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Diels-Alder Reactions of New Methoxysubstituted-6-arylfulvenes

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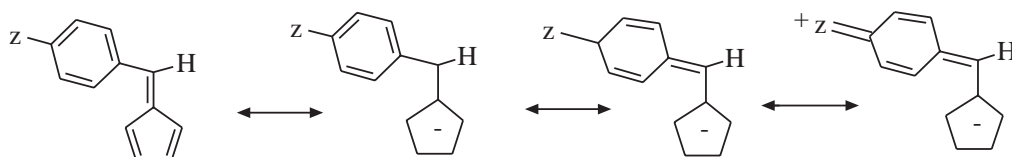
Fulvenes **1**, **2** and **3** were prepared and their Diels-Alder cycloaddition reactions with maleic anhydride, N-phenylmaleimide and dimethyl acetylenedicarboxylate (DMAD) as dienophiles leading to *endo*- and *exo*- [4+2] adducts shown.

Key Words: Fulvenes, Cycloadditions, Isomers, Stereoselectivity.

Introduction

Theoretical and synthetic aspects of fulvenes are of considerable interest in view of the periselectivity of their reactions¹. Fulvenes have found extensive use as key intermediates in the synthesis of natural products such as hirsutene, capnellene, β -vetivone, viburtinal, hinesol and silphinene².

Fulvenes are highly reactive dienes, and 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^{3,4}. Cycloadditions of fulvenes provide versatile and powerful approaches to various polycyclic systems and natural products⁵⁻⁸. Recent interest in substituent effects on 6-arylfulvenes has arisen due to their potential as organic nonlinear optical materials. It has been suggested that the charge transfer interaction resulting from aromaticities of these nonbenzenoid compounds can be as effective in producing nonlinear optical responses as that from electronegativities in heteroatoms, especially when Z is a strong donor substituent⁹ (Scheme 1).



Scheme 1

We report the cycloaddition reactions of methoxy substituted arylfulvenes with dienophiles.

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Experimental

Melting points are uncorrected and were measured in open capillaries with a Gallenkamp melting point apparatus. Infrared spectra were recorded on a Philips PU 9714 spectrometer in KBr pellets unless otherwise indicated. NMR spectra were determined on Bruker Ac 250 MHz and 400 MHz spectrometers in CDCl₃ with TMS as internal standard. Mass spectra were obtained with a Hewlett Packard GC-MS 5989 B spectrometer with 70 eV electron impact ionization. Column chromatography was performed with silica gel 60 (70-230 mesh) purchased from Merck. Thin layer chromatography (TLC) was performed with Merck 5554 silica gel sheets with fluorescent indicator. Pyrrolidine and cyclopentadiene were freshly distilled before use. All reactions were conducted under an atmosphere of dry nitrogen.

2-(Cyclopenta-2,4-dien-1-ylidenemethyl)-1,4-dimethoxybenzene (1, C₁₄H₁₄O₂)

0.332 g of (2 mmol) 2,5-dimethoxybenzaldehyde was added 0.330 g (5 mmol) of freshly distilled cyclopentadiene and 5 mL of methanol containing 0.213 g (3 mmol) of pyrrolidine. The solution was stirred under N₂ at room temperature for 4 h. The reaction mixture was then acidified with 0.18 g of glacial acetic acid. The mixture was diluted with 20 mL of ether, the layers were separated, and the ether layer was washed with water (2 x 15 mL). The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. A red oil, **1** (78%), was obtained after purification with column chromatography on silica gel eluting with n-hexane-ethyl acetate (3:2); ¹H NMR (250 MHz, CDCl₃): δ = 3.81 (s, 3OCH₃), 3.83 (s, 3OCH₃), 6.38-6.35 (m, 1=CH), 6.54-6.51 (m, 1=CH), 6.66-6.65 (t, *J*=3.19, 2=CH), 6.93-6.82 (m, 2CH), 7.18-7.14 (d, *J*= 2.87, 1CH), 7.53 (s, 1CH) ppm; ¹³C NMR (62.5 MHz, CDCl₃): δ = 55.99, 56.24, 112.50, 115.12, 115.15, 124.31, 125.02, 126.08, 130.04, 131.24, 133.72, 134.0, 152.06, 153.89 ppm; IR (KBr): ν = 3054, 3004, 2927, 2825, 1625, 1584, 1491, 1460, 1429, 1337, 1331, 1285, 1223, 1182, 1048, 811, 760 cm⁻¹; GC-MS: *m/z* = 214 (M⁺, 100), 199 (M⁺-CH₃, 77), 184 (M⁺-2CH₃, 33), 183 (M⁺-OCH₃, 41), 156 (M⁺-C₃H₆O, 36), 149 (M⁺+1- Ph, 38), 102 (M⁺-C₆H₈O₂, 26), 77 (Ph, 13).

