Synthesis of New Fulvene Derivatives

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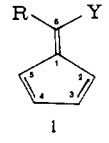
Eight new alkyl or aryl pentafulvene derivatives bearing alkyloxy substituents at C_6 have been prepared by base-induced condensation of cyclopentadiene with appropriately substituted ketones. All new fulvenes were converted to Diels–Alder cycloaddition products by reaction with tetracyanoethylene or maleic anhydride.

We report the preparation of eight new pentafulvene derivatives of type **1** in which R groups are alkyl or aryl and in which



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Y groups are simple, oxygen-containing substituents. These compounds have been prepared in the course of our continuing investigations into the effects on chemical reactivity of the cross-conjugated π electronic structure of fulvenes (*1–3*). Simple alkyloxy-substituted fulvenes are previously unreported. In fact, in the growing literature dealing with fulvenes, virtually no mention is made of derivatives such as **1** in which Y contains any type of heteroatom substitution (*4,5*).

Base-induced condensation of cyclopentadiene with appropriately functionalized ketones affords the title compounds. Thus, condensation of sodium or lithium cyclopentadienide generated from cyclopentadiene by action of sodium alkoxide in alcohol solvent or by *n*-butyllithium in benzene with a variety of ketones gives the new fulvenes. Yields in these reactions are based on isolated products and range from 30 to 60%. Such conversions are typical of many reports of fulvene syntheses employing aldol-type condensation methods. Physical properties and spectral assignments for fulvenes **2–9** are listed in Table I.

For purposes of characterization, the new fulvenes reported here have been converted to Diels–Alder cycloaddition products by reaction with tetracyanoethylene or maleic anhydride. Melting points and NMR spectral assignments for the cycloadducts of fulvenes **2–9** are listed in Table II.

Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses of all Diels–Alder adducts are by Integral Microanalytical Laboratories, Raleigh, NC, or by Galbraith Laboratories, Knoxville, TN, and were within acceptable limits (<0.40%). NMR spectra were recorded on a Varian Model T-60 spectrometer. Mass spectra were recorded by using a Finnigan Model 3100-D mass spectrometer. Infrared spectra were obtained by using a Perkin-Elmer Model 457 spectrometer. Ultraviolet spectra were obtained by using a Beckman DK-2A spectrometer.

General Methods for Preparing New Fulvene Derivatives. The following procedures are typical of the methods used to prepare new derivatives of fulvenes.

Method A. To a slurry of 0.12 mol of lithium cyclopentadienide (from cyclopentadiene and *n*-butyllithium) stirred under N_2 in 70–125 mL of dry benzene was added 0.10 mol of the appropriately substituted ketone dissolved in 50 mL of benzene. On addition of the ketone, the mixture warmed slightly, acquired a dark orange color, and became much more nearly homogeneous. Stirring at room temperature was continued for 3–5 h, after which the reaction mixtures sometimes were heated at reflux for 0.5–1 h. Hydrochloric acid (0.5 M) was added until the mixture was slightly acidic. The reaction miixtures usually became bright orange at this point. Product was extracted into ether or methylene chloride and washed with water until the aqueous extracts were neutral. The organic layers were dried by extraction with brine followed by treatment with anhydrous sodium sulfate. Removal of solvent left orange or red-orange oils. Pure products were obtained by distillation or by chromatographic methods.

Method B. In a flame-dried 2-L flask equipped with magnetic stirring, reflux condenser, N_2 inlet, and an addition funnel was placed 1 L of dry methanol and 11.5 g (0.5 mol) of sodium. Freshly distilled cyclopentadiene (33 g, 0.50 mol) was added under N_2 after the sodium had dissolved, and the resulting solutions were stirred for 15 min. Over a period of 2 h, 0.1 mol of ketone was added, generally causing the formation of clear orange solution. When the addition of ketone was complete, the reaction mixture was stirred for an additional 0.5–2.0 h, at which time dilute HCl was added until the mixture was slightly acidic. Product was extracted into ether, and methanol was removed by washing with water. The ether layer was washed with brine and dried over molecular seives or anhydrous sodium sulfate. Solvent was removed affording orange or red-orange oils. Purification was continued by distillation or by chromatographic methods.

