chemical ionization, argon, 30 eV) m/e 663 [M – SbF$_6$]$^-$, 877 [M – F]$^-$.

Iodosobenzene hexafluorophosphate (3): yield 2.0 g (65%); mp 115–120 °C dec; ^{1}H NMR (20% DMSO-d_6 in CDCl$_3$) δ 7.7 (2 H, d, J = 7.5 Hz), 7.4 (1 H, t, J = 7.2 Hz), 7.3 (2 H, t, J = 7.4 Hz); ^{13}C NMR (20% DMSO-d_6 in CDCl$_3$) δ 132.8, 131.1, 130.3; IR (KBr, cm^{-1}) 3080, 1585 (Ph), 550 (I–O), 430 (I–C).

Hydrolysis of Iodosobenzene Tetrafluoroborate (1). A mixture of reagent 1 (0.3 g, 0.5 mmol) with water (500 mL) was stirred for 2 h. Pale yellow crystals of product were filtered, washed additionally with 500 mL of water, and dried in a vacuum dessicator over phosphorus pentoxide to give 0.25 g (95%) of the hydroxy derivative 4: mp 150–160 °C dec; ^{1}H NMR (DMSO) δ 7.8 (2 H, d, J = 7.8 Hz), 7.7 (2 H, d, J = 7.2 Hz), 7.6 (1 H, t, J = 7.1 Hz), 7.5 (1 H, t, J = 7.4 Hz), 7.45 (2 H, t, J = 7.3 Hz), 7.2 (2 H, t, J = 7.5 Hz), 3.39 (1 H, s); ^{13}C NMR (DMSO) δ 136.9, 133.4, 131.5, 131.4, 130.6, 128.5; IR (Nujol, cm^{-1}) 3420, 3060, 1575, 530, 460. Anal. Calcd for C$_{12}$H$_{11}$BF$_4$I$_2$O$_2$: C, 27.30; H, 2.10. Found: C, 27.70; H, 1.99.

Reactions of Reagents 1–3 with Indene. Reagent (1, 2, or 3) (0.5 mmol) was added to a stirred solution of indene (0.12 g, 1 mmol) in 3 mL of methanol or acetic acid at room temperature. The reaction mixture was stirred at room temperature until its color completely disappeared, diluted with 15 mL of water, and extracted with CH$_2$Cl$_2$. The organic solution was dried with Na$_2$SO$_4$, the solvent was evaporated, and the products were separated by column chromatography (silica gel, ethyl acetate–hexane, 1:2).

cis-1,2-Dimethoxyindan (5): ^{1}H NMR (CDCl$_3$) δ 7.30 (4 H, m), 4.74 (1 H, d, J = 4.2 Hz), 4.10 (1 H, m), 3.57 (3 H, s), 3.47 (3 H, s), 3.32 (1 H, dd, J = 16.0 and 6.9 Hz), 2.80 (1 H, dd, J = 16.0 and 5.4 Hz); MS m/z 178 (M$^+$).

trans-1,2-Dimethoxyindan (6): ^{1}H NMR (CDCl$_3$) δ 7.38 (4 H, m), 4.61 (1 H, d, J = 4.9 Hz), 4.08 (1 H, td, J = 7.2 and 4.9 Hz), 3.51 (3 H, s), 3.42 (3 H, s), 3.90 (2 H, dd, J = 7.2 and 2.8 Hz); MS m/z 178 (M$^+$).

cis-1,2-Diacetoxyindan (7): ^{1}H NMR (CDCl$_3$) δ 7.30 (4 H, m), 6.26 (1 H, d, J = 3.6 Hz), 5.49 (1 H, ddd, J = 7.1, 4.5, and 3.5 Hz), 3.53 (1 H, dd, J = 16.7 and 7.1 Hz), 2.90 (1 H, dd, J = 16.7 and 4.5 Hz), 2.10 (3 H, s), 2.08 (3 H, s); MS m/z 174 (M$^+$ – AcOH).

