mmol) in the solvent mixture H_2O–dioxane (1 mL:2 mL) were added, at 0 °C, 1 N NaOH (0.9 mL, 8 equiv and $(Boc)_2O$ (42 mg, 1.8 equiv). The reaction mixture was stirred for 1 h at 0 °C followed by stirring overnight at room temperature. After acidification with 1 M HCl (pH 4) and evaporation of the solvents, the residue was dissolved in water. Compound **9** was extracted from EtOAc to yield, after evaporation of EtOAc, 16 mg (41%) of a pale yellow solid: R_f 0.25 (F); ^{1}H NMR (DMSO-d_6) δ 1.25 (s, 9 H, Boc), 3.80 and 3.87 (s, 2 H, CH_2PO_3), 3.74 and 3.94 (dd, 2 H, $CH_2CH<$), 3.98 (m, 1 H, CH<), 7.03 (d, 1 H, NH), 7.10 (s, 4 H, aromatic protons); mass spectrum (FAB), m/e $(MH)^+$ calcd 360, found 360.

***p*-(Phosphonomethyl)-DL-phenylalanine Methyl Ester (10).** Compound **8** (50 mg, 0.169 mmol) was lyophilized in 1 N NaOH (5 mL) to eliminate NH_4OH in order to prevent amidification of the COOH function during the reaction. After acidification with 1 M HCl (pH 2–3) and evaporation to dryness, compound **8** was dissolved in dry MeOH (5 mL). Then, thionyl chloride (20 μL, 1.6 equiv) was carefully added at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, 1 h at room temperature, and 6 h at 110 °C. After filtration of mineral salts and evaporation of MeOH, the product was washed with ether, to yield 27 mg (52%) of a white solid: R_f 0.41 (G); ^{1}H NMR (DMSO-d_6) δ 2.86 and 2.94 (s, 2 H, CH_2PO_3), 3.02 and 3.15 (dd, 2 H, $CH_2CH<$), 3.60 (s, 3 H, OCH_3), 4.12 (m, 1 H, CH<), 7.10 and 7.17 (d, 4 H, aromatic protons), 8.80 (large s, 3 H, NH_3^+); mass spectrum (FAB), m/e $(MH)^+$ calcd 310, found 310.

Acknowledgment. We are indebted to Dr. J. Belleney for carrying out the ^{1}H NMR experiments and Dr. A. Gouyette for the FAB-MS spectral analysis. We are grateful to Dr. A. Beaumont for stylistic revision and I. Bonetti for typing the manuscript.

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Preparation of 6-(Silyloxy)-6-alkylfulvenes. A Novel in Situ Trapping of an Enolate with *tert*-Butyldimethylsilyl Chloride

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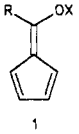
Fulvenes have long attracted the interest of theoreticians as well as inorganic and organic chemists.[1] They have served our research efforts as starting materials in the preparation of molecules of mechanistic interest and natural occurrence.[2] Our development of a new synthetic strategy required a flexible preparation of 6-oxyfulvenes (e.g., **1**, X = alkyl, acyl, or SiR_3) that would allow the



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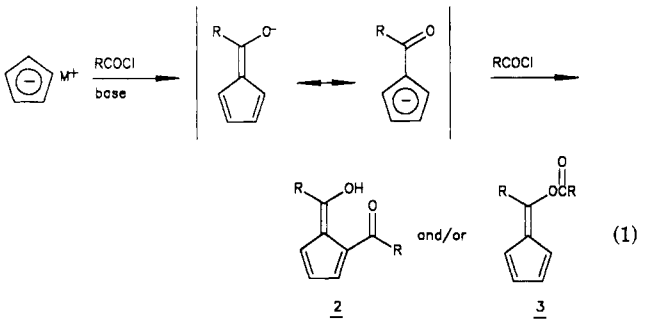
incorporation of a variety of alkyl groups and protection of the oxygen moiety. Herein we report that (1) cyclopentadiene anion (Cp^-) adds efficiently to acid chlorides, leading to the preparation of 6-oxyfulvenes; (2) the product distribution, viz., the formation of **2** vs **3** formed by addition of the presumed enolate intermediate to a second equivalent of the acid chloride, was found to be highly dependent upon the counterion used; (3) *tert*-butyldimethylsilyl (TBDMS) chloride is stable in the presence of CpK at −78 °C and serves admirably in a novel in situ trapping of the intermediate enolate, thereby providing high yields of 6-(silyloxy)-6-alkylfulvenes (**1**, X = TBDMS).

