was evaporated to give 2.28 g of slightly colored crystals which consisted of ca. 94% **15b** and 6% **11** by GLC. Three recrystallizations from hexane followed by sublimation gave an analytical sample: mp 108–109.5 °C; ν_{max} (CCl_4) 3610 (O–H), 3086 cm^{-1} (C–H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.95; H, 10.40.

A similar reaction of **11** with *tert*-butyllithium gave **15c** as colorless crystals: mp 84–86 °C; ν_{max} (CCl_4) 3600 (O–H), 3080 cm^{-1} (C–H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.93; H, 10.45.

The *tert*-butyl derivative **15c** decomposed on Woelm neutral alumina (activity grade 1) and on GLC columns above 190 °C to a complex mixture of alcohols and hydrocarbons.

Iso-Half-Cage Ketoxime 8. A mixture of 34.8 g of **8**, 27.8 g of hydroxylamine hydrochloride, 25 ml of 30% sodium hydroxide solution, 45 ml of water, and 125 ml of ethanol was refluxed for 46 h, poured into 500 ml of water, and extracted three times with ether. The combined ether extracts were dried and evaporated. The colorless, crystalline residue was recrystallized from hexane to yield 34.2 g of **8**, mp 132–136 °C. An analytical sample, mp 134.5–136.0 °C, was obtained by another recrystallization from hexane followed by sublimation.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.55; H, 8.41; N, 7.33.

Registry No.—**1**, 704-02-9; **1b**, 3212-28-0; **2**, 707-05-1; **3**, 60606-96-4; **5**, 60606-97-5; **6**, 60606-98-6; **6** oxime, 60606-99-7; **6** tosylhydrazone, 60607-00-3; **6** Na salt, 60607-01-4; **7**, 60607-02-5; **8**, 707-83-5; **8** oxime, 1603-18-5; **11**, 7509-41-3; **12a**, 60607-03-6; **12b**, 741-42-4; **12c**, 60607-04-7; **12d**, 60607-05-8; **15a**, 7261-85-0; **15b**, 60607-06-9; **15c**, 60607-07-0; isodrin, 465-73-6; endrin, 72-20-8.

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(18) *We obtained half-cage ketone* **11** *as a by-product in the triquinacene synthesis:*[2] ^1H NMR (220 MHz) δ 1.32 (ddm, J = 13, 8 Hz, 1 H), 1.44 (dm, J = 10 Hz, 1 H), 1.56 (dm, J = 11 Hz, 1 H), 1.72–1.89 (m, 3 H), 2.24 (br s, 1 H), 2.30 (br s, 1 H), 2.35–2.65 (m, 6 H).

1-Cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene System[1,2]

Tony Niem and Marvin D. Rausch*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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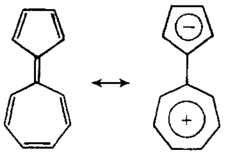
A synthesis of the parent hydrocarbon, 1-cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene (**4**), was attempted. The approach was based on the dehydrogenation of the dihydro derivative **11**. Hydride abstraction of **11** did not lead to the desired tropylium salt **13**. A synthetic approach to the tetraphenyl derivative **17** involved the tropylium salt **16**. Deprotonation of **16** produced an apparent oligomer of **17**. A stable organoiron derivative **7** of **4** was prepared by a three-step synthesis starting with *p*-ferrocenylphenylmagnesium bromide (**19**).

Sesquifulvalene (1) is a cross-conjugated two-ring hydrocarbon of considerable theoretical interest[3] which is expected to have a certain amount of contribution to its structure from the dipolar resonance form. The parent hydrocarbon **1**[4] is unstable and could not be isolated as a solid at low temperature.[5] The tetraphenyl derivative **2** possesses the expected thermal stability.[6] The hydrocarbon **1** can also be stabilized as a ligand in transition metal complexes. This was demonstrated by the synthesis of ferrocenyltropylium fluoroborate (**3**).[7]



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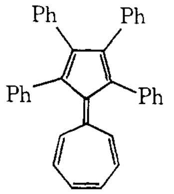

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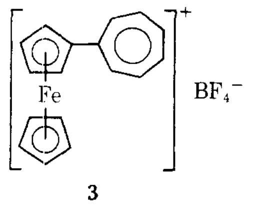
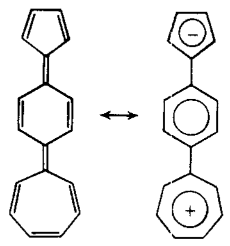


3

The system **4** is a cross-conjugated three-ring hydrocarbon having an inserted *p*-phenylene ring between the two aromatic rings of sesquifulvalene in the dipolar structure. It was of interest to study the synthesis of this long conjugated system about which very little is known. The parent hydrocarbon **4** has not yet been synthesized. Only three derivatives, **5**,[8] **6**,[9] and **7**,[2] with strong electron-withdrawing substituents or metal coordination have recently been reported. The present paper describes the preparation of the dihydro derivative **11**, which was a key intermediate in the attempted synthesis of the parent hydrocarbon **4**, and the isolation of an oligomer of tetraphenyl derivative **17**. Also included is a detailed report of the synthesis of π-cyclopentadienyliron derivative **7**.



