

Linear Acene Derivatives. New Routes to Pentacene and Naphthacene and the First Synthesis of a Triptycene with Two Anthracene Moieties

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The cycloaddition of *o*-xylylene to arene 1,4-endoxides was used to construct linear arene derivatives. For example, heating benzocyclobutene **4** with anthracene 1,4-endoxide (**10**) followed by dehydration and dehydrogenation gave pentacene in three steps and 64% overall yield. An analogous sequence but with naphthalene 1,4-endoxides gave naphthacenes. Dehydration of the di adducts from **4** and anthracene 1,4:5,8-diendoxides (**5**) gave a mixture of 5,9,14,18- and 5,8,15,18-tetrahydroheptacenes **3** and **9**. The previously unknown triptycene **2** was synthesized from 5,14-dihydropentacene (**12**), an intermediate in the new pentacene synthesis, in three steps and 29% overall yield.

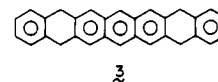
We recently described four short, efficient syntheses of triptycene **1**,^{1,2} a useful synthon for higher iptycenes³ because of the potential for cycloadditions to the anthracene moiety. We describe here the first synthesis of **2** (7,16-[1',2']-benzeno-7,16-dihydroheptacene), the higher analogue of **1** containing two potentially useful anthracene moieties.⁴ During the course of this work, new routes to pentacene and naphthacene and to a variety of linear acene derivatives were also developed.



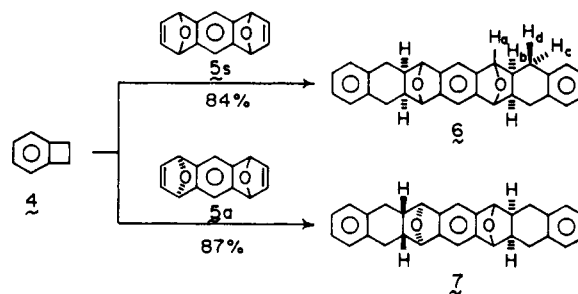
Results and Discussion

First Attempt at 2. Triptycene **2** can be viewed as the cycloadduct of benzyne to the central ring of heptacene. This direct route was not considered seriously, however, because of the high reactivity and difficulty in obtaining pure heptacene^{5,6} and because cycloadditions to internal rings other than the central ring of heptacene are also

likely. Consequently, the tetrahydroheptacene **3** was selected as our initial synthetic target. It should undergo cycloadditions with the desired regiochemistry, and the required anthracene moieties in the product could then be generated by dehydrogenation.



The seven linearly-fused rings needed for **3** were assembled in one step through the cycloaddition of *o*-xylylene⁷ (2 equiv) to the *syn*- or *anti*-anthracene diendoxide **5**.⁸ Thus, when benzocyclobutene **4**⁹ and **5s** were heated



in a sealed tube (toluene as solvent) at 190 °C for 24 h, a single di adduct **6**, mp 238–240 °C, was obtained in 84% yield. The structure of **6** was clear from its spectra. The

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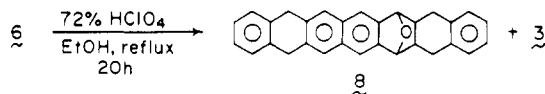
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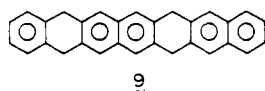
bridgehead protons H_a appeared as a singlet at δ 5.06, and the remaining aliphatic protons gave doublets of doublets at δ 1.97, 2.70, and 2.98 ($J_{bc} = 6$ Hz, $J_{cd} = 14$ Hz, and $J_{bd} = 11$ Hz). The negligible coupling between H_a and H_b is consistent with exo stereochemistry.¹⁰

In a similar manner, 4 and 5a gave a single di adduct 7, mp 272 °C, also with exo stereochemistry.