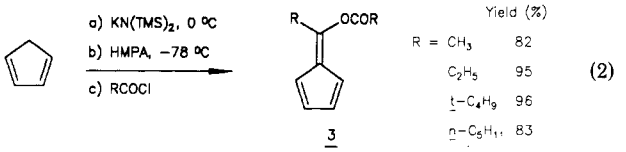


(1)

2 **3**

Although the addition of CpNa to esters has been used for the preparation of 6-oxyfulvenes,[3] we were unable to generalize the reaction and were unable to intercept the acylated intermediates with trapping/protecting agents. The addition of benzoyl chloride to a solution of CpLi, on the other hand, has been known for some time to provide 1-benzoyl-6-hydroxy-6-phenylfulvene (**2**, R = Ph).[4] Presumably, the initially formed benzoylcyclopentadiene adduct is readily deprotonated; the incipient enolate is then C-acylated by a second equivalent of the acid chloride. We reasoned that the nature of the products of the reaction of Cp^- with acid chlorides might be altered by conditions that favor O-acylation. Indeed, when conditions were employed that are known to favor O-acylation (viz., potassium counterion, THF and HMPA as cosolvent), 6-(acyloxy)-6-alkylfulvenes (e.g., **3**) were obtained in high yield, *exclusive* of other fulvene products.

The reaction of CpK in THF containing 1–2 equiv of hexamethylphosphoramide (HMPA) with acid chlorides (−78 °C to room temperature) was found to provide high yields of the 6-(acyloxy)-6-alkylfulvenes (eq 2). Either



(2)

3

potassium hydride or potassium hexamethyldisilazane was found to be suitable for the generation of CpK. Reactions run without HMPA present were found to contain significant amounts of the C-acylated fulvene **2** and generally resulted in lower overall yields of fulvene products. The use of CpNa under the identical reaction conditions, with and without HMPA, gave a mixture of the fulvenes, but favored formation of **3**. Reactions in which the acid chloride was added rapidly or at temperatures significantly above −78 °C also provided mixtures of the **2** and **3**, though again the O-acylated product **3** predominated.

We desired that *only a single equivalent of the acid chloride be consumed* and that the oxygen be suitably protected, thus enabling further synthetic manipulation of the products. A variety of in situ trapping agents were used in attempts at capturing the presumed intermediate enolate. Various electrophilic agents, including methyl iodide, dimethyl sulfate, and benzyl bromide, were added

(1) For reviews, see: (a) Yates, P. *Adv. Alicyclic Chem.* **1968**, *2*, 59. (b) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41.
(2) (a) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. (b) Little, R. D. *Chem. Rev.* **1986**, *86*, 875.
(3) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196.
(4) Linn, W. J.; Sharkey, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 4971.

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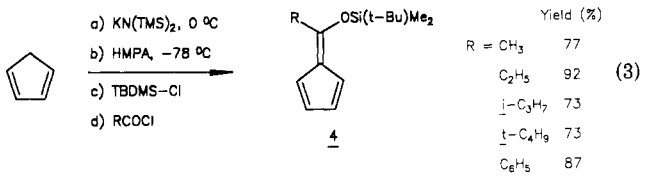
prior to or during addition of the acid chloride, but only the previously observed fulvenes were obtained. Attempted addition of trimethylsilyl chloride (TMS-Cl) prior to addition of the acid chloride provided no fulvene products; instead the anion was apparently quenched by the silylating agent.[5] On the other hand, when a solution of *tert*-butyldimethylsilyl chloride (TBDMS-Cl) was added to a slurry of CpK at −78 °C, prior to addition of the acid chloride, high yields of the 6-[(*tert*-butyldimethylsilyl)oxy]fulvenes could be obtained (eq 3).