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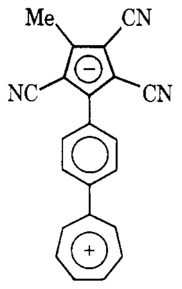

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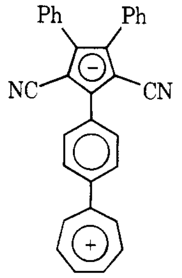

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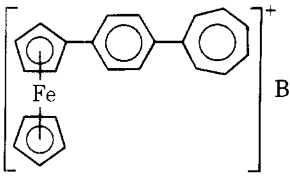
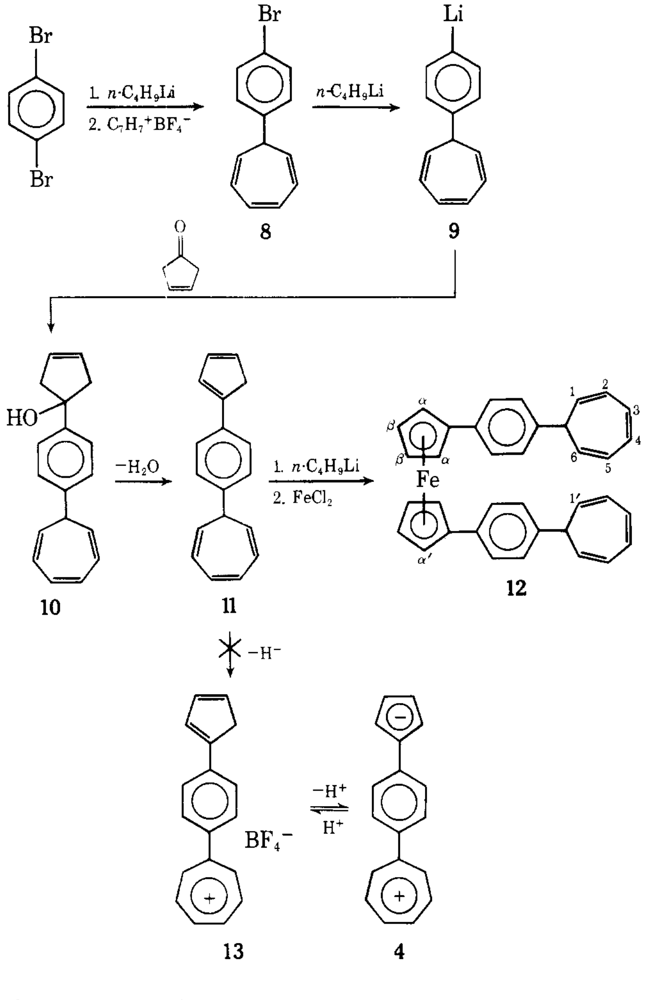


