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# Diels-Alder Reactions of a 6-Arenyl Fulvene with Dienes and Dienophiles and Related Chemistry[1]

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***Abstract***: 6-(2-Phenyl ethenyl) fulvene has been shown to participate both as diene and dienophile in Diels-Alder reactions and a facile photochemical transformation of the resulting bicyclo[2.2.2]-octenediones leading to extensively conjugated benzofulvenes has been accomplished.

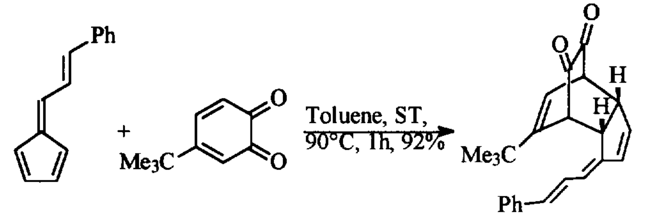
Pentafulvenes are among the most extensively investigated cross-conjugated systems; their chemistry has been of interest to both synthetic organic chemists and theoreticians, largely due to the diverse cycloaddition profiles these molecules can potentially exhibit.[2] Although a substantial amount of work has been done on the cycloadditions of pentafulvenes, such reactions of 6-vinyl fulvenes have received only scant attention.[3] The only work in this area has been the reaction of 6-(2-phenyl ethenyl) and 6-(2,2-diphenyl ethenyl) fulvene with DMAD and the photolysis of the resulting [4+2] adducts leading to heptafulvene derivatives.[4]

As a natural progression of our recent work on the cycloadditions of fulvenes with *o*-benzoquinones,[5] we became interested in exploring the cycloaddition chemistry of 6-arenyl fulvenes. The latter, being 8π conjugated systems, potentially offer the prospect of higher-order cycloadditions also.

## RESULTS AND DISCUSSION

With a view to gaining insight into the cycloaddition chemistry of 6-arenylfulvenes, 6-(2-phenyl ethenyl) fulvene **1**, a typical member of the series was prepared by the condensation of cinnamaldehyde with cyclopentadiene in the presence of pyrrolidine as base.[6] Our initial efforts involved the cycloaddition of **1** with *o*-benzoquinones; the latter are known to participate as carbodienes, heterodienes or dienophiles in cycloaddition reactions.[5]

4-*tert*-butyl-*o*-benzoquinone on treatment with **1** in a sealed tube under argon atmosphere at 90 °C for 1h afforded a yellow crystalline product in 92% yield. This was characterized as the Diels-Alder adduct **3** resulting from the participation of **1** as a $2\pi$ component and *o*-quinone as a carbodiene. It is noteworthy that the reaction is *endo* selective (Scheme 1).



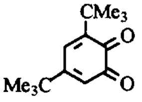
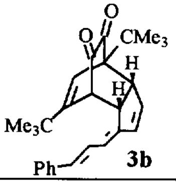
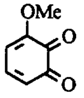
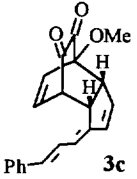
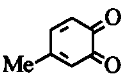
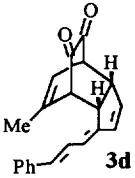
**1** **2a** **3a**

Scheme 1

The IR spectrum of **3** showed a strong carbonyl absorption at 1739 cm$^{-1}$ characteristic of the $\alpha$-diketone. The $^{1}$H NMR spectrum of **3** exhibited a singlet corresponding to the *tert*-butyl group at $\delta$ 1.00 . The two sp$^{3}$ protons at the ring junction appeared as a multiplet at $\delta$ 3.62. The two bridgehead protons adjacent to the carbonyl groups resonated at $\delta$ 3.77 as a multiplet. The $^{13}$C NMR spectrum of **3** revealed the presence of two carbonyl groups ($\delta$ 192.13 and 192.01). The signals discernible at $\delta$ 53.47 and 50.82 were assigned to the bridgehead carbons. The carbons at the ring junction resonated at $\delta$ 46.85 and 39.95.

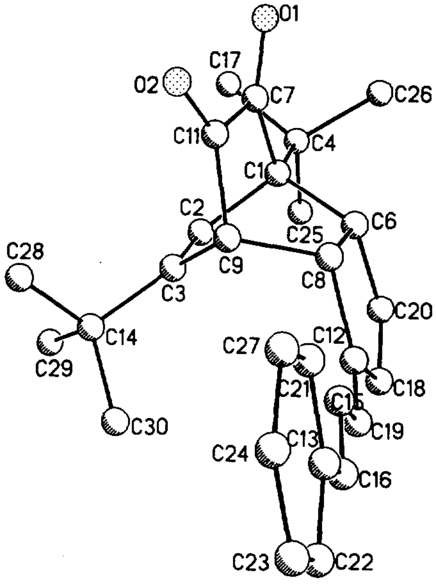
Similar results were obtained with other substituted *o*-benzoquinones and the results are summarised in Table1.

