from the ratios of peak pair integrals at τ 0.29 and 0.35 (17.2-Hz separation) and at τ 1.08 and 1.21 Hz (*o*-aryl, 34.1-Hz separation) was 30% ee.[35] Since the aldehyde sample had $[\alpha]^{20}_D$ −9.24° (*c* 4.5, C_6H_6), the rotation for the enantiomerically pure aldehyde is $[\alpha]^{20}_D$ −30.8 ± 1° (*c* 4.5, C_6H_6). Asymmetric hydroformylation results are summarized in Table II.

Acknowledgment. We thank Mr. D. E. McMackins for the synthesis of certain important starting materials used in this work and Mr. Gerald M. Gasser for GC analyses.

(35) We thank Professor W. H. Urry, University of Chicago, for this determination.

Registry No. (*R,R*)-**1a**, 32305-98-9; (*S,S*)-**1a**, 37002-48-5; (*R,R*)-**1b**, 78870-98-1; (*R,R*)-**1c**, 78890-48-9; (*R,R*)-**1d**, 78870-99-2; (*R,R*)-**1e**, 57221-96-2; (*R,R*)-**1f**, 78871-00-8; (*R,R*)-**2**, 78871-01-9; vinyl propionate, 105-38-4; vinyl benzoate, 769-78-8; (*R*)-2-propionoxypropanal, 78871-02-0; (*S*)-2-propionoxypropanal, 78871-03-1; (*R*)-2-(benzoyloxy)propanal, 78871-04-2; Rh(1,5-COD)[(*S,S*)-*trans*-4,5-bis[5*H*-dibenzophospholyl)methyl]-2,2-dimethyl-1,3-dioxolane] perchlorate, 60594-33-4; bis(1-naphthalenyl)phosphine oxide, 13440-07-8; bis(2-naphthalenyl)phosphine oxide, 78871-05-3; bis(α,α,α-trifluorotolyl)-phosphine oxide, 15929-44-9; bis(1-naphthalenyl)phosphine, 39864-75-0; bis(2-naphthalenyl)phosphine, 78871-06-4; bis(α,α,α-trifluoro-3-tolyl)phosphine, 65796-64-7; tetrakis(1-naphthalenyl)biphosphine, 78890-49-0; (−)-*trans*-4,5-bis[(*p*-tosyloxy)methyl]-2,2-diphenyl-1,3-dioxolane, 78871-07-5; (*S*)-2-acetoxypropanal, 66875-70-5; (*S*)-2-acetoxypropionic acid, 6034-46-4.

Generalization of the Triptycene Concept. Use of Diaryne Equivalents in the Synthesis of Iptycenes

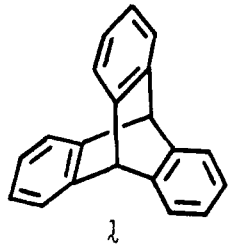
Harold Hart,* Shamouil Shamouilian, and Yoshikazu Takehira

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received June 2, 1981

A simple one-step synthesis of triptycene analogues prepared by reaction of a diaryne equivalent with anthracenes is described. For example, 1,2,4,5-tetrabromobenzene, anthracene, and *n*-butyllithium gave 5,7,12,14-tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene (**2**, R = H; trivially called a *p*-pentiptycene) in good yield. Other tetrabromoarenes were used to similarly prepare **2** (R = CH_3), **2** (R = OCH_3), and the naphtho analogue **13**. Use of 9,10-dimethoxyanthracene gave the tetramethoxy bridgehead-substituted pentiptycene **11**. 4,5-Dibromo-3,6-diiodo-*o*-xylene functioned as an ortho diaryne equivalent to give the *o*-pentiptycene **3** (R = CH_3). The synthesis of heptiptycene **4** (5,6,11,12,17,18-hexahydro-5,18[1′,2′]:6,11[1″,2″]:12,17[1‴,2‴]-tribenzenotrinaphthylene has been improved, and the intermediate cycloalkyne **22** has been trapped with various dienes.

