, 62%) as yellow solid.

IR, KBr : 2968, 2880, 1745, 1733, 1563, 1467, 1368, 1274, 1125, cm^{-1}.
^{1}H NMR : δ 6.75 (d, 1H), 5.9 (d, 1H), 5.75 (s, 1H), 3.8 (d, 1H), 3.62 (d, 2H), 3.45 (d, 1H), 1.45 (m, 2H), 1.25 (s, 9H), 0.96 (s, 9H) 0.85-0.7 (m, 6H), 0.4 (m, 1H), 0.25 (m, 1H).
^{13}C NMR : δ 193.0, 191.0, 151.0, 143.8, 137.0, 133.0, 131.0, 121.0, 61.5, 51.8, 50.0, 42.0, 35.8, 34.2, 28.0, 16.0, 12.0, 7.0, 6.0, 5.5, 5.0.
MS *m/z* : 378 (M$^+$), 297, 184, 132, 120.
HRMS calcd. for $C_{26}H_{34}O_2$: 378.2558, found: 378.2501.

(3a-*cis*)-2-(1-Cyclopenten-1-yl)-5,7-bis(1,1-dimethyethyl)-3a,9a-dihydro-1H-cyclopenta[*b*][1,4]benzodioxin (11)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.503 g, 2.28 mmol.) and 6,6-tetramethylenefulvene (0.5 g, 3.78 mmol) were dissolved in dry benzene (10 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the product was subjected to chromatography on silica gel to afford 11 (0.68 g, 85%) as colourless crystals.

mp. 114-116 °C.
IR, KBr : 2960, 2930, 2872, 1587, 1484, 1421, 1362, 1313, 1289 cm^{-1}.
^{1}H NMR : δ 6.86 (d, 1H), 6.79 (d, 1H), 5.81 (s, 1H), 5.67 (s, 1H), 5.008 (d, J=4.7 Hz, 1H), 4.703 (q, J=4.9 Hz, 1H), 2.84 (d, J=4.7 Hz, 2H), 2.5 (m, 4H), 1.95(m, 2H),1.388 (s, 9H), 1.266 (s, 9H).
^{13}C NMR : 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.
MS *m/z* : 353 (M$^+$ +1), 325, 300, 280, 224, 222, 207, 198, 163, 116, 53.
HRMS calcd. for $C_{24}H_{32}O_2$: 352.2402, found: 352.2389.

Diels-Alder adducts 14 and 15: 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.20 g, 0.91 mmol) and 6,6-pentamethylenefulvene (0.50 g, 3.42 mmol) were dissolved in benzene (5 mL) and it was refluxed under nitrogen for 8 h. The solvent was removed *in vacuo,* and the residue on column chromatography afforded the products **14** (0.174 g, 52%) and **15** (0.109 g, 33%) as viscous oils.

(3a-*cis*)-2-(1-Cyclohexen-1-yl)-5,7-bis(1,1-dimethylethyl)-3a,9a-dihydro-1H-cyclopenta[*b*][1,4]benzodioxin (14)

IR, KBr : 2960, 2870, 1590, 1485, 1422, 1363, 1305, 1236, 1088 cm^{-1}.

^{1}H NMR : 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 : 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 calcd for $C_{25}H_{34}O_2$: 366.2559 , found : 366.2560.

[3a-(3aα,4α,7α,7aα]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(cyclohexyl)methylene]-4,7-ethanoindene-8,9-dione (15)

IR, film : 2963, 2880, 1747, 1625, 1484, 1400, 1266, 1168, 787 cm^{-1}.

^{1}H NMR : δ 6.47 (dd, 1H), 5.85 (d, 1H), 5.75 (s, 1H), 3.67 (d, 1H), 3.57 (s, 1H), 3.31 (d, 1H), 2.24 (m, 4H), 1.55 (m, 6H), 1.221 (s, 9H), 1.01 (s, 9H).

^{13}C NMR : δ 192.0, 190.0, 150.0, 136.0, 135.0, 132.5, 132.0, 120.5, 61.0, 52.0, 49.8, 41.0, 35.0, 34.0, 31.5, 28.0, 27.5, 27.0, 26.5.

HRMS calcd for $C_{25}H_{34}O_2$: 366.2558 , found : 366.2544.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(cycloheptyl)methylene]-4,7-ethanoindene-8,9-dione (16)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.40 g, 1.18 mmol.) and 6,6-hexamethylenefulvene (0.33 g, 2.11 mmol.) were dissolved in dry toluene (5 mL) and refluxed for 2.5 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **16** (0.577 g, 84%) as yellow solid.

IR, KBr : 2928, 2877, 1744, 1732, 1621, 1467, 1368, 1236, 1018 cm^{-1}.

^{1}H NMR : δ 6.4 (dd, 1H), 5.8 (br d, 1H), 5.7 (s, 1H), 3.55 (m, 2H), 3.2 (br d, 1H), 2.25 (m, 4H), 1.45 (m, 8H), 1.15 (s, 9H), 0.9 (s, 9H).

