$MgSO_4$ without neutralization. Concentration on a rotary evaporator gave crude products. The crude oxidation products were analyzed by GLC to determine the product yields. Exceptionally, the produced dicarboxylic acids were directly analyzed by GLC without the treatment as above.

Preparation and Oxidation of Epoxy Alcohol. 1,2-Epoxyoctan-3-ol was prepared according to the our previous method.[9] Fractional distillation under reduced pressure gave the epoxy alcohol. For 1,2-epoxyoctan-3-ol: bp 132–138 °C (13 mm); NMR ($CDCl_3$) δ 0.8–1.7 (m, 11 H, CH_3 and CH_2), 1.97 (br s, 1 H, OH), 2.7–3.1 (m, 3 H, CHO), 3.7–4.0 (m, 1 H, CHO).

Oxidation of 1,2-epoxyoctan-3-ol (430 mg, 3 mmol) and *t*-BuOOH (3.3 g, 30 mmol) in the presence of $MoO_2(acac)_2$ (19.6 mg, 0.06 mmol) was carried out under the same conditions as those described in allylic alcohol oxidations. Hexanoic acid (254 mg, 73% yield) was obtained as the major oxidation product.

Registry No. *t*-BuOOH, 75-91-2; $MoO_2(acac)_2$, 17524-05-9; $Mo(CO)_6$, 13939-06-5; MoO(TPP)OH, 28780-74-7; MoO_3, 1313-27-5; 1-octen-3-ol, 3391-86-4; 2-octen-1-ol, 22104-78-5; 2-ethyl-2-hexen-1-ol, 50639-00-4; 4-methyl-3-penten-2-ol, 4325-82-0; 1-cyclohexyl-2-propen-1-ol, 4352-44-7; 1-phenyl-2-propen-1-ol, 4393-06-0; cinnamyl alcohol, 104-54-1; 2-cyclohexen-1-ol, 822-67-3; 2-methylenecyclohexan-1-ol, 4065-80-9; 1-octene, 111-66-0; 2-octene, 111-67-1; styrene, 100-42-5; α-methylstyrene, 98-83-9.

Synthesis of Substituted Cyclopentadienes: Intramolecular Diels–Alder Precursors[1]

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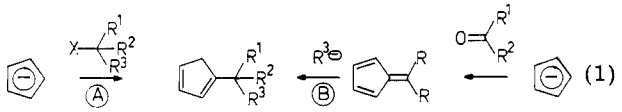
In the course of developing a versatile synthetic route to natural products containing more than one five-membered carbocyclic ring (polyquinanes) we needed a general route to cyclopentadienes substituted with functionalized alkenyl chains. These compounds can serve as precursors for intramolecular Diels–Alder reactions.[1]

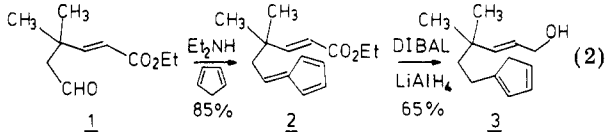
Two complementary routes to substituted cyclopentadienes may be envisioned (eq 1). Route A represents

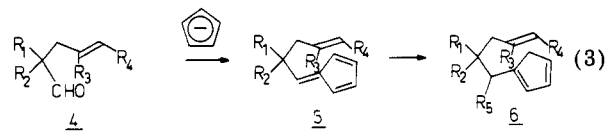

(1)

the well-precedented alkylation of cyclopentadiene anion. This method works well for primary and secondary tosylates (or mesylates)[3] but not for tertiary halides (Brieger[4] has reported alkylation with a tertiary halide but in poor yield). Method B outlines a less explored two-step approach that requires the formation of a fulvene followed by addition of a nucleophile to the polarized exocyclic double bond. A few examples of this type of reaction have been reported.[5-7] In the majority of these examples, the reaction was used to prepare substituted metallocenes by addition of simple alkyllithiums to 6,6-dialkylfulvenes and trapping of the intermediate anions with a metal salt.[5,6] Only in one instance[7] was the reaction used specifically for the preparation of a functionalized cyclopentadiene.

For many of our target molecules, application of method A would require the alkylation of cyclopentadiene with a secondary neopentyllic halide. Since the outlook for such an alkylation was poor, we decided to further explore the use of method B for the preparation of functionalized cyclopentadienes. Herein we report the synthesis of several Diels–Alder precursors by this method.