4-(Cyclopenta-2,4-dien-1-ylidenemethyl)-1,2-dimethoxybenzene (2; C₁₄H₁₄O₂)

The above procedure was applied to cyclopentadiene using 3,4-dimethoxybenzaldehyde. Thus, dark red crystals, **2** (81%), were obtained after purification with column chromatography on silica gel eluted with n-hexane-ethyl acetate (1:1). M.p.: 72 °C; ¹H NMR (200 MHz, CDCl₃): δ = 3.93 (s, 2x3OCH₃), 6.33-6.31 (m, 1=CH), 6.49-6.48 (m, 1=CH), 6.75-6.64 (m, 2=CH), 6.93-6.87 (d, 1CH), 7.25-7.14 (m, 3CH) ppm; ¹³C NMR (50 MHz, CDCl₃): δ = 55.90, 111.0, 113.10, 119.70, 124.70, 127.40, 129.80, 135.0, 138.50, 145.30, 149.80, 150.30 ppm; IR (KBr): ν = 3005, 2927, 2851, 1615, 1595, 1522, 1460, 1409, 1337, 1255, 1142, 1141, 1017, 811, 771 cm⁻¹; GC-MS: *m/z* = 214 (M⁺, 100), 199 (M⁺-CH₃, 63), 184 (M⁺-2CH₃, 33), 183 (M⁺-OCH₃, 60), 171 (M⁺-C₃H₇, 22), 152 (M⁺-2OCH₃, 26), 102 (M⁺-C₆H₈O₂, 22), 77 (Ph, 13).

5-(Cyclopenta-2,4-dien-1-ylidenemethyl)-1,2,3-trimethoxybenzene (3; C₁₅H₁₆O₃)

The above experiment was performed using 3,4,5-trimethoxybenzaldehyde. Dark red oil, **3** (76%), was obtained after purification with column chromatography on silica gel eluted with n-hexane/ethyl acetate (2:1). ¹H NMR (250 MHz, CDCl₃): δ = 3.84 (s, 3x3OCH₃), 6.32-6.28 (m, 1=CH), 6.51-6.45 (m, 1=CH),

6.67-6.60 (m, 2=CH), 6.81 (s, 2CH), 7.25-7.24 (s, 1CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 56.30, 60.90, 109.0, 123.77, 124.66, 130.86, 131.49, 132.06, 133.36, 137.32, 139.11, 153.22$ ppm; IR (KBr): $\nu = 3173, 2998, 2933, 2824, 1622, 1579, 1470, 1339, 1230, 1120, 1011, 902, 836, 771$ cm^{-1} ; GC-MS: $m/z = 244$ (M^+ , 100), 229 ($\text{M}^+ - \text{CH}_3$, 72), 213 ($\text{M}^+ - \text{OCH}_3$, 58), 201 ($\text{M}^+ - \text{C}_3\text{H}_7$, 15), 199 ($\text{M}^+ - 3\text{CH}_3$, 12), 115 ($\text{C}_6\text{H}_8\text{O}_2$, 18), 77 (Ph, 11).

endo-10-(2,5-Dimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**1a**; $\text{C}_{18}\text{H}_{16}\text{O}_5$)

0.178 g of **1** (0.83 mmol) and 0.258 g of maleic anhydride (1.2 mmol) were dissolved in 5 mL of dry toluene and the solution was stirred at 0 °C under N_2 for 55 h. Solvent was removed under reduced pressure and the residue was purified on silica gel column chromatography from n-hexane-ethyl acetate (2:1) and afforded **1a** as first eluent as yellow crystals (40%), M.p.: 101 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.72\text{-}3.61$ (m, 2CH), 3.79 (s, 3OCH₃), 3.80 (s, 3OCH₃), 3.82 (brs, 1H_{bridge}), 4.14 (brs, 1H_{bridge}), 5.95 (s, 1CH), 6.54-6.44 (m, 2=CH), 6.68-6.67 (dt, 1CH), 6.81-6.80 (m, 2CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 45, 46, 49, 54, 56, 107, 112, 113, 116, 125, 136, 137, 152, 153, 154, 171$ ppm; IR (KBr): $\nu = 3093, 2996, 2947, 2826, 1852, 1776, 1579, 1492, 1460, 1350, 1295, 1219, 1077, 1044, 913, 804$ cm^{-1} ; GC-MS: $m/z = 312$ (M^+ , 58), 284 ($\text{M}^+ - \text{CO}$, 13), 239 ($\text{M}^+ + 1 - \text{CO}_2$, 46), 214 ($\text{M}^+ - \text{maleic anhydride}$, 83), 183 (fulvene-OCH₃, 38), 152 (fulvene-2OCH₃, 17), 128 (42), 54 (25).

exo-10-(2,5-Dimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**1b**; $\text{C}_{18}\text{H}_{16}\text{O}_5$)