Table 1. Cycloaddition reactions of **1** with *o*-benzoquinones.

| Entry | *o*-Quinone | Reaction condition | Product[1] | Yield[2] (%) |
|---|---|---|---|---|
| 1 |  **2b** | Toluene, ST<br>90°C, 24 h |  **3b** | 40 |
| 2* |  **2c** | Benzene,<br>Reflux,<br>30 min. |  **3c** | 82 |
| 3* |  **2d** | Benzene,<br>Reflux,<br>15 min. |  **3d** | 83 |

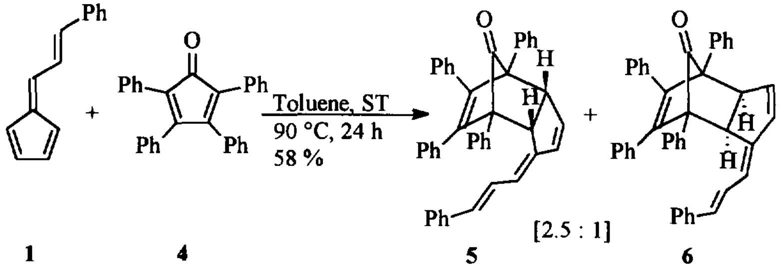
1. Trace amount of *exo* isomer also formed . 2. Isolated yield. *Quinones in entries 2 and 3 were prepared *in situ* by $Ag_2CO_3$ oxidation of corresponding catechols.

All the products were characterized on the basis of spectral analysis. The assigned stereochemistry of the adducts were confirmed by single crystal X-ray analysis of **3b**.



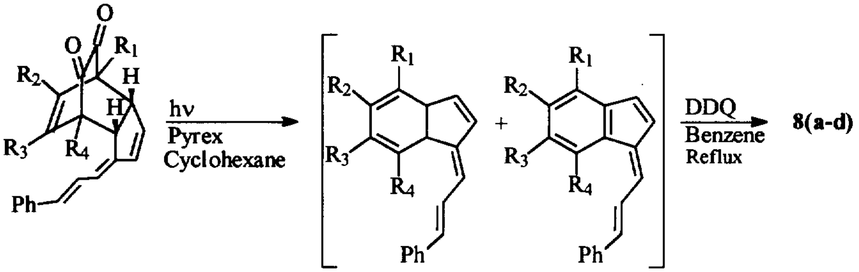
X-ray structure of **3b**

A similar reactivity was observed when **1** was treated with tetracyclone yielding both *endo* and *exo* isomers as illustrated below (Scheme 2).



Scheme 2

The structures were assigned on the basis of spectral analysis and X-ray crystallography of **5**. The bicyclo systems obtained from the reactions of **1** with *o*-benzoquinones and tetracyclone appeared attractive for further synthetic transformations.[7] In this context, we have carried out some photodecarbonylation studies.[8] The photolysis of the bicyclo[2.2.2]octene dione systems **3(a-d)** in cyclohexane using a medium pressure mercury vapour lamp afforded the doubly decarbonylated products **7(a-d)** and **8(a-d)**. The two products were not separable by column chromatography due to their highly non-polar nature. The mixture was filtered through a silicagel column and was subjected to DDQ oxidation in benzene under reflux conditions, which converted the dihydroproduct **7(a-d)** to **8(a-d)**. The reactions are summarised in Scheme 3.



**3(a-d)** **7(a-d)** **8(a-d)**

| Entry | Dione | Substituents | Photolysis time | Yield * (%) | DDQ Oxidation time | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | **3a** | $R_1$, $R_2$, $R_4$= H, $R_3$= $CMe_3$ | 1 h | 67 | 4 h | 55 |
| 2 | **3b** | $R_1$, $R_3$= $CMe_3$, $R_2$, $R_4$= H | 2 h | 97 | 1 h | 85 |
| 3 | **3c** | $R_1$= OMe, $R_2$, $R_3$, $R_4$= H | 1.25 h | 84 | 3 h | 31 |
| 4 | **3d** | $R_1$, $R_2$, $R_4$= H, $R_3$= Me | 1 h | 59 | 2 h | 59 |

*Combined isolated yields of 7 and 8.

