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Diels-Alder Reactions of *o*-Benzoquinones with 6-Substituted Fulvenes: Facile Synthesis of 1-Aryl and 1,1-Diarylmethylene-4,7-Ethanoindene-8,9-Diones [1]

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Abstract: 3,5-Di-*tert*-butyl-, 4-*tert*-butyl- and 3-methoxy-*o*-benzoquinones have been shown to undergo facile thermal cycloaddition to symmetrical and unsymmetrical fulvenes to give bicyclo[2.2.2]octene diones in high yields.

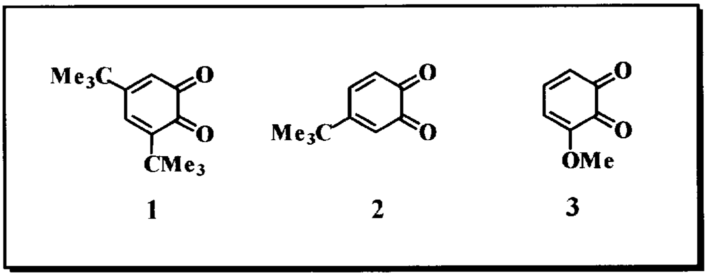
The Diels-Alder reaction, being one of the most powerful carbon-carbon bond forming processes, has been the subject of extensive research during the past seven decades.[2,3] Among others, *p*-quinones have been shown to be excellent dienophiles in Diels-Alder reaction. In contrast, however, the reactivity profile of *o*-quinones has received less attention, attributable, at least in part to the instability of these compounds. Potentially *o*-quinones can function as carbodienes, heterodienes and dienophiles. Although such varied reactivity has been revealed in a number of instances there have been very few systematic investigations in this area.[4-13]

As a part of our quest to gain insight into the reactivity of *o*-quinones towards dienes and trienes[14] an investigation of the cycloaddition of selected *o*-quinones with fulvenes appeared particularly interesting. 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 on the reactivity and stereoselectivity in Diels-Alder reactions of *p*-substituted 6-phenyl-6-methylfulvenes have been reported recently.[16] The current interest on the use of fulvenes as synthons for substituted cyclopropanones[17] and the synthesis of vinylfulvenes is also noteworthy.[18]

Our interest in the cycloaddition of *o*-quinones to fulvenes stems from the realization that the quinone or the fulvene can function as the diene or the dienophile.[1,19] In addition, the intriguing possibility of higher order cycloaddition also exists in such systems. There has been some work on the cycloaddition of *o*-quinones to fulvenes, but for the most part, this is concerned with the cycloaddition of tetrachloro-*o*-benzoquinone with 2,3,4,5-tetraaryl- and 6,6-dimethylfulvenes. In these cases, the quinone functions as a heterodiene leading to inverse electron demand Diels-Alder reaction. In addition to the [4+2] cycloaddition, products arising from [6+4] addition with the fulvene acting as the 6π component were also isolated. There are isolated examples of the [4+2]cycloaddition of methyl substituted *o*-quinones with diaryl fulvenes in which the quinone participates as a carbodiene.[20-22]

Results and Discussion

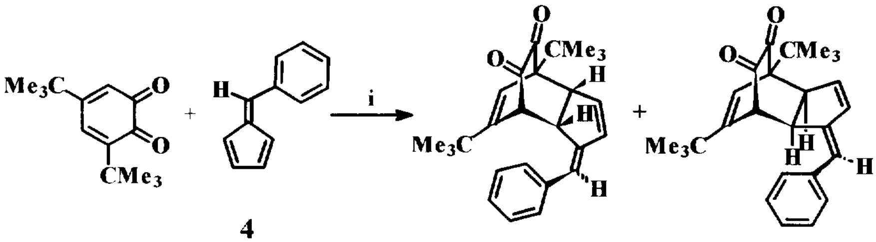
With the stated objective of probing the reactivity profile of *o*-benzoquinones in cycloaddition reaction with fulvenes, the following *o*-benzoquinones (**1-3**), readily accessible from the corresponding catechols, were selected for our studies.



1 **2** **3**

The required substituted fulvenes were synthesized by Little's procedure utilizing the condensation of cyclopentadiene with the appropriate aldehyde or ketone in presence of pyrrolidine.[23,24] The fulvenes were obtained in good yields and these have been characterized by spectroscopic methods.