The second eluent from the above chromatography was **1b**, a yellow oil, (21%); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.18\text{-}3.14$ (m, 2CH), 3.80 (s, 3OCH₃), 3.76 (s, 3OCH₃), 3.81 (brs, 1H_{bridge}), 4.16-4.15 (brs, 1H_{bridge}), 6.21 (s, 1CH), 6.57-6.48 (m, 2=CH), 6.71-6.70 (t, 1CH), 6.80-6.77 (m, 2CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 46, 49, 51, 54, 56, 57, 112, 113, 114, 115, 126, 138, 147, 152, 154, 171$ ppm; IR (KBr): $\nu = 3093, 2935, 2843, 1857, 1775, 1579, 1498, 1463, 1359, 1278, 1220, 1082, 1047, 908, 850$ cm^{-1} ; GC-MS: $m/z = 312$ (M^+ , 55), 284 ($\text{M}^+ - \text{CO}$, 13), 239 ($\text{M}^+ + 1 - \text{CO}_2$, 36), 214 ($\text{M}^+ - \text{maleic anhydride}$, 87), 183 (fulvene-OCH₃, 42), 152 (fulvene-2OCH₃, 17), 128 (42), 54 (22).

endo-10-(3,4-Dimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**2a**; $\text{C}_{18}\text{H}_{16}\text{O}_5$)

0.178 g of **2** (0.83 mmol) and 0.258 g of maleic anhydride (1.2 mmol) were dissolved in 5 mL of dry toluene and the solution was stirred at 0 °C under N_2 for 48 h. Solvent was removed under reduced pressure and the residue on silica gel column chromatography from n-hexane-ethyl acetate (3:2) afforded **2a** as first eluent as yellow crystals (52%). M.p.: 40 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.67\text{-}3.65$ (t, $J = 4.1$ Hz, 2CH), 3.77 (brs, 1H_{bridge}), 3.88 (s, 2x3OCH₃), 4.30 (brs, 1H_{bridge}), 5.81 (s, 1CH), 6.56-6.51 (m, 2=CH), 6.71-6.70 (d, 1CH), 6.86-6.76 (m, 2CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 45.0, 46.54, 46.60, 50.16, 56.33, 56.35, 111.61, 120.88, 128.64, 135.89, 136.49, 136.94, 148.84, 152.25, 164.57, 170.79$ ppm; IR (KBr): $\nu = 3012, 3005, 2988, 2940, 2843, 1856, 1783, 1602, 1589, 1516, 1455, 1419, 1322, 1261, 1237, 1140, 1079, 1018,$

812, 776 cm^{-1} ; GC-MS: $m/z = 312$ (M^+ , 41), 284 ($\text{M}^+ - \text{CO}$, 13), 239 ($\text{M}^+ + 1 - \text{CO}_2$, 32), 214 ($\text{M}^+ - \text{maleic anhydride}$, 100), 183 (fulvene- OCH_3 , 41), 152 (fulvene- 2OCH_3 , 18), 128 (36), 54 (45).

exo-10-(3,4-Dimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2b; C₁₈H₁₆O₅)

The second eluent from the above chromatography was **2b**, a yellow oil (26%); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.18$ (s, 2CH), 3.71 (brs, $1\text{H}_{\text{bridge}}$), 3.88 (s, 3OCH_3), 3.85 (s, 3OCH_3), 4.23 (brs, $1\text{H}_{\text{bridge}}$), 6.00 (s, 1CH), 6.54-6.51 (m, $2=\text{CH}$), 6.81-6.70 (m, 3CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 46, 48, 51, 54, 56, 112, 113, 115, 121, 128, 139, 145, 148, 149, 169, 171$ ppm; IR (KBr): $\nu = 3005, 2964, 2916, 2843, 1856, 1783, 1613, 1516, 1455, 1419, 1358, 1322, 1249, 1237, 1080, 1018, 909, 848$ cm^{-1} ; GC-MS: $m/z = 312$ (M^+ , 68), 284 ($\text{M}^+ - \text{CO}$, 11), 239 ($\text{M}^+ + 1 - \text{CO}_2$, 26), 214 ($\text{M}^+ - \text{maleic anhydride}$, 100), 183 (fulvene- OCH_3 , 38), 152 (fulvene- 2OCH_3 , 16), 128 (28), 54 (26).

endo-10-(3,4,5-Trimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (3a; C₁₉H₁₈O₆)