7

Results and Discussion

Scheme I

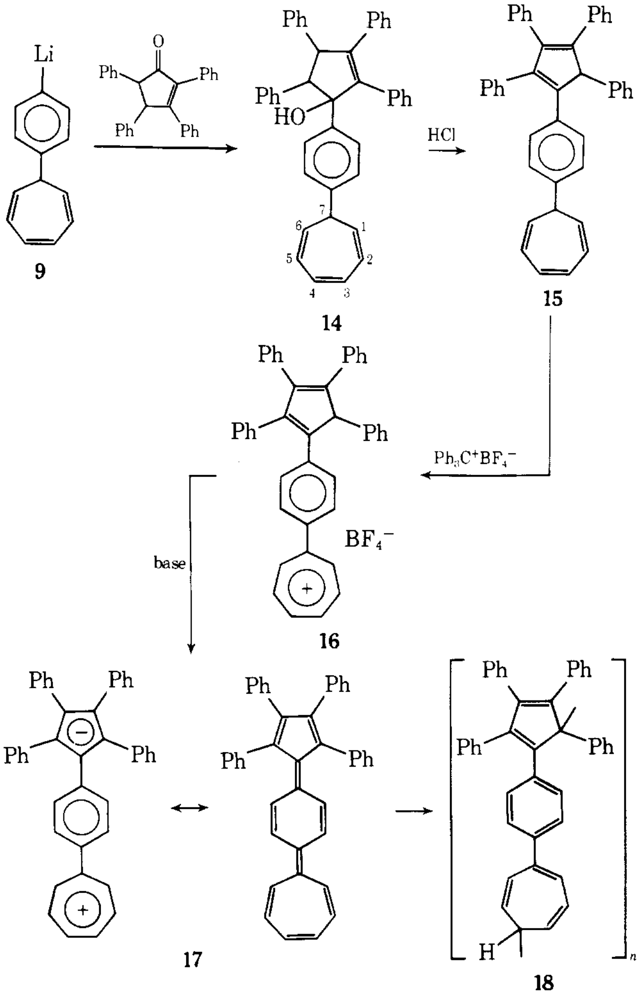


Dihydro Derivative 11 (Scheme I). The dihydro derivative 11 was synthesized from p-dibromobenzene by the sequence outlined in Scheme I. Thus, lithiation of p-dibromobenzene, followed by addition of tropylium fluoroborate, gave p-tropylbromobenzene (8)[10] in 56% yield. The NMR spectrum exhibited a methine proton (H_7) triplet at τ 7.34, characteristic of 7-arylcycloheptatrienes.[12,13] p-Tropylphenyllithium (9) was prepared via addition of n-butyllithium to a solution of 8, at 0 °C.[14] The lithium reagent 9 was then treated with 3-cyclopentenone at 0 °C to yield the hydroxy derivative 10 in 26% yield. The IR spectrum of carbinol 10 exhibited a hydroxy absorption peak at 3600 cm^{-1}. The NMR spectrum exhibited a multiplet at τ 7.1–7.5 for the methine and methylene protons and a broad singlet at τ 4.30 for the olefinic protons.

Treatment of 10 with phosphoryl chloride and pyridine at 0 °C gave the dihydro derivative 11. This compound was thermally unstable and decomposed fairly rapidly when exposed to air.[15] 1-Phenyl-1,3-cyclopentadiene also behaved similarly.[16] The mass spectrum of 11 exhibited a parent ion peak at m/e 232. The NMR spectrum of 11[24] showed a triplet for a methine proton (H_7) at τ 7.30 and an apparent doublet for two methylene protons (H_{11}) at τ 6.65.[17] The structure of 11 was further substantiated by treatment with n-butyllithium followed by ferrous chloride to give the disubstituted ferrocene derivative 12. The mass spectrum of 12 showed the expected parent peak at m/e 518. The NMR spectrum of 12 exhibited two triplets at τ 5.60 and 5.87, characteristic of 1,1′-diarylferrocenyl group.[19]

Treatment of 11 with triphenylmethyl fluoroborate failed to give the expected tropylium derivative 13 and afforded only intractable polymeric materials. Hydride abstraction from 11 did occur as evidenced by the isolation of triphenylmethane; however, the tropylium derivative 13 was apparently very unstable and could not be isolated. The instability of 13 could be due to the dissociation of the slightly acidic proton in cyclopentadiene to form the parent hydrocarbon 4, which was so reactive that it in turn was converted to polymeric material.[20]

Scheme II



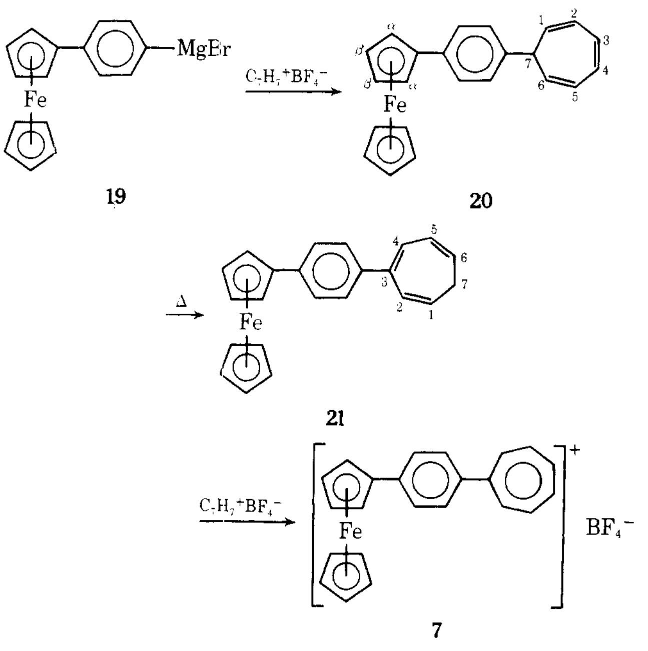
Oligomer of Tetraphenyl Derivative 17 (Scheme II). Addition of 2,3,4,5-tetraphenyl-2-cyclopentenone[40] to p-tropylphenyllithium (9) yielded the carbinol 14. The crude product **14** was heated at reflux with hydrochloric acid in ethanol to form the cyclopentadiene derivative **15** in 19% yield. The NMR spectrum[24] of **15** exhibited a singlet at τ 4.95 for the methine proton of the cyclopentadienyl group.[22] The mass spectrum exhibited a parent ion peak at m/e 536.

