(4-Methoxyphenyl)acetylene. Potassium hydroxide (2.75 g, 49 mmol) was placed in a 25-mL three-neck round-bottom flask fitted for distillation. The system was maintained under ca. 30 mmHg pressure throughout the procedure. The flask was heated slowly until the KOH melted (170–175 °C). β-Bromo-4-methoxystyrene (2.12 g, 10 mmol) was added slowly to molten KOH. While the β-bromo-4-methoxystyrene was being added, the temperature of the oil bath was kept below 185 °C to avoid distillation of starting material. The distillate was separated, and the organic layer was dried with KOH and distilled under reduced pressure. The main fraction boiled at 85 °C (11 mmHg):[9] ^{1}H NMR (CD_3Cl) δ 3.01 (s, 1 H), 3.81 (s, 3 H), 6.85 (d, 2 H), 7.44 (d, 2 H). Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.50; H, 6.22.

Potassium [(4-Fluorophenyl)ethynyl]triphenylborate. A THF solution of (4-fluorophenyl)acetylene (10 mmol, 1.2 g) was placed in a 100-mL round-bottom flask equipped with a low-temperature thermometer and a N_2 inlet. A hexane solution of nBuLi (1.6 M, 10 mmol) was added slowly to the reaction mixture at −78 °C. This mixture was stirred for 1 h, and then a THF solution of triphenylborane (2.42 g, 10 mmol) was added. The reaction solution was warmed to room temperature, the solvent was evaporated, and the residue was dissolved in water. After extraction with hexane, the solution was filtered and an aqueous solution of KCl (ca. 1 g) was added. The white solid that formed was removed by filtration, washed with water, and then dried under high vacuum: ^{1}H NMR ($(CD_3)_2CO$) δ 6.83 (t, 2 H), 6.98 (t, 9 H), 7.37 (dd, 2 H), 7.52 (bd, 6 H); ^{11}B NMR (THF) δ −12.6; UV-vis λ_{max} (CH_3CN) 258 nm (ε = 22 000 M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{19}BFK$: C, 78.00; H, 4.78; B, 2.70; F, 4.75; K, 9.77. Found: C, 77.78; H, 4.81; B, 2.92; F, 4.63; K, 9.53.

Tetramethylammonium [(4-Fluorophenyl)ethynyl]triphenylborate. The same procedure was followed as in the preparation of the potassium salt of this borate except that tetramethylammonium bromide was added to the filtered aqueous solution: ^{1}H NMR (CD_3CN) δ 2.90 (s, 12 H), 6.91–7.08 (m, 11 H), 7.35–7.42 (m, 8 H); ^{11}B NMR (CH_3CN) δ −12.2; UV-vis λ_{max} (CH_3CN) 255–260 nm (ε = 19 000 M^{-1} cm^{-1}). Anal. Calcd for $C_{30}H_{31}NBF$: C, 82.76; H, 7.18; N, 3.22; B, 2.48; F, 4.36. Found: C, 82.62; H, 7.29; N, 3.26; B, 2.59; F, 4.23.

Potassium [(4-Methoxyphenyl)ethynyl]triphenylborate. The procedure described for [(4-fluorophenyl)ethynyl]triphenylborate was followed with (4-methoxyphenyl)acetylene: ^{1}H NMR ($(CD_3)_2CO$) δ 3.74 (s, 3 H), 6.80 (m, 5 H), 6.96 (t, 6 H), 7.29 (d, 2 H), 7.52 (bd, 6 H); ^{11}B NMR (THF) δ −12.7; UV-vis λ_{max} (CH_3CN) 260 nm (ε = 24 100 M^{-1} cm^{-1}), 270 (24 200). Anal. Calcd for $C_{27}H_{22}OBF$: C, 78.64; H, 5.38; B, 2.62; K, 9.48. Found: C, 78.62; H, 5.42; B, 2.78; K, 9.32.

Tetramethylammonium [(4-methoxyphenyl)ethynyl]triphenylborate: ^{1}H NMR ($(CD_3)_2CO$) δ 3.13 (s, 12 H), 3.74 (s, 3 H), 6.77–6.81 (m, 5 H), 6.96 (t, 6 H), 7.28 (d, 2 H), 7.51 (bd, 6 H); ^{11}B NMR (CH_3CN) δ −12.2; UV-vis λ_{max} (CH_3CN) 260 nm (ε = 28 000 M^{-1} cm^{-1}), 269 (28 000). Anal. Calcd for $C_{31}H_{34}BNO$: C, 83.22; H, 7.66; N, 3.58; B, 2.42. Found: C, 82.86; H, 7.68; N, 3.68; B, 2.59.