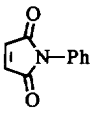
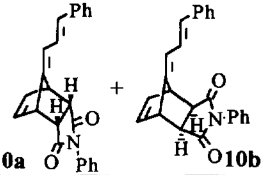
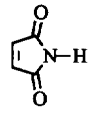
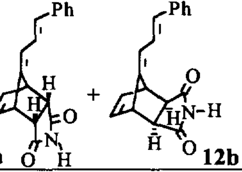
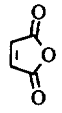
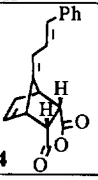
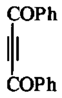
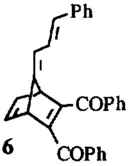
Scheme 3

The conjugated benzofulvene derivatives **8(a-d)** were characterized by spectral analysis. Attempted photodecarbonylation experiments of Diels-Alder adduct **5** obtained from the reaction of **1** with tetracyclone, resulted in retro Diels-Alder reaction. The benzofulvene derivative **8c** contains an extensively conjugated π system with an electron donating ($-OCH_3$) group and electron withdrawing phenyl group, rendering it a potential push-pull system. Irradiation of **8c** using the 1064 nm fundamental output of Nd:YAG laser produces second harmonic at 532 nm . This is indicative of the appreciable Non Linear Optical (NLO) activity of **8c**.

Subsequently we have investigated the cycloaddition profile of **1** with other electron deficient dienophiles, in which the former participated as a 4π addend. The results are summarised in Table 2.

All the products were characterized by spectroscopic analysis and final proof for the assigned structure was obtained from single crystal X-ray analysis of a representative compound **10b**.

Table 2. Cycloaddition reactions of **1** with dienophiles.

| Entry | Dienophile | Reaction conditions | Products | Isomeric ratio | Yield* (%) |
|---|---|---|---|---|---|
| 1 | <br>**9** | Benzene, rt, 24 h | <br>**10a** + **10b** | 1.9:1 | 89 |
| 2 | <br>**11** | Benzene, rt, 24 h | <br>**12a** + **12b** | 1:1 | 98 |
| 3 | <br>**13** | Toluene, rt, 20 h | <br>**14** | – | 57 |
| 4 | <br>**15** | Benzene, rt, 48 h | <br>**16** | – | 91 |

*Isolated yield

In order to explain the observed reactivity and periselectivity in the cycloaddition reactions of **1** with dienes and dienophiles, we have carried out some MNDO and AM1 calculations using MOPAC program.[8] The results obtained are illustrated in Figure 1 in which the correlation diagram for the reactions of **1** with N-phenyl maleimide and 3,5-di-*tert*-butyl-*o*-benzoquinone is presented.

From the correlation diagrams, it is evident that the reaction of **1** with electron deficient dienophiles (N-phenylmaleimide) follows the normal Diels-Alder pathway. The size and shape of orbital coefficients of the reacting carbon centers show that NHOMO(1)- LUMO(dienophile) interaction is favourable. In those reactions in which 6-vinyl fulvene participates as a dienophile with electron deficient dienes, the energy gaps of the interacting orbitals show that the reaction is controlled by LUMO(diene)-NHOMO(**1**) interaction, which is classified as inverse electron demand Diels-Alder reaction .