0.253 g of **3** (0.83 mmol) and 0.366 g of maleic anhydride (1.2 mmol) were dissolved in 5 mL of dry toluene and the solution was stirred at 0 °C under N_2 for 48 h. Solvent was removed under reduced pressure and the residue on silica gel column chromatography from n-hexane-ethyl acetate (1:1) afforded **3a** (45%) as first eluent as yellow oil; ^1H NMR (250 MHz, CDCl_3): $\delta = 3.66$ - 3.65 (t, $J=4.03$ Hz, 2CH), 3.80 (brs, $1\text{H}_{\text{bridge}}$), 3.85 (s, 9OCH_3), 4.28 (brs, $1\text{H}_{\text{bridge}}$), 6.37 (s, 1CH), 6.54-6.52 (q, $J = 6.41$ Hz, $2=\text{CH}$), 7.02 (s, 2CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 45.95, 47.31, 48.02, 56.30, 60.90, 109.92, 124.18, 131.30, 131.98, 134.52, 145.08, 147.92, 152.65, 173.27$ ppm; IR (KBr): $\nu = 3010, 2922, 2863, 1860, 1778, 1578, 1460, 1365, 1224, 1118, 1071, 1000, 906, 812$ cm^{-1} ; GC-MS: $m/z = 342$ (M^+ , 62), 314 ($\text{M}^+ - \text{CO}$, 17), 299 ($\text{M}^+ + 1 - \text{CO}_2$, 50), 244 ($\text{M}^+ - \text{maleic anhydride}$, 95), 213 (fulvene- OCH_3 , 43), 182 (fulvene- 2OCH_3 , 22), 158 (46), 84 (28).

exo-10-(3,4,5-Trimethoxybenzylidene)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (3b; C₁₉H₁₈O₆)

The second eluent from the above chromatography was **3b**, a yellow oil (32%); ^1H NMR (250 MHz, CDCl_3): $\delta = 3.20$ (s, 2CH), 3.71 (brs, $1\text{H}_{\text{bridge}}$), 3.84 (s, $3 \times 3\text{OCH}_3$), 4.24 (brs, $1\text{H}_{\text{bridge}}$), 6.01 (s, 1CH), 6.37 (s, $2=\text{CH}$), 7.02 (s, 2CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 46.01, 47.52, 48.12, 56.35, 60.82, 109.98, 124.18, 131.30, 131.98, 134.75, 145.08, 147.92, 154.25, 173.32$ ppm; IR (KBr): $\nu = 3005, 2922, 2844, 1857, 1780, 1581, 1460, 1360, 1239, 1128, 1073, 1007, 907, 786$ cm^{-1} ; GC-MS: $m/z = 342$ (M^+ , 62), 314 ($\text{M}^+ - \text{CO}$, 19), 299 ($\text{M}^+ + 1 - \text{CO}_2$, 52), 244 ($\text{M}^+ - \text{maleic anhydride}$, 98), 213 (fulvene- OCH_3 , 39), 182 (fulvene- 2OCH_3 , 25), 158 (46), 84 (25).

endo-10-(2,5-Dimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (1c; C₂₄H₂₁NO₄)

0.122 g of N-phenylmaleimide (1 mmol) in 5 mL of dry toluene was refluxed in a 2-necked flask as N_2 was passed through. The solution was treated with 0.150 g of **1** (1 mmol) in 5 mL of dry toluene by dropping

with an injector from the septum neck. The mixture was refluxed for 8 h and was freed of solvent in vacuo. The residue was subjected to column chromatography on silica gel using a n-hexane-ethyl acetate (3:2) mixture as first eluent to afford **1c** (46%) as dark yellow crystals. M.p.: 163 °C; ¹H NMR (250 MHz, CDCl₃): δ = 3.59-3.49 (m, 2CH), 3.78 (s, 2x3OCH₃), 3.82 (brs, 1H_{bridge}), 4.19 (brs, 1H_{bridge}), 5.98 (s, 1CH), 6.48-6.41 (m, 2=CH), 6.78-6.73 (m, 3CH), 7.16-7.12 (m, 2CH), 7.47-7.32 (m, 3CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 46.27, 47.82, 47.99, 55.99, 56.24, 111.93, 115.11, 115.22, 124.50, 126.19, 127.84, 128.39, 129.20, 130.07, 133.28, 134.43, 143.18, 151.49, 153.96, 169.83 ppm IR (KBr): ν = 3021, 2952, 2832, 1768, 1711, 1584, 1492, 1458, 1389, 1285, 1193, 1182, 1044, 883, 808 cm⁻¹; GC-MS: m/z = 387 (M⁺, 100), 372 (M⁺-CH₃, 9), 356 (M⁺-OCH₃, 15), 240 (M⁺-C₈H₅NO₂, 7), 214 (fulvene, 36), 183 (fulvene-OCH₃, 17), 175 (N-phenylmaleimide, 20), 129 (C₉H₇N, 6).

exo-10-(2,5-Dimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**1d**; C₂₄H₂₁NO₄)