Reactions of Reagents 1–3 with Cyclohexene in the Presence of LiClO$_4$. A mixture of the reagent (1, 2, or 3) (0.05 mmol), cyclohexene (0.2 mL), lithium perchlorate (0.5 g), and ethyl acetate (3 mL) was stirred until its color completely disappeared, diluted with CH$_2$Cl$_2$, washed with water, and dried. The solvent was removed by evaporation. Iodobenzene and diperchlorate 8 were separated by column chromatography (silica gel, ethyl acetate–hexane, 1:5). For 1,2-bis(perchloryloxy)cyclohexane 8:[4b] ^{1}H NMR (CDCl$_3$) δ 5.17 (2 H, m, W = 12 Hz), 2.0–1.5 (8 H, m). **Caution:** neat diperchlorate 8 can explode violently on contact or heating.

Reactions of Reagents 1 and 3 with Silyl Enol Ethers. A mixture of reagent (1 or 3) (0.05 mmol), silyl enol ether (0.2 mmol), and CH$_2$Cl$_2$ (2 mL) was stirred at room temperature until the reagent completely disappeared. The reaction mixture was washed with water and dried with Na$_2$SO$_4$, and the solvent was evaporated. Crystals of 1,4-butanedione that formed were washed with hexane to remove iodobenzene and dried. Physical characteristics and spectral data for products 14–16[7e] and 17[12] were the same as previously reported.

Reactions of Reagents 1–3 with 1-Pentyne. A mixture of reagent (1, 2, or 3) (0.05 mmol) and 0.2 mL of 1-pentyne in 3 mL of CH$_2$Cl$_2$ was stirred at room temperature until the reagent completely disappeared. The solution was dried with Na$_2$SO$_4$, and the solvent was evaporated. Washing of the crude product with hexane to remove excess alkyne gave the alkynyliodonium salts 18–20 as unstable oils.

1-Pentynylphenyliodonium tetrafluoroborate (18): ^{1}H NMR (CDCl$_3$) δ 8.01 (2 H, m), 7.61 (3 H, m), 2.58 (2 H, t, J = 7.1 Hz), 1.59 (2 H, m), 0.94 (3 H, t, J = 7.3 Hz); IR (Nujol, cm^{-1}) 2200 (C≡C).

1-Pentynylphenyliodonium hexafluoroantimonate (19): ^{1}H NMR (CDCl$_3$) δ 8.05 (2 H, m), 7.71 (1 H, m), 7.58 (2 H, m), 2.63 (2 H, t, J = 7.1 Hz), 1.62 (2 H, m), 0.95 (3 H, t, J = 7.2 Hz); IR (Nujol, cm^{-1}) 2190 (C≡C).

1-Pentynylphenyliodonium hexafluorophosphate (20): ^{1}H NMR (CDCl$_3$) δ 8.04 (2 H, m), 7.51 (3 H, m), 2.52 (2 H, t, J = 6.8 Hz), 1.61 (2 H, m), 0.94 (3 H, t, J = 7.0 Hz); IR (Nujol, cm^{-1}) 2200 (C≡C).

Iptycene Synthesis. A New Method for Attaching a 2,3-Anthracene Moiety to the 9,10-Positions of Another Anthracene Moiety. Exceptional Conditions for a Lewis Acid Catalyzed Diels–Alder Reaction[1]

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An efficient three-step method for appending a 2,3-anthracene moiety to the 9,10-positions of an existing anthracene moiety is described. The first step uses excess 1,4-anthraquinone (3 equiv) and aluminum chloride (6 equiv) to obtain the anthracene–quinone cycloadduct (omission of the AlCl$_3$ resulted in no adduct). The resulting diketone was reduced to the corresponding diol (excess LiAlH$_4$), which was dehydrated to the arene with phosphorus oxychloride and pyridine. Specific examples include the preparation of heptiptycene 8 from pentiptycene 6 (66% overall yield) and a similar conversion of 8 to the noniptycene 13 (75% overall yield). The methodology led to a markedly improved synthesis of tritriptycene 9 and the first synthesis of undecaiptycene 14.

Iptycenes have a rigid carbon framework, show exceptional thermal stability, and have well-defined molecular cavities that may trap small molecules.[2] The development

of general methodology for their synthesis therefore constitutes a significant synthetic challenge.

One method for rapidly constructing higher iptycenes[2,3] involves attaching a 2,3-anthracene moiety to the 9,10-

(1) Presented at the Midwest-America Chinese Science and Technology Conference, St. Louis, MO, June 4, 1988.

(2) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* 1986, *42*, 1641–1656.

(3) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* 1981, *46*, 4427–4432.