6-Methyl-6-(Dimethoxymethyl)fulvene (2). Compound **2** was prepared by method A in 59% yield from cyclopentadiene and dimethylglyoxal dimethyl acetal. **2** had bp 63 °C (0.9 mm). IR (CCl_4): 3105, 3075, 3028, 2993, 2928, 2810, 1662, 1644, 1610, 1477, 1441, 1375, 1360, 1339, 1260, 1211, 1187, 1155, 1100, 1090, 1070, 990, 954, 914, 698, 631 cm^{-1}.

6-Methyl-6-(2,2-dimethoxyethyl)fulvene (3). Fulvene **3**, bp 78–80 °C (1.5 mm) was prepared by method B in 34% yield from cyclopentadiene and the dimethyl acetal of acetylacetaldehyde. IR (CCl_4): 3110, 3080, 3002, 2960, 2938, 2900, 2848, 1665, 1613, 1528, 1470, 1440, 1360, 1290, 1230, 1195, 1130, 1105, 1090, 1060, 1025, 995, 965, 940, 915, 870, 830, 740, 620, 565 cm^{-1}.

6-Methyl-6-(tetrahydropyran-2-yloxy)fulvene (4). Fulvene **4** was prepared in 34% yield by using method A from cyclopentadiene and (tetrahydropyran-2-yloxy)acetone. All attempts to distill **4** led to decomposition. Pure product was obtained by chromatography on silica gel, 4:1 hexane/benzene as eluent. Dry column chromatography of **4** on grade III alumina using hexane as eluent (R_f = 0.71) also afforded pure product. IR (neat): 3108, 3086, 2950, 2946, 2888, 2856, 1664, 1642, 1473, 1452, 1440, 1384, 1368, 1350, 1321, 1260, 1208, 1201, 1184, 1136, 1120, 1021, 972, 905, 827, 618 cm^{-1}.

(Tetrahydropyran-2-yloxy)acetone. A solution of freshly distilled 2*H*-dihydropyran (2.0 mol), hydroxyacetone (1.3 mol), 0.8 mL of concentrated HCl, and 800 mL of anhydrous ethyl ester was stirred under N_2 at room temperature. GLC analysis (5 ft 10% Carbowax 20M on Chromosorb W) indicated that all of the hydroxyacetone had reacted after 24 h. After the mixture was neutralized with aqueous sodium bicarbonate, washed with brine, and dried over anhydrous sodium sulfate, and the solvent was removed, distillation gave a 74% yield of colorless liquid bp 65–67 (0.2 mm). IR (neat): 2948, 2930, 2872, 2854, 1724, 1465, 1450, 1440, 1384, 1353, 1319, 1280, 1260, 1208, 1200, 1182, 1131, 1075, 1047, 1020, 960, 905, 822 cm^{-1}. NMR

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Table I. Spectral Assignments for New Fulvene Derivatives