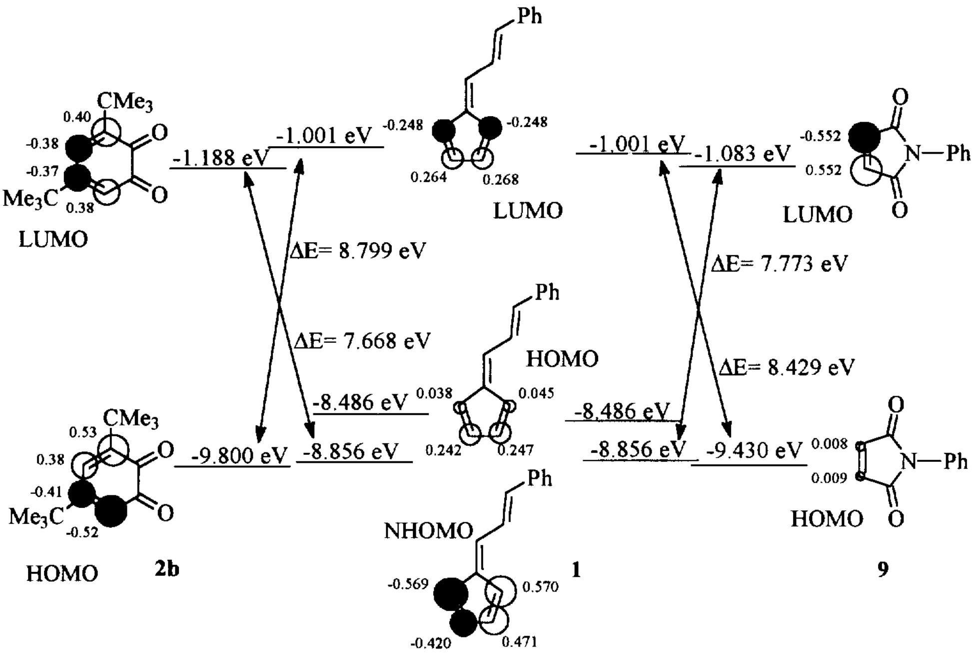


Figure 1. Correlation diagrams for the cycloadditions of **1** with 3,5-di-*tert*-butyl-*o*-benzoquinone and N-phenyl maleimide.

In conclusion, the present investigation shows that **1** participates as a 4π addend in Diels- Alder reaction involving electron deficient dienophiles whereas it reacts as a 2π addend with electron deficient dienes. These observations have been rationalized by MNDO and AM1 calculations. The photodecarbonylation of bicyclo[2.2.2]octene diones resulting from the cycloaddition of **1** with *o*-benzoquinones has been shown to be an efficient method for the synthesis of conjugated benzofulvenes.

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## EXPERIMENTAL DETAILS

All reactions were carried out in oven dried glassware (120 °C) under an atmosphere of argon. 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 hexane were used as eluents. Melting points are uncorrected. IR spectra were run on a Perkin-Elmer Model 882 infrared spectrophotometer. Electronic spectra were recorded on a Shimadzu UV-2100 spectrophotometer. $^{1}$H and $^{13}$C NMR were recorded in the δ scale with TMS as internal reference. All steady-state irradiations were carried out in an immersion well equipment using a Hanovia 450 W medium pressure mercury vapour lamp.

**6-*tert*-Butyl-1-(3-phenyl-allylidene)-3a,4,7,7a-tetrahydro-1H-4,7-ethano-indene-8,9-dione (3a) (*Endo* adduct).**[1]

6-(2-Phenylethenyl)fulvene **1** (0.164 g, 0.91 mmol) and 4-*tert*-butyl-*o*-benzo-quinone (0.100 g, 0.6 mmol) were dissolved in dry toluene (2 mL) and sealed under argon in a Schlenk glass tube. The mixture was heated at 90 °C for 1 h and then subjected to silica gel column chromatography (10% ethyl acetate-hexane) to afford **3a** (0.193 g, 92%) as yellow crystals. MP. 195-197 °C.

**4,6-Di-*tert*-butyl-1-(3-phenyl-allylidene)-3a,4,7,7a-terahydro-1H-4,7-ethanoindene-8,9-dione (3b) (*Endo* adduct).**

6-(2-Phenylethenyl)fulvene 1 (0.298 g, 1.65 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (0.300 g, 1.36 mmol) were dissolved in dry toluene (2 mL) in a Schlenk glass tube, sealed under argon and heated at 90 °C for 24 h. The reaction mixture was subjected to column chromatography on silica gel (5% ethylacetate-hexane) to afford **3b** (0.220 g, 40%) as yellow crystals. MP. 203-205 °C.

IR, KBr : 2967, 1739, 1627, 1574, 1500, 1371, 1236, 1117, 965, 748 cm$^{-1}$.

$^1$H NMR : δ 7.34 (m, 5H), 6.90 (dd, J=11 Hz, 1H), 6.56 (d, J=15 Hz, 1H), 6.30 (dd, 1H), 6.20 (d,J=11 Hz, 1H), 6.08 (dd, 1H), 5.78 (d, 1H), 3.76 (m, 2H), 3.56 (m, 1H), 1.28 (s, 9H), 1.01 (s,9H).

$^{13}$C NMR : δ 193.00, 190.00, 152.00, 147.50, 139.31, 136.33, 133.40, 128.80, 127.81, 126.48, 124.26, 122.21, 120.77, 61.75, 52.38, 50.65, 40.98, 35.16, 28.07.

Analysis calcd. for $C_{28}H_{33}O_2$: C, 83.95%; H, 8.05%. Found: C, 83.60%; H, 8.08%.