Bartlett[1] was the first to synthesize triptycene (**1**), for

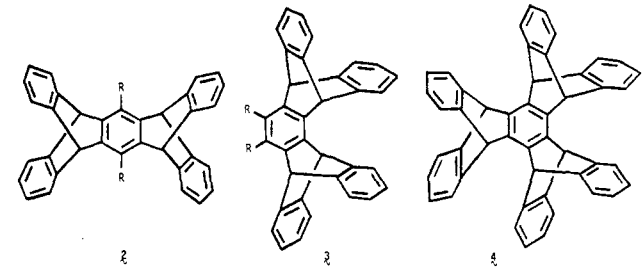


1

the purpose of testing certain concepts in physical-organic chemistry. For example, bridgehead-substituted triptycenes were used to generate the corresponding carbonium ions, radicals, and carbanions, and these were compared with their trityl analogues.[2] Interest in triptycene rose sharply when it was shown by Wittig that it could be synthesized easily in one step from benzyne and anthracene,[3] and at one point the formation of triptycene actually became a test for the efficacy of various benzyne precursors.[4] Eventually, the synthesis of triptycene became a standard undergraduate laboratory "experiment".[5]

Many substituted triptycenes are known, and the benzene rings have also been replaced with a variety of other aromatic rings.[6] The rigid framework is attractive and has been used to study such diverse phenomena as intramolecular charge transfer[7] and restricted rotation about single bonds.[8] In the many structural variations on triptycene, the triptych or triplanar nature of the structures has been preserved.[9]

If triptycene is viewed *not* as a benzyne derivative of anthracene but rather as a benzene which is ortho-disubstituted by attachment to the 9,10-positions of anthracene, then one quickly observes that this concept might be extended by connection to two or three anthracenes as shown in **2**–**4**. We propose that these substances be given the trivial name of "iptycenes".[11,12]

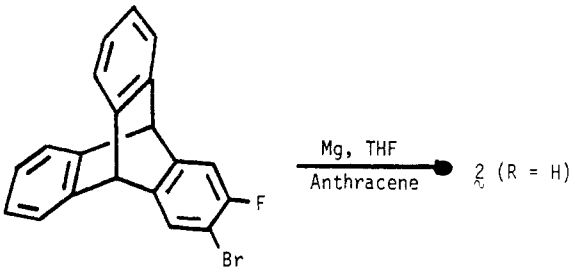


2 **3** **4**

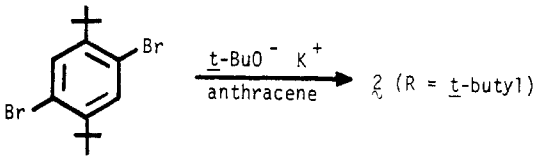
(1) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649.
(2) Bartlett, P. D.; Lewis, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 1005. Bartlett, P. D.; Greene, F. D. *Ibid.* **1954**, *76*, 1088. Wittig, G.; Tochtermann, W. *Justus Liebigs Ann. Chem.* **1962**, *660*, 23. Theilacker, W.; Beyer, K.-H. *Chem. Ber.* **1961**, *94*, 2968. Streitwieser, A., Jr.; Caldwell, R. A.; Granger, M. *J. Am. Chem. Soc.* **1964**, *86*, 3578.
(3) Wittig, G.; Ludwig, R. *Angew. Chem.* **1956**, *68*, 40.
(4) For examples, see: Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press: New York, 1967; Table 3.5, entries 107–113, p 225.
(5) Fieser, L. F. "Organic Experiments"; Heath: Boston, 1964; p 315.
(6) For a review, see: Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 951.
(7) Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* **1977**, *99*, 1996. Iwamura, H.; Makino, K. *J. Chem. Soc., Chem. Commun.* **1978**, 720.
(8) Ōki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87.
(9) This is also true of the nonbenzo analogues such as barrelene[10] and its mono- and dibenzo derivatives.
(10) Zimmermann, H. E.; Paufler, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 1514.