Scheme I
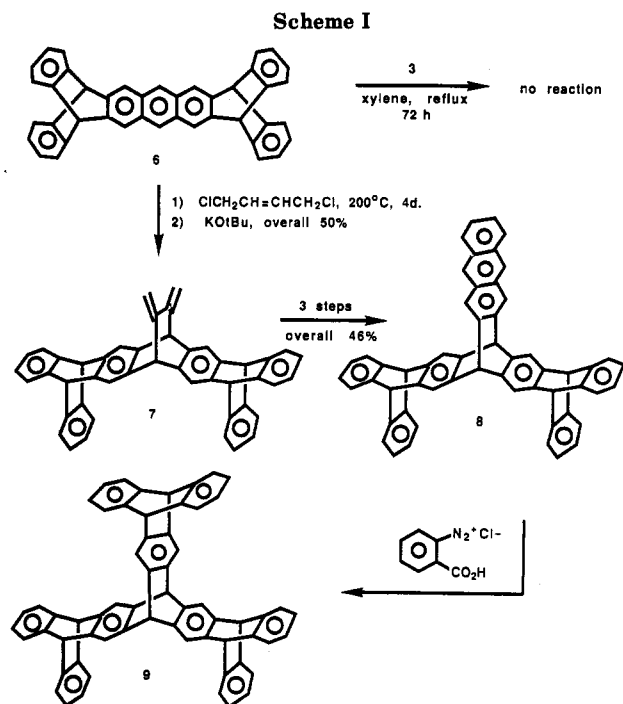
positions of an existing anthracene moiety (1 → 2). Benzyne or other cycloaddition, or repetition of the reactions which convert 1 to 2, results in higher iptycenes.
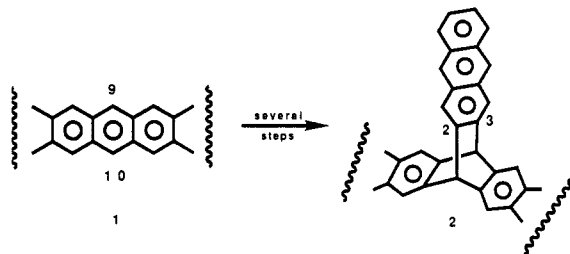
A two-step version of this transformation was used to convert anthracene itself to triptycene 4,[2] using as the first step cycloaddition of endoxide 3 to anthracene. The utility of this sequence is illustrated by repetition of the sequence to give pentiptycene 5.[2]
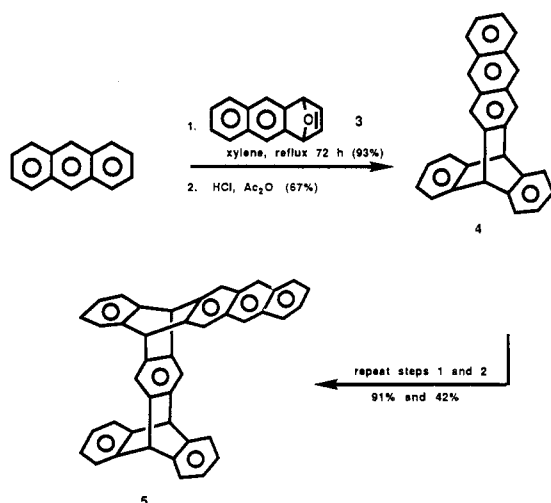
This methodology failed when applied to the anthracene moiety of pentiptycene 6,[4] and an alternative strategy was
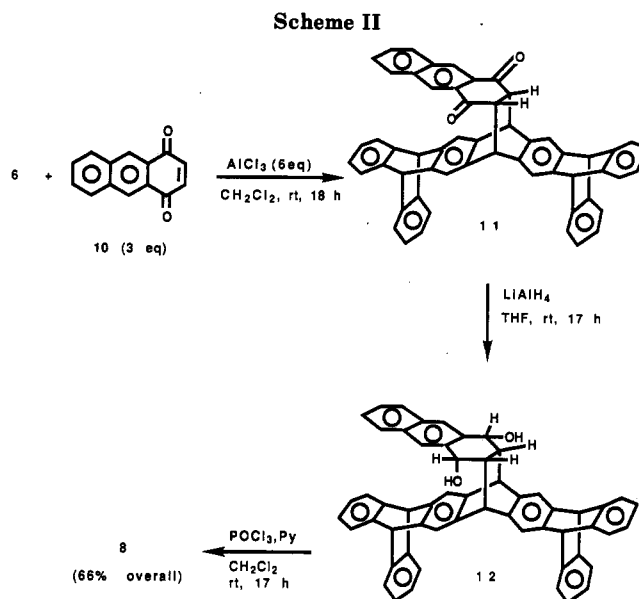
Scheme II