Photolysis of Potassium [(4-Fluorophenyl)ethynyl]triphenylborate. A N_2-purged THF solution of the borate (0.08 M) was irradiated at 254 nm in the presence of undecane as an internal standard. The solution turned dark red. When the photolysis solution was monitored by ^{11}B NMR spectroscopy, the resonance of starting borate at δ −12.6 disappeared and was replaced by a peak at δ −16.3. Acetic acid was added to the reaction mixture when the NMR spectrum showed complete consumption of the starting borate. The red color disappeared, and analysis by GC showed that a mixture of *cis*- and *trans*-4-fluorostilbene (42% and 17%, respectively) had been formed. When this photolysis was carried out in the presence of CH_3OD, the reaction solution did not turn red and analysis by GC/MS showed the formation of dideuterated 4-fluorostilbene.

Tetramethylammonium 1,1,3-Triphenyl-2-(4′-fluorophenyl)boratirene (5). A THF solution of borate 2 (0.01 M, 150 mL) in a quartz round-bottom flask was degassed, sealed, and irradiated at 254 nm. When the reaction was complete, the solution was opened in a drybox and diluted with 200 mL of hexane. The yellow solid that formed was isolated by filtration (crude isolated yield = 35%): ^{1}H NMR (CD_3CN) δ 2.96 (s, 12 H), 6.8–7.1 (m, 10 H), 7.23 (t, 1 H), 7.4–7.5 (m, 8 H); ^{11}B (CH_3CN) δ −16.5; UV-vis λ_{max} (CH_3CN) 270 (ε = 20 000 M^{-1} cm^{-1}), 330 (7000), 390 (1300). The absorption at 390 nm was bleached when the boratirene solution is exposed to air. Anal. Calcd for $C_{30}H_{31}NBF$: C, 82.76; H, 7.18; N, 3.22; B, 2.48; F, 4.36. Found: C, 81.20; H, 7.23; N, 3.25; B, 2.77; F, 4.10. We commonly observe insufficient carbon in boron-containing compounds, perhaps due to formation of boron carbide. The ^{1}H NMR spectrum of this compound is included in the supplementary material.

Photolysis of Potassium [(4-Methoxyphenyl)ethynyl]triphenylborate. A N_2-saturated THF solution of borate 3 (0.08 M) containing undecane as an internal standard was irradiated at 254 nm. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. During the irradiation, the solution became dark red and the resonance of starting borate at δ −12.7 was replaced by one at δ −16.8. Acetic acid was added to the reaction mixture when borate 3 was completely consumed. Analysis of this solution by GC showed *cis*- and *trans*-4-methoxystilbene (27% and 14%, respectively). When the photolysis was performed in the presence of CH_3OD, dideuterated 4-methoxystilbenes were obtained.

Tetramethylammonium 1,1,3-Triphenyl-2-(4′-methoxyphenyl)boratirene (6). A THF solution of borate 3 (0.0075 M) was degassed and sealed in a quartz round-bottom flask. This solution was irradiated at 254 nm and, when reaction was complete, diluted with hexane in a drybox. A yellow solid precipitated when this solution was stored in a freezer overnight: ^{1}H NMR (CD_3CN) δ 2.76 (s, 12 H), 3.77 (s, 3 H), 6.8–7.2 (m, 10 H), 7.2–7.6 (m, 9 H); ^{11}B NMR (CH_3CN) δ −16.9; UV-vis λ_{max} (CH_3CN) 260 nm (ε = 20 300 M^{-1} cm^{-1}), 340 (6000), 400 (1900). When an acetonitrile solution of this solid is exposed to air or water, the absorption at 400 nm is bleached. Despite repeated attempts, we were unable to obtain a satisfactory elemental analysis of this compound. This is a consequence of its high reactivity toward oxygen when the last traces of solvent are removed. The ^{1}H NMR spectrum of this compound is included in the supplementary material.