Crystal data for **3b**: $C_{28}H_{32}O_2$, Fw-400.54, 0.20x0.30x0.40 mm, Triclinic, Space group P1, Unit cell dimensions a=9.635 Å, α= 102.37°; b= 10.04340(10) Å, β= 110.4980 (10)°; c= 13.0685(2) Å, γ= 90.4910(10)°. Rindices(all data) R1=0.0845, WR2= 0.1528. Volume, Z= 1152.24(2) Å$^3$, 2. Dcalc= 1.154 Mg/m$^3$. F(000)= 432. Absorption Coefficient= 0.071 mm$^{-1}$; Reflections collected = 32272. (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).

**4-Methoxy-1-(3-phenyl-allylidene)-3a,4,7,7a-tetrahydro-1H-4,7-ethanoindene-8,9-dione (3c) (*Endo* adduct).**

3-Methoxycatechol (0.231 g, 1.64 mmol) was dissolved in dry benzene (5 mL) and silver carbonate (0.680 g, 2.46 mmol) was added and stirred under argon. 6-(2-Phenylethenyl)fulvene **1** (0.200 g, 1.1 mmol) was added to the above solution and refluxed for 30 minutes. The inorganic material was removed by passing through a short celite column and washed with diethyl ether. The solvent was removed *in vacuo* and the residue purified by silica gel column chromatography (20% ethylacetate-hexane) to afford **3c** (0.289 g, 82%) as yellow crystals. MP. 157-160 °C.

IR, KBr : 3065, 2941, 1745, 1450, 1352, 1238, 1070, 967, 760, 692 cm$^{-1}$.

$^1$H NMR : δ 7.33 (m, 5H), 6.89 ( dd, J=11.53 Hz, 1H0, 6.57 (d, J=15.37 Hz, 1H), 6.40 (dd, 1H), 6,23 (m, 3H), 6.01 (dd, 1H), 3.81 (m, 2H), 3.66 (s, 3H), 3.58 (m, 1H).

$^{13}$C NMR : δ 191.13, 188.10, 157.50, 142.20, 137.10, 134.00,132.00, 128.80, 128.05, 127.00, 126.48, 124.80, 123.00, 88.10, 54.80, 52.30, 51.00, 39.92.

HRMS : $C_{21}H_{18}O_3$: 318.12558. Found: 318.12533.

**6-Methyl-1-(3-phenyl-allylidene)-3a,4,7,7a-tetrahydro-1H-4,7-ethano-indene-8,9-dione (3d) (*Endo* adduct).**

4-Methylcatechol (0.206 g, 1.6 mmol) was dissolved in dry benzene (5 mL) and silver carbonate (0.660 g, 2.4 mmol) was added and stirred under argon. To the solution, 6-(2-phenylethenyl)fulvene **1** (0.200 g, 1.1 mmol) was added and refluxed for 15 minutes. The inorganic material was removed by passing through a short celite column and washed with diethyl ether. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography to afford **3d** (0.281 g, 83%) as yellow semisolid.

IR, KBr : 3064, 3034, 2976, 2916, 2257, 1740, 1647, 1598, 1503, 1446, 1313, 1234, 1173, 1150, 1094, 1025, 968, 912, 797, 729 $cm^{-1}$.

$^1$H NMR : δ 7.3 (m, 5H), 6.85 (m, 6H), 3.55 (m, 4H), 1.80 (s, 3H).

$^{13}$C NMR : δ 190.10, 189.89, 147.61, 139.65, 136.93, 134.61, 133.23, 131.15, 128.55, 128.46, 126.25, 126.07, 122.52, 121.06, 57.33, 51.37, 47.04, 39.40, 21.65.

Analysis calcd.for $C_{21}H_{18}O_2$: C,83.41%; H,6.00%. Found: C,83.23%; H,5.93%.

**Diels-Alder adducts 5 and 6.**

6-(2-Phenylethenyl)fulvene **1** (0.180 g, 1 mmol) and tetracyclone (0.422 g, 1.1 mmol) were dissolved in dry benzene (2 mL) in a Schlenk glass tube. It was sealed under argon and heated at 90 °C for 24 h. The reaction mixture was subjected to silica gel column chromatography (1% ethylacetate-hexane) to afford *endo* adduct **5** (0.235 g, 42%) as colourless crystals and *exo* adduct **6** (0.093 g, 16%) as colourless amorphous solid.

**4,5,6,7,-Tetraphenyl-1-(3-phenyl-allylidene)-3a,4,7,7a-tetrahydro-1H-4,7-methano-indene-8-one(5)**

**Data for *endo* adduct** [1]

***Exo* adduct (5).**

IR, KBr : 3032, 2920, 1771, 1584, 1482, 958, 900 $cm^{-1}$.