required[4] to build the anthracene moiety of **8**. This strategy, although it succeeded in ultimately achieving the synthesis of tritriptycene **9**, suffered because of the first step (Scheme I). Cycloaddition of 1,4-dichloro-2-butene to **6** required severe and carefully controlled reaction conditions, was somewhat erratic, and when successful proceeded to diene **7** in only 50% overall yield. Consequently we sought an alternative solution to this problem, and present our results here.

Results and Discussion

In place of endoxide **3**, we decided to try the more reactive dienophile 1,4-anthraquinone **10** for attaching an anthracene moiety to the central ring of **6**. However, when **6** and **10** were heated with xylene at reflux or in a sealed tube for 3 days at 190 °C, none of the cycloadduct **11** was obtained. Even when a solution of **6** and 5 equiv of **10** was heated in methylene chloride at 80 °C for 24 h under 15 kbar of pressure[5] most of the starting material was recovered; some adduct **11** was formed, but the yield was <10% (Scheme II). We were finally successful in obtaining the desired cycloadduct by using rather exceptional Lewis acid conditions for the Diels–Alder reaction. By treating **6** with 3 equiv of 1,4-anthraquinone and 6 equiv of aluminum chloride in methylene chloride at room temperature for 18 h, we obtained a good yield of **11**, mp 220–222 °C.[6] The adduct was identified by its spectra and further conversions. In particular, the ^{1}H NMR spectrum showed four two-proton singlets for the aliphatic protons (three bridgehead sets at δ 4.88, 4.99, and 5.48 and a peak at δ 3.23 for the protons α to the carbonyls; the angle between the latter protons and the adjacent bridgehead protons is such that there is essentially no coupling between them) and three two-proton singlets for the isolated aromatic protons (δ 7.06, 7.35, and 8.12) as well as appropriate peaks for the remaining aromatic protons.

Adduct **11** was converted to the known heptiptycene **8** in two steps. Lithium aluminum hydride reduction afforded a single crystalline diol **12**, mp 248–250 °C, which was then dehydrated to **8** with phosphorus oxychloride and pyridine. By not purifying intermediates, it was possible

(4) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675–6679. See also the correction, *J. Am. Chem. Soc.* **1988**, *110*, 5237.

(5) We are indebted to Bruce Kowalczyk and Prof. W. G. Dauben for carrying out this reaction; workup was performed by Y.-S.C.

(6) There is precedent for using aluminum chloride to catalyze the cycloaddition of benzoquinone to anthracene: Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436–4437.

Scheme III
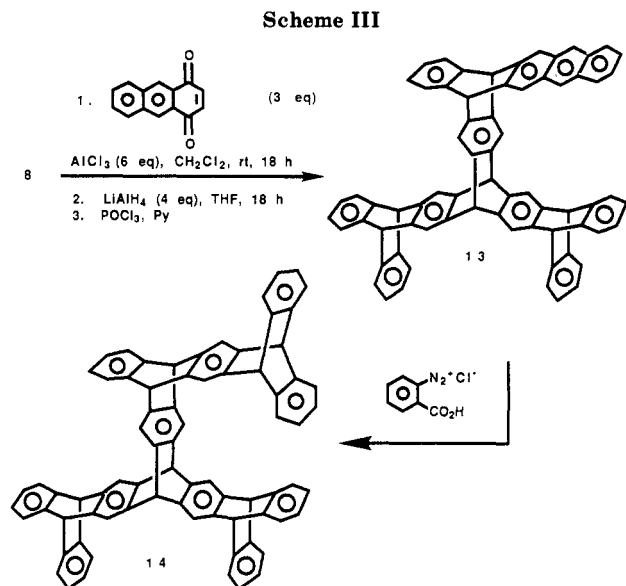
to obtain a 66% overall yield of **8** from **6** in three steps. Under the conditions described for the first step, no **6** remained unreacted, and the only other substantial product at the stage of final purification was recovered excess 1,4-anthraquinone.

