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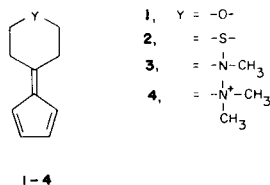
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Four new fulvene derivatives bearing heterocyclic substituents have been prepared. Base-promoted condensation of cyclopentadiene with tetrahydropyran-4-one, tetrahydrothiopyran-4-one, and 1-methyl-4-piperidone afforded 4-(cyclopentadienylidene)tetrahydropyran **1**, 4-(cyclopentadienylidene)tetrahydrothiopyran **2**, and *N*-methyl-4-(cyclopentadienylidene)piperidine **3** in yields ranging from 28% to 75%. Methylation of **3** with methyl iodide gave the corresponding ammonium salt, **4**.

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Fulvenes bearing heteroatom substituents which are not in conjugation with the fulvene π electronic system are not common (1,2,3). We report the preparation of four new fulvenes of type **1** bearing heteroatomic substituents which are part of heterocyclic rings.



To lithium cyclopentadienide, prepared by treating cyclopentadiene with *n*-butyllithium in benzene was added either tetrahydropyran-4-one, tetrahydrothiopyran-4-one or 1-methyl-4-piperidone. The new fulvene derivatives 4-(cyclopentadienylidene)tetrahydropyran (**1**), 4-(cyclopentadienylidene)tetrahydrothiopyran (**2**) or *N*-methyl-4-(cyclopentadienylidene)piperidine (**3**) were obtained in 28-75% isolated yields. Yields in this range are commonly encountered in fulvene syntheses employing aldol-type condensations of ketones. Fulvenes **1**, **2** and **3** were bright yellow, non-distillable liquids. Chromatographic methods were employed in their purification. Elemental analyses were not positive for **1**, **2** and **3** because of their instability.

Methylation of fulvene amine **3** with methyl iodide in benzene afforded the corresponding ammonium salt.

For purposes of characterization, fulvenes **1** and **2** were converted to crystalline Diels-Alder adducts by cycloaddition with maleic anhydride.

EXPERIMENTAL

Ultraviolet spectra were obtained using a Beckman DK-2A spectrometer. Infrared spectra were taken on a Perkin-Elmer Model 457 Spectrometer. The nmr spectra were recorded on a Varian Model T-60 Spectrometer. Elemental analyses are by Galbraith Laboratories, Knoxville, Tennessee.

All glassware used in the preparation of **1**, **2** and **3** had been oven-dried overnight, assembled while hot and allowed to cool with a current of dry nitrogen. All reactions were carried out under an atmosphere of dry nitrogen.

4-(Cyclopentadienylidene)tetrahydropyran (**1**).

n-Butyllithium in hexane (0.12 mole) was added to 500 ml of dry benzene. Freshly prepared cyclopentadiene (0.30 mole) was added and the white heterogeneous mixture was stirred at room temperature for 20 minutes. Over a period of 2 hours, tetrahydropyran-4-one, (Aldrich Chemical Co.), (0.065 mole) in 110 ml of dry benzene was added dropwise. Following the addition of the ketone, the mixture was allowed to stir at room temperature for 12 hours. The resulting yellow reaction mixture was poured into 700 ml of 0.9 *M* hydrochloric acid and was stirred for 2 hours. The benzene layer was separated, washed with water and dried over anhydrous magnesium sulfate. Solvent was removed under reduced pressure leaving a yellow-orange oil. The crude product was purified by dry-column chromatography on silica gel, using 80:20 hexane:benzene as eluent. A slow moving lemon-yellow band was isolated. A non-mobile orange band remained at the top of the column. The yield was 0.03 mole, 42%, based on starting keto ether; ir (liquid film): 3104, 3088, 2970, 2920, 2860, 2760, 1645, 1620, (sh), 1470, 1435, 1420, 1382, 1370, 1355 (sh), 1323, 1292, 1240, 1150, 1132, 1100, 1010, 990, 955, 928, 900, 862, 855, 834, 815, 804, 775, 735, 705, 680, and 612 cm⁻¹.

4-(Cyclopentadienylidene)tetrahydrothiopyran (**2**).

Fulvene **2** was prepared in the same manner as was **1**. Tetrahydrothiopyran-4-one (0.043 mole) was treated with 0.080 mole of lithium cyclopentadienide in 600 ml of dry benzene. The mixture was stirred at room temperature under nitrogen for 12 hours. Work up as in **1** gave a yellow oil which was purified using dry column chromatography on silica gel using 85:15 hexane:benzene as eluent. The yield was 75%; ir