0022-3263/81/1946-4427$01.25/0

Some compounds of this type already appear in the literature. Thus **2** (R = H) was prepared by the addition of 2,3-triptycyne to anthracene.[13] The yield was 10%, and

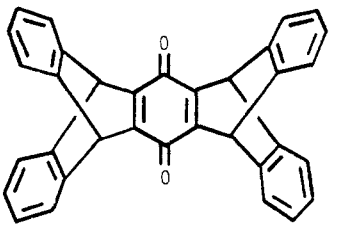


the required fluorobromotriptycene had to be synthesized from anthracene (in four steps, via nitro-, amino-, and 2-bromo-3-aminotriptycenes), so that the overall yield from readily accessible starting materials was quite low. Compound **2** (R = *t*-Bu) was synthesized in low yield (3.7% crude, 2% purified) via diaryne equivalent **5** by treatment



5

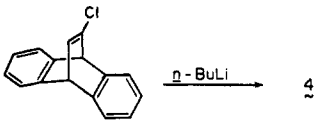
with strong base.[14] Although not fully aromatic, the pentiptycene quinone **6** properly belongs among these compounds. It was originally reported 50 years ago[15] and can be considered as a substance readily available in high yield from inexpensive precursors, benzoquinone and anthracene.



6

As far as we are aware, no *o*-iptycenes such as structure **3** have been previously described.

Compound **4** was obtained in low, unspecified yield as a minor product from the reaction 11-chloro-9,10-dihydro-9,10-ethenoanthracene (**7**) with butyllithium.[16] The



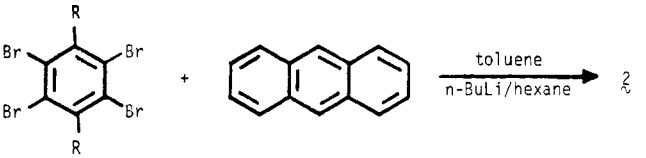
7

structure assignment was based on spectra and the space group of its crystalline 1:1 chlorobenzene complex. Compound **4** has the remarkable melting point, without decomposition, of 580 °C.

We recently found that tetrahalobenzenes can be used as diaryne equivalents, and described their dicycloadditions to such dienes as furans, pyrroles, cyclopentadienes, and fulvenes.[17] Extension of this technology to cycloadditions with anthracenes has led to a short general synthesis of pentiptycenes **2** and **3** which we describe here. We have also reexamined and improved the synthesis of **4** and trapped the cycloalkyne intermediate derived from **7** with several dienes.

Results and Discussion

Pentiptycenes with General Structure 2. A toluene solution of anthracene and 1,2,4,5-tetrabromobenzene, when treated with *n*-butyllithium in hexane at room temperature, gave the parent pentiptycene **2** (R = H) in high yield. The structure is based on spectroscopic properties.



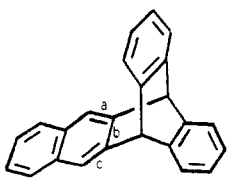
8

The mass spectrum showed a parent and base peak at *m/e* 430 and major fragmentation peaks at *m/e* 252 (M^+ – anthracene) and 178 (anthracene$^+$).[18] The ^{13}C NMR

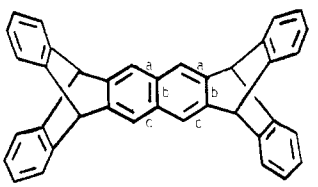
(11) This name was first developed during a lunchtime conversation with Professor Joel F. Liebman, whom we thank.

(12) The name "iptycene" emphasizes the relationship between these compounds and the parent structure triptycene. A prefix indicates the number of separated arene planes; thus **1** is triptycene (three planes), **2** and **3** are pentiptycenes (five planes), and **4** is a heptiptycene (seven planes). We believe that only three descriptors need be added to these names to precisely define the structures. The use of two of these descriptors is illustrated in the following names: for **2** (R = H), [1.1.1^b.1.1]pentiptycene; for **3** (R = H), [1.1.1^a.1.1]pentiptycene; for **4**, [1.1.1^{ac}.1.1.1.1]heptiptycene. The 1's indicate that each ring is benzenoid, and the appropriate number would be replaced by 2 if naphthalenoid or 3 if anthracenoid or phenanthrenoid, etc. The superscripts refer to the bond (a, b, or c) to which the sp^3 carbons are attached. We further suggest that these trivial names be abbreviated for prototype compounds. Thus we will use the names *p*- and *o*-pentiptycene for **2** and **3** (R = H), respectively.