Unfortunately, neither 6 nor 7 could be cleanly dehydrated to the desired 3. For example, heating 6 with 72% perchloric acid in refluxing ethanol for 20 h gave mainly the monodehydration product 8, together with some of the desired 3 (ratio 4:1). Longer reflux (60 h) or other deh-



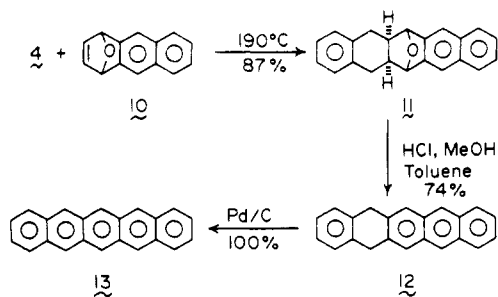
hydrating agents (HCl in acetic anhydride or $HClO_4$ in methanol/toluene) completed the dehydration but gave inseparable mixtures of 3 and its thermodynamically more stable¹¹ isomer 9. Attempts to separate 3 from 9 were



complicated by the conversion of 3 to 9 during recrystallization. Since similar difficulties were encountered in dehydration of the anti-adduct 7, this approach to 2 was dropped.

New Routes to Pentacene and Naphthacene. Despite the lack of success in developing a clean synthesis of the heptacene equivalent 3, the rapid assembly of linearly fused, six-membered rings from benzocyclobutene and arene 1,4-endoxides suggested that this reaction should be explored further. In extending this methodology to a new pentacene synthesis, an intermediate was prepared that led to a short synthesis of the desired triptycene 2.

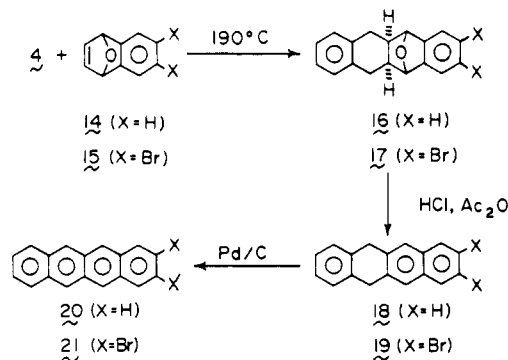
Pentacene was prepared in three steps and 64% overall yield as follows. Benzocyclobutene was heated with anthracene 1,4-endoxide 10¹² in toluene (sealed tube, 190 °C, 24 h) to give 11 in 87% yield. Dehydration of 11 with acid



gave 5,14-dihydropentacene (12) in 74% yield. This dihydropentacene was previously obtained¹³ by allowing the 6,13-dihydro isomer to stand for about 3 months. Its ¹H NMR spectrum showed a singlet at δ 4.13 for the methylene protons, two doublets of doublets at δ 7.23 and 7.36 for the isolated benzenoid ring, and singlets at δ 7.92 and 8.36 plus doublets of doublets at δ 7.42 and 7.98 for the anthracene moiety. Dehydrogenation of 12 over Pd/C gave

pentacene in quantitative yield. This short, efficient route to pentacene is at least comparable to the literature methods,¹³⁻¹⁸ and it is the method of choice for 5,14-dihydropentacene (12).

Similar methodology afforded naphthacene (20) and 2,3-dibromonaphthacene (21) as illustrated, starting from 4 and endoxides 14¹⁹ or 15,¹ respectively. The overall yield of 20 from 4 and 14 was 77% for the three steps, generally superior but at least comparable to the better literature methods.^{12b,18,20-23}



Synthesis of 2. 5,14-Dihydropentacene (12), the readily available intermediate in our pentacene synthesis, provided an excellent starting point for a three-step synthesis of the desired triptycene 2. The strategy was to use the anthracene group in 12 in a cycloaddition with 10, thus creating the two potential anthracene moieties needed for 2.

A solution containing equivalent amounts of 10 and 12 in xylene was heated at reflux for 5 days to give a 3:2 mixture of adducts 22 and 23 in 63% yield. The compounds were not cleanly separable, but their structures were clear from the ¹H NMR spectrum of each. In particular the two sets of bridgehead protons and the methine ring-juncture protons between them all appeared as singlets (at δ 2.35, 4.46, and 5.06 in 22 and at δ 2.32, 4.45, and 5.07 in 23). The lack of coupling is only consistent with exo stereochemistry in each isomer. The benzylic protons in the major isomer (22) appeared as a four-proton singlet at δ 3.82, whereas in the minor isomer (23), these protons appeared as an AB quartet at δ 3.97 and 3.86, $J = 16.1$ Hz, presumably as a consequence of one pair being close to the oxygen bridge.