6-Phenylfulvene (**4**), prepared from benzaldehyde and cyclopentadiene, undergoes cycloaddition with 3,5-di-*tert*-butyl-*o*-benzoquinone to afford the products **5** and **6** in 82 and 8% yields respectively and these were separated by crystallization. The major product was identified as the *endo* adduct **5**. The reaction can be illustrated as follows.



4

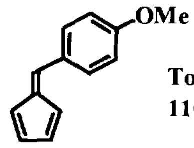
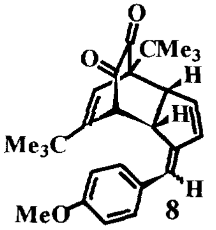
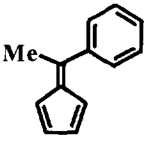
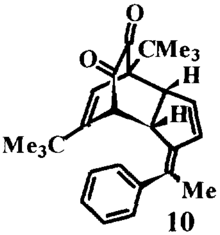
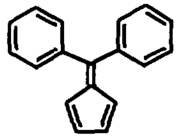
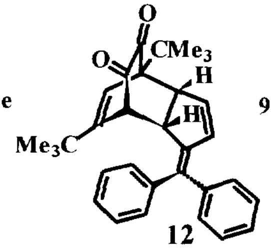
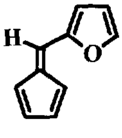
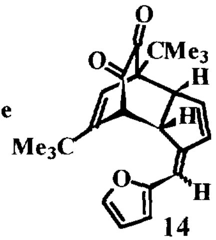
i, Toluene, sealed tube, 120 °C, 24 h **5 (82%)** **6 (8%)**

IR spectrum of **5** showed a strong absorption at 1731 cm^{-1} which indicated the presence of α-diketone. The ^{1}H NMR spectrum of **5** showed two singlets corresponding to nine protons each at δ 0.8 and 1.2. These are assigned to the two *tert*-butyl groups. The one bridgehead and two ring junction protons appeared as an overlapping multiplet at δ 3.7 (3H). The ^{1}H NMR spectrum also exhibited a singlet at δ 7.1 due to the aromatic protons and a multiplet at δ 6.2-5.6 due to the olefinic protons (4H). The ^{13}C NMR spectrum of **5** revealed the C=O resonances at δ 190.0 and 192.0. The ring junction and bridgehead carbons resonated at δ 41.0, 49.0, 51.0 and 61.0. The mass spectrum of **5** showed molecular ion peak at 374 and this also is in accordance with assigned structure. The conclusive assignment of *endo* stereochemistry to **5** rests solidly on the X-ray crystal structure of **8**[1] and its correlation with **5**.

The structure of the *exo* adduct (**6**) has been similarly confirmed by spectral analysis. The IR spectrum of **6** showed a strong absorption at 1737 cm^{-1} indicating the presence of α-diketone. In the ^{1}H NMR spectrum, the two *tert*-butyl groups resonated at δ 0.85 and 1.20. The ring junction protons appeared at δ 3.8 as a multiplet corresponding to three protons. The olefinic protons appeared at δ 5.78 (1H), 6.1 (1H) and 6.35 (2H) as multiplets. The phenyl ring protons resonated at δ 7.3. The ^{13}C NMR spectrum of **6** is similar to that of the *endo* adduct. The *tert*-butyl groups resonated at δ 27.5, 28.0, 34.5 and 35.0. The bridgehead and ring junction carbons appeared at δ 41.5, 48.5, 51.0 and 52.0. The olefinic and aromatic carbons resonated in the region δ 121.0-150.5 and the C=O resonances were visible at δ 192.0 and 193.0.

Similar results were obtained with a number of aryl fulvenes and the results are summarised in the following Table 1.