compd	R	Y	UV λ_{max}, nm (log ϵ)	NMR δ (ppm from Me_4Si)	mass spectrum[a] (*m/e*)
2	CH_3	$(OCH_3)_2$	(EtOH) 354 (2.47), 262 (4.33)	(CCl_4) 2.07 (s, 3 H, $-CH_3$), 3.25 (s, 6 H, OCH_3), 5.08 (s, 1 H, methinyl), 6.43 (s, 4 H, ring vinyl)	166 (M^+), 151, 135, 123, 92, *91*, 89, 79, 77, 75, 65, 63, 51, 47, 43, 39
3	CH_3	$-CH(OCH_3)_2$	(MeOH) 348 (2.60), 268 (4.17)	(neat) 2.13 (s, 3 H, $-CH_3$), 2.73 (d, 2 H, -CH2-), 3.20 (s, 6 H, OCH_3), 4.48 (t, 1 H, methinyl), 6.42 (s, 4 H, ring vinyl)	180 (M^+), 117, 101, 84, 78, *77*, 66, 59, 47, 43, 33
4	CH_3	-OThp[b]	(MeOH) 357, 270	(CCl_4) 1.20-1.93 (br m, 8 H, ring CH_2), 2.20 (s, 3 H, CH_3), 4.37 (s, 2 H, $-CH_2-$), 4.55 (br s, 1 H, methinyl), 6.40 (br s, 4 H, ring vinyl)	206 (M^+), 105, 91, 79, 78, 77, 66, 65, 57, 56, 55, 43, *41*, 39, 31, 29, 27
5	CH_3	OH	(pentane) 360 (2.52), 267 (4.26), 262 (4.25)	(acetone-d_6) 2.23 (s, 3 H, CH_3), 3.72 (br s, 1 H, OH), 4.45 (s, 2 H, $-CH_2-$), 6.27-6.63 (m, 4 H, ring vinyl)	122 (M^+), 93, 91, 79, 77, 65, 63, 39, *31*, 29, 27
6	CH_3	OCH_3	(EtOH) 355 (2.37), 267 (4.26), 262 sh (4.15)	(neat) 2.11 (s, 3 H, CH_3), 3.21 (s, 3 H, OCH_3), 4.20 (s, 2 H, $-CH_2-$), 6.46 (br s, 4 H, ring vinyl)	136 (M^+), 121, 106, 105, 103, 93, 91, 79, 78, 77, 67, *66*, 65, 63, 56, 54, 52, 51, 50, 49, 44, 42, 40, 39, 38
7	C_6H_5	OCH_3	(hexane) 365 (2.48), 294 (4.08), 237 sh (3.85)	($CDCl_3$) 3.26 (s, 3 H, OCH_3), 4.61 (s, 2 H, $-CH_2-$), 6.48 (m, 4 H, ring vinyl), 7.35 (br s, 5 H, aryl)	*198* (M^+), 197, 183, 168, 167, 166, 165, 155, 154, 153, 152, 121, 115, 105, 100, 91, 77
8	C_6H_5	OThp[b]	(EtOH) 385 sh (2.3), 282 (4.23), 241 (4.11)	($CDCl_3$) 1.53 (br m, 6 H, $-CH_2-$), 3.53 (br m, 2 H, O-CH_2-), 4.67 (br s, 1 H, methinyl), 4.82 (s, 2 H, $-CH_2-O$), 6.07-6.87 (m, 4 H, ring vinyl), 7.37 (br s, 5 H, aryl)	268 (M^+), 169, 168, 167, 165, 153, 152, 92, 91, *85*, 67, 57
9	C_6H_5	OH	(EtOH) 385 sh (2.4), 294 (4.11), 240 (3.85)	($CDCl_3$) 2.47 (br s, 1 H, OH), 4.70 (s, 2H, $-CH_2-$), 6.00-6.23 (m, 1 H, ring vinyl), 6.37-6.70 (m, 3 H, ring vinyl), 7.32 (br s, 5 H, aryl)	184 (M^+), 175, 156, *155*, 154, 153, 152, 151, 141, 129, 128, 127, 115, 105, 100, 91, 85, 83, 77, 76

[a] *m/e* greater than 10% of base peak included. Molecular ions observed in all cases. [b] Tetrahydropyranyl ether.

Table II. Diels-Alder Adducts of Fulvenes 2-9 with Tetracyanoethylene or Maleic Anhydride

adduct	R	Y	mp, °C	NMR[a] (δ, ppm from Me_4Si)
10	CH_3	$-(OCH_3)_2$	141-142	1.78 (s, 3 H, $-CH_3$), 3.31 (s, 6 H, $-OCH_3$), 4.97 (m, 2H, bridgehead and methinyl), 5.23 (m, 1 H, bridgehead), 6.90 (t, 2 H, vinyl)
11	CH_3	$-CH(OCH_3)_2$	137.5-138	1.88 (s, 3 H, $-CH_3$), 2.45 (t, 2 H, $-CH_2$), 3.28 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 4.52 (t, 1 H, methinyl), 4.98 (br t, 2 H, bridgehead), 6.95 (br t, 2 H, vinyl)
12	CH_3	-OThp[b]	127-129	1.65 (br s, 5 H, ring methylene), 1.87 (s, 3 H, CH_3), 3.68 (m, 2 H, ThpOCH_2), 4.13 (t, 2 H, $-CH_2$OThp), 4.50 (m, 1 H, O-CH-O), 5.00 (br t, 1 H, bridgehead), 5.13 (br t, 1 H, bridgehead), 6.88 (br t, 2 H, vinyl)
13	CH_3	-OH	122.5-123.5	1.83 (s, 3 H, CH_3), 4.17 (d, 2 H, $-CH_2O$), 4.93 (m, 1 H, bridgehead), 5.15 (m, 1 H, bridgehead), 6.85 (t, 2 H, vinyl), 7.30 (s, 1 H, OH)
14	CH_3	$-OCH_3$	118.4-119	1.83 (s, 3 H, CH_3), 3.33 (s, 3 H, OCH_3), 4.07 (s, 2 H, $-CH_2-O$), 5.03 (m, 1 H, bridgehead), 5.20 (m, 1 H, bridgehead), 6.98 (t, 2 H, vinyl)
15	C_6H_5	$-OCH_3$	128.5-130	3.32 (s, 3 H, OCH_3), 4.35 (s, 2 H, $-CH_2-O$), 4.55 (m, 1 H, bridgehead), 5.17 (m, 1 H, bridgehead), 6.95 (m, 2 H, vinyl), 7.35 (br s, 5 H, aryl)
16[c]	C_6H_5	-OThp[b]	124-125	1.55 (br s, 6 H, ring methylene), 3.80 (br m, 5 H, bridgehead, methinyl, and ring $-OCH_2$), 4.25 (br s, 1 H, bridgehead), 4.40 (s, 2 H, $-CH_2-O$), 4.67 (br m, 1 H, O-CH-O), 6.57 (m, 2 H, vinyl), 7.42 (s, 5 H, aryl)
17[c]	C_6H_5	-OH	95-100	3.42 (br s, 2 H, methinyl), 3.91 (m, 2 H, bridgehead), 4.42 (s, 2 H, $-CH_2-$), 6.33 (m, 2 H, vinyl), 7.32 (s, 5 H, aryl)