Dehydration of the mixture using HCl in acetic anhydride at reflux (12 h) gave a single product 24, mp >205 °C dec, in 48% yield. The methine and bridgehead protons appeared as four- and two-proton singlets at δ 3.84

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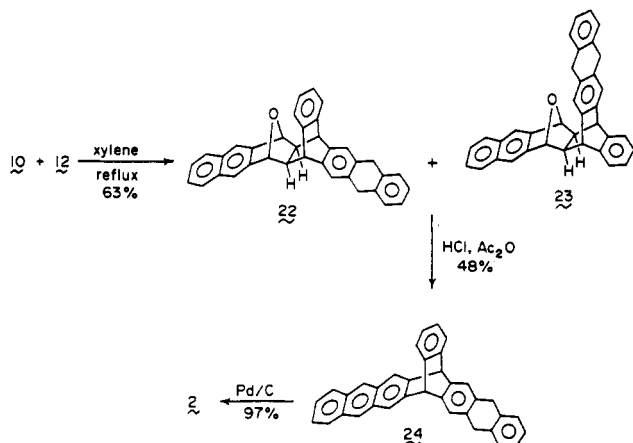
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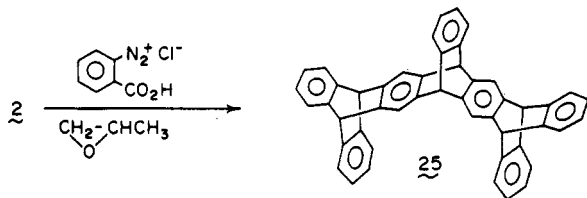
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and 5.52, respectively. The isolated aromatic protons gave rise to three two-proton singlets at δ 7.36, 7.87, and 8.22, with the remaining aryl protons as doublets of doublets as expected.

Dehydrogenation of **24** over Pd/C gave **2**, mp >360 °C dec, in essentially quantitative yield. The ^1H NMR spectrum of **2** showed a singlet at δ 5.68 for the bridgehead protons and two four-proton singlets at δ 7.98 and 8.28 for the uncoupled aromatic protons in the anthracene moieties. The remaining aromatic protons appeared as doublets of doublets at δ 7.11 and 7.52 for the lone benzenoid ring (2 H each) and at δ 7.41 and 7.93 for the "outer" ring of the anthracene moieties (4 H each). The ^{13}C NMR spectrum of **2** showed one aliphatic carbon (δ 53.30) and 10 aromatic carbons as required by the C_{2v} symmetry.

The structure of **2** was confirmed by reaction with 2 equiv of benzyne, which gave the known heptyptycene **25**⁸ in 50% yield.



In summary, we have demonstrated here the utility of the cycloadditions of *o*-xylylene (benzocyclobutene) with arene 1,4-endoxides in constructing linear acene derivatives and have illustrated that methodology by short, efficient syntheses of pentacene and naphthacene and their 5,14- and 5,12-dihydro derivatives, respectively. We then used the dihydropentacene for a three-step 29% overall yield synthesis of the novel triptycene **2**.

Experimental Section²⁴

Syn-Diendoxide 6. A mixture of benzocyclobutene,⁹ (5.20 g, 50 mmol), *syn*-1,4,5,8-tetrahydroanthracene 1,4:5,8-diendoxide (**5a**)⁸ (5.25 g, 25 mmol), and toluene (60 mL) was heated in a sealed tube at 185–195 °C for 24 h. The precipitate that deposited on cooling was collected. The filtrate was concentrated (Rotavap) and triturated with hexane. The resulting solid was washed with hexane, dried, and combined with the initial precipitate to give 8.78 g (84%) of **6**, mp 238–240 °C; ^1H NMR δ 1.97 (dd, 4 H), 2.70 (dd, 4 H), 2.98 (dd, 4 H), 5.06 (s, 2 H), 7.09 (br s, 8 H), 7.18 (s, 2 H); ^{13}C NMR δ 33.11, 42.82, 84.57, 110.46, 126.15, 126.83, 138.96, 144.66; mass spectrum, m/e (relative intensity) 288 (10), 270 (1), 158 (100), 130 (7), 129 (11), 128 (9), 115 (8), 102 (4), 40 (51). Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_2$: C, 86.09; H, 6.26. Found: C, 85.96; H, 6.30.