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Supplementary Material Available: ^{1}H NMR spectra of compounds 5 and 6 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Syntheses of Dipentafulvenes: Bichromophoric Effects Correlated with Structure

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Introduction

The polarity of the carbon–carbon double bond exocyclic to pentafulvenes is a major contributor to the overall dipole moment in monofulvenes. For example, 6,6-dimethylfulvene, 1, has a dipole moment of 0.44 D.[1] The exocyclic bond polarizability of pentafulvenes results in ketone-like reactivity. Alkyl- and aryllithium reagents add to the exocyclic carbon–carbon double bond,[2,3] and strong bases

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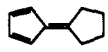
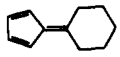
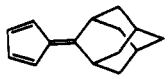
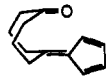
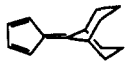
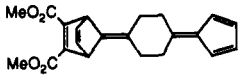
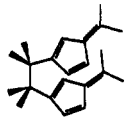
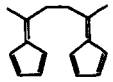
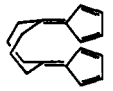
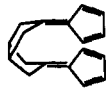
Table I. Monopentafulvene and Dipentafulvene Physical and Spectral Properties

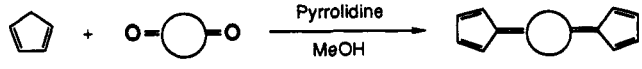
	compound	λ_{max} (nm)	ϵ ($\times 10^{-4}$ L·mol^{-1} cm^{-1})	mp or bp/mmHg (°C)	% yield (ref)
1		265	1.35	76–77/5	95 (25)
2		274	1.70	55–57/2	93 (12)
3		268	2.08	78–89/3	96 (12)
4		280	2.20	91–92	51 (26)
9		276	1.49	85	trace
11		270 278	1.59 1.58	48–49	66
13		282	2.14	95–96	37
5		278	2.99	144	82 (15)
6		286 294	4.74 3.76	205 dec	77
7		279	2.59	85–95/0.3–0.4	25
8		286	1.42	123–124	26
10		286	3.57	122–124	37

deprotonate α to this carbon atom in pentafulvenes.[4] Selective exocyclic double bond reduction in pentafulvenes is facile with lithium aluminum hydride[5] or with dissolving metal conditions.[6]

Pentafulvenes were among the first synthetic colored hydrocarbons to be discovered. Pentafulvenes with hydrogen or alkyl 6,6-substituents (unstabilized) are typically bright yellow compounds.[7] The visible wavelength absorption that is responsible for the color of pentafulvenes is due to a weak broad band that usually extends from 360 to 440 nm. Unstabilized pentafulvenes also exhibit a strong absorption band in the UV around 275 nm with fine structure which is also strongly influenced by substituents and by the rigidity of the molecule.

Fulvenes can be synthesized using several methods.[8] The most widely used method involves the base-catalyzed condensation of cyclopentadiene with aldehydes and ketones, yielding the corresponding fulvenes.[9,10] Up to the early 1980s, yields for base-catalyzed reactions averaged 50% for alkoxides and alcoholic solutions of hydroxides, while a method by Freiesleben using primary and secondary amines gave yields of greater than 95% for 1.[11] In 1983, Stone and Little developed a versatile and convenient synthesis of pentafulvenes by the condensation of ketones and aldehydes with cyclopentadiene in methanol, catalyzed by pyrrolidine.[12] Modifications of this method gave the best yields of the dipentafulvenes reported here.

Scheme I



Dipentafulvenes are of interest as precursors to organometallic biscyclopentadienyl compounds. We anticipated that intramolecular reductive coupling of the exocyclic double bonds of dipentafulvenes would be facile when the exocyclic double bonds were held in close proximity. While this goal remains elusive, the synthesis of dipentafulvenes, spectroscopic properties, and bichromophoric effects are the subjects of this paper. Many of these compounds have been studied via single-crystal X-ray diffraction. These structural studies allow a correlation

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between spectral properties and structures of the dipentafulvenes.

Experimental Section

General Procedures. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were measured at 200 and 50 MHz, respectively, on a Bruker AC 200 spectrometer. Chemical shifts are reported in δ or ppm downfield from tetramethylsilane. IR spectra were recorded with a Perkin-Elmer 283B infrared spectrophotometer. UV spectra were recorded with a Cary 219 spectrophotometer and a Hewlett-Packard HP 8451A diode array spectrophotometer in spectrograde cyclohexane and extinction coefficients were calculated by a Beer's law plot using several serial dilutions. MS were recorded on Hewlett-Packard 5985A mass spectrometer. High-resolution MS were obtained from the Midwestern Regional Mass Spectroscopy Facility. Elemental analysis for all new compounds were obtained from Desert Analytics (Tucson, AR) or Oneida Research Services, Inc. (Whiteboro, NY).