The tropylium salt **16** was obtained as a red solid in 83% yield by hydride abstraction of **15** with triphenylmethyl fluoroborate. This IR spectrum of **16** showed a strong absorption at 1060 cm^{-1}, indicating the presence of fluoroborate ion. The NMR spectrum exhibited a singlet for the methine proton at τ 4.31, a multiplet for the tropylium protons at τ 0.6–1.10, and a quartet for para-disubstituted aromatic ring protons at τ 2.40. The UV spectrum of **16** was markedly solvent dependent.[25] It showed λ_{max} at 355 (log ϵ 4.04) and 600 nm (3.90) in $CHCl_3$, and 377 (log ϵ 4.17) and 527 nm (4.23) in CH_3CN.

Treatment of **16** in acetonitrile with triethylamine afforded a yellow solid, mp 250 °C. A molecular weight determination by vapor pressure osmometry in benzene solution[27] indicated that the product was the dimer **18**.[28] The elemental analysis was consistent with either the monomer **17** or an oligomer **18**. The absorption spectrum of **18** exhibited no visible band as expected for an oligomer. The spectrum showed λ_{max} at 300 nm (log ϵ 4.67). The NMR spectrum exhibited broad resonances in the regions τ 3.00–5.00 (olefinic) and 7.00–7.60 (methine), indicating the presence of a substituted cycloheptatrienyl group[21,35a] as a result of polymeric linkage.[29] Presumably the tetraphenyl derivative **17** was formed as an intermediate;[30] however, its highly polar nature rendered it so reactive that it was converted to the oligomer **18**.[31]

π-Cyclopentadienyliron Derivative 7. The synthetic sequence for the preparation of **7** is outlined in Scheme III.

Scheme III



Addition of p-ferrocenylphenylmagnesium bromide (**19**)[32] to tropylium fluoroborate in THF gave the tropyl derivative **20** as an orange solid, mp 129–130 °C, in 25% yield. The NMR spectrum of **20** exhibited a triplet for the methine proton (H_7) at τ 7.73, a singlet at τ 6.06 for protons of the unsubstituted cyclopentadienyl group, and two triplets at τ 5.51 and 5.81 for the aryl-substituted cyclopentadienyl group.[33] The mass spectrum exhibited a parent ion peak at m/e 325.

In order to facilitate hydride ion removal from the tropyl ring,[12,34] the derivative **20** was isomerized to **21** in refluxing xylene. The structural assignment of **21** was based on its NMR spectrum, which exhibited a triplet at τ 7.72 for two methylene protons (H_7).

Treatment of **21** with tropylium fluoroborate in methylene chloride–acetonitrile produced the thermally stable salt **7** as a dark green solid in 50% yield. This complex did not melt below 300 °C. The ir spectrum of **7** displayed a strong absorption at 1060 cm^{-1} characteristic of fluoroborate ion. The NMR spectrum exhibited a multiplet at τ 0.7–1.31 indicating the presence of an aryl tropylium group.[35] The low-field NMR signals at τ 0.70–1.31 indicated that most of the positive charge was located on the seven-membered ring. Derivatives **5** and **6**,[8,9] having strong electron-withdrawing substituents on the five-membered ring, also displayed these characteristic low-field signals. Thus, the success of preparing a stable derivative of **4** required the presence of strong electron-withdrawing substituents or metal coordination on the five-membered ring.

Experimental Section

Infrared spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated vs. polystyrene. NMR spectra were recorded on a Varian A-60 spectrometer or Perkin-Elmer R12A spectrometer with tetramethylsilane as internal standard. Ultraviolet spectra were obtained on a Cary 14 recording spectrometer. Mass spectral data were obtained on a Hitachi Perkin-Elmer RMU 6L mass spectrometer by Dr. A. Siegel, University of Massachusetts.

Melting points were determined on a Mel-Temp apparatus. They are not corrected. Elemental analysis and molecular weight determinations were performed by Mr. Charles Meade of the University of Massachusetts Microanalytical Laboratory.

Ethyl ether and tetrahydrofuran were purified by drying over potassium hydroxide and sodium respectively, and were distilled from lithium aluminum hydride. Benzene was dried by azeotropic distillation. Pentane was washed with sulfuric acid and distilled from calcium hydride.

Thin layer chromatography experiments were performed with CAMAG silica gel containing ultraviolet-sensitive fluorescent indicator. Column chromatography experiments were performed with CAMAG alumina (neutral).

Commercial n-butyllithium in hexane solution was obtained from Alfa Inorganics, Inc. Tropylium fluoroborate,[36] 3-cyclopentenone,[37] ferrous chloride,[38] triphenylmethyl fluoroborate,[36] 3,4-diphenyl-2-cylopentenone,[39] and tetraphenyl-2-cyclopentenone[40] were prepared by published methods.