Anti-Diendoxide 7. In a procedure and workup as described for **6**, from 4.16 g (40 mmol) of **4**, 4.20 g (20 mmol) of **5a**⁸ in toluene

(50 mL) there was obtained 7.27 g (87%) of **7**, mp 272 °C dec; ^1H NMR δ 1.94 (dd, 4 H), 2.69 (dd, 4 H), 3.01 (dd, 4 H), 5.08 (s, 4 H), 7.12 (br s, 8 H), 7.15 (s, 2 H); ^{13}C NMR: δ 33.10, 42.77, 84.53, 110.70, 126.20, 126.87, 138.87, 144.66; mass spectrum, m/e (relative intensity) 288 (15), 270 (1), 158 (100), 130 (7), 129 (11), 128 (9), 115 (7), 102 (6).

Dehydration of 6. To a suspension of **6** (1.254 g, 3 mmol) in ethanol (200 mL) was added slowly 15 mL of 72% perchloric acid. The resulting solution was heated at reflux for 20 h, cooled, and poured into ice-water, and the resulting precipitate was washed with water and dried. Recrystallization from benzene gave 690 mg of a mixture of **8** and **3** (4:1 by NMR). For **8**: ^1H NMR δ 2.11 (dd, 2 H), 2.75 (dd, 2 H), 3.04 (dd, 2 H), 4.06 (s, 4 H), 5.24 (s, 2 H), 7.13 (br s, 4 H), 7.20 (dd, 2 H), 7.32 (dd, 2 H), 7.57 (s, 2 H), 7.71 (s, 2 H). For **3**: δ 4.12 (s, 8 H), 7.20 (dd, 4 H), 7.33 (dd, 4 H), 7.89 (s, 4 H), 8.29 (s, 2 H).

From a similar reaction using 1.672 g (4 mmol) of **6**, 300 mL of ethanol, and 20 mL of 72% perchloric acid heated at reflux for 60 h, there was obtained, after recrystallization from 1,2-dichloroethane, 932 mg (61%) of a mixture of **3** and **9** (1:2 by NMR). For **9**: ^1H NMR δ 4.06 (s, 4 H), 4.21 (s, 4 H), 7.15–7.42 (m, 6 H), 7.69 (s, 2 H), 7.71 (s, 2 H), 7.77 (s, 2 H), 7.78 (dd, 2 H); mass spectrum m/e (relative intensity) [for the mixture] 382 (M^+ , 1), 280 (6), 165 (4), 149 (5), 139 (6), 108 (8), 99 (100), 55 (46).

5,5a,6,13,13a,14-Hexahydropentacene 6,13-Endoxide (11). A mixture of benzocyclobutene **4** (2.08 g, 20 mmol), endoxide **10**¹² (3.88 g, 20 mmol), and toluene (70 mL) was heated in a sealed tube at 190 °C for 24 h. Workup as for **6** gave **11** (5.18 g, 87%): mp 235–237 °C, from toluene; ^1H NMR δ 2.12 (dd, 2 H), 2.78 (dd, 2 H), 3.04 (dd, 2 H), 5.25 (s, 2 H), 7.13 (br s, 4 H), 7.44 (dd, 2 H), 7.62 (s, 2 H), 7.79 (dd, 2 H); ^{13}C NMR δ 32.89, 43.50, 84.55, 117.13, 125.69, 126.25, 126.90, 128.12, 132.82, 138.69, 143.67; mass spectrum, m/e (relative intensity) 298 (M^+ , 1), 168 (100), 140 (5), 129 (3), 91 (7).

5,14-Dihydropentacene (12). To a solution of **11** (2.98 g, 10 mmol) in 40 mL of methanol and 160 mL of toluene was slowly added 15 mL of concentrated hydrochloric acid. The solution was heated at reflux for 14 h. The solid which formed on cooling was washed with methanol, dried, and recrystallized from 1,2-dichloroethane to give 2.07 g (74%) of **12** as yellowish crystals: mp 305–307 °C (lit.¹³ mp 300–310 °C); ^1H NMR δ 4.13 (s, 4 H), 7.20–7.44 (m, 6 H), 7.92 (s, 2 H), 7.98 (dd, 2 H), 8.36 (s, 2 H); mass spectrum, m/e (relative intensity) 280 (M^+ , 100), 279 (73), 278 (49), 265 (6), 139 (9), 133 (6), 91 (33), 81 (14).