Materials and Methods. Cyclopentadiene was freshly cracked from dicyclopentadiene (Aldrich). 1,4-Cyclohexadione, acetonylacetone, *N,N*-dimethylnaphthylamine, and pyrrolidine were used as received from Aldrich. Cyclohexanone, cyclopentanone (Baker), and dimethyl 2-butynedioate (Aldrich) were distilled just before use. THF was distilled from potassium under argon. 6,6-Dimethylfulvene, 2,4-cyclopentadien-1-ylidenecyclopentane (**2**), 2,4-cyclopentadien-1-ylidenecyclohexane (**3**), adamantylidenefulvene (**4**), and 2,3-bis[3-(1-methylethylidene)cyclopenta-1,4-dienyl]-2,3-dimethylbutane (**5**)[13,14] were prepared according to literature methods. Reagent-grade methanol, benzene, and chloroform were used as received.

1,4-Bis(2,4-cyclopentadien-1-ylidene)cyclohexane (6). A methanol solution (8 mL) of 1,4-cyclohexanedione (1.00 g, 8.92 mmol) under argon was cooled to 0 °C before the addition of 1,3-cyclopentadiene (1.5 mL, 18.2 mmol) and pyrrolidine (3.0 mL, 35.9 mmol). After 4 h, water (100 mL) was added, the suspension was extracted with diethyl ether (3 × 100 mL) and dried over magnesium sulfate, and solvent was removed at reduced pressure to yield 1.53 g (82.4% yield) of crude 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane. This crude material was 95% pure according to ^1H NMR; 0.22 g can be sublimed at 100 °C (0.1 mm) to give 0.17 g (77% recovery) of analytically pure material that decomposes at 205 °C: IR ($CDCl_3$) 3115, 2980, 2855, 1650, 1475, 1380, 1345, 1110, cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.90 (s), 6.58 (m); ^{13}C NMR ($CDCl_3$) 33.56, 120.1, 131.7, 140.6, 153.1 ppm; MS *m/z* (relative intensity) 209 ($M^+ + 1$, 17.9), 208 (M^+, 100), 207 (44.4), 193 (10.5), 191 (22.1), 178 (23.0), 165 (24.8), 141 (23.6), 115 (29.5), 76 (16.4), 65 (7.9).

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.75.

2,5-Bis(2,4-cyclopentadien-1-ylidene)hexane (7). A solution of acetonylacetone (5.0 mL, 0.043 mol) and cyclopentadiene (7.0 mL, 0.085 mol) in anhydrous methanol (35 mL) is treated under argon with pyrrolidine (7.1 mL, 0.085 mol). After the addition, the mixture is stirred for 15 min at room temperature. The resulting red solution is then cooled to 0 °C and neutralized with glacial acetic acid (7 mL). After warming to room temperature, the solution is diluted in water and extracted with ether. The organic layer is then dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Bulb-to-bulb distillation yields a bright yellow viscous liquid (2.25 g, 25.2%): bp 85–95 °C (0.3–0.4 mmHg); IR (thin film, cm^{-1}) 3130, 3080, 2975, 2940, 2920, 2870, 1645, 1620, 1478, 1465, 1440, 1378, 1095, 860, 770, 635; ^1H NMR ($CDCl_3$) δ 2.25 (s, 6 H), 2.75 (s, 4 H), and 6.48 (s, 8 H); ^{13}C NMR ($CDCl_3$, ppm) 21.0, 36.8, 120.0, 120.8, 131.2, 143.0, 151.5 (one ^{13}C peak absent); MS *m/z* 210 (46.1), 195 (100.0), 182 (75.7), 167 (68.6), 153 (30.9), 129 (28.1), 115 (24.1), 103 (33.7), 77 (58.6); HRMS *m/z* (M^+) calcd 210.1409, obsd 210.1416.

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.48; H, 8.67.