The numbering of positions in all structures is arbitrary for the convenience of proton assignments.

p-(7-Cycloheptatrienyl)bromobenzene (8). n-Butyllithium (68 mmol) was added under nitrogen to a stirred solution of p-dibromobenzene (16 g, 68 mmol) in 100 ml of dry ethyl ether at 0 °C over 20 min and stirring was continued for an additional 30 min. The reaction mixture was then added under nitrogen through an addition funnel to a stirred suspension of 6.4 g (36 mmol) of tropylium fluoroborate in 100 ml of dry ethyl ether at room temperature. Following completion of the addition, the reaction mixture was allowed to stir at room temperature for 4 h. The reddish solution was then poured onto 300 ml of cold 2 N hydrochloric acid and the layers were separated. The ether layer was washed twice with 10% sodium carbonate solution and twice with sodium chloride solution, and dried (Na_2SO_4). The solvent was evaporated and the residue was extracted twice with 250 ml of hot Skellysolve B. The combined extracts were evaporated and the liquid residue was vacuum distilled (95–108 °C, 0.05 mm), affording 4.5 g (56%) of product as a pale yellow oil. The product was further purified by low temperature recrystallization from pentane. The pure product obtained was a white solid: mp 31–32 °C; bp 108–109 °C (0.05 mm) [lit.[11] bp 108 °C (0.001 mm)]; NMR ($CDCl_3$) τ 7.34 (1 H, t, H_7), 4.55–4.90 (2 H, m, $H_{1,6}$), 3.63–3.97 (2 H, m, $H_{2,5}$), 3.24–3.41 (2 H, m, $H_{3,4}$), 2.47–3.00 (4 H, m, H_{Ar}).

Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.49; Br, 32.33. Found: C, 63.11; H, 4.34; Br, 32.30.

p-(7-Cycloheptatrienyl)phenyllithium (9). To a stirred solution of **8** in ether at 0 °C was added slowly an equimolar amount of n-butyllithium under nitrogen. The initially colorless reaction mixture turned to yellow at the end of addition. After an additional stirring for 15 min, the reagent was ready for use.

1-p-(7-Cycloheptatrienyl)phenyl-3-cyclopenten-1-ol (10). A solution of p-tropylphenyllithium (**9**) was prepared from 5.1 g (23 mmol) of p-tropylbromobenzene in 60 ml of dry ethel ether and 10.5 ml (23 mmol) of n-butyllithium in 20 ml of dry ether. To this solution was added a solution of 1.9 g (23 mmol) of 3-cyclopentenone[37] in 25 ml of dry ether at 0 °C over a period of 15 min. Stirring was continued at this temperature for 5 h. The mixture was hydrolyzed with an aqueous solution of ammonium chloride and layers were separated. The ether layer was washed with water, dried (Na_2SO_4), and evaporated in vacuo to a yellow solid. The latter was triturated with cold Skellysolve B and recrystallized three times from ethyl ether at −78 °C to produce 1.2 g (26%) of white crystals: mp 101–102 °C; NMR ($CDCl_3$) τ 7.92 (1 H, s, H_{OH}), 7.10–7.50 (5 H, m, $H_{7,\text{methylene}}$), 4.30 (2 H, broad s, $H_{\text{olefinic of Cp}}$), 4.50–4.86 (2 H, m, $H_{1,6}$), 3.67–4.00 (2 H, m, $H_{2,5}$), 3.28–3.50 (2 H, m, $H_{3,4}$), 2.50–2.90 (4 H, m, H_{Ar}).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.24; O, 6.39. Found: C, 85.99; H, 6.92; O, 6.93.

1-*p*-(7-Cycloheptatrienyl)phenyl-1,3-cyclopentadiene (11). To a solution of the carbinol **10** (0.8 g, 3.2 mmol) in 8 ml of dry pyridine at 0 °C, 0.3 ml (3.4 mmol) of phosphoryl chloride was added by a syringe. The reaction mixture was stirred at this temperature under nitrogen for 6 h and then hydrolyzed by pouring it onto ice-cold dilute hydrochloric acid. The mixture was extracted with 150 ml of ether; the extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The brown residue was extracted twice with 15-ml portions of Skellysolve B. The extracts were evaporated under reduced pressure to produce 0.52 g (70%) of a yellow product. A purer sample was obtained by trituration with Skellysolve B at −78 °C. The product was thermally unstable, even under nitrogen at 0 °C: NMR ($CDCl_3$) τ 7.30 (1 H, t, H_7), 6.65 (2 H, d, $H_{\text{methylene}}$), 2.70–3.20 (4 H, m, H_{Ar}), 4.65–5.00 (2 H, m, $H_{1,6}$), 3.30–4.20 (7 H, $H_{2,5,3,4,\text{olefinic of Cp}}$).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94; mol wt, 232. Found: C, 93.21; H, 5.91; mol wt. (mass spectroscopic), 232.