The second adduct was **1d** (27%), a viscous yellow oil; ¹H NMR (250 MHz, CDCl₃): δ = 3.09 (s, 2CH), 3.79 (s, 3OCH₃), 3.82 (s, 3OCH₃), 3.84 (brs, 1H_{bridge}), 4.22 (brs, 1H_{bridge}), 6.30 (s, 1CH), 6.66-6.58 (m, 2=CH), 6.80 (s, 3CH), 7.21-7.17 (m, 2CH), 7.51-7.37 (m, 3CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 46.01, 48.31, 51.11, 53.89, 56.27, 110.11, 110.19, 112.04, 114.32, 114.40, 114.52, 125.66, 127.38, 129.20, 129.56, 129.73, 132.32, 138.41, 138.46, 138.32, 148.67, 151.76, 153.93, 176.87 ppm; IR (KBr): ν = 3068, 2947, 2923, 2850, 1771, 1710, 1589, 1492, 1467, 1383, 1261, 1255, 1188, 1103, 1043, 861, 800 cm⁻¹; GC-MS: m/z = 387 (M⁺, 100), 372 (M⁺-CH₃, 12), 356 (M⁺-OCH₃, 21), 240 (M⁺-C₈H₅NO₂, 9), 214 (fulvene, 42), 199 (fulvene-CH₃, 36), 183 (fulvene-OCH₃, 15), 175 (N-phenylmaleimide, 23), 129 (C₉H₇N, 9).

endo-10-(3,4-Dimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**2c**; C₂₄H₂₁NO₄)

The above experiment was performed using **2**. The residue was subjected to column chromatography on silica gel using n-hexane-ethyl acetate (1:2). **2c** (53%) was isolated as pale yellow crystals. M.p.: 153 °C; ¹H NMR (250 MHz, CDCl₃): δ = 3.55-3.53 (q, *J* = 4.45 Hz, 2CH), 3.80-3.79 (brs, 1H_{bridge}), 3.90 (s, 2x3OCH₃), 4.34 (brs, 1H_{bridge}), 5.84 (s, 1CH), 6.52-6.44 (m, 2=CH), 6.74 (s, 1CH), 6.84 (s, 2CH), 7.17-7.16 (d, 2CH), 7.45-7.38 (m, 3CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 46.27, 47.82, 47.99, 55.85, 111.85, 112.25, 124.24, 127.84, 125.10, 128.39, 128.60, 129.20, 130.07, 133.28, 134.43, 143.84, 148.54, 149.53, 169.43 ppm; IR (KBr): ν = 3071, 3002, 2963, 2917, 2833, 1763, 1703, 1583, 1512, 1452, 1416, 1368, 1249, 1177, 1141, 1021, 890, 866 cm⁻¹; GC-MS: m/z = 387 (M⁺, 95), 372 (M⁺-CH₃, 15), 356 (M⁺-OCH₃, 18), 240 (M⁺-C₈H₅NO₂, 5), 214 (fulvene, 36), 199 (fulvene-CH₃, 41), 183 (fulvene-OCH₃, 19), 175 (N-phenylmaleimide, 22), 129 (C₉H₇N, 5).

exo-10-(3,4-Dimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione
(**2d**; C₂₄H₂₁NO₄)

The second eluent from the above column chromatography was **2d** as yellow crystals (27%). M.p.: 184 °C; ¹H NMR (250 MHz, CDCl₃): δ = 3.05 (s, 2CH), 3.67 (brs, 1H_{bridge}), 3.87 (s, 3OCH₃), 3.82 (s, 3OCH₃),

4.24 (s, 1H_{bridge}), 6.01 (s, 1CH), 6.59-6.51 (m, 2=CH), 6.83-6.75 (m, 3CH), 7.07-7.03 (m, 2CH), 7.37-7.32 (m, 3CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 46.23, 48.42, 48.78, 51.54, 56.57, 111.19, 111.53, 114.75, 121.26, 127.38, 129.45, 129.85, 131.12, 138.25, 138.64, 147.52, 149.28, 149.62, 177.05 ppm; IR (KBr): ν = 3006, 2960, 2833, 1769, 1704, 1596, 1519, 1495, 1378, 1335, 1248, 1193, 1189, 1161, 1019, 867, 802 cm⁻¹; GC-MS: m/z = 387 (M⁺, 100), 372 (M⁺-CH₃, 9), 356 (M⁺-OCH₃, 14), 240 (M⁺-C₈H₅NO₂, 8), 214 (fulvene, 33), 199 (fulvene-CH₃, 44), 183 (fulvene-OCH₃, 23), 175 (N-phenylmaleimide, 21), 129 (C₉H₇N, 6).

endo-10-(3,4,5-Trimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (3c; C₂₅H₂₃NO₅)

The above procedure was applied to **3**. The residue was subjected to column chromatography on silica gel using n-hexane-ethyl acetate (2:3). **3c** (51%) was isolated as first eluent and a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ = 3.56-3.55 (m, 2CH), 3.83 (brs, 1H_{bridge}), 3.87 (s, 3OCH₃), 3.90 (s, 2x3OCH₃), 4.34 (brs, 1H_{bridge}), 5.86 (s, 1CH), 6.54-6.49 (s, 2=CH), 7.28-7.18 (m, 2CH), 7.48-7.38 (m, 5CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 44.89, 45.10, 45.16, 50.01, 56.63, 61.38, 105.62, 111.18, 129.22, 129.60, 131.96, 132.11, 134.83, 135.47, 137.77, 126.99, 153.69, 176.12 ppm; IR (KBr): ν = 3063, 3005, 2925, 2845, 1775, 1713, 1586, 1505, 1461, 1421, 1379, 1290, 1241, 1187, 1029, 907, 837 cm⁻¹; GC-MS: m/z = 417 (M⁺, 100), 402 (M⁺-CH₃, 6), 386 (M⁺-OCH₃, 10), 270 (M⁺-C₈H₅NO₂, 6), 244 (fulvene, 30), 229 (fulvene-CH₃, 40), 213 (fulvene-OCH₃, 20), 173 (M⁺-fulvene, 8), 115 (8).