The fulvenes may be formed by condensation of cyclopentadiene with an aldehyde in the presence of base. For relatively unhindered aldehydes (i.e., aldehydes with α protons), a dialkylamine may be used as the base[8] (eq 2) while for α,α-disubstituted aldehydes preformation of sodium cyclopentadienide is necessary to obtain good yields of fulvenes (eq 3).


(2)


(3)

Conversion of the resulting fulvenes into substituted cyclopentadienes has been carried out in two different ways. When no additional substituent is desired, reduction of the exocyclic fulvene double bond with $LiAlH_4$ affords fair to good yields of substituted cyclopentadienes (eq 2 and Table I, entry a). Attempts at selectively reducing a fulvene in the presence of an α,β-unsaturated ester (i.e., **2**) failed. Either the reagent had no effect on the fulvene ($NaBH_4$ or DIBAl-H at −78 °C) or complex mixtures resulted ($LiAlH_4$ or CuI/Vitride), presumably by subsequent reactions of the cyclopentadiene anion with the α,β-unsaturated ester. Finally, we found that when the ester functionality was intentionally reduced first with diisobutylaluminum hydride at room temperature, subsequent reduction of the fulvene with $LiAlH_4$ to **3** occurred in good yield (65%). Reduction of the ester might be circumvented by the use of method A (requiring alkylation with a primary halide). However, attempts at suitable alkylations did not result in the formation of the desired product.[9]

The addition of alkyllithiums was generally carried out by addition of the fulvene to a solution of the desired lithium compound at 0–25 °C. In all examples mixtures of double bond isomers in the cyclopentadiene ring were formed. In addition, when the fulvene contained a chiral center, a mixture of epimers at the newly formed chiral center was obtained (Table I, entries c–e).

In all cases the fulvenes were characterized by ^1H and ^{13}C NMR and IR. The substituted cyclopentadiene

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(2) Undergraduate research participant.
(3) (a) Breitholle, E. G.; Fallis, A. G. *J. Org. Chem.* **1978**, *43*, 1964. (b) Glass, R. S.; Herzog, J. D.; Sobczau, R. L. *Ibid.* **1978**, *43*, 3209.
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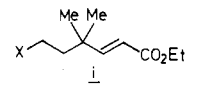
(9) When i (X = I, OMs) was treated with cyclopentadiene anion, a more complex product was formed. The nature of this product and its formation are being investigated further.



(10) Luche, J.-L.; Damiano, J.-C. *J. Am. Chem. Soc.* **1980**, *102*, 7926.

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Table I. Synthesis of Diels-Alder Precursors

entry	R_1	R_2	R_3	R_4	% yield of 5	R_5	% yield of 6
a	EtO	EtO	H	CH_2CH_2OTHP	73	H	28
b	EtO	EtO	H	CH_2CH_2OTHP		CH_3	61
c	CH_3	BnO	H	H	74	CH_2=COEt	71
d	CH_3	BnO	H	H		CH_2=CCH_3	94 (crude)
e	CH_3	MeO	H	H	60	CH_2=CCH_3	93
f	CH_3	CH_3	CH_3	H	68	CH_2=COEt	77

[a] Isopropenyllithium was prepared according to ref 9.

products, however, were always mixtures of double bond isomers in the cyclopentadiene ring, therefore having complex NMR spectra.[11] These compounds have been best characterized by further reaction to give Diels–Alder adducts.

Experimental Section

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. THF was dried by distillation from sodium–benzophenone, and methanol was dried by distillation from magnesium. Column chromatography was done on Aldrich chromatographic grade alumina which had been deactivated to activity II–III. ^{1}H NMR was done on an IBM NR-80 instrument, ^{13}C NMR on a JEOL FX-90Q spectrometer, and IR spectra on a PE 297 spectrometer. All NMR results are reported relative to Me_4Si.