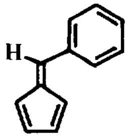
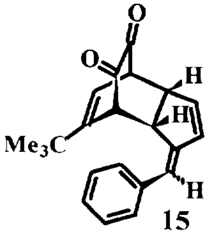
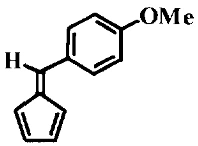
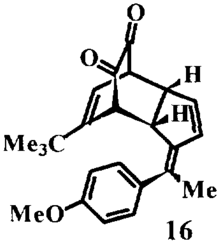
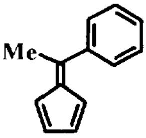
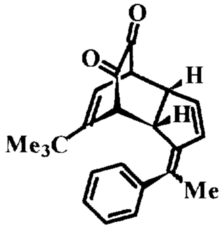
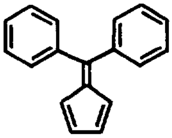
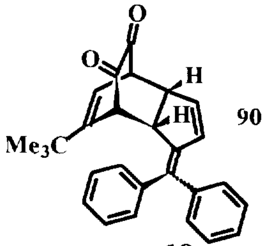
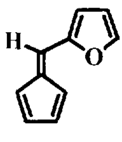
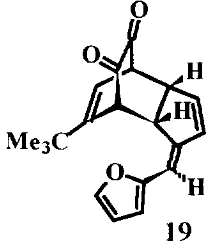
Table 1 Cycloaddition reactions of 3,5-di- *tert*-butyl-*o*-benzoquinone with fulvenes

Entry	Fulvene	Conditions	Product(s)[1]	Yield[2]	MP. °C
1	 7	**Toluene, sealed tube 110 °C, 5h.**	 8	**56%**	**178-180**
2	 9	**Toluene, sealed tube 110 °C, 13h**	 10	**85%**	**184-185**
3	 11	**Toluene, sealed tube 100 °C, 12h**	 12	**90%**	**202-204**
4	 13	**Benzene, sealed tube 100 °C, 2h**	 14	**91%**	**168-170**

[1] Trace amounts of *exo* isomer was also detected [2] Isolated yield

The reactions of 4-*tert*-butyl-*o*-benzoquinone follows the same trend and the results are given in the following Table 2.

Table 2 Cycloaddition reactions of 4- *tert*-butyl-*o*-benzoquinone with fulvenes

Entry	Fulvene	Conditions	Product(s)[1]	Yield[2]	MP. °C
1		**Toluene** **90 °C, 4h**	 **15**	**87%**	**180-182**
2		**Benzene** **reflux, 8h**	 **16**	**64%**	---
3		**Toluene** **reflux, 6h**	 **17**	**68%**	---
4		**Toluene** **reflux, 12h**	 **18**	**90%**	**216-218**
5		**Benzene** **reflux, 12h**	 **19**	**92%**	---

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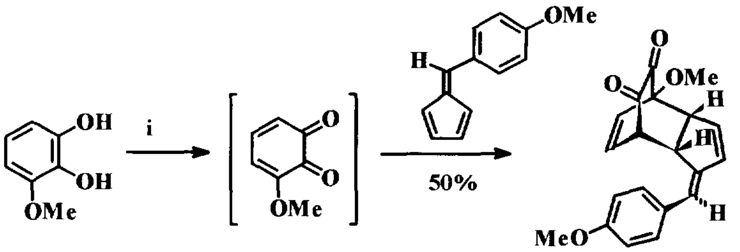
[1] Only *endo* isomer was formed [2] Isolated yield

In continuation of the above investigations, we have studied the reactions of 3-methoxy-*o*-benzoquinone with various fulvenes and the results are discussed below.

First we studied the reaction of 3-methoxy-*o*-benzoquinone with 6-(4-methoxy) phenylfulvene, and the bicyclo[2.2.2]adduct **20** was isolated in 50% yield. The quinone was prepared *in situ* by the oxidation of 3-methoxycatechol in benzene with silver carbonate.



i, Ag_2CO_3, Benzene, reflux, 30 min.