[a] Acetone-d_6 solvent. [b] Tetrahydropyranyl ether. [c] Adducts of maleic anhydride.

(CCl_4): δ = 1.31-1.90 (br m, 8 H, ring-CH_2-), 2.08 (s, 3 H, CH_3), 4.02 (s, 2 H, -CH_2-), 4.63 ppm (br s, 1 H, methine).

6-Methyl-6-(hydroxymethyl)fulvene (5). Optimized conditions for preparing alcohol **5** from the tetrahydropyranyl ether **4** are the following: In a 500-mL flask under N_2 was placed 5.4 g of **4** and a mixture of 142 mL of methanol, 36 mL of water, 0.7 mL of concentrated HCl, and 0.5 g of diphenyl ether (present as GLC reference). The resulting cloudy mixture was stirred, and periodically aliquots were removed for GLC analysis (10% SE-30 on Chromosorb W, 5 ft column). The maximum yield (GLC) of alcohol formed after 3 h at room temperature. Significant losses were noted for longer reaction times. The reaction mixture was extracted into ether, and the organic layer was washed with water and with brine. After drying of the mixture over anhydrous sodium sulfate, solvent was removed giving 4.8 g of crude, orange oil. Purification by dry column chromatography on grade III alumina (chloroform eluent), gave 2.2 g (69%) of pure **5**, which solidified on standing to give yellow needles, mp 54.0-54.5 °C (pentane). IR (neat): 3623, 3413, 3118, 3083, 3008, 2958, 2923, 2883, 1811, 1648, 1618, 1481, 1442, 1381, 1373, 1261, 1194, 1151, 1123, 1094, 1014, 998, 919, 860, 773, 661, 619 cm^{-1}.

6-Methyl-6-(methoxymethyl)fulvene (6). Fulvene **6** was prepared by method B in 40% yield from cyclopentadiene and methoxyacetone. **6** had bp 68-70 °C (3.2 mm). IR (neat): 3117, 3080, 2990, 2937, 2825, 1660, 1645, 1617, 1478, 1453, 1372, 1322, 1282, 1255, 1194, 1153, 1098, 1070, 1030, 995, 958, 920, 903, 862, 810, 770, 740, 670, 622 cm^{-1}.

6-Phenyl-6-(methoxymethyl)fulvene (7). Fulvene **7** was prepared by method A in 35% yield from cyclopentadiene and 2-methoxyacetophenone. The product was purified by column chromatography on silica gel by using 70:30 hexane/benzene as eluent. On removal of solvent, an orange-red oil was obtained. IR (neat liquid): 3100, 3082, 3045, 3010, 2945, 2920, 2882 (sh), 2843, 1630, 1615 (sh), 1505, 1482, 1455, 1376, 1200, 1140, 1108, 1038, 965, 908, 790, 780, 715, 650 cm^{-1}.