$^1$H NMR : δ 7.12 (m, 27H), 6.36 (d, J=5.86 Hz, 1H), 5.98 (d, J=15.36 Hz, 1H), 5.33 (d, J=14.7 Hz, 1H), 4.40 (d, J=7.5 Hz, 1H), 3.74 (d, J=7.49 Hz, 1H).

$^{13}$C NMR : δ 200.92, 147.25, 145.03, 142.90, 137.33, 134.83, 134.14, 134.08, 133.86, 131.11, 130.25, 130.15, 129.08, 128.36, 127.86, 127.51, 127.12, 127.05, 126.92, 126.67, 126.56, 126.04, 125.44, 125.29, 66.12, 63.45, 54.62, 53.07.

Analysis calcd. for $C_{43}H_{32}O$: C, 91.45%; H, 5.71%. Found: C, 91.18%; H, 5.98%.

**Typical procedure for the photolytic double decarbonylation of α-diones.**

**6-*tert*-Butyl-1-(3-phenyl-allylidene)-1H-indene (8a).**

The adduct **3a** (90 mg, 0.26 mmol) was dissolved in cyclohexane (250 mL) and the solution was purged with argon for 10 min with stirring. It was then irradiated for 1 h using a 450 W mercury vapour lamp and a pyrex filter. The solvent was evaporated *in vacuo* and the residue was charged on a silica gel column. Elution with hexane afforded a mixture (50 mg, 67%) of diene **7a** and benzofulvene **8a** as a viscous yellow liquid.

To a stirred solution of the mixture (50 mg, 0.17 mmol) of **7a** and **8a**, in dry benzene (5 mL), DDQ (44 mg, 0.19 mmol) was added and the mixture was refluxed with stirring for 3 h. The solvent was evaporated *in vacuo* and the residue was charged on a silica gel column. Elution with hexane afforded the benzofulvene **8a** (26 mg, 55%) as a yellow semisolid.

IR, film : 2971, 2936, 2863, 1617, 1457, 1264, 1100, 910, 735 cm$^{-1}$.

$^1$H NMR : δ 7.30 (m, 13H), 1.35 (s, 9H).

$^{13}$C NMR : δ 137.65, 137.29, 136.90, 132.64, 128.76, 128.40, 127.77, 127.06, 126.91, 125.69, 124.67, 122.02, 118.94, 118.29, 31.50, 30.75.

EIMS, *m/z* : 287(M$^+$+1, 5), 286 (M$^+$, 3), 165(20), 115 (48), 57 (80).

**4,6-Di-*tert*-butyl-1-(3-phenyl-allylidene)-1H-indene (8b).**

The adduct **3b** (100 mg, 0.25 mmol) was irradiated for 1 h as in the case of **3a**. Processing of the reaction mixture followed by chromatographic separation on silica gel column afforded the mixture (83 mg, 97%) of diene and benzofulvene. This mixture (55 mg, 0.16 mmol) was then subjected to oxidation using DDQ (43 mg, 0.19 mmol) in refluxing benzene (5 mL) for 4 h. Purification of the product by silicagel column chromatography using hexane as the eluent gave **8b** (46 mg, 85%) as a yellow semisolid.

IR, film : 2952, 2925, 2864, 1608, 1481, 1407, 1360, 1313, 1232, 1165, 1031, 964, 796 cm$^{-1}$.

$^1$H NMR : δ 7.49 (m, 7H), 7.04 (m, 5H), 1.50 (s, 9H), 1.40 (s, 9H).

$^{13}$C NMR : δ 147.67, 142.96, 140.75, 137.47, 137.14, 136.90, 133.09, 128.67, 128.31, 127.39, 126.85, 125.66, 122.73, 121.72, 114.17, 35.52, 34.87, 31.56, 31.23, 29.62.

EIMS, *m/z* : 343 (M$^+$+1, 3), 342 (M$^+$, 4), 285 (7), 165 (10), 116 (15), 57 (100), 41 (69).

**4-Methoxy-1-(3-phenyl-allylidene)-1H-indene (8c).**

The adduct **3c** (100 mg, 0.31 mmol) in cyclohexane (250 mL) was irradiated for 1 h. The reaction mixture on usual work up, followed by purification on a silica gel column using hexane as eluent afforded the mixture (68 mg, 84%) of diene and benzofulvene. This mixture (87 mg, 0.33 mmol) was then subjected to oxidation with DDQ (90 mg, 0.39 mmol) in refluxing benzene (10 mL) for 1 h. The reaction mixture was purified by chromatogrphy on a silica gel column using hexane as the eluent to obtain **8c** (27 mg, 31%) as a reddish yellow semisolid.