exo-10-(3,4,5-Trimethoxybenzylidene)-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (3d; C₂₅H₂₃NO₅)

The second eluent from the above column chromatography was **3d** as a yellow oil (31%). ¹H NMR (400 MHz, CDCl₃): δ = 3.08 (s, 2CH), 3.70 (brs, 1H_{bridge}), 3.82 (s, 2x3OCH₃), 3.86(s, 3OCH₃), 4.24 (brs, 1H_{bridge}), 6.05 (s, 1CH), 6.60-6.53 (m, 2=CH), 7.13-7.10 (m, 2CH), 7.43-7.35 (m, 5CH), ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 46.10, 48.10, 48.55, 51.08, 56.52, 61.31, 105.20, 114.74, 127.13, 129.31, 129.66, 131.85, 132.07, 137.84, 138.50, 148.47, 153.70, 176.76, 177.06 ppm; IR (KBr): ν = 3070, 3008, 2923, 2845, 1779, 1718, 1591, 1504, 1459, 1417, 1380, 1288, 1247, 1189, 1033, 912, 841 cm⁻¹; GC-MS: m/z = 417 (M⁺, 100), 402 (M⁺-CH₃, 5), 386 (M⁺-OCH₃, 15), 270 (M⁺-C₈H₅NO₂, 8), 244 (fulvene, 35), 229 (fulvene-CH₃, 48), 213 (fulvene-OCH₃, 25), 173 (M⁺-fulvene, 10), 115 (13).

7-(2,5-Dimethoxybenzylidene)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (1e; C₂₀H₂₀O₆)

0.150 g of **1** (0.54 mmol) and 0.184 g of DMAD (0.66 mmol) were dissolved in dry benzene in a Schlenk glass tube sealed under N₂ and stirred at rt for 100 h. The solvent was evaporated under reduced pressure and the residue on silica gel column chromatography from n-hexane-ethyl acetate (3:2) afforded **1e** (48%) as yellow crystals. M.p.: 109°C; ¹H NMR (400 MHz, CDCl₃): δ = 3.75 (s, 3OCH₃), 3.81 (s, 3OCH₃), 3.82 (s, 3OCH₃), 3.84 (s, 3OCH₃), 4.30 (brs, 1H_{bridge}), 4.62 (brs, 1H_{bridge}), 5.58 (s, 1CH), 6.71-6.62 (m, 2=CH), 7.10-7.01 (m, 3CH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 52.64, 53.61, 56.11, 56.4, 57.23, 95.58, 112, 112.97, 115.41, 125.59, 141.96, 142.63, 151.32, 151.70, 153.72, 164.99, 167.85 ppm; IR (KBr): ν = 3023,

2947, 2850, 1734, 1627, 1574, 1494, 1427, 1334, 1281, 1214, 1107, 1040, 800, 791 cm^{-1} ; GC-MS: $m/z = 356$ (M^+ , 100), 326 ($\text{M}^+ - 2\text{CH}_3$, 11), 296 ($\text{M}^+ - 4\text{CH}_3$, 24), 238 ($\text{M}^+ - 2\text{COOCH}_3$, 48), 152 (fulvene- 2OCH_3 , 17), 59 (COOCH_3 , 32).

7-(3,4-Dimethoxybenzylidene)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (2e; C₂₀H₂₀O₆)