20

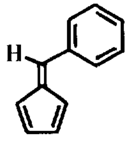
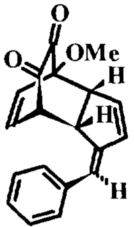
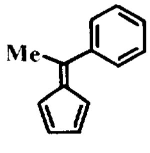
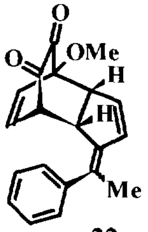
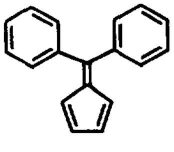
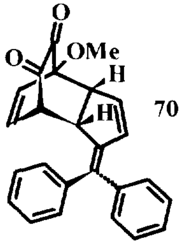
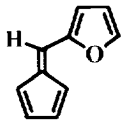
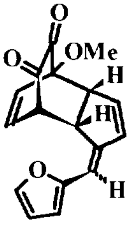
The IR spectrum of **20** showed a strong absorption at 1742 cm^{-1} indicating the presence of an α-diketone. The regio- and stereochemistry of the adduct **20** were derived from extensive NMR analysis. ^1H NMR spectrum of **20** showed the presence of 18 protons. The two methoxy groups appeared at δ 3.65 and 3.83. The bridgehead and ring junction protons resonated at δ 3.86 (1H) and 3.77 (2H) as multiplets. The olefinic protons showed five signals at δ 5.99 (dd, 1H), 6.06 (dd, 1H), 6.18 (dd, 1H), 6.39 (d, 1H) and 6.41 (dd, 1H). The aromatic ring protons gave two doublets at δ 6.92 (2H) and 7.27 (2H). The proton connectivity of the molecule **20** was established by 2D COSY experiments. Carbon-13 spectrum of **20** showed the presence of 20 carbon atoms. The ^{13}C- 90° DEPT showed that 12 -CH- moieties are present. Examination of the ^{13}C- 135° DEPT showed no $-CH_2-$ groups present, and the two $-CH_3$ groups whose carbons resonated at δ 55.3 and 54.0 are clearly the $-OCH_3$ groups. The signals at δ 188.1 and 190.3 in the ^{13}C NMR spectrum have been assigned to the carbonyl groups. The compound **20** showed four quaternary carbons, at δ 87.6, 128.8, 145.0 and 158.7. The $-OCH_3$ group at δ 3.65 is connected to the carbon at δ 87.6. The $-OCH_3$ group on the aromatic ring is connected to the carbon at δ 158.7. Similar results were obtained with other aryl fulvenes and these are presented in the Table 4.

Inorder to explain the observed reactivity, we have carried out some MNDO and AM1 calculations using MOPAC program. The energies of the starting materials were optimized by this method. The HOMO and LUMO energies of some of the reactants were derived from this program and are given below (Table 3).

Table 3. HOMO - LUMO energies of the quinones and fulvenes.

	REACTANT	$HOMO_{eV}$	$LUMO_{eV}$
1.	3,5-Di-*tert*-butyl-*o*-benzoquinone	-9.800	-1.188
2.	4-*tert*-Butyl-*o*-benzoquinone	-10.009	-1.435
3.	3-Methoxy-*o*-benzoquinone	-9.106	-2.006
4.	6-Phenylfulvene	-8.891	-0.487
5.	6-Furylfulvene	-8.851	-0.893

Table 4 Cycloaddition reactions 3-methoxy- *o*-benzoquinone with fulvenes

Entry	Fulvene	Conditions	Product(s)[1]	Yield[2]	MP. ^{o}C
1		**Benzene reflux, 30 min.**	 **21**	56%	146-148
2		"	 **22**	57%	---
3		"	 **23**	70%	175-177
4		"	 **24**	63%	138-140

[1] Only *endo* isomer was detected [2] Isolated yield

From the Table 3, it is clear that all the reactions described in this chapter can be classified as inverse electron demand Diels-Alder reactions. The LUMO$_{quinone}$-HOMO$_{fulvene}$ interaction is favourable in every case.

In conclusion, the present investigations clearly demonstrate that *o*-quinones participate as 4π component in facile cycloadditions with 6-arylfulvenes leading to the bicyclo[2.2.2]diones. It is noteworthy that bicyclo[2.2.2]octene diones are potentially amenable to a number of synthetic transformations.

Acknowledgements: S. K. thanks Regional Research Laboratory and Department of Science and Technology, Govt. of India, for research fellowships.

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. Melting points are uncorrected. The IR spectra were recorded using potassium bromide pellets. ^{1}H and ^{13}C NMR spectra were recorded in the δ scale with TMS as internal reference. The purity of the adducts has been checked by HPLC.

Diels-Alder Adducts 5 and 6. 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.5 g, 2.26 mmol) and 6-phenylfulvene (0.57 g, 3.71 mmol) were dissolved in toluene (1 mL) and taken in a tube. The tube was then sealed under nitrogen and heated at 120 °C for 24 h. The solvent was removed *in vacuo* and the cycloadducts 5 (0.692 g, 82%) and 6 (0.068 g, 8%) were isolated by crystallization from benzene.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(phenyl)methylene]-4,7ethano-indene -8,9-dione (5) (*Endo* adduct).