6-[(*E*)-4-Carbethoxy-2,2-dimethyl-3-butenyl]fulvene (2) (Method of Little and Miller[8]). Aldehyde 1 (92 mg, 0.50 mmol) and 83 mg (1.2 mmol) of cyclopentadiene were dissolved in 1 mL of methanol at 0 °C. A solution of 55 mg (0.75 mmol) of diethylamine in 0.8 mL of methanol was added dropwise, and the mixture was stirred for 1.5 h at room temperature. Saturated NH_4Cl solution was added and the solution was extracted with ether. The ether extract was washed with brine, dried with $MgSO_4/K_2CO_3$, and concentrated to give 96 mg (83%) of essentially pure fulvene 2: yellow oil; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 6.99 (d, J = 15.9 Hz, 1 H), 6.1–6.6 (m, 5 H), 5.76 (d, J = 15.9 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 2.58 (d, J = 8.1 Hz, 2 H), 1.29 (t, J = 7.1 Hz, 2 H), 1.12 (s, 6 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 166.8, 156.7, 148.1, 137.7, 133.7, 131.1, 125.5, 119.1, 118.6, 60.4, 42.8, 37.6, 26.6, 14.3; IR ($CDCl_3$) 3080 (w), 2975 (s), 1715 (s), 1650 (m), 1470 (m), 1375 (m), 1315 (s), 1195 cm^{-1} (s).

[(*E*)-3,3-Dimethyl-6-hydroxy-4-hexenyl]cyclopentadiene (3). A 1.0-mL sample of a 1.53 M toluene solution of DIBAL-H (1.6 mmol) was added to 2 mL of THF at room temperature, 121 mg of fulvene 2 (0.52 mmol) in 2 mL of THF was added dropwise, and the solution was stirred 15 min. Under a nitrogen flush, 15 mg (0.52 mmol) of solid $LiAlH_4$ was added to the reaction flask, and the mixture was stirred another 15 min. After the reaction was quenched with water, dilute H_2SO_4 was carefully added to neutralize the metal hydroxide precipitate. The solution was extracted with ether, and the ether extract was washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4/K_2CO_3$. Evaporation gave 64 mg (65%) of 3, homogeneous by TLC. ^{1}H NMR showed a mixture of cyclopentadiene isomers.

6-(1,1,3-Trimethyl-3-butenyl)fulvene (5f). A 4.60-g (200.0 mmol) sample of a 50% NaH/oil dispersion was washed three times with hexane under N_2, 225 mL of THF was added, and the suspension was cooled to 0 °C. Freshly distilled cyclopentadiene (16.4 mL, 200.0 mmol) was added in portions, and the solution was stirred for 30 min at 0 °C to complete the anion formation. The cooling bath was removed, and a solution of aldehyde 4f (5.00 g, 40.0 mmol) in 25 mL of THF was added dropwise while the reaction mixture was warmed to room temperature. The resulting brown solution was stirred for 15 min and quenched with saturated NH_4Cl solution. The mixture was extracted with ether. The ether layer was washed successively with saturated NH_4Cl, water, and brine, dried with $MgSO_4/K_2CO_3$, and concentrated to give 8.06 g of a dark orange oil. The fulvene was purified by chromatography on activity II–III neutral alumina (250 g, hexane elution) to yield 4.66 g (68%) of fulvene 5f: light orange oil; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 6.10–6.70 (m, 5 H), 4.82 (dq, J = 2.4, 1.5 Hz, 1 H), 4.68 (dtq, J = 2.44, 0.73, 0.98 Hz, 1 H), 2.27 (d, J = 0.73 Hz, 2 H), 1.68 (dd, J = 1.5, 0.98 Hz, 3 H), 1.30 (s, 6 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 151.7 (d), 141.7 (s), 141.5 (s), 132.8 (d), 127.1 (d), 118.6 (d), 113.2 (t), 51.1 (t), 38.0 (s), 27.9 (q), 23.3 (q); IR ($CDCl_3$) 3075 (w), 2970 (s), 2930 (m), 1635 (m), 1470 (m), 1380 cm^{-1} (m).