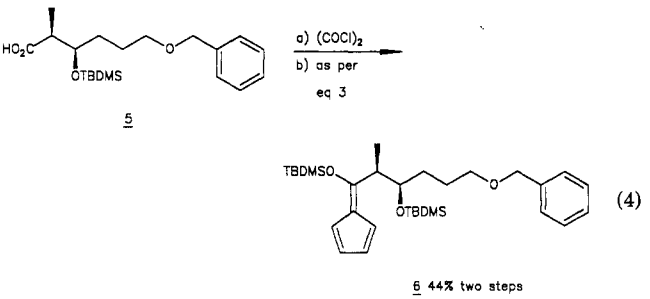


4

	Yield (%)
R = CH_3	77
C_2H_5	92
i-C_3H_7	73
t-C_4H_9	73
C_6H_5	87

(3)

The reaction appears quite general for simple alkyl acid chlorides, and the conditions were compatible with a functionalized acid chloride. Reaction of the acid chloride derived from the single epimer of carboxylic acid **5**,[6] bearing benzyl and silyl protected alcohols, gave the desired (silyloxy)fulvene in reproducible yields; however, the product was obtained as a 6.6:1 mixture of diastereomers.[7] The in situ enolate trapping was highly efficient with TBDMS-Cl. The attempted use of TMS-Cl or diphenylmethylsilyl chloride resulted in apparent quenching of Cp^- prior to the addition of the acid chloride, and no fulvene was obtained.[5] A similar side reaction was thought responsible for low yields when the TBDMS-Cl solution was not precooled prior to addition. The use of sterically hindered *tert*-butyldiphenylsilyl chloride resulted in a mixture of the corresponding 6-(silyloxy)- and 6-(acyloxy)fulvenes.



5

6 44% two steps

(4)

The use of a cosolvent was necessary for complete selectivity and high yields in the reaction sequence. The highest yields were obtained when HMPA was added at low temperature following formation of Cp^-. Addition of HMPA at 0 °C typically resulted in slightly lower yields. The use of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone[8] (DMPU) was found to be superior to the use of THF alone, but traces of the C-acylated fulvene could be observed.

In summary, the addition of CpK to acid chlorides provides an efficient entry to 6-oxyfulvenes. Conditions may be altered to provide 6-(acyloxy)-6-alkylfulvenes in a straightforward manner or 6-(silyloxy)-6-alkylfulvenes by in situ interception of the intermediate enolates with TBDMS-Cl. The fulvene products may find utility in the synthesis of organometallic fulvene ligands or may offer promise as masked acyl cyclopentadiene anion equivalents.[9] We are currently pursuing the use of these materials as precursors to diyl intermediates as novel entries to natural product syntheses[2] and will report our findings in due course.

Experimental Section

Proton magnetic resonance spectra (^{1}H NMR) were recorded on a Nicolet NT-300 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard, unless otherwise specified. Infrared data (IR) were recorded on a Digilab FT-IR instrument on NaCl plates as the neat film or as KBr pellets. Yields are reported in the equation and refer to isolated yields of the pure compounds. All fulvenes were determined to be of greater than 97% purity, as determined by capillary gas chromatography (GC) measured on a Hewlett-Packard 5890-A gas chromatograph equipped with a Hewlett-Packard 3392-A digital integrator and an Ultra II, 5% phenylmethylsilicone column (25 m × 0.20 mm). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Although several analytically pure fulvenes were submitted for elemental analysis, most proved too labile. Mass spectra (MS) were obtained by Dr. H. M. Webb of UCSB using a VG7070 mass spectrometer. Ionization was initiated by either electron impact (EI) or chemical ionization (CI) using methane.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Hexamethylphosphoramide (HMPA) was distilled under reduced pressure from BuLi and stored under N_2. Cyclopentadiene was distilled after cracking through a column packed with coarse steel wool and collected in a cooled vessel at 0 °C. All attempted syntheses of fulvenes were carried out under inert atmospheres using nitrogen.

Column chromatography was carried out on silica gel 60, 230–400 mesh. Thin-layer chromatography was performed on silica gel 60 precoated glass plates (EM) and visualized with *p*-anisaldehyde reagent or UV light. High-performance liquid chromatography (HPLC) was accomplished with an Altex 110 A pump, Rheodyne injector (100 μL), and an Altex 1.0 × 25 cm silica column using refractive index detection. Solvent systems were prepared with low-boiling petroleum ether (petroleum ether bp 45–50 °C, Fischer), ethyl acetate (reagent grade, Fisher), and triethylamime (TEA, Fischer).