With substantial amounts of **8** in hand, we were also able to improve the yield of the benzyne addition step, to give tritriptycene **9** in 90% yield from **8**. Thus **6** can now be converted to **9** in four steps and 59% yield (compared with six steps and 11%[4]).

To illustrate the generality of this method, we subjected **8** to the same four-step sequence, to obtain the undecaiptycene **14**, mp >460 °C, in 71% overall yield, via the anthracene intermediate **13** (Scheme III).

The structure of **13** was clear from its spectra. The ^{1}H NMR spectrum showed four two-proton singlets for the four sets of bridgehead protons (δ 5.07, 5.12, 5.17, and 5.31) and five two-proton singlets for the five sets of isolated aromatic protons (at δ 7.72 and 8.11 for the anthracene moiety and at δ 7.20, 7.25, and 7.31 for the central triptycene moiety). The UV spectrum was typical for an anthracene.

The structure of **14** was evident from the method of synthesis and from its spectral properties. In particular, the ^{1}H NMR spectrum showed five two-proton singlets for the bridgehead protons (δ 5.02, 5.06, 5.12, 5.15, 5.17) and four two-proton singlets for the isolated aromatic protons (δ 7.14, 7.19, 7.21, 7.24) as well as other appropriate peaks. Compound **14** has two U-shaped cavities similar to those in **9**, and a somewhat more enclosed cavity that includes five benzene rings.

In summary, the use of a large excess of aluminum chloride facilitates the cycloaddition of dienophile **10** to an anthracene moiety in cases where no reaction occurs otherwise. This observation permitted the development of a three-step efficient method for appending a 2,3-anthracene moiety to the 9,10-positions of another anthracene moiety, even if the latter is somewhat hindered.

Experimental Section

Cycloadduct 11. Aluminum trichloride (4.46 g, 33.5 mmol) was added in portions (1 h) to a stirred solution of pentiptycene **6**[4] (2.96 g, 5.58 mmol) and 1,4-anthraquinone **10**[7] (3.48 g, 16.74 mmol) in methylene chloride (250 mL) at room temperature under

(7) Purchased from Lancaster Synthesis, Windham, NH.

argon. The mixture was stirred for 17 h, poured into a mixture of ice and concentrated hydrochloric acid, and extracted with methylene chloride (3 × 300 mL). The organic layer was washed with water (3 × 150 mL), dried (MgSO$_4$), and concentrated to yield 6.0 g of a dark green solid, which (by NMR) consisted only of **11** and excess **10**. For characterization, a small portion was purified by preparative TLC using 30% ethyl acetate in hexane as the eluent to give pure **11** as a pale yellow solid: mp 220–222 °C; IR (CHCl$_3$) 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 3.22 (s, 2 H), 4.84 (s, 2 H), 4.99 (s, 2 H), 5.36 (s, 2 H), 6.43 (dd, J = 5.3, 3.2 Hz, 2 H), 6.74 (dd, J = 5.3, 3.2 Hz, 2 H), 6.84 (dd, J = 5.3, 3.2 Hz, 2 H), 6.88 (dd, J = 5.3, 3.2 Hz, 2 H), 7.00 (dd, J = 5.3, 3.2 Hz, 2 H), 7.06 (s, 2 H), 7.09 (dd, J = 5.3, 3.2 Hz, 2 H), 7.25 (dd, J = 5.3, 3.2 Hz, 2 H), 7.35 (s, 2 H), 7.39 (dd, J = 5.3, 3.2 Hz, 2 H) 7.46 (dd, J = 6.3, 3.2 Hz, 2 H), 7.69 (dd, J = 6.3, 3.2 Hz, 2 H), 8.12 (s, 2 H); mass spectrum, m/e (relative intensity) 530 (M$^+$ – anthraquinone,[8] 23.9), 352 (1.2), 263 (5.1), 208 (anthraquinone, 100), 180 (25.1), 152 (67.2), 126 (60.3); FAB mass spectrum, m/e (relative intensity) 739 (M + 1, 20.3), 530 (M$^+$ - anthraquinone, 30.6), 307 (16.6), 154 (100), 137 (88.7); high-resolution mass spectrum calcd for C$_{56}$H$_{34}$O$_2$ 738.2559, obsd 738.2568.