A third descriptor, to indicate points of ring fusion, may also be necessary; it consists again of a bond (a, b, or c) and is placed in parentheses. The following examples illustrate the system:



[2^b.1.1]triptycene



[1.1.2(b)^b.1.1]pentiptycene

These trivial names are, we believe, simpler to use than the systematic CAS names [for **2** (R = H), 5,7,12,14-tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene; for **3** (R = H), 5,8,13,14-tetrahydro-5,14[1′,2′]:8,13-[1″,2″]-dibenzenopentaphene; for **4**, 5,6,11,12,17,18-hexahydro-5,18-[1′,2′]:6,11[1″,2″]:12,17[1‴,2‴]-tribenzenotrinaphthylene.

It should be a fairly simple matter, when the need arises, to add further descriptors (for example, to accommodate tropylium, cyclopentadienide, or heterocyclic rings).

(13) Skvarchenko, V. R.; Shalaev, V. K. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1974**, *216*, 110; *Dokl. Akad. Nauk SSSR (Engl. Transl.)*, **1974**, *216*, 307.

(14) Cadogan, J. I. G.; Harger, M. J. P.; Sharp, J. T. *J. Chem. Soc. B* **1971**, 602.

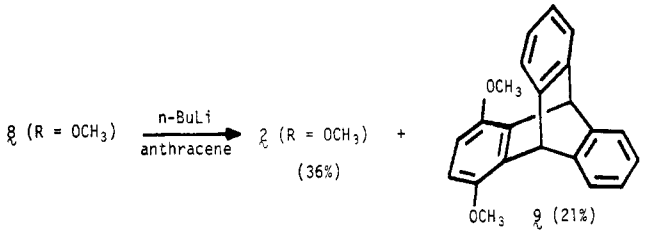
(15) Clar, E. *Chem. Ber.* **1931**, *64*, 1676. See also: Theilacker, W.; Berger-Brose, U.; Beyer, K. H. *Ibid.* **1960**, *93*, 1658; Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. Polyquinones of the [1.1.1^b.1.1^b.1.1]-heptiptycene type have been described: Nishizawa, Y.; Oosumi, T.; Iwamura, H. "Institute for Molecular Science, Annual Review"; Okazaki, Japan, 1980; p 106.

(16) Huebner, C. F.; Puckett, R. T.; Brzechfta, M.; Schwartz, S. L. *Tetrahedron Lett.* **1970**, 359. Huebner, C. F. U.S. Patent 3 641 179, Feb 8, 1972.

(17) Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649.

spectrum of this 34-carbon compound showed only six peaks, consistent with its D_{2h} symmetry. The bridgehead carbons appeared at δ 53.68[19] and the remaining five peaks were in the aromatic region. The proton NMR spectrum of **2** (R = H) consisted of a singlet at δ 5.18 for the bridgehead protons[20] and aromatic multiplets at δ 7.0–7.3 (10 H) and 6.68–7.0 (8 H). These data are quite different from those reported previously[13] with PCl_3 as the solvent.[21] We accordingly ran the spectrum in that solvent and found relatively little change (δ 5.10 for the bridgehead protons, multiplets at δ 6.90–7.13 and 6.53–6.80, and a singlet at δ 7.18). It appears that our spectrum is similar to the literature spectrum but that the latter is shifted downfield about 0.5 ppm from ours. We checked the calibration of our instrument against benzene, and, consequently, believe our data are accurate. Our ultraviolet spectrum agrees well with the reported[13] spectrum. Finally, there is a substantial difference in melting points. We find that **2** (R = H) melts (with decomposition) at 483 °C, whereas the literature value[13] is 413–416 °C.[22]

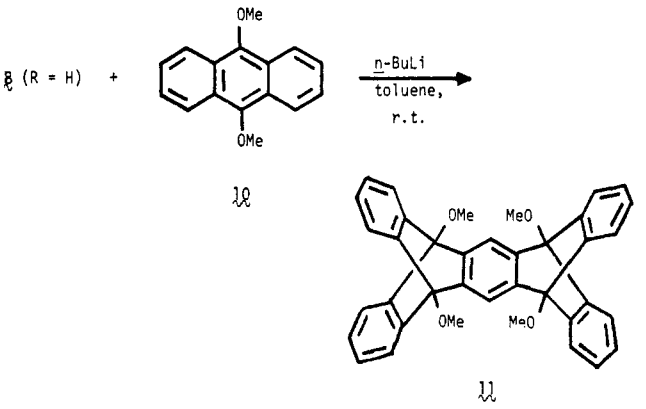
We have synthesized several substituted pentiptycenes. For example, **2** ($R = CH_3$) and **2** ($R = OCH_3$) were prepared in one step from the reaction of tetrabromo-*p*-xylene (**8**, $R = CH_3$) or tetrabromohydroquinone dimethyl ether (**8**, $R = OCH_3$), respectively, with anthracene and *n*-butyllithium. The yields were modest and were not optimized. In the methoxy example, some reduced monoadduct **9** was also formed.