General Procedure for the Preparation of 6-[(*tert*-Butyldimethylsilyl)oxy]-6-alkylfulvenes. 6-[(*tert*-Butyldimethylsilyl)oxy]-6-ethylfulvene. To a solution of cyclopentadiene (0.5 mL) in THF (20 mL) at 0 °C was added KN(TMS)$_2$ (4.0 mL, 2.0 mmol, 0.5 M solution in toluene). The gray slurry was cooled to −78 °C, and HMPA (0.7 mL, 4 mmol, distilled from BuLi) was added. After 10 min, a precooled solution of *tert*-butyldimethylsilyl chloride (1.08 g, 5.0 mmol) in THF (5 mL) was added. Within 2 min, propionyl chloride (0.17 mL, 2.0 mmol) was added as a solution in THF (2 mL). The slurry became yellow within 5 min. After addition was complete, the solution was slowly warmed to room temperature for 10 min, and saturated NH_4Cl was added. Petroleum ether was added, and the organic material was transferred to a separatory funnel. The bright yellow organic layer was washed three times with water and then brine. The crude solution was concentrated in vacuo at room temperature

(5) Reactions in which TMS-Cl or diphenylmethylsilyl chloride was added prior to the addition of an acid chloride failed to provide any fulvene. The silyl chlorides likely reacted with Cp^-; however, no attempt was made to isolate the silylated cyclopentadiene product one would expect from such a reaction. The term "quenched" is used to indicate that Cp^- was consumed prior to addition of the acid chloride. In a few instances, TMS-Cl has been reported to be compatible with basic and/or nucleophilic species. (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. (b) Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155. (c) Taylor, S. L.; Lee, D. Y.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. (d) Tobia, D.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 3849.

(6) The acid was prepared following the Heathcock aldol procedure by condensation with 4-(benzyloxy)butanal, prepared in two steps from 1,4-butanediol: (a) Young, S. D.; Buse, C. T.; Heathcock, C. H. *Org. Synth.* **1984**, *63*, 79. (b) Bal, B.; Buse, C. T.; Heathcock, C. H. *Org. Synth.* **1984**, *63*, 89. The stereochemistry was established by comparison of spectral data to that of similar aldol products: (c) Heathcock, C. H. *Asymmetric Synthesis*; J. D. Morrison: New York, 1984; Vol. 3, pp 111–212. A single epimer of an intermediate acid was obtained after recrystallization as the dicyclohexylamine salt.

(7) The diastereomeric mixture could be observed by ^{1}H NMR (300 MHz); the epimers could be separated by capillary gas chromatography.

(8) Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 385.

(9) Most η^5-cyclopentadienyl metal compounds do not undergo ring substitution, as does ferrocene; acylated cyclopentadiene anion equivalents may offer an alternative entry to substituted η^5-cyclopentadiene metal compounds. See ref 3 and references therein.

with care to avoid direct light. The thick yellow oil was chromatographed on silica gel (2% EtOAc, balance petroleum ether). The yellow band was collected and concentrated in vacuo: ^{1}H NMR ($CDCl_3$) δ 6.58 (m, 1), 6.56 (m, 1), 6.41 (m, 1), 6.36 (m, 1), 2.62 (q, 2, J = 7.5 Hz), 1.26 (t, 3, J = 7.5 Hz), 1.03 (s, 9), 0.27 (s, 6); ^{13}C NMR ($CDCl_3$) δ 166.2, 128.7, 127.9, 127.2, 121.3, 118.9, 28.5, 25.6, 24.0, 13.3, -4.0; IR (neat) 2957, 2861, 1626, 1472, 1464, 1370, 1333, 1276, 1192, 1084 cm^{-1}; MS, m/e 236, 207, 179, 151, 105, 73; exact mass calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1586. Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.39. Found: C, 70.93; H, 10.39.