Table I
Spectral Assignments for New Fulvene Derivatives

Compound	Y	UV λ_{max} nm (log ϵ)	NMR δ (ppm from tetramethylsilane)
1	-O-	(Ethanol) 350 (2.60), 269 (4.33)	(deuteriochloroform): 2.72 (br, 4H, -CH ₂), 3.82 (tr, 4H, -CH ₂ -O-), 6.53 (s, 4H, ring vinyl)
2	-S-	(Methanol) 353 (2.58), 270 (4.28)	(deuteriochloroform): 2.87 (br m, 8H, ring, -CH ₂), 6.52 (s, 4H, ring vinyl)
3	-N-CH ₃	(Acetonitrile) 347 (2.49) 270 (4.17)	(deuteriochloroform): 2.33(s, 3H, methyl), 2.70 (br m, 8H, ring methylene), 6.57 (s, 4H, ring vinyl)
4	-N ⁺ (CH ₃) ₂	(Methanol) 359 (2.50), 266 (4.45), 259 (4.45), 220 (4.27)	(DMSO-d ₆): 3.13 (br m, 4H, ring methylene), 3.35, (s, 6H, N ⁺ -CH ₃), 3.67 (br m, 4H, ring N ⁺ -CH ₂), 6.57 (s, 4H, ring vinyl)

(liquid film): 3110, 3080, 2970, (sh), 2920, 2860, 1805, 1655, 1638, 1620, (sh), 1515, 1475, 1430, 1375, 1360, (sh), 1327, 1295, 1275, 1228, 1180, 1130, (sh), 1110, 1092, 1030, 985, 957, 935, 905, 840, 813, 772, 690, 660, cm^{-1} .

1-Methyl-4-(cyclopentadienyliidene)piperidine (3).

n-Butyllithium (0.24 mole) was added to 500 ml of dry benzene. Cyclopentadiene (0.25 mole) in 75 ml of benzene was added and the resulting mixture was stirred for 30 minutes. Freshly distilled 1-methyl-4-piperidone (Aldrich Chemical Co.) in 150 ml of benzene was added dropwise over a 2 hour period. On addition of the ketone the white suspension become yellow, and after 15 minutes became much more homogeneous. The mixture was stirred at room temperature for 12 hours. The reaction mixture was poured into one ℓ of 0.5 *M* hydrochloric acid and stirred for 1 hour. The yellow aqueous layer was separated and was made basic ($\text{pH} = 12$) by slow addition of 3 *M* sodium hydroxide. The basic mixture was extracted with 3 portions of methylene chloride. The organic layer was washed with water, and with saturated brine, and was dried over anhydrous magnesium sulfate. Removal of solvent at reduced pressure gave a dark orange oil. The crude fulvene was isolated by preparative layer chromatography on Grade III silica gel plates using chloroform as eluent. The product, a bright orange oil, $R_f = 0.83$, was obtained in 28% yield; ir (liquid film): 3110, 3067, 2965, (sh), 2938, 2900, 2847, 2782, 1647, 1557, 1462, 1447, 1430, 1368, 1353 (sh), 1320, 1279, 1233, 1168, 1133, 1089, 1065, 991, 922, 850, 802, 770, 705, 612 cm^{-1} .

1,1-Dimethyl-4-(cyclopentadienyliidene)piperidinium Iodide (4).

In a dry 25 ml flask was placed 0.50 g (0.0031 mole) of fulvene **3** dissolved in 7 ml of dry benzene. Methyl iodide (1.4 g, 0.010 mole) was added and the mixture was stirred under nitrogen. A yellow, crystalline solid (0.90 g, 96%) was collected by filtration. Careful recrystallization from an anhydrous mixture of methanol and ether gave 0.78 g of yellow needles, mp 235-255° dec. The mp varied somewhat with the rate of heating; ir (potassium bromide): 3068, 3002, 2908, 2900, 1644, 1640 (sh),

1475, 1461, 1424, 1412, 1388 (sh), 1361, 1357, 1301, 1267, 1256, 1219 (sh), 1207, 1162, 1115, 1089, 1031, 996, 978, 962, 928, 911 (sh), 840, 785, 722, 704 (sh), 620 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{IN}$: C, 47.54; H, 5.98; N, 4.62. Found: C, 47.29; H, 6.05; N, 4.53.

Diels-Alder Adducts of Maleic Anhydride and Fulvene 1 and 2.

In a dry round bottom flask under nitrogen was placed 0.5 g of either fulvene **1** or **2** in 3 ml of benzene. An equivalent amount of maleic anhydride dissolved in 5 ml of benzene was added and the resulting yellow mixtures were held at room temperature overnight. After reaction was complete, the yellow color had been bleached and hexane was added to precipitate the crude adducts. Products were recrystallized from either ethyl acetate/anhydrous ether or ethyl acetate/hexane.

Adduct of Maleic Anhydride and Fulvene 1.

A white crystalline adduct of maleic anhydride and **1** was obtained mp 132-133° (mixture melting point with maleic acid 118-129°).

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_4$: C, 68.29; H, 5.73; O, 25.98. Found: C, 68.51; H, 5.95.

Adduct of Maleic Anhydride and Fulvene 2.

A white crystalline adduct of maleic anhydride and **2** was obtained, mp 150-151.5°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{SO}_3$: C, 64.11; H, 5.38; S, 12.22; O, 18.29. Found: C, 64.30; H, 5.38.

REFERENCES AND NOTES

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