MP. : 178-179 °C
IR, KBr, : 2968, 2910, 2878, 1731, 1632, 1470, 1397, 1367, 1230, 1166, 1121,1025, 954, 874 cm^{-1}.
^{1}H NMR : δ 7.1 (s, 5H), 6.2-5.6 (m, 4H), 3.7 (m, 3H), 1.2 (s, 9H), 0.8 (s, 9H).
^{13}C NMR : δ 192.0, 190.0, 150.0, 146.0, 141.0, 136.0, 135.0, 129.0, 128.0, 127.0, 123.0, 121.0, 61.0, 51.0, 49.0, 41.0, 35.0, 34.0, 28.0
MS *m/z* : 374 (M^{+}), 348, 301, 220, 183.
HRMS : $C_{26}H_{30}O_2$: 374.4991; found : 374.4923.

***Exo* adduct 6.** MP. : 184-186 °C
IR, KBr : 2967, 1737, 1630, 1470 cm^{-1}.
1H NMR : δ 7.3 (m, 5H), 6.35 (m, 2H), 6.1 (m, 1H), 5.78 (m, 1H), 3.85- 3.7 (m, 3H), 1.2 (s, 9H), 0.85 (s, 9H).
13C NMR : δ 193.0, 192.0, 150.5, 147.0, 141.0, 137.0, 135.0, 129.0, 128.0, 127.0, 122.5, 121.0, 52.0, 51.0, 48.5, 41.5, 35.0, 34.5, 28.0, 27.5.
MS *m/z* : 374 (M^{+}), 348, 147, 96.
HRMS : $C_{26}H_{30}O_2$: 374.4991; found : 374.4945.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(4-methoxyphenyl)methylene] 4,7-ethano-1H-indene-8,9-dione (8)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.23 g, 1.07 mmol) and 6-(4-methoxy) phenylfulvene (0.5 g, excess) were taken in a glass tube and toluene (1 mL) was added. The tube was then sealed under nitrogen and heated at 110 °C for 5 h. The solvent was removed *in vacuo* and the residue on chromatography afforded **8** (0.225 g, 56%) as yellow crystalline solid. MP. 178-180 °C

IR, KBr : 2969, 1732, 1674, 1610, 1517, 1449, 1373, 1301, 1252, 1178, 1032, 960, 876 cm^{-1}.
^{1}H NMR : δ 7.0-6.75 (m, 4H), 6.15-5.60 (m, 4H), 3.7-3.65 (m, 6H), 1.2 (s, 9H), 0.85 (s, 9H).
^{13}C NMR : δ 192.5, 190.0, 158.5, 150.0, 144.5, 141.0, 134.0, 129.0, 122.0, 121.0, 114.4, 61.0, 55.0, 51.0, 48.5, 41.0, 35.0, 34.0, 28.0, 27.5
MS *m/z* : 404 (M^+), 349, 321, 241, 195.
Analysis calcd for $C_{27}H_{32}O_3$: C, 80.16 ; H, 7.97. found : C, 80.09 ; H, 7.86.

[3a-(3aα,4α,7α,7aα)]4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(methylphenyl)methylene]-4,7-ethanoindene-8,9-dione (10)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.2 g, 0.90 mmol) and 6-methyl-6-phenylfulvene (0.221 g, 1.30 mmol) were dissolved in toluene (1 mL) and taken in a glass tube. The tube was then sealed under nitrogen and heated at 110 ^{o}C for 13 h. The solvent was removed *in vacuo* and the product was subjected to chromatography on silica gel using petroleum ether ethyl acetate mixture as eluent to afford **10** (0.30 g, 85%) as yellow crystals. MP. 184-185 ^{o}C