1,5-Bis(cyclopenta-2,4-dien-1-ylidene)cyclooctane (8). A methanol (2 mL) solution of 1.00 g (7.14 mmol) of 1,5-cyclooctanedione was cooled to 0 °C, and 1.20 mL (14.5 mmol) of 1,3-cyclopentadiene and 0.6 mL (7.2 mmol) of pyrrolidine were added. The reaction was stirred for 8 h at 0 °C and for 24 h at room temperature. Ether (30 mL) and water (20 mL) were added, and the the organic layer was washed once with dilute hydrochloric acid and 3 × 100 mL portions of water. The organic layer is then dried over magnesium sulfate, filtered, and concentrated under reduced pressure. A few crystals sublimed on to the neck of the flask, which were identified as the monofulvene (**9**) by X-ray crystal structure analysis.[15] Silica gel column chromatography (3 × 60 cm) by elution with hexane gave a single yellow band. Solvent removal and flash crystallization of the resulting oil from hexane at −78 °C and recrystallization from hexane gave 0.44 g (26% yield) of **8**. Recrystallization of **8** from hexane again gave X-ray-quality crystals as yellow plates: mp 123–124 °C; IR ($CDCl_3$, cm^{-1}) 3110, 2960, 2885, 1635, 1460, 1380; 200-MHz ^1H NMR ($CDCl_3$) δ 2.17 (m, 4 H), 2.71 (m, 8 H) 6.33 (m, 8 H); 50-MHz ^{13}C NMR ($CDCl_3$) 33.1, 33.9, 119.9, 130.5, 144.1, 156.0 ppm; MS *m/z* (relative intensity) 237 ($M^+ + 1$, 20), 236 (M^+, 100), 209 (20), 207 (39), 194 (54), 193 (54).

***cis*-3,7-Bis(cyclopenta-2,4-dien-1-ylidene)bicyclo[3.3.0]octane (10).** A suspension of *cis*-bicyclo[3.3.0]octane-3,7-dione (1.00 g, 7.24 mmol) and calcium chloride (0.53 g, 4.8 mmol) in 3 mL of methanol was cooled to 0 °C, and 1,3-cyclopentadiene (3.60 mL 43.7 mmol) and pyrrolidine (2.40 mL, 28.8 mmol) were added. The suspension immediately turned light yellow, and stirring was continued for 2 h at 0 °C. The yellow solid was filtered and washed with copious amounts of water. The gummy solid was dried under a high vacuum for 1 h to remove unreacted cyclopentadiene. The solid was taken up in dichloromethane, filtered, concentrated, and chromatographed on a 300-mm × 22-mm column filled with 80–200-mesh silica gel. A single yellow band eluted with hexane. Concentration of the yellow fraction and flash crystallization from hexane at −78 °C gave 0.63 g (37% yield) of pure **10**. X-ray-quality crystals were obtained by slow cooling (25 to −10 °C) of a concentrated hexane solution: mp 122–124 °C; ^1H NMR ($CDCl_3$) δ 2.72 (m, 8 H), 3.11 (m, 2 H) 6.38 (m, 8 H); ^{13}C NMR ($CDCl_3$) 38.2, 43.0, 121.3, 130.6, 139.8, 160.4 ppm; IR ($CDCl_3$, cm^{-1}) 3095, 3065, 2930, 1653, 1465, 1420, 1365, 1080, 855; MS *m/z* (relative intensity) 235 (18), 234 (M^+, 100), 219 (18), 167 (17), 141 (17), 129 (56), 128 (88), 127 (28), 115 (26), 106 (21), 91 (25), 77 (23); HRMS M^+ (calcd, obsd) $C_{18}H_{18}$ (234.1428, 234.1402).

9-(2,4-Cyclopentadien-1-ylidene)bicyclo[3.3.1]nonane (11). A solution of bicyclo[3.3.1]nonan-9-one (0.5 g, 5 mmol) in methanol (5 mL) was treated with cyclopentadiene (2 mL, 24 mmol) and pyrrolidine (2 mL, 24 mmol) and stirred for 2 h under argon at 25 °C. A yellow precipitate formed, which was filtered and dried under vacuum. Bright yellow crystals suitable for X-ray structure analysis[16] sublimed between 30 and 40 °C under high vacuum: mp 48–49 °C (0.6 g, 66% yield); ^1H NMR (200 MHz, $CDCl_3$) δ 1.5–1.67 (m broad, 4 H), 1.83–2.20 (m broad, 8 H), 3.22 (broad, 2 H), 6.54 (dd, 4 H); ^{13}C (50 MHz, $CDCl_3$) δ 21.69, 34.81, 119.19, 130.55; IR (thin film, cm^{-1}) 3099, 3067, 2982, 2926, 2876, 2866, 2849, 2348, 1640, 1484, 1464, 1447, 1374, 1358; MS 198 (M^+, 100), 183 (6), 141 (17), 103 (4.4), 91 (19), 63 (7).