6-[(*tert*-Butyldimethylsilyl)oxy]-6-methylfulvene: ^{1}H NMR ($CDCl_3$) δ 6.67 (m, 1), 6.55 (m, 1), 6.42 (m, 2), 2.35 (s, 3), 1.07 (s, 9), 0.33 (s, 6); ^{13}C NMR ($CDCl_3$) δ 160.9, 129.3, 127.6, 127.1, 121.5, 118.6, 25.5, 21.3, 18.3, -3.7; IR (neat) 2945, 2861, 1633, 1471, 1464, 1257, 1197 cm^{-1}; MS, m/e 222, 207, 165, 151, 91, 73; exact mass calcd for $C_{13}H_{22}OSi$ 222.1442, found 222.14224.

6-[(*tert*-Butyldimethylsilyl)oxy]-6-(2-propyl)fulvene: ^{1}H NMR ($CDCl_3$) δ 6.63 (m, 1) 6.56 (m, 1), 6.40 (m, 1), 6.33 (m, 1), 3.32 (m, 1, J = 6.9 Hz), 1.22 (d, 6, J = 6.9), 1.05 (s, 9), 0.33 (s, 6); ^{13}C NMR ($CDCl_3$) δ 169.6, 128.2, 127.7, 126.4, 121.8, 119.2, 33.7, 25.9, 23.9, 20.7, 19.0, -3.6; IR (neat) 2958, 2861, 1612, 1471, 1466, 1374, 1320, 1196, 1085 cm^{-1}; UV ($CHCl_3$) λ 294 nm (ϵ 11 400); MS, m/e 250, 207, 193, 151, 119, 105, 91; exact mass calcd for $C_{15}H_{26}OSi$ 250.1721, found 250.1728. Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.99; H, 10.41. Found: C, 71.93; H, 10.46.

6-[(*tert*-Butyldimethylsilyl)oxy]-6-*tert*-butylfulvene: ^{1}H NMR ($CDCl_3$) δ 6.78 (m, 1), 6.52 (m, 1), 6.36 (m, 1), 6.27 (m, 1) 1.41 (s, 9), 1.06 (s, 9), 0.28 (s, 6); ^{13}C NMR ($CDCl_3$) δ 173.1, 128.2, 127.1, 125.0, 121.8, 121.6, 40.0, 31.3, 26.2, 19.2, -2.7; IR (neat) 2958, 2861, 1586, 1472, 1464, 1371, 1272, 1175, 873 cm^{-1}; MS, m/e 264, 249, 207, 192, 177, 151, 133, 105; exact mass calcd for $C_{16}H_{28}OSi$ 264.1909, found 264.1898.

6-[(*tert*-Butyldimethylsilyl)oxy]-6-phenylfulvene: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2), 7.49 (m, 3), 6.77 (m, 1), 6.50 (m, 1), 6.41 (m, 1), 6.29 (m, 1), 1.02 (s, 9), -0.02 (s, 6); ^{13}C NMR ($CDCl_3$) δ 169 (?), 134.4, 127.1, 126.9, 126.1, 125.8, 125.2, 121.6, 117.4, 28.3, 0.1; IR (neat) 2960, 2860, 1613, 1471, 1463, 1367, 1328, 1291, 1279, 1255, 1164, 1073, 996 cm^{-1}; UV ($CHCl_3$) λ 310 nm (ϵ 20 400); MS, m/e 284, 227, 179, 135, 105, 91; exact mass calcd for $C_{18}H_{24}OSi$ 284.1597, found 284.1615.

***syn*-2-Methyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-(benzyloxy)hexanoic acid**: ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5), 4.49 (s, 2), 3.99 (m, 1, J = 4.4, 8.9 Hz), 3.45 (m, 2), 2.61 (m, 1, J = 4.4, 6.9 Hz), 1.57 (m, 4), 1.12 (d, 3, J = 6.9 Hz), 0.89 (s, 9), 0.09 (s, 3), 0.07 (s, 3); ^{13}C NMR ($CDCl_3$) δ 179.7, 138.3, 129.1, 128.3, 127.6, 127.5, 106.7, 73.2, 73.0, 70.1, 44.4, 31.0, 25.7, 25.6, 17.9, 10.8, -4.4, -4.8; IR (neat) 2957, 2900, 1709, 1472, 1462, 1361, 1253, 1096 cm^{-1}; MS, m/e 366, 320, 259, 257, 217, 201, 181, 157, 143, 127, 105, 91; MS (CI, CH_4), m/e 367 (M + 1), 349, 309, 201, 127, 105, 91; exact mass calcd for $C_{20}H_{34}O_4Si$ (M + 1) 367.2304, found 367.22845.