IR, film : 3035, 2966, 2938, 2844, 1610, 1591, 1478, 1434, 1390, 1264, 1185, 1118, 1061, 1013, 968, 803, 752, 692 cm$^{-1}$.

$^1$H NMR : δ 7.22 (m, 13H), 3.89 (s, 3H).

$^{13}$C NMR : δ 141.29, 137.92, 136.78, 129.30, 128.73, 128.49, 126.97, 126.28, 125.54, 122.40, 112.65, 109.96, 55.40.

EIMS, *m/z* : 261 ($M^+$+1, 21), 260 ($M^+$, 100), 259 (29), 245 (44), 229 (64), 215 (58), 202 (52), 139 (31), 115 (54), 94 (18).

**6-Methyl-1-(3-phenyl-allylidine)-1H-indene (8d).**

The adduct **3d** (100 mg, 0.33 mmol) in cyclohexane (250 mL) was irradiated for 1 h. The reaction mixture was processed as usual and purificaiton by column chromatography afforded the mixture (48 mg, 59%) of diene and benzofulvene. This mixture (62 mg, 0.25 mmol) was then oxidised by DDQ (70 mg, 0.30 mmol) in refluxing benzene (5 mL) for 3 h. Purification of the reaction mixture by silica gel column chromatography afforded **8d** (36 mg, 59%) as a yellow semisolid.

IR, film : 3038, 2967, 2935, 2866, 1617, 1581, 1502, 1455, 1297, 1261, 1142, 1101, 1068, 1011, 965 $cm^{-1}$.

$^1$H NMR : δ 7.12 (m, 13H), 1.28 (s, 3H).

$^{13}$C NMR : δ 145.14, 142.87, 140.72, 137.26, 132.61, 132.25, 128.70, 128.34, 127.74, 127.06, 126.91, 125.57, 124.73, 121.93, 119.12, 118.97, 31.50, 21.62.

EIMS, *m/z* : 245 ($M^+$+1, 19), 244 ($M^+$, 90), 243 (28), 229 (100), 228 (59), 202 (19), 165 (26), 152 (24), 115 (36), 91 (13), 63 (24), 51(25).

**Diels-Alder adducts 10a and 10b.**

6-(2-Phenylethenyl)fulvene **1** (0.180 g, 1 mmol) and N-phenyl maleimide (0.190 g, 1.1 mmol) were dissolved in dry benzene (4 mL) and stirred at room temperature under argon atmosphere for 24 h. The solvent was removed under reduced pressure and the residue was subjected to chromatography on silica gel column (10% ethylacetate-hexane), which afforded the *endo* adduct **10a** (0.205 g, 58%) and *exo* adduct **10b** (0.110 g, 31%) as colourless solids. The products were recrystallised from dichloromethane-hexane solvent system.

**4-Phenyl-10-(3-phenyl-allylidene)-4-aza-tricyclo[5.2.10.2.6]dec-8-ene-3,5-dione (10a) (*Endo adduct*).**

MP. : 150-152 °C

IR, KBr : 3035, 1778, 1717, 1601, 1500, 1379, 1184, 963, 738 $cm^{-1}$.

$^1$H NMR : δ 7.32 (m, 10H), 6.76 (dd, J=10.9 Hz, 1H), 6.51 (m, 3H), 5.67 (d, J=10.78 Hz, 1H), 4.24 (s, 1H), 3.78 (s, 1H), 3.49 (brs, 2H).

$^{13}$C NMR : δ 175.66, 175.60, 155.32, 136.95, 135.03, 134.19, 132.28, 131.65, 129.09, 128.68, 128.61, 127.60, 126.50, 126.16, 123.82, 110.52, 48.30, 44.84, 44.54, 44.12.

Analysis calcd. for $C_{24}H_{19}O_2N$: C, 81.56%; H, 5.41%; N, 3.96%. Found: C, 81.28%; H, 5.38%; N,3.78%.