Anal. Calcd for $C_{15}H_{18}$ (198.31): C, 90.26; H, 9.74. Found: C, 90.38; H, 9.61.

1,9-Di(*N*-pyrrolidinyl)-10-oxaheptacyclo[7.1.$1^{1,4}$.$1^{6,9}$.$0^{2,8}$.$0^{3,7}$.$0^{11,12}$]dodecane (12). A solution of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (1.0 g, 5.7 mmol) in methanol (5 mL) was stirred under argon at room temperature while cyclopentadiene (4.7 mL, 57 mmol) was slowly added followed by the quick addition of pyrrolidine (4.7 mL, 57 mmol). The resulting solution was stirred for 2.5 h, and the white solid produced was filtered and dried under vacuum overnight. The mother liquor was neutralized with glacial acetic acid (5 mL), diluted with water, and extracted with ether. The resulting ether extract was dried with magnesium sulfate, and solvent was removed under reduced pressure yielding an amber liquid. After

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^{1}H NMR analysis, the amber liquid was identified as dicyclopentadiene. The white powder recrystallized from ethanol, affording fine white needles (0.42 g, 25%): mp 163–165 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.52 (dt, 1 H), 1.74–1.84 (m, 8 H), 1.85 (dt, 1 H), 2.55 (broad m, 2 H), 2.78 (d, 2 H), 2.81 (d, 2 H), 2.91 (t, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.48, 41.87, 42.97, 44.04, 44.88, 47.75, 55.61, 106.26. IR (thin film, in cm^{-1}) 2984, 2920, 2880, 2845, 1388, 1347, 855; MS *m/z* 298 (M^+), 228, 200, 160, 134, 91, 70, 55; HRMS M^+ (calcd, obsd) $C_{19}H_{26}N_2O$ (298.2049, 298.2043), $C_{18}{}^{13}CH_{26}N_2O$ (299.2090, 299.2074) $C_{15}H_{18}NO$ (228.1415, 228.1381), $C_{14}H_{18}N$ (200.1474, 200.1431), $C_{11}H_{14}N$ (160.1155, 160.1121), $C_9H_{12}N$ (134.1001, 134.0965).

Dimethyl 7-[1-(2,4-Cyclopentadien-1-ylidene)cyclohex-4-ylidene]bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (13). A solution containing **6** (1.500 g, 7.213 mmol), 2,6-di-*tert*-butyl-4-methylphenol (6.8 mg), and dimethyl 2-butynedioate (0.997 g, 7.02 mmol) in reagent-grade benzene was refluxed for 3 days, and solvent was removed under reduced pressure. A short alumina column (1:1 hexane to diethyl ether) was used to filter the crude product to remove unwanted polymer. Further purification was accomplished using a silica gel column (2 cm × 32 cm) with 1:1 hexane–diethyl ether gave 0.525 g (37.3% yield) of **13**, from which the X-ray structure was solved:[17] mp 95–96 °C; IR ($CDCl_3$, cm^{-1}) 2850, 1735, 1640, 1440, 1335, 1285, 1265, 1225, 1105; 200-MHz ^{1}H NMR ($CDCl_3$) δ 2.42 (m), 3.81 (s), 4.49 (s), 6.53 (s), 7.03 (s); 100-MHz ^{13}C NMR ($CDCl_3$) 33.27, 29.73, 52.15, 52.89, 105.42, 120.00, 131.15, 140.11, 142.24, 151.53, 155.39, 160.13, 164.13; MS *m/z* (relative intensity) 350 (M^+, 68.4), 318 (80.7), 303 (50.5), 259 (100), 231, (100), 141 (21.1), 128 (36.4), 115 (39.4), 91 (19.4), 77 (17.0), 59 (16.2).

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.52; H, 6.33.

General Procedures for the Intramolecular Reductive Coupling of Dipentafulvenes 5, 6, 8, and 10. A. Via Magnesium. A solution of dipentafulvene (2.04 mmol) and CCl_4 (0.3 mL) in 10 mL of THF was slowly added to magnesium turnings (0.4 g, 16 mmol) under argon. A slight exotherm resulted, with the surface of the magnesium turning black and a black precipitate forming. Both hydrolysis of the reaction mixture or treatment with $TiCl_3$·3THF yielded no products derived from intramolecular coupling.