^{13}C NMR : δ 192.5, 190.2, 150.5, 138.5, 135.8, 134.0, 132.5, 121.0, 61.0, 51.5, 50.2, 41.5, 35.0, 34.0, 32.5, 32.3, 30.5, 29.0, 27.9, 27.0.

HRMS calcd for $C_{26}H_{36}O_2$: 380.5460 , found : 380.5369.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(dimethyl)methylene]-4,7-ethanoindene-8,9-dione (17)

4-*tert*-Butyl-*o*-benzoquinone (0.44 g, 2.72 mmol) and 6,6-dimethylfulvene (0.58 g, 4.7 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 8 h. The solvent was removed *in vacuo* and the residue on chromatography (pet. ether/ EtOAc-eluent) afforded **17** (0.588 g, 80%) as yellow semi solid.

IR, film : 2870, 1734, 1625, 1370, 1284, 1165 cm^{-1}.

^{1}H NMR : δ 6.44 (m, 1H), 5.9 (m, 1H), 5.8 (m, 1H), 3.7 (m, 2H), 3.6 (m, 2H), 1.8 (s, 3H), 1.77 (s, 3H), 1.21 (s, 9H).

^{13}C NMR : δ 193.0, 192.0, 151.0, 140.0, 135.0, 132.5, 124.0, 121.0, 59.0, 52.0, 50.5, 42.0, 35.1, 27.6, 21.3, 20.8

MS *m/z* : 270 (M^+), 216, 194, 82, 63.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.58; H, 8.16.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(methylethyl)methylene]-4,7-ethanoindene-8,9-dione (18)

4-*tert*-Butyl-*o*-benzoquinone (0.2g,1.21 mmol) and 6-methyl-6-ethylfulvene (0.3 g, 2.4 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **18** (0.27 g, 78%) as yellow semi solid.

IR, film : 2869, 1735, 1384, 1285, 1160 cm^{-1}.

^{1}H NMR : δ 6.6 (m, 1H), 6.2 (m, 2H), 3.75 (m, 2H), 3.5 (m, 2H), 1.85 (s, 3H), 1.35 (q, 2H), 1.25 (s,9H), 1.2 (t, 3H).

^{13}C NMR : δ 192.0, 191.5, 150.5, 140.0, 135.5, 133.0, 132.5, 125.0, 59.0, 51.0, 50.0, 41.5, 35.0, 28.0, 27.0, 18.5, 12.5

MS *m/z* : 284 (M^+), 212, 182, 78, 64.

HRMS Calcd for $C_{19}H_{24}O_2$: 284.1776 , found : 284.1705.

(3a-*cis*)(1-Cyclopenten-1-yl)-7-(1,1-dimethyethyl)-cyclopenta[*b*][1,4]benzodioxin (19)

4-*tert*-Butyl-*o*-benzoquinone (0.342 g, 2.08 mmol) and 6,6-tetramethylenefulvene (0.5 g, 3.78 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded 19 (0.518 g, 84%) as pale yellow semi solid.

IR, film : 2930, 2869, 1584, 1480, 1423, 1314 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 3H), 5.85 (m, 1H), 5.75 (m, 1H), 4.95 (m, 1H), 4.65 (q, 1H), 2.75 (br d,2H), 2.15 (m,4H), 1.6 (m, 4H), 1.25 (s, 9H).

^{13}C NMR : δ 146.5, 142.5, 133.0, 132.0, 128.5, 128.0, 120.5, 118.0,116.5, 114.0, 78.5, 74.0, 36.5, 34.0, 31.5, 26.0, 25.5, 22.5, 22.0.

MS *m/z* : 297 (M^+ +1), 296 (M^+), 231, 176, 86, 75.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.96; H, 8.01.

Diels-Alder Adducts 20 and 21: 4-*tert*-Butyl-*o*-benzoquinone (0.8 g, 4.87 mmol) and 6,6-pentamethylenefulvene (0.9 g, 6.15 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the residue on chromatography afforded **20** (0.138 g, 10 %) and **21** (1.11 g, 74%) as viscous oils.

(3a-*cis*)(1-Cyclohexen-1-yl)-7-(1,1-dimethylethyl)-cyclopenta[*b*][1,4]benzodioxin (20)

IR, film : 2869, 1591, 1485, 1420, 1350 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 3H), 5.8 (br d, 2H), 5.0 (br s, 1H), 4.65 (q, 1H), 2.75 (br d, 2H), 2.15 (m, 4H), 1.6 (m, 4H), 1.25 (s, 9H).