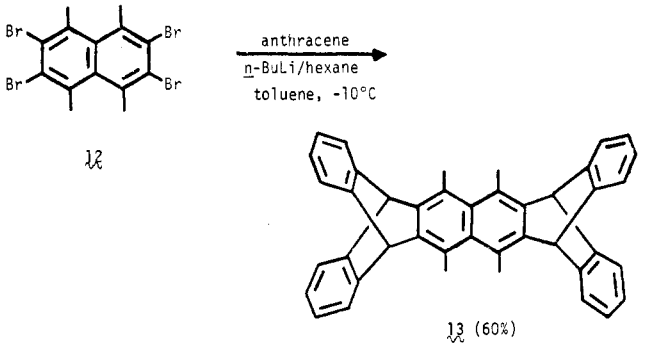


The substituted pentiptycene structures were clear from their spectra. Thus **2** ($R = CH_3$; mp 460–462 °C), with 36 carbons, showed only seven peaks in its ^{13}C spectrum, and the same was true for **2** ($R = OCH_3$; mp 400–402 °C). Cleavage of the dimethyl ether with hydrogen iodide and acetic acid gave **2** (R = OH; mp 427–430 °C dec) which was oxidized with ceric ammonium nitrate to the known yellow quinone **6**. A single-crystal X-ray structure determination of **2** ($R = OCH_3$) also confirmed the structure.[23]

Reaction of tetrabromobenzene **8** (R = H) with 9,10-dimethoxyanthracene **10** and *n*-butyllithium gave the first example of a bridgehead-substituted pentiptycene, **11** (mp 472–475 °C), whose structure was clear from its spectra.

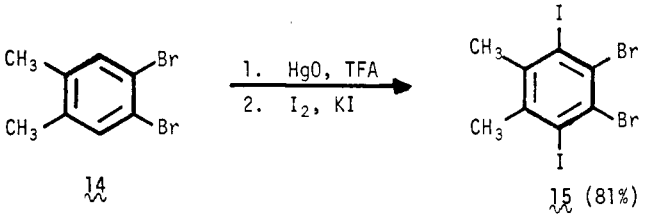
A pentiptycene with a central naphthalene ring was obtained in good yield from tetrabromotetramethylnaphthalene **12**.[24] The structure of **13** (mp 358–360 °C) follows from its method of synthesis and spectra.





Pentiptycenes with General Structure 3. As far as we are aware, no examples of compounds with this general structure were previously known. The technique of ortho bisannelation, however, has been used previously.[25]

The diaryne equivalent selected was 4,5-dibromo-3,6-diiodo-*o*-xylene (**15**), which was synthesized in two steps



and high yield from the corresponding dibromo compound **14**.[26] This ortho diaryne precursor was selected in order that initial lithiation, which is faster at iodine than at bromine, be directed in such a way as to produce the desired product. If the tetrabromo analog of **15** is used, initial lithiation and lithium bromide elimination can occur in an undesired manner.

Treatment of **15** with anthracene and butyllithium gave **3** ($R = CH_3$): 14% yield; mp 382–384 °C. The C_{2v} symmetry of **3** ($R = CH_3$) requires only 12 different "kinds" of carbons, and this is precisely what is seen in the ^{13}C spectrum. There is one methyl signal (δ 15.32), but there are two bridgehead carbon signals (δ 50.18, 50.93) and appropriate aromatic peaks. The mass spectrum of **3** ($R = CH_3$) showed an intense M^+ peak (*m/e* 458, intensity 97), a base peak at *m/e* 280 (M^+ – anthracene), and a fairly

$$\mathbf{15} + \text{anthracene} \xrightarrow[\text{toluene, } -23\ ^\circ\text{C}]{n\text{-BuLi}} \mathbf{3}\ (R = CH_3)$$

(18) In the mass spectrum reported in the original preparation of **2** (R = H),[13] the peaks at *m/e* 430 and 252 were much less intense than the peak at *m/e* 178, which was the base peak.