B. Via Sodium Amalgam. A sodium amalgam was prepared by adding Na (0.052 g, 2.3 mmol) to Hg (4.02 g) under argon. A solution containing dipentafulvene (0.86 mmol) and $TiCl_3$·3THF (0.32 g, 0.86 mmol) in 70 mL of THF was slowly added to the sodium amalgam and allowed to stir for 36 h at room temperature. The reaction mixture was cooled to −40 °C, 6 M HCl (0.20 mL) was added, and the mixture was warmed to room temperature, stirring for 3 h. The reaction mixture was concentrated under reduced pressure, redissolved in DCM, and separated from insolubles by filtration. The solvent was removed under reduced pressure. The resulting residue contained numerous products analyzed by GC/MS but did not show signs of a titanocene dichloride that should have resulted from intramolecular coupling.

C. Via Sodium/*N,N*-Dimethylnaphthylamine. A solution of *N,N*-dimethylnaphthylamine (0.20 mL, 1.2 mmol) in THF (10 mL) was added to sodium (0.91 g, 40 mmol) under argon. After the resulting naphthylide anion solution was cooled to −78 °C, a solution of dipentafulvene (9.8 mmol) in THF (10 mL) was added slowly over 45 min and stirred at −78 °C for 3 h. The reaction mixture was warmed to room temperature and stirred for an additional 24 h. After aqueous workup and extraction, an insoluble polymer resulted which was not be further characterized.

Results and Discussion

Many standard pentafulvene synthetic techniques were investigated during the course of this work, and simple modifications of the method by Stone and Little gave the best yields of the mono- and dipentafulvenes. There are two limitations of this method: diketones that have strong prevalence for aldol cyclization during the reaction fail to yield dipentafulvenes under any conditions tried. Side reactions that are evident, but do not cause complete failure of the synthesis are competing Diels–Alder dimerization of cyclopentadiene and pyrrolidine addition to the dipentafulvene product. Diels–Alder dimerization of cyclopentadiene occurs over the reaction time at room temperature for unreactive diketones such as 1,5-cyclooctanedione. Pyrrolidine addition to the diketone starting material led to the major product (**12**) in the attempted synthesis of 3,8-bis(2,4-cyclopentadien-1-ylidene)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**14**). Dipentafulvenes **7** and **8** are very sensitive to the environment and polymerize quickly; therefore, they were prepared and purified immediately before spectra were recorded. Single crystals of **8** and **10** were sufficiently stable to allow X-ray structural studies.

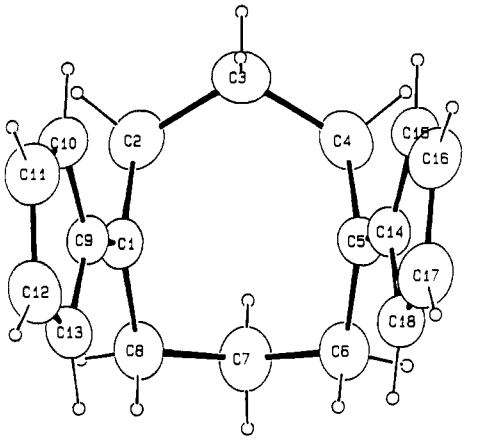

Figure 1. ORTEP diagram of **8**.

Correlation of the ^{1}H and ^{13}C NMR spectral properties, along with the UV λ_{max} and extinction coefficients reveal, no significant differences within the dipentafulvene and monopentafulvene series, except that **8** has a substantially lower ε than expected when compared with **6** and **10**. The X-ray structure of **6** shows that the six-membered ring adopts a near ideal chair conformation in the solid state.[18] The dominant solution structure of **6** is probably the same as its solid-state structure since it exhibits center of inversion symmetry according the simplicity of its NMR spectra. In contrast, the single-crystal X-ray and solution structure of 1,4-cyclohexanedione is a twist boat.[19,20] Compounds **5**, **6**, and **7** do not show any unusual bichromophoric effects. However, powerful bichromophoric effects are not expected with two carbon linkages connecting the chromophores.

The X-ray structure of **8** shows that the eight-membered ring adopts a chair–boat conformation with a close interannular distance of 2.95 Å between the 1 and 5 carbon atoms (Figure 1).[21] This distance is well within the sum of the van der Waals radii (3.4 Å) of sp^2 carbons, which made it a good candidate for possible intramolecular reductive coupling. The small nonbonding distance in **8** may also be responsible for the pronounced hypochromic shift in absorbance. The structure of **8** does not indicate that pentafulvenes prefer a ground state with significant interactions, but instead, the structure is the result of the preferred conformation of the eight-membered ring. The

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molecular structures of the monopentafulvene 9[15] and 1,5-cyclooctanedione[22] are very similar. In 8, there is considerable distortion in the ring methylenes with bond angles ranging from 113° for C6-C7-C8 to 116° for C2-C3-C4. Similar ring methylene distortions are found in 9 and in 1,5-cyclooctanedione but are smaller by approximately 2°.