6-[(*E*)-1,1-Diethoxy-6-[(2-tetrahydropyranyl)oxy]-3-hexenyl]fulvene (5a). The preparation was the same as for 5f: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 6.75 (m, 1 H), 6.45 (m, 2 H), 6.15 (m, 2 H), 5.40 (m, 2 H), 4.55 (br s, 1 H), 3.20–4.00 (m, 8 H), 2.60 (m, 2 H), 2.30 (m, 2 H); 1.60 (m, 6 H), 1.15 (t, J = 7.6 Hz, 6 H); ^{13}C NMR (22.5 MHz) δ 146.3 (s), 140.3 (d), 134.8 (d), 131.2 (d), 130.3 (d), 126.3 (d), 125.3 (d), 121.4 (d), 102.1 (s), 98.6 (d), 66.9 (t), 62.3 (t), 56.4 (t), 32.9 (t), 31.7 (t), 30.4 (t), 25.2 (t), 22.7 (t), 19.5 (t), 15.2 (q); IR ($CDCl_3$) 3040 (w), 2945 (s), 1705 (w), 1645 (w), 1440 (m), 1120 (s), 1015 cm^{-1} (s).

6-[1-(Benzyloxy)-1-methyl-3-butenyl]fulvene (5c). The preparation was the same as for 5f: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.29 (m, 5 H), 5.6–6.7 (m, 6 H), 4.9–5.3 (m, 2 H), 4.45 (s, 2 H), 2.58 (d, J = 7.0 Hz, 2 H), 1.52 (s, 3 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 145.6 (s), 144.4 (d), 139.1 (s), 134.8 (d), 133.4 (d), 130.3 (d), 128.2 (d), 127.3 (d), 127.2 (d), 126.9 (d), 121.0 (d), 118.2 (t), 78.5 (s), 65.0 (t), 46.2 (t), 25.4 (q); IR ($CDCl_3$) 3075 (m), 3040 (w), 2980 (s), 2940 (m), 1640 (m), 1455 (m), 1375 (m), 1160 (m), 1040 cm^{-1} (5).

6-(1-Methoxy-1-methyl-3-butenyl)fulvene (5e). The preparation was the same as for 5f: ^{1}H NMR ($CDCl_3$ 80 MHz) δ 6.7–5.6 (m, 6 H), 5.2–5.0 (m, 2 H), 3.21 (s, 3 H), 2.48 (d, J = 6.97 Hz, 2 H), 1.42 (s, 3 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 145.4, 144.0, 134.6, 133.3, 130.2, 126.8, 120.8, 118.6, 78.3, 50.7, 45.8, 24.7; IR ($CDCl_3$) 3090 (m), 2995 (s), 2950 (s), 2845 (m), 1645 (m), 1480 (m), 1380 (m), 1085 (s), 1080 (s), 780 cm^{-1} (s).

The following is a representative procedure for the addition of alkenyllithiums to fulvenes.

[1-(1-Ethoxyvinyl)-2,2,4-trimethyl-4-pentenyl]cyclopentadiene (6f). To a solution of 11.4 mmol of 1-ethoxyvinyllithium in 11 mL of THF (prepared according to Boeckman[12]) at 0 °C was added dropwise a solution of fulvene 5f (1.00 g, 5.70 mmol) in 6 mL of THF. The resulting purple solution was stirred 15 min and quenched with saturated NH_4Cl solution. The mixture was extracted with ether, and the ether extract washed with saturated NH_4Cl, water, and brine and dried with $MgSO_4/K_2CO_3$. After concentration, the crude product (1.30 g) was chromatographed on activity II–III neutral alumina (40 g, hexane elution) to give 1.07 g (77%) of 6f.

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Registry No. 1, 82351-48-2; 2, 87937-84-6; 3, 87648-94-0; 4a, 87952-97-4; 4c, 87937-85-7; 4e, 87937-86-8; 4f, 39482-50-3; 5a, 87937-87-9; 5c, 87937-88-0; 5e, 87937-89-1; 5f, 87937-90-4; 6a, 87937-91-5; 6b, 87937-92-6; 6c, 87648-91-7; 6d, 87648-92-8; 6e, 87648-93-9; 6f, 87953-07-9; cyclopentadiene, 542-92-7; sodium cyclopentadienide, 4984-82-1.

(11) While the ^{1}H NMR spectra of the cyclopentadienes were complex, they were in each case in agreement with the proposed structures (complex multiplets between 6 and 7 ppm for the cyclopentadiene olefin protons and multiplets at approximately 3 ppm for the cyclopentadiene methylene). In addition, each cyclopentadiene has been fully characterized as the intramolecular Diels–Alder product. Except for 6a, these are reported in ref 1.

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