IR, KBr : 2970, 1735, 1602, 1423, 1369, 1238, 1069 cm^{-1}
^{1}H NMR : δ 6.95 (m, 5H), 6.0 (m, 1H), 5.5 (m, 2H), 3.6 (m, 2H), 3.4 (m, 2H), 2.0 (s, 3H), 1.1 (s, 9H), 1.0 (s, 9H).
^{13}C NMR : δ 192.0, 190.0, 154.0, 150.0, 141.5, 137.0, 135.5, 135.0, 128.5, 128.0, 127.5, 126.5, 121.0, 61.0, 51.0, 48.5, 42.0, 35.0, 34.0, 28.0, 27.0, 21.0
MS *m/z* : 388 (M^+), 361, 302, 298, 204.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(diphenyl)methylene]4,7-ethanoindene-8,9-dione (12)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.14 g, 0.63 mmol) and 6,6-diphenyl fulvene (0.175 g, 0.712 mmol) were dissolved in toluene (1 mL) and taken in a glass tube. It was then sealed and heated at 110 ^{o}C for 12 h. The solvent was removed *in vacuo* and the product was subjected to chromatography to afford **12** (0.257 g, 90%) as yellow crystals. MP. 202-204 ^{o}C

IR, KBr : 2974, 1734, 1604, 1516, 1450, 1302, 1254 cm^{-1}.
^{1}H NMR : δ 7.3 (m, 10H), 6.5 (dd, 1H), 6.15 (d, 1H), 5.8 (d, 1H), 3.55 (br s, 2H), 3.2 (br s, 1H), 1.25 (s, 9H), 0.7 (s, 9H).
^{13}C NMR : δ 189.92, 189.5, 153.94, 142.6, 141.86, 141.53, 138.07, 136.93, 129.71, 129.48, 128.61, 127.98, 127.24, 127.12, 123.12, 59.84, 53.01, 48.3, 48.06, 35.1, 33.82, 27.25, 27.08
MS *m/z* : 450 (M^+), 412, 385, 201.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(furyl)methylene]-4,7-ethanoindene-8,9-dione (14)

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.50 g, 2.27 mmol) and 6-furylfulvene (0.5 g, 3.4 mmol) were dissolved in benzene (1 mL) and taken in a glass tube . The tube was then sealed under nitrogen and heated at 100 ^{o}C for 2 h. The solvent was removed *in vacuo* and the product subjected to chromatography to yield **14** (0.925 g, 91%) as yellow crystals. MP. 168-170 ^{o}C

IR, KBr, : 2960, 2880, 1731, 1617, 1481, 1398, 1368, 1232, 1167, 912, 733 cm^{-1}.
^{1}H NMR : δ 7.25 (d, 1H), 6.3-5.6 (m, 6H), 3.8 (br s, 1H), 3.65 (br s, 2H), 1.2 (S, 9H), 0.9 (s, 9H).
^{13}C NMR : δ 193.0, 190.0, 152.5, 150.0, 145.0, 143.0, 140.0, 136.0, 121.0, 112.0, 110.0, 109.5, 61.0, 51.0, 50.5, 41.0, 35.0, 34.0, 28.0
MS *m/z* : 364 (M^+), 331, 298, 205, 169.

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

4-*tert*-Butyl-*o*-benzoquinone (0.5 g, 3.04 mmol) and 6-phenylfulvene (0.617 g, 4.0 mmol) were dissolved in toluene (10 mL) and heated at 90 °C for 4 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **15** (0.84 g, 87%) as a yellow crystals. MP. 180-182 °C

IR, film : 2884, 1732, 1630, 1745, 1368 cm^{-1}.
^{1}H NMR : δ 7.1 (s, 5H), 6.25 (m, 2H), 5.6 (m, 2H), 3.6 (m, 4H), 1.0 (s, 9H).
^{13}C NMR : δ 190.5, 190.0, 151.5, 147.0, 140.0, 136.5, 135.0, 128.5, 127.5, 126.5, 122.5, 118.0, 53.0, 47.0, 40.0, 35.0, 28.0
Analysis calcd for $C_{22}H_{22}O_2$: C, 41.39; H, 4.37. Found : C, 41.37; H, 4.30.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(4-methoxyphenyl)methylene]-4,7-ethanoindene-8,9-dione (16)

4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6-(*p*-methoxy) Phenylfulvene (0.4 g, 2.17 mmol) were dissolved in benzene (10 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **16** (0.407 g, 64%) as yellow solid.