Pentacene (13). A solution of **12** (560 mg, 2 mmol) in xylene (20 mL) containing 80 mg of 10% Pd/C was heated at reflux under argon for 3 days. The hot solution was filtered to remove the catalyst, and the red-purple filtrate was concentrated to give 512 mg (92%) of pentacene as blue-violet crystals. Infrared, ultraviolet, and mass spectra were identical with those of a commercial sample.

5,5a,6,11,11a,12-Hexahydronaphthacene 5,12-Endoxide (16). From 1.04 g (10 mmol) of **4** and 1.44 g (10 mmol) of **14**¹⁹ in 45 mL of toluene, following a procedure and workup as for **11**, there was obtained 2.13 g (86%) of **16** as colorless crystals: mp 161–163 °C; ^1H NMR δ 2.02 (dd, 2 H), 2.74 (dd, 2 H), 3.04 (dd, 2 H), 5.13 (s, 2 H), 7.12 (br s, 4 H), 7.14 (dd, 2 H), 7.24 (dd, 2 H); ^{13}C NMR δ 33.07, 42.84, 84.57, 118.90, 126.17, 126.55, 126.84, 138.93, 145.62; mass spectrum, m/e (relative intensity) 248 (M^+ , 1), 128 (6), 118 (100), 90 (5).

5,12-Dihydronaphthacene (18). To a solution of **16** (1.86 g, 7.5 mmol) in 40 mL of acetic anhydride was added slowly (through a condenser) 8 mL of concentrated hydrochloric acid. The solution was heated at reflux for 8 h, cooled, and poured into ice-water. The resulting solid was washed with water and methanol, dried, and recrystallized from toluene to give 1.54 g (89%) of **18**: mp 207–208 °C (lit.²⁵ mp 209–210 °C); ^1H NMR δ 4.09 (s, 4 H), 7.21 (dd, 2 H), 7.34 (dd, 2 H), 7.41 (dd, 2 H), 7.76 (s, 2 H), 7.78 (dd, 2 H); mass spectrum, m/e (relative intensity) 230 (M^+ , 100), 229 (97), 228 (74), 226 (18), 215 (10), 202 (5), 114 (54), 107 (16), 101 (22), 88 (7).

Naphthacene (20). A solution of **18** (1.15 g, 5 mmol) in 30 mL of xylene containing 150 mg of 10% Pd/C was heated at reflux

(24) For general procedures, see ref 2.

(25) Friedman, S.; Metlin, S.; Svedi, A.; Wender, I. *J. Org. Chem.* **1959**, *24*, 1287.

under argon for 2 days. Filtration of the catalyst and solvent removal (Rotavap) gave 1.08 g (95%) of naphthacene (**20**) as orange crystals: mp 339–341 °C (lit.²³ mp 341 °C); ¹H NMR δ 7.40 (dd, 4 H), 8.00 (dd, 4 H), 8.67 (s, 4 H).

2,3-Dibromo-5,5a,6,11,11a,12-hexahydronaphthacene 5,12-Endoxide (17). From 1.04 g (10 mmol) of **4** and 3.02 g (10 mmol) of **15**¹ in 60 mL of toluene, in a reaction and workup as for **16**, there was obtained 3.61 g (89%) of **17** as colorless crystals: mp 179–181 °C, after recrystallization from methylene chloride–hexane; ¹H NMR δ 1.99 (dd, 2 H), 2.70 (dd, 2 H), 2.98 (dd, 2 H), 5.07 (s, 2 H), 7.13 (br s, 4 H), 7.49 (s, 2 H); ¹³C NMR δ 32.75, 42.47, 83.96, 122.32, 124.38, 126.35, 126.90, 138.35, 146.65; mass spectrum, *m/e* (relative intensity) 278 (62), 276 (100), 274 (55), 248 (1), 195 (5), 169 (10), 167 (8), 128 (18), 115 (13).