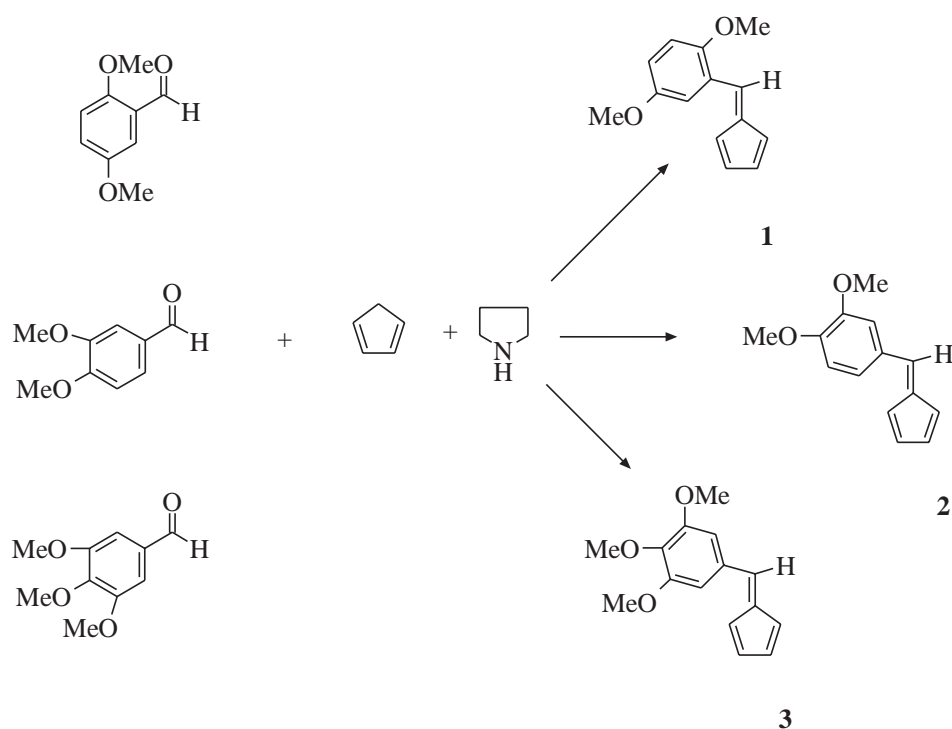
The above experiment was applied using **2**. The residue on silica gel column chromatography from n-hexane-ethyl acetate (3:2) afforded **2e** as a yellow oil (57%); ^1H NMR (250 MHz, CDCl_3): $\delta = 3.77$ (s, 3OCH_3), 3.79 (s, 3OCH_3), 3.83 (s, 3OCH_3), 3.85 (s, 3OCH_3), 4.29-4.27 (brt, $J = 4.83$ Hz, $1\text{H}_{\text{bridge}}$), 4.75-4.73 (brt, $J = 5.3$ Hz, $1\text{H}_{\text{bridge}}$), 5.31 (s, 1CH), 6.71-6.68 (m, $2=\text{CH}$), 7.09-6.77 (m, 3CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 43.48, 51.38, 52.30, 55.85, 112.25, 113.52, 122.45, 123.18, 124.28, 126.77, 129.28, 133.54, 134.21, 140.96, 148.54, 149.53, 164.26, 164.36$ ppm; IR (KBr): $\nu = 3005, 2947, 2850, 1722, 1625, 1516, 1443, 1322, 1261, 1172, 1143, 1024, 875, 816$ cm^{-1} ; GC-MS: $m/z = 356$ (M^+ , 100), 326 ($\text{M}^+ - 2\text{CH}_3$, 13), 296 ($\text{M}^+ - 4\text{CH}_3$, 26), 238 ($\text{M}^+ - 2\text{COOCH}_3$, 48), 152 (fulvene- 2OCH_3 , 19), 59 (COOCH_3 , 34).

7-(3,4,5-Trimethoxybenzylidene)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (3e; C₂₁H₂₂O₇)

The above procedure was applied using **3**. The residue on silica gel column chromatography from n-hexane-ethyl acetate (2:1) afforded **3e** as yellow crystals (53%). M.p.: 118 °C; ^1H NMR (250 MHz, CDCl_3): $\delta = 3.78$ (s, 3OCH_3), 3.81 (s, $2 \times 3\text{OCH}_3$), 3.83 (s, 3OCH_3), 3.84 (s, 3OCH_3), 4.33-4.30 (brq, $J = 5.69$ Hz, $1\text{H}_{\text{bridge}}$), 4.79-4.77 (brq, $J = 5.64$ Hz, $1\text{H}_{\text{bridge}}$), 5.34 (s, 1CH), 6.40 (s, $2=\text{CH}$), 7.04-7.00 (q, $J = 9.04$ Hz, 1CH), 7.12-7.08 (q, $J = 8.95$ Hz, 1CH) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 43.48, 51.38, 52.30, 56.30, 60.90, 110.95, 122.45, 123.36, 124.28, 132.28, 133.54, 134.21, 140.96, 147.92, 152.65, 164.26, 164.36$ ppm; IR (KBr): $\nu = 3006, 2965, 1706, 1617, 1579, 1452, 1351, 1325, 1287, 1122, 1008, 869, 729, 653$ cm^{-1} . GC-MS: $m/z = 386$ (M^+ , 100), 355 ($\text{M}^+ - \text{OCH}_3$, 18), 341 ($\text{M}^+ - \text{CH}_3$, 32), 326 ($\text{M}^+ - 4\text{CH}_3$, 43), 244 (fulvene, 18), 182 (fulvene- 2OCH_3 , 12), 168 ($\text{M}^+ - 2\text{COOCH}_3$, 52), 59 (COOCH_3 , 34).