Diol 12. To a stirred suspension of crude **11** (6.0 g, vide supra) in tetrahydrofuran (600 mL) was added under argon at 0 °C 1.8 g (47.4 mmol) of lithium aluminum hydride. The mixture was warmed to room temperature and stirred for 17 h, quenched with water, and extracted with ethyl acetate (3 × 500 mL). The organic layer was washed with water (2 × 300 mL), dried (MgSO$_4$), and concentrated to give 6.3 g of crude **12**. Chromatography of a small portion of the crude mixture gave pure **12** as a pale yellow crystalline solid: mp 248–250 °C; IR (CHCl$_3$) 3460 (br), 2930 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.49 (br s, 2 H), 2.04 (br s, 2 H, exchanges with D$_2$O), 3.90 (br s, 2 H), 4.49 (br s, 2 H), 5.23 (s, 2 H), 5.33 (s, 2 H), 6.81 (dd, J = 5.3, 3.1 Hz, 4 H), 6.88–6.91 (m, 2 H), 6.95 (dd, J = 5.3, 3.1 Hz, 4 H), 7.09 (s, 2 H), 7.22 (s, 2 H), 7.23–7.48 (m, 10 H), 7.76 (br s, 2 H); FAB mass spectrum, m/e (relative intensity) 743 (M + 1, 1.6), 742 (M$^+$, 2.0), 707 (1.8), 530 (45.3), 454 (8.1), 352 (7.8), 289 (8.4), 195 (17.1), 154 (100); high-resolution mass spectrum calcd for C$_{56}$H$_{38}$O$_2$ 742.2872, obsd 742.2895.

Heptiptycene 8 from Diol 12. To a stirred solution of crude **12** (6.3 g, vide supra) and pyridine (13.5 mL, 0.173 mol) in methylene chloride (600 mL) was added under argon at 0 °C 6.3 mL (68.3 mmol) of phosphorus oxychloride.[9] The mixture was warmed to room temperature and stirred for 17 h. After the mixture was cooled to −78 °C, water (10 mL) was added to destroy the excess phosphorus oxychloride. The resulting mixture was warmed to room temperature, diluted with methylene chloride (1 L), washed successively with water (300 mL), 10% aqueous hydrochloric acid (2 × 100 mL), water (300 mL), saturated aqueous sodium bicarbonate (200 mL), and water (300 mL), and dried (MgSO$_4$). Concentration of the solution gave 5.2 g of crude **8** as a red-brown solid. Flash chromatography on silica gel with 0–30% methylene chloride in hexane gave pure **8** (2.60 g, 3.68 mmol, 66% overall yield from **6**) as a white solid, mp 354–356 °C, with an ^{1}H NMR spectrum identical with that previously reported.[4]

Improved Preparation of 9 from 8. Propylene oxide (0.70 mL, 10 mmol) was added to a stirred suspension of **8** (707 mg, 1.0 mmol) and benzenediazonium 2-carboxylate hydrochloride (738 mg, 4.0 mmol) in 1,2-dichloroethane (60 mL) at room temperature under argon. The resulting mixture was heated at reflux for 4 h, cooled to room temperature, and diluted with methylene chloride (600 mL). The solution was washed with water (3 × 150 mL), dried (MgSO$_4$), and concentrated to give 1.05 g of crude **9** as a brown-yellow solid. Recrystallization from methylene chloride–hexane gave 705 mg (0.90 mmol, 90%) of pure **9** as a white solid with NMR data identical with those reported.[4]

Noniptycene 13. The same procedures were followed as for the preparation of **8** from **6**. From 706.9 mg (1 mmol) of heptiptycene **8**, 1,4-anthraquinone (625 mg, 3 mmol), and aluminum trichloride (800 mg, 6 mmol) there was obtained 1.21 g of a crude cycloadduct, a portion of which (420 mg) was purified by chromatography to give the diketone as a pale yellow solid: mp

(8) The m/e 208 fragment lost here and in the analogous cycloadduct involved in the synthesis of **13** is presumably 1,4-anthraquinone.

(9) This dehydration procedure was adapted from Reuvers, J. T. A.; de Groot, A. *J. Org. Chem.* 1984, 49, 1110–1113.