***syn*-2-Methyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-(benzyloxy)hexanoyl Chloride.** The silyloxy acid (800 mg, 2.17 mmol) was dissolved in benzene (5 mL). The solution was cooled in an ice bath until the benzene began to freeze, and oxalyl chloride (0.38 mL, 4.3 mmol) was added. A drop of DMF was then added, and the mixture began to foam. The ice bath was removed, and foaming increased. The foaming ceased after 15 min at room temperature. The mixture was stirred for 1 h and concentrated in vacuo (0.10 mm). The crude acid chloride was used immediately for the formation of the fulvene: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 5), 4.41 (s, 2), 4.22 (m, 1), 3.40 (m, 2), 2.85 (m, 1), 1.4-1.6 (m, 4), 1.11 (d, 3, J = 7.2 Hz), 0.77 (s, 9), -0.03 (s, 3), -0.04 (s, 3).

6-[(*tert*-Butyldimethylsilyl)oxy]-6-[*syn*-1-methyl-2-[(*tert*-butyldimethylsilyl)oxy]-5-(benzyloxy)pentyl]fulvene. The crude 2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-(benzyloxy)hexanoyl chloride was used as described in the general procedure above to provide the fulvene in 44% yield for the two steps from the acid: ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 5), 6.53 (m, 1), 6.47 (m, 1), 6.38 (m, 1), 6.30 (m, 1), 4.35 (s, 2), 3.93 (m, 1, J = 3.9, 9.4 Hz), 3.34 (t, 2, J = 6.5 Hz), 3.15 (m, 1, J = 9.4, 6.8 Hz), 1.66 (m, 2, J = 7.5 Hz), 1.52 (m, 2), 1.23 (d, 3, J = 6.8 Hz), 1.00 (s, 9), 0.90 (s, 9), 0.31 (s, 3), 0.28 (s, 3), 0.06 (s, 3), 0.05 (s, 3); ^{13}C NMR ($CDCl_3$) δ 166.5, 138.7, 128.1, 127.6, 127.4, 126.8, 122.4, 118.9, 73.6, 72.0, 70.5, 44.8, 31.7, 25.9, 25.8, 23.1, 18.9, 18.1, 17.3, -3.7, -3.8, -4.1, -4.4; IR (neat) 2958, 2860, 1612, 1472, 1463, 1373, 1362, 1273, 1260, 1191, 1105 cm^{-1}; MS (CI, CH_4), m/e 528, 503, 471, 422, 326, 293, 187, 145; exact mass calcd for $C_{31}H_{52}O_3Si_2$ 528.3454, found 528.3434.

General Procedure for the Preparation of 6-(Acyloxy)-6-alkylfulvenes. 6-(Propionyloxy)-6-ethylfulvene. To a solution of cyclopentadiene (0.5 mL) in THF (20 mL) at 0 °C was added $KN(TMS)_2$ (4.0 mL, 2.0 mmol, 0.5 M solution in toluene). The gray slurry was cooled to -78 °C, and HMPA (0.7 mL, 4 mmol, distilled from BuLi) was added. After 10 min, the addition of propionyl chloride (0.34 mL, 4.0 mmol) in THF (2 mL) was begun. The slurry became yellow within 5 min. After addition was complete, the solution was slowly warmed to room temperature for 10 min, and saturated NH_4Cl was added. Petroleum ether was added, and the organic material was transferred to a separatory funnel. The bright yellow organic layer was washed three times with water and then brine. The crude solution was concentrated in vacuo at room temperature with care to avoid direct light. The thick yellow oil was chromatographed on silica gel (5% EtOAc, balance petroleum ether). The yellow band was collected and concentrated in vacuo to give the fulvene (339 mg, 95%): ^{1}H NMR ($CDCl_3$) δ 6.45 (m, 3), 6.30 (m, 1), 2.78 (q, 2, J = 7.5 Hz), 2.57 (q, 2, J = 7.5 Hz), 1.27 (t, 3, J = 7.5 Hz), 1.18 (t, 3 J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 171.9, 158.3, 134.1, 131.6, 131.4, 121.2, 119.3, 27.4, 25.6, 11.9, 9.0; IR (neat) 2979, 1759, 1661, 1462, 1422, 1367, 1154 cm^{-1}; MS, m/e 178, 149, 122, 93, 71, 57; exact mass calcd for $C_{11}H_{14}O_2$ 178.100, found 178.0993.