IR, film : 2969, 1730, 1610, 1517, 1254 cm^{-1}.
^{1}H NMR : δ 6.9 (m, 2H), 6.8 (m, 2H), 6.15 (m, 2H), 5.75 (m, 1H), 5.6 (m, 1H), 3.7 (s, 3H), 3.6 (m, 2H), 3.58 (m, 2H), 1.20(s, 9H).
^{13}C NMR : δ 192.0, 190.0, 158.5, 150.5, 145.0, 141.5, 134.5, 129.5, 123.0, 122.0, 115.0, 61.0, 55.5, 51.5, 49.0, 41.5, 35.0, 28.0
MS *m/z* : 348 (M^+), 301, 287, 148, 78.
HRMS : $C_{23}H_{24}O_3$: 348.4212 ; found : 348.4202.

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

4-*tert*-Butyl-*o*-benzoquinone (0.2 g, 1.21 mmol) and 6-phenyl-6-methylfulvene (0.28 g, 1.66 mmol) were dissolved in toluene (10 mL) and refluxed for 6 h under nitrogen. The solvent was removed *in vacuo* and the residue on chromatography afforded **17** (0.275 g, 68 %) as yellow solid.

IR, KBr : 2969, 1734, 1603, 1425, 1367, 1068 cm^{-1}.
^{1}H NMR : δ 6.9 (s, 5H), 5.4 (m, 3H), 3.6 (m, 2H), 3.4 (m, 2H), 2.0 (s, 3H), 1.2 (s, 9H).
^{13}C NMR : δ 191.5, 190.0, 154.5, 151.0, 140.5, 138.0, 135.5, 135.0, 128.5, 128.0, 127.5, 126.0, 121.5, 61.0, 51.0, 49.0, 43.0, 35.0, 28.0, 22.0
MS *m/z* : 332 (M^+), 306, 229, 147, 91.

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

4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6,6-diphenylfulvene (0.5 g, 2.17 mmol) were dissolved in toluene (10 mL) and refluxed for 12 h. The solvent was removed *in vacuo* and the residue was subjected to column chromatography to afford **18** (0.648 g, 90%) as yellow solid. MP. 216-218 °C

IR, KBr : 2974, 1735, 1605, 1516, 1450, 1255 cm^{-1}.
^1H NMR : δ 7.1(m, 10 H), 6.4 (m, 1H), 6.2 (m, 2H), 5.85 (d, 1H), 3.5 (m,2H), 3.3 (m, 2H), 1.25 (s, 9H).
^{13}C NMR : δ 190.0, 189.0, 153.0, 143.0, 142.0, 141.5, 138.6,135.0, 130.0, 129.48, 128.71, 127.9, 127.24, 127.0, 123.0, 59.5, 53.0, 48.5, 48.0, 35.1, 27.2
MS *m/z* : 394 (M^+), 361, 294, 263, 174, 83.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(furyl)methylene]-4,7-ethanoindene-8,9-dione (19)

4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6-furylfulvene (0.35 g, 2.42 mmol) were dissolved in benzene (10 mL) and refluxed under nitrogen for 12 h. The solvent was removed *in vacuo* and the residue on column chromatography yielded **19** (0.518 g, 92%) as yellow semi solid.

IR, film : 2878, 1733, 1618, 1480, 1378 cm^{-1}.
^1H NMR : δ 7.5 (d, 1H), 6.3-5.7 (m, 6H), 3.9 (br s, 1H), 3.8 (m, 1H), 3.7 (m, 2H), 1.25 (s, 9H).
^{13}C NMR : δ 193.5, 191.5, 152.5, 151.0, 145.5, 143.0, 140.0, 136.5, 121.5, 112.0, 110.5, 109.5, 61.0, 51.5, 50.0, 41.0, 35.0, 28.0
MS *m/z* : 308 (M^+), 271, 204, 188, 96.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(4-methoxyphenyl)methylene]-4,7-ethanoindene-8,9-dione (20)

3-Methoxycatechol (0.588 g, 4.2 mmol) was dissolved in benzene (10 mL) and silver carbonate (2.0 g) was added and stirred under nitrogen. To the above solution 6-(4-methoxy) phenylfulvene (0.72 g, 4.0 mmol) was added and refluxed for 30 minutes. The inorganic material was removed by passing through a short column of celite and washed with benzene. The solvent was removed *in vacuo* and the residue on chromatography afforded **20** (0.53 g, 50%) as yellow crystals. MP. 170-172 °C