(19) Compared with δ 54.13 for triptycene, the aromatic protons in triptycene appear at δ 123.58, 125.12, and 145.29 (unpublished results).

(20) $CDCl_3$ solvent; compare with δ 5.37 reported for triptycene: Sadtler spectrum No. 4346. In CS_2, the reported value is δ 5.21: Kidd, K. G.; Kotowycz, G.; Schaefer, T. *Can. J. Chem.* **1967**, *45*, 2155.

(21) Bridgehead at δ 5.62, aromatic multiplets at δ 7.22 and 7.63, and a singlet for the central ring protons at δ 7.76.

(22) We call attention to the fact that the starting material anthracene and the product **2** (R = H) have nearly identical calculated percentage compositions, so that microanalysis is useless as a criterion of purity. We also note that the literature mass spectrum[13] has a considerably more intense anthracene peak, *m/e* 178, than we observe for **2** (R = H). The remote possibility that the compound described in ref 13 is **3** (R = H) requires checking.

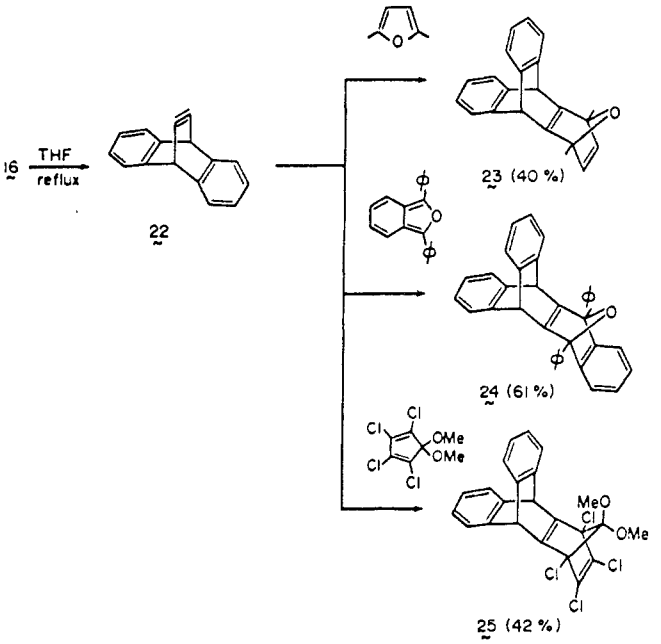
(23) Details will be published elsewhere with D. L. Ward.

(24) Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7.

(25) For examples, see: Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, 3831.

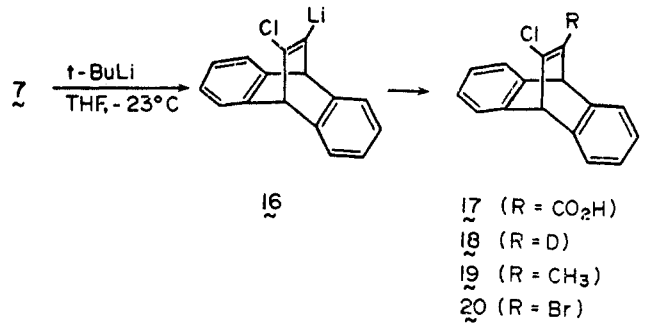
(26) Jacobsen, O. *Chem. Ber.* **1884**, *17*, 2372.

Scheme I

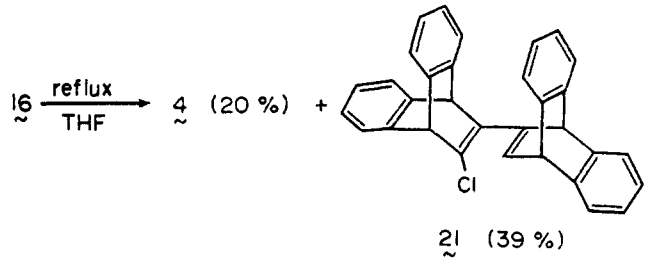


intense peak at m/e 178 (anthracene, intensity 52).