231–233 °C; IR (CHCl₃) 1680 cm⁻¹; ¹H NMR (CDCl₃) δ 3.22 (s, 2 H), 4.86 (s, 2 H), 5.17 (s, 4 H), 5.27 (s, 2 H), 6.62 (dd, *J* = 5.3, 3.2 Hz, 2 H), 6.76 (dd *J* = 5.3, 3.2 Hz, 2 H), 6.81 (dd, *J* = 5.3, 3.2 Hz, 2 H), 6.83 (dd, *J* = 5.3, 3.2 Hz, 2 H), 6.88 (dd, *J* = 5.3, 3.2 Hz, 2 H), 6.94 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.16 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.19 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.23 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.27 (s, 2 H)8 7.28 (s, 2 H), 7.28 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.37 (s, 2 H), 7.55 (dd, *J* = 6.3, 3.2 Hz, 2 H), 7.88 (dd, *J* = 6.3, 3.2 Hz, 2 H), 8.34 (s, 2 H); *m/e* (relative intensity) 208 (anthraquinone, 100), 180 (12.3), 152 (44.2), 126 (25.2), 44 (10.9); FAB mass spectrum, *m/e* (relative intensity) 915 (M + 1, 6.9), 914 (M⁺, 8.0), 707 (21.8), 528 (3.7), 307 (23.5), 154 (100); high-resolution mass spectrum calcd for C₇₀H₄₂O₂ 914.3185, obsd 914.3140.

The crude diketone (778 mg) was reduced with 4 equiv of lithium aluminum hydride as in the preparation of **12**. Crude diol (889 mg) was reserved for the next step. A small amount of the product was chromatographed to give pure diol: mp 237–239 °C; ¹H NMR (CDCl₃) δ 2.04 (br s, 2 H, exchanges with D₂O), 2.19 (br s, 2 H), 4.33 (s, 2 H), 4.99 (s, 2 H), 5.09 (s, 2 H), 5.17 (s, 2 H), 5.21 (s, 2 H), 6.72–6.97 (m, 10 H), 7.09–7.24 (m, 16 H), 7.29 (s, 2 H), 7.36–7.44 (m, 4 H), 7.64–7.75 (m, 2 H); FAB mass spectrum, *m/e* (relative intensity) 919 (M + 1, 38.0), 918 (M⁺, 40.0), 883 (5.6), 707 (98.9), 677 (18.5), 621 (63.0), 531 (72.5), 154 (100); high-resolution mass spectrum calcd for C₇₀H₄₆O₂ 918.3498, obsd 918.3470.

The crude diol (889 mg) was dehydrated following the same procedure as for the dehydration of **12**. Flash chromatography of the crude hydrocarbon (800 mg) on silica gel with 0–50% methylene chloride–hexane as eluent gave the desired pure noniptycene **13**¹⁰ (431 mg, 0.488 mmol, 75% overall from **8**): mp 240 °C dec; ¹H NMR (CDCl₃) δ 5.07 (br s, 2 H), 5.12 (s, 2 H), 5.17 (s, 2 H), 5.31 (s, 2 H), 6.67 (dd, *J* = 5.4, 3.2 Hz, 2 H), 6.75–6.84 (m, 8 H), 6.88 dd, *J* = 5.4, 3.2 Hz, 2 H), 7.09 (dd, *J* = 5.3, 3.2 Hz,

2 H), 7.20 (s, 2 H), 7.25 (s, 2 H), 7.31 (s, 2 H), 7.33 (dd, *J* = 6.4, 3.2 Hz, 2 H), 7.08–7.35 (m, 6 H), 7.72 (s, 2 H) 7.85 (dd, *J* = 6.4, 3.2 Hz, 2 H), 8.11 (s, 2 H); UV (cyclohexane) λ_max (ε) 374 (6300), 355 (9400), 338 (8200), 296 (60 400), 265 (139 900), 226 (228 800); FAB mass spectrum, *m/e* (relative intensity) 883 (M + 1, 70.6), 882 (M⁺, 66.8), 806 (6.75), 706 (10.1), 626 (13.1), 587 (30.0), 526 (17.8), 154 (100); high-resolution mass spectrum calcd for C₇₀H₄₂ 882.3286, obsd 882.3272.