8,9-Dibromo-5,12-dihydronaphthacene (19). From 2.84 g (7 mmol) of **17**, 70 mL of acetic anhydride, and 15 mL of concentrated hydrochloric acid, in a procedure and workup as for **18**, there was obtained 2.44 g (90%) of **19** as light yellow crystals, mp 224–226 °C, after recrystallization from toluene: ¹H NMR δ 4.06 (s, 4 H), 7.22 (dd, 2 H), 7.34 (dd, 2 H), 7.63 (s, 2 H), 8.07 (s, 2 H); ¹³C NMR δ 36.78, 124.11, 126.49, 127.27, 131.54, 132.07, 136.44, 137.46, 137.77; mass spectrum, *m/e* (relative intensity) 390 (M⁺ + 4, 65), 388 (M⁺ + 2, 100), 386 (M⁺, 55), 309 (39), 307 (42), 228 (87), 226 (74), 114 (38), 113 (34).

2,3-Dibromonaphthacene (21). From 1.16 g (3 mmol) of **19** in 50 mL of xylene containing 150 mg of 10% Pd/C there was obtained, in a procedure and workup as for **20**, 1.10 g (96%) of **21** as orange crystals, mp 336–338 °C. The compound was too insoluble to obtain an NMR spectrum. Mass spectrum, *m/e* (relative intensity) 388 (M⁺ + 4, 4), 386 (M⁺ + 2, 6), 384 (M⁺, 4), 308 (4), 306 (4), 228 (9), 226 (13), 113 (10), 33 (100). Anal. Calcd for C₁₈H₁₀Br₂: C, 55.60; H, 2.61. Found: C, 55.26; H, 2.78.

Cycloadducts 22 and 23. A solution of **12** (1.40 g, 5 mmol) and **10** (0.97 g, 5 mmol) in 160 mL of xylene was heated at reflux for 5 days. The solid that deposited in the cooled solution was unreacted **12** (0.21 g). The filtrate was concentrated (Rotavap) and the residue chromatographed on silica gel with methylene chloride–hexane (1:3) as eluent to give 1.49 g (63%) of a mixture of **22** and **23**, mp 294–296 °C. For **22**: ¹H NMR δ 2.35 (s, 2 H), 3.82 (s, 4 H), 4.46 (s, 2 H), 5.06 (s, 2 H), 7.13 (dd, 2 H), 7.18 (s, 2 H), 7.20–7.31 (m, 6 H), 7.39 (dd, 2 H), 7.49 (s, 2 H), 7.72 (dd, 2 H). For **23**: ¹H NMR δ 2.32 (s, 2 H), 3.86 and 3.97 (AB q, 4 H, *J* = 16.1 Hz), 4.45 (s, 2 H), 5.07 (s, 2 H), 6.99 (dd, 2 H), 7.15–7.30 (m, 8 H), 7.39 (dd, 2 H), 7.50 (s, 2 H), 7.72 (dd, 2 H). For the mixture: mass spectrum, *m/e* (relative intensity) 474 (M⁺, 9), 456 (4), 388 (6), 374 (4), 305 (9), 293 (46), 280 (16), 278 (19), 207 (21), 194 (26), 181 (67), 168 (56), 139 (13), 44 (100).

5,7,16,18-Tetrahydro-5,16[1',2']-benzenoheptacene (24). To a mixture of **22** and **23** (1.422 g, 3 mmol) in 60 mL of acetic anhydride there was added slowly (through the condenser) 12 mL of concentrated hydrochloric acid. After 12 h at reflux, the cooled

mixture was poured into ice–water and extracted with methylene chloride. The organic extract was washed with 10% sodium carbonate and water, dried, and reduced in volume (Rotavap). Chromatography of the residue over silica gel with methylene chloride–hexane (1:4) as the eluent gave 656 mg (48%) of **24**, mp >205 °C dec; ¹H NMR δ 3.84 (s, 4 H), 5.52 (s, 2 H), 7.03 (dd, 2 H), 7.11 (dd, 2 H), 7.21 (dd, 2 H), 7.36 (s, 2 H), 7.38 (dd, 2 H), 7.40 (dd, 2 H), 7.87 (s, 2 H), 7.93 (dd, 2 H), 8.22 (s, 2 H); mass spectrum, *m/e* (relative intensity) 456 (M⁺, 53), 455 (59), 454 (80), 453 (100), 452 (45), 374 (2), 227 (35), 226 (52), 225 (36), 210 (28), 194 (2), 151 (2), 121 (4).