**Data for *Exo adduct* (10b).**[1]

**10-(3-Phenyl-allylidene)-4-aza-tricyclo[5.2.1.0.2.6]dec-8-ene-3,5-dione (12a and 12b)**

**( Mixture of *endo* and *exo* isomers).**

6-(2-Phenylethenyl)fulvene **1** (0.180 g, 1 mmol) and maleimide (0.117 g, 1.2 mmol) were dissolved in dry benzene (5 mL) and stirred at room temperature under argon atmosphere for 24 h. The solvent was evaporated *in vacuo* and the residue was subjected to chromatography on silica gel column (10% ethylacetate-hexane) to afford an inseparable mixture of adducts **12a** and **12b** (0.272 g, 98%) as colourless crystals (mp. 177-180 °C) in 1:1 isomeric ratio.

IR, film : 3188, 3069, 1771, 1711, 1346, 1292, 1187, 964, 743 cm$^{-1}$.

$^1$H NMR : δ 8.26 (brs, 2H), 7.31 (m, 10H), 6.50 (m, 8H), 5.75 (d, J=10.53 Hz, 1H), 5.60 (d, J=10.64 Hz, 1H), 4.10 (brs, 1H), 3.99 (brs, 1H), 3.59 (brs, 1H), 3.55 (brs, 1H), 3.32 (m, 2H), 2.85 (brs, 2H).

$^{13}$C NMR : δ 177.03, 177.01, 176.92, 176.66, 155.42, 148.96, 137.82, 137.05, 135.08, 134.26, 133.13, 132.34, 128.60, 127.65, 126.40, 126.24, 123.90, 123.67, 114.24, 110.56, 49.12, 48.98, 47.94, 46.46, 46.15, 44.83, 43.71.

Analysis calcd. for $C_{17}H_{14}O_2N$: C, 77.95%; H, 5.45%; N, 5.05%. Found: C, 77.88%; H, 5.48%; N, 5.01%.

**10-(3-Phenyl-allylidene)-4-oxa-tricyclo[5.2.1.0.2.6]dec-8-ene-3,5-dione (14) (*Endo* adduct).**

6-(2-Phenylethenyl)fulvene **1** (0.150 g, 0.83 mmol) and maleic anhydride (0.122 g, 1.2 mmol) were dissolved in dry toluene (4 mL) and the solution was stirred at room temperature under argon atmosphere for 20 h. Solvent was evaporated and the residue was subjected to a rapid chromatographic separation on short silica gel column (20% ethylacetate-hexane) to afford **14** (0.159 g, 57%) as colourless crystals.(mp.131-133°C).

IR, KBr : 3035, 1865, 1785, 1685, 1599, 1498, 1453, 1358, 1285, 1225, 1077, 914, 803, 757 cm$^{-1}$.

$^1$H NMR : δ 7.33 (m, 5H), 6.60 (m, 4H), 5.63 (d, J=10.20 Hz, 1H), 4.20 (brs, 1H), 3.77 (brs, 1H), 3.64 (m, 2H).

$^{13}$C NMR : δ 170.15, 170.13, 153.99, 136.86, 136.16, 135.34, 133.25, 128.71, 127.90, 126.33, 123.38, 111.36, 48.68, 46.32, 46.07, 44.44.

Analysis calcd. for $C_{17}H_{13}O_3$: C, 77.68%; H, 5.07%. Found: C, 77.78%; H, 5.09%.

**7-(3-Phenyl-allylidene)-2,3-dibenzoyl-bicyclo[2.2.1]hept-2,4-diene (16).**

6-(2-Phenylethenyl)fulvene **1** (0.100 g, 0.54 mmol) and dibenzoylacetylene (0.156 g, 0.66 mmol) were dissolved in dry benzene (5 mL). The reaction mixture was stirred at room temperature under argon atmosphere for 48 h. The solvent was evaporated under reduced pressure and the residue on silica gel column chromatography (10% ethylacetate-hexane) afforded **16** (0.210 g, 91%) as a deep yellow semisolid.

IR, film : 3068, 3037, 2937, 1663, 1642, 1602, 1558, 1452, 1327, 1274, 1178, 966 cm$^{-1}$.

$^1$H NMR : δ 7.27 (m, 17H), 6.79 ( dd, J=11 Hz, 1H), 6.48 (d, J=15.29 Hz, 1H), 5.37 (d, J=10.49 Hz, 1H), 4.89 (brs, 1H), 4.48 (brs, 1H).

$^{13}$C NMR : δ 192.90, 168.32, 157.61, 156.48, 142.54, 141.89, 137.56, 137.44, 137.26, 132.76, 130.85, 128.49, 128.37, 128.16, 127.21, 126.04, 123.60, 100.98, 57.57, 53.60.

Analysis calcd. for $C_{29}H_{21}O_2$: C, 86.75%; H, 5.27%. Found: C, 86.72%; H, 5.26%.

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