Heptiptycene 4 and Cycloalkyne 22. Huebner et al. showed[16] that at −70 °C in THF, 7 was metalated by *n*-butyllithium to give the α-lithio derivative 16 which on



carbonation gave the chloro acid 17. We verified this result using *tert*-butyllithium at −42 °C. Quenching of 16 with CH_3OD, CH_3I, or $BrCH_2CH_2Br$ gave 18–20, respectively. Thus 16 is relatively stable toward elimination of lithium chloride. When a solution of 16 (prepared at −42 °C with *tert*-butyllithium) was warmed quickly to room temperature and then heated under reflux for 2 h, a 20% yield of the heptiptycene 4 and a 39% yield of coupling product



21[16] was obtained. This procedure represents some yield improvement over the literature,[16] but we are working to further improve the yield of 4.

The presumed intermediate in the formation of 4 is the cycloalkyne 22 (see Scheme I). To trap this intermediate, solutions of 16 were prepared at −42 °C and added dropwise to refluxing THF containing various dienes. In this way, adducts 23–25 were prepared in reasonable yields.[27]

Cycloalkyne 22 appears not to have been trapped previously, and we are exploring the synthetic utility of this easily accessible reactive intermediate and the formation of related derivatives. In the Experimental Section we describe an improved synthesis of its precursor 7.

Conclusions. We have developed a short, reasonably efficient synthesis of pentiptycenes with the general structures 2 and 3, a synthesis which will permit exploration of the chemistry of these novel compounds and their derivatives. We have also improved the yield of heptiptycene 4 by using *tert*-butyllithium in place of *n*-butyllithium in the metalation of 7 and have trapped the presumed intermediate in its formation, cycloalkyne 22, with various dienophiles. The chemistry of triptycene analogues such as 2–4 can now be explored.

Experimental Section

General Procedures. ^1H NMR spectra were measured at 60 MHz (Varian T-60) with $(CH_3)_4Si$ as an internal standard. Chemical shifts are reported in parts per million (δ). ^{13}C NMR spectra were measured on a Varian CFT-20 spectrometer. IR spectra were determined on a Perkin-Elmer 167 spectrometer. UV spectra were obtained on a Cary 219 spectrometer. Mass spectra were measured at 70 eV by using a Finnigan 4000 with the INCOS data system, operated by Mr. Ernest Oliver. Melting points were determined with an electrothermal melting point apparatus (Fisher Scientific) but with the thermometer replaced by an iron–constantan thermocouple. To extend the range above 360 °C, we connected the apparatus to one or two Variacs (in series), each of which could nominally boost line voltage from 110 to 140 V. The thermometer well was blocked with a glass rod to minimize heat loss, and the thermocouple was placed in a melting point tube well adjacent to the well holding the sample tube. After the approximate melting point range was determined, the block was preheated to approximately 50 °C below the expected melting point before the sample was inserted. Microanalyses were by Spang Microanalytical Laboratory. The silica gel for chromatography was 230–400 mesh.

5,7,12,14-Tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene (2, R = H). To a stirred solution of 1,2,4,5-tetrabromobenzene[28] (2.0 g, 5 mmol) and anthracene (1.78 g, 10 mmol) in dry toluene (250 mL) at room temperature under a continuous nitrogen flow was added dropwise a solution of *n*-butyllithium (12.6 mmol) in dry hexane (100 mL) over 3 h. After 5 h of additional stirring the reaction mixture was quenched with methanol (10 mL). Concentration on a rotary evaporator gave a yellow sticky solid which was resolved by flash chromatography on silica gel. With hexane as eluant, the first fraction was unreacted anthracene (1.29 g). With benzene as eluant, the second fraction was 0.56 g (1.3 mmol, 94% based on consumed anthracene) of 2 (R = H). The product was recrystallized from carbon tetrachloride to give colorless needles: mp 483 °C; ^1H NMR ($CDCl_3$) δ 5.18 (s, 4 H), 6.68–7.0 (m, 8 H), 7.0–7.3 (m, 10 H); ^1H NMR (PCl_3) δ 5.10 (s, 4 H), 6.53–6.80 (m, 8 H), 6.90–7.13 (m, 8 H), 7.18 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 53.68, 119.40, 123.07, 124.67, 142.10, 145.03; UV (CH_2Cl_2) λ_{max} 273 nm (sh, ε 6800), 280 (8700), 285 (sh, 8000), 291 (9100); mass spectrum, m/e (relative intensity) 430 (M^+, 100), 252 (M^+ − anthracene, 48), 178 (anthracene, 16).