1,1′-Di[*p*-(7-cycloheptatrienyl)phenyl]ferrocene (12). To a stirred solution of 0.52 g (2.3 mmol) of dihydro derivative 11 in 30 ml of dry ethyl ether at 0 °C was added under nitrogen *n*-butyllithium (2.6 mmol) in 10 ml of dry ethyl ether over 10 min. Stirring at this temperature was continued for 30 min and 0.14 g (2.3 mmol) of ferrous chloride was added in one portion. The reaction mixture was then stirred at 0 °C for 2 h and at room temperature for 12 h, and hydrolyzed with 100 ml of 2 N hydrochloric acid. The mixture was extracted two times with 300-ml portions of ether; the combined ether extracts were washed twice with water and dried over Na_2SO_4. The dried ethereal solution was evaporated to dryness in vacuo and the residue was dissolved in 40 ml of benzene. The benzene solution was placed on a column of alumina. Elution with benzene gave an orange solid. The solid was crystallized from benzene to yield 0.25 g (22%) of product. An analytical sample was obtained by recrystallization from benzene: mp 163–165 °C; NMR ($CDCl_3$) τ 7.40 (2 H, t, $H_{7,7}$), 5.60 (4 H, t, $H_{\alpha \text{ and } \alpha'}$), 5.87 (4 H, t, $H_{\beta \text{ and } \beta'}$), 4.46–4.83 (4 H, m, $H_{1,6,1',6'}$), 3.67–4.00 (4 H, m, $H_{2,5,2',5'}$), 3.25–3.46 (4 H, m, $H_{3,4,3',4'}$), 2.64–2.95 (4 H, m, H_{Ar}).

Anal. Calcd for $C_{36}H_{30}Fe$: C, 83.40; H, 5.83; Fe, 10.77; mol wt, 518. Found: C, 83.57; H, 5.95; Fe, 10.15; mol wt (mass spectroscopic), 518.

Attempted Preparation of *p*-(1,3-Cyclopentadienyl)phenylcycloheptatrienylium Fluoroborate (13). The dihydro derivative 11 (0.2 g, 0.86 mmol) in 5 ml of methylene chloride and 0.28 g (0.86 mmol) of triphenylmethyl fluoroborate in 10 ml of methylene chloride were combined in a 25-ml flask with argon. The reaction mixture was left in a refrigerator for 2 days. After filtration, the black precipitate collected was found to be intractable material. The filtrate was evaporated to dryness; the residue was purified by column chromatography on alumina and eluted with Skellysolve B to produce 94 mg (45%) of triphenylmethane. The NMR spectrum of this compound was identical with that of an authentic sample.

1,2,3,5-Tetraphenyl-4-*p*-(7-cycloheptatrienyl)phenyl-1,3-cyclopentadiene (15). A solution of *p*-tropylphenyllithium (**9**) was prepared from 2.4 g (10.7 mmol) of *p*-tropylbromobenzene **8** in 100 ml of dry ethyl ether and 4.9 ml (10.7 mmol) of *n*-butyllithium in 30 ml of dry ether. To this solution was added a solution of 2.8 g (7.25 mmol) of 2,3,4,5-tetraphenyl-2-cyclopentenone[40] in 150 ml of benzene over 30 min at 0 °C. Stirring was continued at this temperature for 7 h. The reaction mixture was hydrolyzed with 250 ml of 2 N hydrochloric acid. The layers were separated. The organic layer was washed twice with 10% sodium carbonate solution and twice with sodium chloride solution, and dried (Na_2SO_4). The solvent was evaporated, and an IR spectrum of the residue showed an O–H stretching frequency at 3600 cm^{-1} ($CHCl_3$). The crude carbinol **14** was dissolved in 150 ml of hot ethanol. The ethanolic solution was allowed to cool to room temperature and filtered. The filtrate was then stirred at reflux under nitrogen in a 250-ml flask while 15 ml of 12 N hydrochloric acid was added dropwise through an addition funnel over 30 min. Stirring was continued under reflux for 1 h. The product gradually crystallized from the hot solution and was collected on a Buchner funnel after the solution had been cooled. Recrystallization first from chloroform–ethanol, then from ether, and again from chloroform–ethanol afforded 0.76 g (19%) of light yellow crystals: mp 180–181 °C; NMR ($CDCl_3$) τ 7.50 (1 H, t, H_7), 4.60–5.05 (2 H, m, $H_{1,6}$), 3.72–4.05 (2 H, m, $H_{2,5}$), 3.28–3.50 (2 H, m, $H_{3,4}$), 2.73–3.20 (24 H, m, H_{Ar}), 4.95 (1 H, s, $H_{\text{methine of Cp}}$); UV ($CHCl_3$) λ_{max} (log ϵ) 247 (4.46) and 347 nm (4.11).

Anal. Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01; mol wt, 536. Found: C, 94.01; H, 5.89; mol wt (mass spectroscopic), 536.