7,16[1',2']-Benzeno-7,16-dihydroheptacene (2). A solution of **24** (547 mg, 1.2 mmol) in 20 mL of mesitylene containing 80 mg of 10% Pd/C was heated at reflux for 60 h. The hot solution was filtered, and the filtrate was concentrated to give 528 mg (97%) of **2** as pale yellow crystals, mp >360 °C dec; ¹H NMR δ 5.68 (s, 2 H), 7.11 (dd, 2 H), 7.41 (dd, 4 H), 7.52 (dd, 2 H), 7.93 (dd, 4 H), 7.98 (s, 4 H), 8.28 (s, 4 H); ¹³C NMR δ 53.30, 121.66, 123.95, 125.02, 125.72, 126.24, 127.99, 130.69, 131.71, 140.35, 143.35; mass spectrum, *m/e* (relative intensity) 454 (M⁺, 59), 453 (35), 452 (24), 290 (4), 274 (13), 227 (100), 226 (97), 213 (34), 197 (11), 165 (6), 149 (6), 105 (5); UV (cyclohexane) λ_{max} 378 nm (ε 14 298), 358 (14 480), 342 (14 361), 325 (14 217), 283 (31 700), 254 (20 762), 212 (15 070). Anal. Calcd for C₃₆H₂₂: C, 95.12; H, 4.88. Found: C, 94.87; H, 5.04.

Heptytycene 25.⁸ A mixture of **2** (227 mg, 0.5 mmol), benzenediazonium-2-carboxylate hydrochloride (222 mg, 1.2 mmol) and propylene oxide (2 mL) in 20 mL of 1,2-dichloroethane was heated at reflux for 5 h. Diethylcarbitol (4 mL) was added, and the solvent was distilled until the head temperature reached 150 °C. Maleic anhydride (55 mg) was added to remove unreacted **2**, and the mixture was heated at reflux for 15 min. To the cooled mixture was added 0.2 g of KOH in 3 mL of methanol–water (2:1). The mixture was chilled in ice and the resulting solid was filtered, washed with methanol–water (4:1), and dried. Recrystallization from chloroform gave 152 mg (50%) of **25**, whose ¹H NMR spectrum was identical with that reported.⁸

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Registry No. **2**, 110372-75-3; **3**, 110391-11-2; **5a**, 87207-46-3; **5s**, 87248-22-4; **6**, 110372-76-4; **7**, 110454-01-8; **8**, 110391-12-3; **9**, 40476-38-8; **10**, 22187-13-9; **11**, 110372-77-5; **12**, 20244-36-4; **13**, 135-48-8; **14**, 573-57-9; **15**, 106750-88-3; **16**, 110372-78-6; **17**, 110372-79-7; **18**, 959-02-4; **19**, 110372-80-0; **20**, 92-24-0; **21**, 110372-81-1; **22**, 110372-82-2; **23**, 110454-02-9; **24**, 110372-83-3; **25**, 87207-52-1; benzenediazonium-2-carboxylate hydrochloride, 4661-46-5; benzocyclobutene, 4026-23-7; propylene oxide, 75-56-9.

Highly Stereocontrolled Synthesis of Some Polyfunctionalized Cyclohexenes. A Short Formal Total Synthesis of (±)-Chorismic Acid

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Lewis acid catalysis or high pressure is an effective means for promoting stereocontrolled 2 + 4 cycloaddition between pyrone sulfoxide **1** and vinyl ethers and vinyl thioethers. The bridged, bicyclic lactone cycloadducts are versatile synthons carrying much structural and stereochemical information. The allylic sulfoxide groups in such cycloadducts are used ultimately in [2,3]-sigmatropic rearrangements to generate allylic alcohols, and the phenylthio group in cycloadduct **10** is used, after oxidation, to generate the second double bond in 1,3-cyclohexadiene **17**, which is a key intermediate in a total synthesis of chorismic acid.

We have reported recently that some pyridone¹ and pyrone² sulfones 2 + 4 cycloadd to vinyl ethers under mild

conditions to produce stable, bridged, bicyclic lactams and lactones in very good to excellent yields; cleavage of the

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(1) Posner, G. H.; Switzer, C. *J. Org. Chem.* 1987, 52, 1642.