Undecaiptycene 14. The pure noniptycene **13** (210 mg, 0.238 mmol) was treated with benzenediazonium 2-carboxylate hydrochloride as in the improved procedure for converting **8** to **9** (vide supra) to give 336 mg of crude **14**. Flash chromatography on silica gel with 0–40% methylene chloride in hexane as the eluent gave 217 mg (0.226 mmol, 95%) of pure **14**¹¹ as a white solid: mp >460 °C; ¹H NMR (CDCl₃) δ 5.02 (s, 2 H), 5.06 (s, 2 H), 5.12 (s, 2 H), 5.15 (s, 2 H), 5.17 (s, 2 H), 6.72 (dd, *J* = 5.3, 3.1 Hz, 2 H), 6.75–6.80 (m, 10 H), 6.84 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.08 (dd, *J* = 5.3, 3.2 Hz, 2 H), 7.11–7.24 (m, 12 H), 7.14 (s, 2 H), 7.19 (s, 2 H), 7.21 (s, 2 H), 7.24 (s, 2 H); FAB mass spectrum, *m/e* (relative intensity) 960 (M + 1, 87.3), 959 (M⁺, 87.0), 307 (18.6), 154 (100), 137 (93.7); UV (cyclohexane) λ_max (ε) 298 (34 040), 227 (218 000), 211 (145 000); high-resolution mass spectrum calcd for C₇₆H₄₆ 958.3598, obsd 958.3588.¹²

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(11) 5,18:9,14[1′,2′:1″,2″]-dibenzeno-7,16[2‴,3‴]-(5‴,14‴:7‴,12‴-[1‴″,2‴″:1″″,2″″]-dibenzeno-5‴,7‴,12‴,14‴-tetrahydropentaceno)-5,7,9,14,16,18-hexahydroheptacene.

(12) Most complex iptycenes tenaciously cling to recrystallization or chromatographic solvents, making it exceedingly difficult to obtain satisfactory elemental analyses (see, for example, footnote 15 in ref 4). Therefore we have used throughout this paper the somewhat less desirable purity criterion of high-resolution mass spectra.

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(10) 5,18:9,14[1′,2′:1″,2″]-dibenzeno-7,16[2‴,3‴]-(5‴,14‴[1″″,2‴″]-benzeno-5‴,14‴-dihydropentaceno)-5,7,9,14,16,18-hexahydroheptacene.

A Method for the Synthesis of Angular Iptycenes

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Dienes **9** and **13** are useful starting points for the synthesis of angular iptycenes. Cycloaddition of *trans*-1,2-dichloroethylene to **9** gives chloropentiptycene **12** (two steps, 68%); similarly, **13** gives previously unknown angular pentiptycene **3** (two steps, 79%). Cycloaddition of cyclohexene to **13** gave pentiptycene **16** (two steps), which could also be prepared in one step from the lithio derivative of **9** and 1,2-dibromobenzene. Cycloaddition of 1,4-epoxynaphthalene to **13** gave pentiptycene **20** (three steps, 64%), and dichloropentiptycene **22** was similarly prepared. The structure of **20** was proven by addition of benzyne to give the known heptiptycene **8**. Thus cycloaddition of various dienophiles to dienes **9** and/or **13** provides a general route to angular iptycenes.

Triptycene **1** is the first member of a large class of compounds called iptycenes,¹,² derived by the fusion of 9,10-anthradiyl-type³ moieties to the arene rings of **1** or themselves. Thus pentiptycenes **2** and **3** (five separated arene planes) can be regarded as derived by fusing a 9,10-anthradiyl moiety, to a b or an a bond of **1**. It is convenient to use the terms linear and angular to describe

the fusions in **2** and **3**, respectively, analogous to the descriptors used for acenes such as anthracene (linear) and phenanthrene (angular).

Most of the iptycenes synthesized to date are of the linear type.¹,²,⁴ Exceptions are the angular pentiptycene **5** synthesized in low yield from the 1,3-benzadiyne

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(1) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* 1981, *46*, 4427–4432.

(2) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* 1986, *42*, 1641–1654.

(3) The fused groups may be 9,10-anthradiyl itself, or analogues such as 5,12-naphthacenyl, etc.

(4) Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* 1983, *48*, 4357–4360. Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* 1986, *108*, 6675–6679. Luo, J.; Hart, H. *J. Org. Chem.* 1987, *52*, 3631–3636.

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