1,2,3,4,5-Pentaphenylcyclopentadiene. A solution of 0.5 g (1.3 mmol) of 2,3,4,5-tetraphenyl-2-cyclopentenone in 45 ml of benzene was added under nitrogen over 15 min to a stirred solution of phenyllithium prepared from 0.3 g (1.9 mmol) of bromobenzene and 0.86 ml (1.9 mmol) of *n*-butyllithium in 10 ml of dry ethyl ether at 0 °C. After stirring for 4 h, the reaction mixture was hydrolyzed with 2 N hydrochloric acid and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated in vacuo. An IR spectrum of the residue showed an O–H stretching frequency at 3600 cm^{-1}. The crude carbinol was dissolved in 30 ml of ethanol and added to a nitrogen-flushed 100-ml flask. After the solution was heated to reflux, 30 ml of 12 N hydrochloric acid was added dropwise through an addition funnel over 30 min. Stirring was continued under reflux for 1.5 h. The product gradually crystallized from the hot solution and was collected by filtration after cooling. Four recrystallizations from benzene yield 0.19 (33%) of white crystals: mp 259–260 °C (lit.[23] 250 °C); NMR ($CDCl_3$) τ 5.00 (1 H, s, H_{methine}), 2.70–3.18 (25 H, m, H_{Ar}).

Anal. Calcd for $C_{35}H_{26}$: C, 94.12; H, 5.87. Found: C, 94.01; H, 5.87.

***p*-(2,3,4,5-Tetraphenyl-1,3-cyclopentadienyl)phenyltropylium Fluoroborate (16).** A mixture of 1.7 g (3.16 mmol) of the dihydro derivative **15** in 120 ml of methylene chloride, and 1.0 g (3 mmol) of triphenylmethyl fluoroborate in 30 ml of methylene chloride was left in a refrigerator for 4 days. The reaction mixture was concentrated to 30 ml via a stream of nitrogen and again left in a refrigerator overnight. Filtration gave 1.5 g (83%) of red crystals. An analytical sample was obtained by seven recrystallizations from methylene chloride, followed by drying in vacuo at 100 °C: mp 195 °C dec; NMR (acetone-d_6) τ 4.31 (1 H, s, H_{methine}), 2.77–3.20 (20 H, m, H_{Ar}), 2.13–2.70 (4 H, q, $H_{\text{disub Ar}}$), 0.60–1.10 (6 H, m, $H_{\text{tropylium}}$); IR (KBr) 1060 cm^{-1} (s, BF_4); UV ($CHCl_3$) λ_{max} (log ϵ) 355 (4.04) and 600 nm (3.90); UV (CH_3CN), λ_{max} (log ϵ) 337 (4.17) and 527 nm (4.23).

Anal. Calcd for $C_{42}H_{31}BF_4$: C, 81.04; H, 5.02; B, 1.74; F, 12.21. Found: C, 81.14; H, 5.06; B, 1.70; F, 12.12.

The filtrate from the reaction mixture was evaporated to dryness. The residue was extracted several times with hot Skellysolve B. The extracts were concentrated to a small volume and chromatographed on a column of alumina. Elution with Skellysolve B gave 0.47 g (64%) of crude triphenylmethane. Recrystallization from ethanol afforded white crystals. The NMR spectrum of this compound was identical with that of an authentic sample.

Oligomeric 1-Cycloheptatrienylidene-4-(tetraphenylcyclopentadienylidene-2,5-cyclohexadiene) (18). To a nitrogen-flushed 50-ml flask was added 1 g (1.6 mmol) of tropylium derivative **16** in 15 ml of acetonitrile. The deep red solution was cooled to 0 °C, and 0.48 g (4.8 mmol) of triethylamine in 5 ml of acetonitrile was added dropwise over 15 min. Before half of the amine was added, the deep red color of the solution was discharged. After stirring for 1 h at 0 °C, the product was collected on a Hirsch funnel. The yellow solid was transferred to an Erlenmeyer flask containing 5 ml of acetonitrile cooled at 0 °C. The suspension was stirred for 30 min and filtered. The same procedure was repeated once again to produce 0.62 g (72%) of analytically pure **18:** mp 250 °C (red liquid); bp 350 °C (decomposition with gas evolution); UV ($CHCl_3$) λ_{max} (log ϵ) 300 nm (4.67); NMR ($CDCl_3$) τ 7.00–7.60, 4.10–4.90, 3.30–3.90, 2.00–3.30.

Anal. Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66; mol wt, 534. Found: C, 94.30; H, 5.71, mol wt (osmometric in benzene), 1243.

The filtrate from the reaction mixture was evaporated and the residue was extracted with water. The aqueous extract was evaporated in vacuo to give 0.22 g (75%) of triethylammonium fluoroborate. The salt was identical with an authentic sample.