6-Phenyl-6-(tetrahydropyran-2-yloxy)fulvene (8). Fulvene **8** was prepared by method A in 33% yield from cyclopentadiene and 2-(tetrahydropyran-2-yloxy)acetophenone. Purification was accomplished by column chromatography on activity IV alumina, 70:30 hexane/benzene as eluent. A red-orange oil was obtained on removal of solvent. IR (neat): 3070, 3060, 2950, 2870, 2850, 1640, 1610, 1495, 1480, 1465, 1450, 1395, 1375, 1330, 1290, 1285, 1270, 1210, 1190, 1170, 1145 (sh), 1130, 1280, 1045, 1035, 980, 915, 880, 813, 775, 710, 645 cm^{-1}.

2-(Tetrahydropyran-2-yloxy)acetophenone. In a flame-dried flask under N_2 was placed 0.18 mol of 2-hydroxyacetophenone in 500 mL of anhydrous ether. To the yellow-tinted slurry was added 0.52 mol of dihydropyran (distilled from sodium) and 1.5 mL of concentrated HCl. The mixture became homogeneous on stirring for 10 min. Stirring was continued overnight at which time the reaction was quenched by addition of aqueous sodium bicarbonate. The ether layer was washed with water and brine and was dried over anhydrous Na_2SO_4. On removal of solvent, a yellow oil was recovered which crystallized from hexane. On recrystallization from hexane, an 86% yield of white crystals, mp 50-53 °C, was obtained.

6-Phenyl-6-(hydroxymethyl)fulvene (9). Fulvene **9** was prepared in 35% yield by hydrolysis of tetrahydropyranyl ether **8** using conditions that were similar to those employed in the hydrolysis of **4**. To an orange-red solution of 0.0048 mol of **8** in 26 mL of methanol under N_2 was added 7 mL of water. The resulting mixture was not completely homogeneous. To this mixture was added 0.2 mL of concentrated HCl. After being stirred for 5 min, the mixture became homogeneous. Stirring was continued for 3 h, at which time 500 mL of water was added. Product was extracted into ether and washed with water to remove methanol. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Removal of solvent left an orange-red oil which was chromatographed on silica gel, deactivated by the addition of 10% water, using chloroform as eluent. IR (neat): 3580 (sh), 3425 (br), 3100, 3082 (sh), 3045, 2980, 2950, 2910, 1630, 1610, 1583, 1505, 1485, 1455, 1380, 1335, 1300, 1130, 1105, 1070, 1045, 1015, 940, 905, 820, 798, 780, 715, 650 cm^{-1}.

Formation of Tetracyanoethylene Adducts of Fulvenes 2-7. Fulvenes **2-7** were converted to Diel-Alder adducts by reaction with tetracyanoethylene (TCNE). Typically, 0.5 g of fulvene dissolved in 5 mL of toluene was added at room temperature to solutions containing equivalent amounts of TCNE dissolved in 5-10 mL of toluene. In all cases a transient dark green or black color formation was observed which quickly vanished, leaving yellow-orange solutions. Approximately equal volumes of hexane were added to the reaction mixtures, and crystals were observed, either immediately or on standing in a freezer. The solid adducts were collected and recrystallized from 1:1 hexane/toluene. Physical constants and NMR spectra in acetone-d_6 are recorded in Table II.

Formation of Adducts of Maleic Anhydride and Fulvenes 8 and 9. Approximately 0.5 g of fulvenes **8** and **9** dissolved in benzene were added to a solution of a slight excess of maleic anhydride in about 5 mL of benzene. The mixtures were stirred under N_2 at 40 °C for about 3 h. Dry column chromatography (alumina adsorbent, benzene eluent) was employed to purify the products. On removal of the solvent, the residue was crystallized from benzene/hexane. Physical constants and NMR spectra in acetone-d_6 are recorded in Table II.

Literature Cited

(1) Hine, J.; Knight, D. B. *J. Org. Chem.* **1970**, *35*, 3946.
(2) Knight, D. B.; Hartless, R. L.; Jarvis, D. A. *J. Org. Chem.* **1972**, *37*, 688.
(3) Lewis, N. J.; Collins, W. J.; Knight, David B. *J. Med. Chem.* **1979**, *22*, 1505.
(4) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41.
(5) Yates, P. *Adv. Alicycl. Chem.* **1968**, *2*, 20.

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Preparation and Properties of Nickel(II) Complex Dyes

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The preparation and properties of five new dyes derived from nickel(II) ions and aromatic azo derivatives of ethylenebis(β-ketoesters) are reported.

Metal complexes containing phenylazo functionalities have been potentially used as pigments and dyes (*1*). We have been investigating the properties of the metal complexes derived from

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