The X-ray structure of the *cis*-3,7-substituted-bicyclo-[3.3.0]octane difulvene[23] shows an increased intramolecular distance between the electrophilic carbons of the pentafulvene chromophores compared to 8 and exhibits a much smaller hypochromic effect.

Monopentafulvenes are known to undergo reductive intermolecular coupling in low yields when treated with metals such as Mg and Na(Hg),[6] and with sodium *N,N*-dimethylnaphthylamine.[24] It was hoped that selected dipentafulvenes would undergo facile intramolecular reductive coupling to form novel metallocene compounds. Ideal candidates included dipentafulvenes 8 and 10 because the crystal structures showed the cyclopentadienyl rings and exocyclic π-systems to be proximate, and upon intramolecular coupling, two new five-membered rings would be formed. Intramolecular reductive couplings were attempted on dipentafulvenes 5, 6, 8, and 10 but were unsuccessful. Instead, a black polymer coated the surface of the metal and no coupling product was isolated or an inseparable mixture of products resulted.

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Supplementary Material Available: ^{13}C NMR spectra of compounds 8, 10, and 12 (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Diastereoselective Synthesis of *all-cis*-Perhydropyrrolo[3,2,1-*hi*]indol-7-one. A Building Block for the Synthesis of D-Norpandolane-Type Alkaloids

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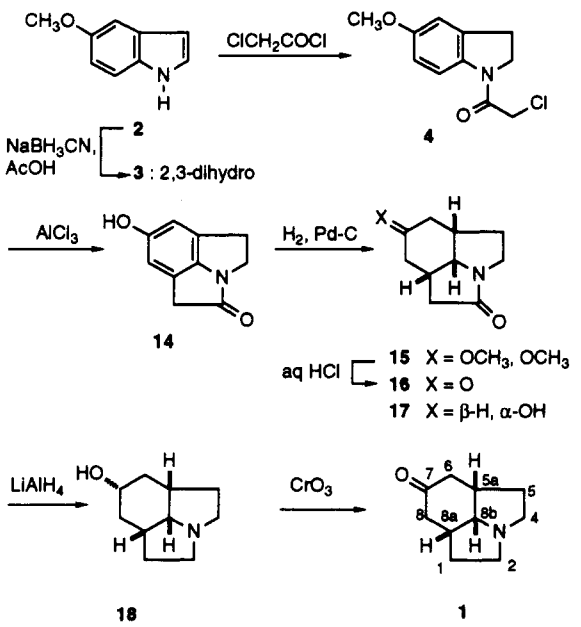
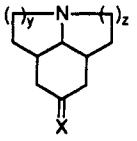
Azatricyclic systems Ia (hexahydrojulolidine) and Ib (hexahydrolilolidine) have been subject of intense synthetic interest because they constitute substructures of *Lycopodium*,[1] *Aspidosperma*,[2] and some *Amaryllidaceae*[3] alkaloids, respectively. Several total syntheses of the former two groups of these alkaloids use functionalized derivatives of Ia or Ib as synthetic precursors.[1,2] However, the lower homologue system Ic has received little synthetic attention.[4] This tricyclic ring system incorporates the characteristic CDE ring moiety of pentacyclic D-norpandolane-type alkaloids,[5] which are a group of indole alkaloids with a rather unusual skeletal type having the piperidine D ring present in *Aspidosperma* alkaloids contracted to a pyrrolidine.

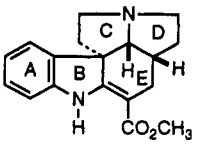
We report here a short, diastereoselective synthesis of the all-cis isomer 1 of ketone Id, which is potentially a key intermediate for the synthesis of the alkaloid deethylibophyllidine.[6,7]

Scheme I





Ia X = H, H; y = z = 2
b X = H, H; y = 1; z = 2
c X = H, H; y = z = 1
d X = O; y = z = 1



Deethylibophyllidine

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(7) Although it has been claimed[8a] that the alkaloid strychnochromine incorporates the tricyclic ring system Ic, recent work[8b] has demonstrated that it has a different skeletal type.

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