IR, film : 2940, 2842, 1742, 1609, 1510, 1462, 1352, 1300, 1252, 1177, 1032, 882, 777 cm^{-1}.
^1H NMR : δ 7.3-6.6 (m, 4H), 6.4-5.8 (m, 5H), 4.0-3.6 (m, 3H), 3.8 (s, 3H), 3.6 (s, 3H).
^{13}C NMR : δ 190.0, 188.0, 159.0, 145.0, 142.0, 132.0, 131.0, 129.0, 128.5, 127.0, 123.0, 114.0, 87.5, 55.5, 54.0, 51.0, 48.0, 40.0
MS *m/z* : 322 (M^+), 291, 263, 248, 191, 97, 65.
Analysis calcd for $C_{20}H_{18}O_4$: C, 74.51; H, 5.63 : found : C, 74.49; H,5.58.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(phenyl)methylene]-4,7-ethanoindene-8,9-dione (21)

3-Methoxycatechol (0.45 g, 3.25 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-phenylfulvene (1.0 g, 6.5 mmol) was added. It was refluxed for 30 minutes and worked up as usual. The residue on column chromatography afforded **21** (0.529 g, 56%) as yellow crystals. MP. 146-148 °C

IR, KBr : 2944, 2842, 1744, 1627, 1450, 1359, 1077 cm^{-1}.
^1H NMR : δ 7.0 (m, 5H), 5.9 (m, 5H), 3.45 (s, 3H), 3.34 (m, 3H).

^{13}C NMR : δ 190.5, 189.0, 146.0, 45.0, 142.5, 132.5, 131.0, 129.5, 128.5, 127.5, 123.0, 114.0, 87.3, 54.0, 51.5, 48.0, 40.5
HRMS : $C_{19}H_{16}O_3$: 292.1098 ; found : 292.1099.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(methyl phenyl)methylene]-4,7-ethanoindene-8,9-dione (22)

3-Methoxycatechol (0.5 g, 3.6 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-phenyl-6-methylfulvene (0.7 g, 4.16 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **22** (0.632 g, 56%) as yellow semi solid.

IR, film : 2940, 2839, 1745, 1628, 1465, 1360 cm^{-1}.
^{1}H NMR : δ 6.85 (m, 5H), 5.6 (m, 4H), 3.45 (s, 3H), 3.3 (m, 3H), 2.0 (s 3H).
^{13}C NMR : δ 192.5, 191.0, 146.0, 145.0, 142.0, 133.5, 131.0, 129.5, 128.5, 128.0, 127.0, 123.5, 115.0, 87.0, 55.0, 51.0, 49.0, 42.0, 22.0
MS *m/z* : 306 (M^{+}), 276, 257, 194, 84, 73.

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

3-Methoxycatechol (0.4 g, 2.89 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6,6-diphenylfulvene (0.7 g, 3.039 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **23** (0.746 g, 70%) as yellow crystals. MP. 175-177 °C

IR, KBr : 2940, 2841, 1739, 1605, 1468, 1375 cm^{-1}.
^{1}H NMR δ:7.25 (m, 10 H), 6.5 (m, 2H), 6.15(m, 2H), 3.4 (s, 3H), 3.25 (m, 2H).
^{13}C NMR : δ 192.0, 190.5, 150.0, 143.0, 141.5, 140.0, 138.5, 135.0, 130.0, 129.8, 128.5, 127.5, 127.0, 125.0, 123.0, 87.0, 58.0, 53.0, 42.0
MS *m/z* : 368 (M^{+}), 324, 289, 258, 87,57.

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

3-Methoxycatechol (0.508 g, 3.6 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-furylfulvene (0.527 g, 3.6 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **24** (0.652 g, 63%) as yellow crystals. MP. 138-140 °C.

IR, KBr : 2940, 1745, 1520, 1470, 1360, 1250, 885 cm^{-1}.
^{1}H NMR : δ 7.4 (d, 1H), 6.4-5.9 (m, 7H), 3.9 (m, 1H), 3.7 (br s, 2H), 3.6 (s, 3H).
^{13}C NMR : δ 190.5, 188.0, 152.0, 145.0, 143.0, 141.0, 133.5, 131.0, 127.0, 112.0, 10.0, 88.0, 54.0, 50.5, 50.0, 40.5
MS *m/z* : 282 (M^{+}), 241, 159, 142, 73, 56.

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