6-(Acetyloxy)-6-methylfulvene: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.43 (m, 3), 6.36 (m, 1), 2.37 (s, 3), 2.25 (s, 3); ^{13}C NMR ($CDCl_3$) δ 167.9, 153.1, 134.4, 131.5, 131.0, 121.2, 118.7, 20.4, 18.3; IR (neat) 2982, 1748, 1675, 1373, 1194, 1016 cm^{-1}; MS, m/e 150, 108, 93, 77, 65; exact mass calcd for $C_9H_{10}O_2$ 150.0680, found 150.0692.

6-[(Trimethylacetyl)oxy]-6-*tert*-butylfulvene: ^{1}H NMR ($CDCl_3$) δ 6.73 (m, 1), 6.46 (m, 1), 6.35 (m, 1), 6.13 (m, 1), 1.39 (s, 9), 1.38 (s, 9); ^{13}C NMR ($CDCl_3$) δ 176.6, 164.5, 134.0, 132.2, 129.7, 121.7, 121.3, 39.5, 39.0, 30.3, 27.4; IR (neat) 2982, 1747, 1629, 1479, 1369, 1114 cm^{-1}; MS, m/e 234, 150, 135, 108, 107, 85, 57; exact mass calcd for $C_{15}H_{22}O_2$ 234.1619, found 234.1608.

6-(Hexanoyloxy)-6-pentylfulvene: ^{1}H NMR ($CDCl_3$) δ 6.43 (m, 3), 6.31 (m, 1), 2.74 (t, 2, J = 7.5 Hz), 2.52 (t, 2, J = 7.5 Hz), 1.75 (m, 2, J = 7.5 Hz), 1.58 (m, 2, J = 7.5 Hz), 1.35 (m, 8), 0.92 (m, 6); ^{13}C NMR ($CDCl_3$) δ 173.7, 159.9, 137.2, 133.9, 133.8, 123.8, 121.7, 36.6, 34.7, 33.7, 33.6, 29.3, 27.0, 24.7, 24.6, 16.2 (2 C); IR (neat) 2956, 2856, 1761, 1661, 1465, 1367, 1137, 1101 cm^{-1} MS, m/e 262, 164, 121, 108, 99, 92, 71; exact mass calcd for $C_{17}H_{26}O_2$ 262.1953, found 262.19038.

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Registry No. **3** (R = C_2H_5), 114837-46-6; **3** (R = CH_3), 701-12-2; **3** (R = t-C_4H_9), 114837-47-7; **3** (R = n-C_5H_{11}), 114837-48-8; **4** (R = C_2H_5), 114837-38-6; **4** (R = CH_3), 114837-39-7; **4** (R = i-C_6H_7), 114837-40-0; **4** (R = t-C_4H_9), 114837-41-1; **4** (R = C_6H_5), 114837-42-2; **5**, 114837-43-3; **6** (isomer 1), 114837-45-5; **6** (isomer 2), 114860-78-5; TBDMS-Cl, 18162-48-6; C_5H_5COCl, 79-03-8; CH_3COCl, 75-36-5; i-C_3H_7COCl, 79-30-1; t-C_4H_9COCl, 3282-30-2; C_6H_5COCl, 98-88-4; n-$C_5H_{11}COCl$, 142-61-0; *syn*-2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]-6-(benzyloxy)hexanoyl chloride, 114837-44-4; cyclopentadiene, 542-92-7; oxalyl chloride, 79-37-8.

The Quest for a Neutral Homoaromatic Hydrocarbon. A Study of Pentacyclo[7.2.1.0^{4,11}.0^{6,9}.0^{6,10}]dodeca-1,4-diene, an Annelated Semibullvalene Derivative

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The concept of homoaromaticity was first proposed by Doering[1] over three decades ago. The idea was generalized