Results and Discussion

The fulvenes **1**, **2** and **3** were prepared by the condensation of cyclopentadiene with 2,5-dimethoxybenzaldehyde, 3,4-dimethoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde, respectively, in the presence of pyrrolidine as base using Little's procedure¹⁰; the cycloadducts were characterized by spectroscopic analysis (Scheme 2).



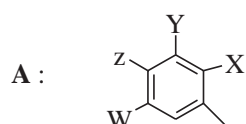
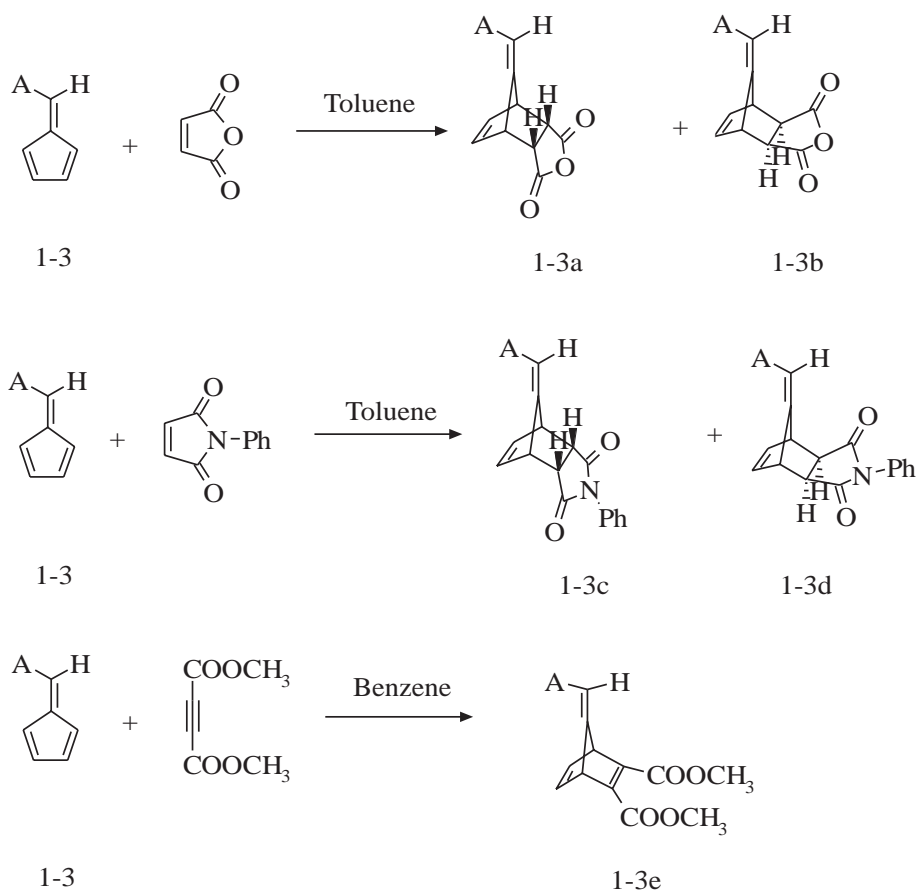
Scheme 2

We investigated the cycloaddition reactions of these fulvenes with maleic anhydride, N-phenylmaleimide and dimethyl acetylenedicarboxylate (DMAD), in which the former participated as a 4π cycloaddend. These reactions were closely monitored by thin-layer chromatography. The isomeric products were separated by column chromatography and the structures were characterized by ^1H NMR, ^{13}C NMR, IR and GC-MS spectroscopic data. The results are summarized in Scheme 3.

In general the Diels-Alder reactions are favored by electron releasing groups in dienes. Fulvenes with methoxy groups are potentially important. We chose 3 different aromatic aldehydes having methoxy groups that could activate the ring from the different positions (2,5 , 3,4 and 3,4,5). Fulvene **2** derived from 3,4-dimethoxybenzaldehyde and its Diels-Alder adducts were obtained in higher yields than the other fulvenes and their cycloadducts.

The Diels-Alder reactions of the synthesized fulvene compounds gave *endo*- and *exo*-cycloaddition adducts with the predominant isomer arising from *endo*- addition, which seems to arise from favorable secondary orbital interactions between the diene and dienophile.

The isomers gave characteristic ^1H NMR spectra and were easily distinguished from each other. The most diagnostic signals that distinguish the *endo*- and *exo*-adducts are the signals of α -carbonyl protons. In the *endo*-adduct, these protons are *exo*- on the norbornene ring and couple to the adjacent bridgehead protons³. On the other hand, in the *exo*-isomer, no such a coupling can be observed. Therefore, in the NMR spectrum of the *endo*-adduct these protons can be seen as a doublet or multiplet at lower field around δ 3.5 ppm, while the *exo* isomer's α -carbonyl protons are at a higher field of around δ 3 ppm, generally as a singlet.



	X	Y	Z	W
1	OCH ₃	H	H	OCH ₃
2	H	OCH ₃	OCH ₃	H
3	H	OCH ₃	OCH ₃	OCH ₃

Scheme 3

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