***p*-(7-Cycloheptatrienyl)phenylferrocene (20).** To a stirred suspension of 3.6 g (20 mmol) of tropylium fluoroborate in 150 ml of dry ethyl ether was added dropwise under nitrogen over 20 min a solution of *p*-ferrocenylphenylmagnesium bromide (**19**)[32] prepared from 3.4 g (10 mmol) of *p*-bromophenylferrocene, 1.1 g (10 mmol) of ethyl bromide, and 0.73 g (30 mmol) of magnesium in 100 ml of dry tetrahydrofuran. Stirring was continued for 2 h at room temperature and then for 20 min at reflux. The reaction mixture was hydrolyzed with

150 ml of 2 N hydrochloric acid. The ether layers were washed twice with 10% sodium carbonate solution and twice with water, dried (Na_2SO_4), and evaporated to dryness. The residue was dissolved in 5 ml of benzene, chromatographed on a 14 × 2 in. column of alumina (activity II), and eluted with Skellysolve B. The first orange band consisted of a mixture of phenylferrocene and *p*-bromophenylferrocene. The second orange band, eluted with 2:1 Skellysolve B–benzene, gave 0.75 g (21%) of product. Three recrystallizations from Skellysolve B afforded analytically pure orange crystals: mp 129–130 °C; NMR ($CDCl_3$) τ 7.73 (1 H, t, H_7), 4.50–4.82 (2 H, m, $H_{1,6}$), 3.69–4.00 (2 H, m, $H_{2,5}$), 3.26–3.48 (2 H, m, $H_{3,4}$), 6.06 (5 H, s, $H_{\text{unsub Cp}}$), 5.51 (2 H, t, H_α), 5.81 (2 H, t, H_β), 2.53–3.00 (4 H, m, H_{Ar}).

Anal. Calcd for $C_{23}H_{20}Fe$: C, 78.42; H, 5.72; Fe, 15.85; mol wt, 352. Found: C, 78.15; H, 5.56; Fe, 15.80; mol wt (mass spectroscopic), 352.

***p*-(3-Cycloheptatrienyl)phenylferrocene (21).** A solution of 1.0 g (2.8 mmol) of *p*-tropylphenylferrocene (**20**) in 12 ml of toluene was heated to reflux under nitrogen for 24 h. The solvent was evaporated in vacuo and the residue was recrystallized from Skellysolve B to yield 9.5 g (95%) of product: mp 123–126 °C; NMR ($CDCl_3$) τ 7.72 (2 H, t, H_7), 4.32–4.78 (2 H, m, $H_{1,6}$), 3.57–3.97 (2 H, m, $H_{2,5}$), 3.03–3.20 (1 H, d, H_4), 6.07 (5 H, s, $H_{\text{unsub Cp}}$), 5.80 (2 H, t, H_β), 5.54 (2 H, t, H_α), 2.70 (4 H, s, H_{Ar}).

***p*-Ferrocenylphenyltropylium Fluoroborate (7).** To a solution of 0.6 g (1.7 mol) of *p*-tropylphenylferrocene (**21**) in 20 ml of methylene chloride and 5 ml of acetonitrile was added 0.32 g (1.7 mmol) of tropylium fluoroborate in one portion. The reaction mixture was stirred at room temperature for 18 h. The final suspension was suction filtered to produce dark green crystals. The product was purified by consecutive trituration with water, ether, and benzene. The analytical sample was obtained by consecutive trituration with carbon tetrachloride, water, and ethyl ether, and dried at 110 °C for 4 days. The compound does not melt below 300 °C: IR (KBr) 1060 cm^{-1} (s, BF_4^-); NMR (CH_3CN) τ 0.70–1.30 (6 H, m, H_{1-6}), 2.10–2.30 (4 H, d, H_{Ar}), 5.10 (2 H, t, H_α), 5.45 (2 H, t, H_β), 5.90 (5 H, s, $H_{\text{unsub Cp}}$).

Anal. Calcd for $C_{23}H_{19}BF_4Fe$: C, 63.06; H, 4.37; Fe, 12.75. Found: C. 63.38; H. 4.62; Fe, 12.50.

Registry No.—**7,** 60595-05-3; **8,** 54615-31-5; **9,** 60582-51-6; **10,** 60582-52-7; **11,** 60582-53-8; **12,** 60595-03-1; **14,** 60582-54-9; **15,** 60582-55-0; **16,** 60582-57-2; **18,** 60582-59-4; **20,** 60595-01-9; **21,** 60595-02-0; *p*-dibromobenzene, 106-37-6; tropylium fluoroborate, 27081-10-3; 3-cyclopentenone, 14320-37-7; ferrous chloride, 7758-94-3; 2,3,4,5-tetraphenyl-2-cyclopentenone, 7317-52-4; 1,2,3,4,5-pentaphenylcyclopentadiene, 2519-10-0; triphenylmethyl fluoroborate, 341-02-6; *p*-bromophenylferrocene, 58482-65-8.

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