^{13}C NMR : δ 146.5, 142.5, 133.0, 132.0, 128.5, 128.0, 120.5, 118.0, 116.5, 114.0, 78.5, 74.0, 36.5, 34.0, 31.5, 26.0, 25.5, 22.5, 22.0

MS *m/z* : 311 (M^+ +1), 310 (M^+), 283, 189, 154, 130.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 80.98; H, 8.31.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(cyclohexyl)methylene]-4,7-ethanoindene-8,9-dione (21)

IR, film : 2830, 1746, 1485, 1400 cm^{-1}.

^1H NMR : δ 6.45 (dd, 1H), 5.85 (dd, 1H), 5.6 (dd, 1H), 3.7 (t, 1H), 3.55 (m, 2H), 3.35 (br d, 1H), 2.25 (br s, 4H), 1.55 (br s, 6H), 1.0 (s,9H).

^{13}C NMR : δ 190.5, 190.3, 151.5, 136.0, 134.0, 133.0, 132.0, 118.0, 53.5, 51.5, 46.0, 39.5, 35.0, 32.0, 31.0, 28.0, 26.0

MS *m/z* : 310 (M^+), 280, 172, 140, 96, 56.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.11; H, 8.29.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(cycloheptyl)methylene]-4,7-ethanoindene-8,9-dione (22)

4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6,6-hexamethylenefulvene (0.35 g, 2.18 mmol) were dissolved in benzene (15 mL) and refluxed under nitrogen for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **22** (0.44 g, 75%) as yellow solid.

IR, film : 2925, 1743, 1623, 1236 cm^{-1}.

^1H NMR : δ 6.43 (dd, 1H), 5.8 (m, 2H), 3.5 (m, 2H), 3.3 (m, 2H), 2.2 (m, 4H), 1.6 (m,8H),1.2 (s, 9H).

^{13}C NMR : δ 193.0, 192.0, 149.5, 138.0, 134.5, 134.0, 132.5, 120.0, 60.0, 51.5, 50.0, 40.5, 35.0, 32.5, 34.4, 32.0, 30.0, 29.0, 27.5, 27.0

MS *m/z* : 324 (M^+), 286, 231, 197, 146, 86.

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 80.98; H, 8.59.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(cyclohexyl)methylene]-4,7-ethanoindene-8,9-dione (23)

3-Methoxycatechol (0.409 g, 2.9 mmol) was dissolved in benzene (10 mL) and silver carbonate (1.5 g) was added and stirred under nitrogen. To this solution 6,6-pentamethylenefulvene (0.42 g, 2.9 mmol) was added and refluxed for 30 minutes. Worked up as in the previous case and the residue on column chromatography afforded **23** (0.57 g, 68%) as yellow crystalline solid. mp. 119-121 °C.

IR, film : 2931, 2855, 1746, 1702, 1668, 1550, 1451, 1358, 1230, 1079, 1032, 788cm^{-1}.

^1H NMR : δ 6.5-5.6 (m, 4H), 3.65 (s, 3H), 3.45 (m, 3H), 2.2 (m, 4H), 1.6 (m, 6H).

^{13}C NMR : δ 190.0, 188.0, 136.0, 135.5, 134.0, 132.0, 130.0, 127.0, 87.5, 54.0, 52.0, 49.0, 39.0, 32.0, 31.0, 28.0, 26.0

MS *m/z* : 284 (M^+), 212, 180, 76.

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.91; H, 6.94.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(cycloheptyl)methylene]-4,7-ethanoindene-8,9-dione (24)

3-Methoxycatechol (0.502 g, 3.58 mmol) and silver carbonate (1.5 g) were taken in benzene (10mL) and 6,6-hexamethylenefulvene (0.7 g, 4.37 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **24** (0.788 g, 75%) as yellow solid.

IR, KBr : 2927, 2877, 1743, 1621, 1467, 1368, 1090 cm^{-1}.

^1H NMR : δ 6.5 (dd, 1H), 6.1 (m, 2H), 5.7 (dd, 1H), 3.85 (m, 1H), 3.65 (s, 6H), 3.4 (m, 2H), 2.4 (m, 4H), 1.6 (m, 8H).

^{13}C NMR : δ 190.0, 188.0, 138.5, 136.5, 135.0, 131.5, 130.0, 126.5, 88.0, 53.5, 51.0, 49.0, 39.5, 32.0, 30.0, 28.0, 27.7, 27.3

MS *m/z* : 299 (M^+ +1), 298 (M^+), 270, 255, 199, 171, 160, 104, 78,

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.32; H, 7.42.

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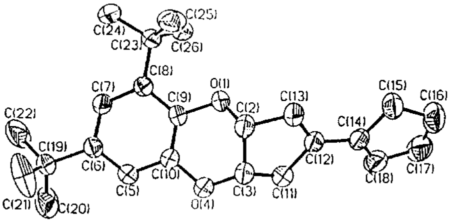

30. Recently in experiments designed to isomerize **10a** to **13a** we have isolated a dimer which seems to arise from **13a**. Nair, V.; Kumar, S.; Nair, J. S.; Williard, P. G, unpublished results.

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