Anal. Calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.80; H, 5.15.

6,13-Dimethyl-5,7,12,14-tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene (2, R = CH_3). To a stirred suspension of 2.11 g (5 mmol) of tetrabromo-*p*-xylene and 1.78 g (10 mmol) of anthracene in 250 mL of dry toluene under argon at −10 °C was added dropwise over 4 h 12 mmol of *n*-butyllithium in 100 mL of hexane. The mixture was allowed to gradually warm to room temperature. Reaction was quenched with methanol, and the mixture was washed with water and dried ($MgSO_4$). After removal

(27) The [2.2.2]cycloalkyne 22 is apparently appreciably longer lived than the recently reported [2.2.1]cycloalkyne norbornyne, since analogous trapping experiments with it failed: Gassman, P.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6863. Personal communication from I. Gennick.

(28) Scheufelen, A. *Justus Liebigs Ann. Chem.* **1885**, *231*, 152.

of the solvent (rotavap), the solid residue was chromatographed on silica gel. Hexane eluted the unreacted anthracene (1.07 g). Further elution with 9:1 hexane–methylene chloride gave 0.327 g (0.71 mmol, 35% based on consumed anthracene) of **2** (R = CH_3) which was recrystallized from chloroform: mp 460–462 °C; ^1H NMR ($CDCl_3$) δ 2.65 (s, 6 H), 5.59 (s, 4 H), 6.90 (m, 8 H), 7.287 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 14.36, 50.84, 123.43, 124.32, 125.01, 140.48, 145.75; mass spectrum, *m/e* (relative intensity) 458 (88), 443 (41), 427 (30), 280 (100), 265 (34), 229 (80), 214 (66), 221 (49), 178 (53); UV (CH_3CN) λ_{max} 232 nm (log ε 4.66), 261 (3.75), 278 (sh, 3.66); IR (KBr) 3010, 3000, 1465, 1460, 750 cm^{-1}.

Anal. Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.16; H, 5.71.

6,13-Dimethoxy-5,7,12,14-tetrahydro-5,14[1′,2′]:7,12-[1″,2″]-dibenzenopentacene, (2, R = OCH_3). The procedure and scale were as with **2** (R = CH_3). After recovery of the unreacted anthracene (0.88 g) by elution with hexane, further elution with 4:1 hexane–methylene chloride gave first 0.375 g (1.19 mmol, 21%) of 1,4-dimethoxytriptycene (**9**): mp 238–240 °C (lit.[29] mp 239–241 °C); ^1H NMR ($CDCl_3$) δ 3.73 (s, 6 H), 5.76 (s, 2 H), 6.33 (s, 2 H), 6.83 (m, 4 H), 7.20 (m, 4 H); mass spectrum, *m/e* (relative intensity) 314 (62), 283 (100), 252 (35), 239 (54), 149 (48), 142 (71), 85 (64), 83 (93). Continued elution with the same solvent gave 0.511 g (1.04 mmol, 37%) of **2** (R = OCH_3) which was recrystallized from acetonitrile: mp 400–402 °C; ^1H NMR ($CDCl_3$) δ 3.76 (s, 6 H), 5.50 (s, 4 H), 6.73 (m, 8 H), 7.10 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 48.23, 62.85, 123.55, 125.23, 136.38, 145.34, 147.00; mass spectrum, *m/e* (relative intensity) 490 (19), 459 (9), 283 (100), 222 (22), 214 (14), 202 (12), 178 (15); UV (CH_3CN) λ_{max} 277 nm (log ε 3.71), 261 (3.93); IR (KBr) 2920, 2820, 1460, 1450, 1300, 1260, 1045, 755, 740 cm^{-1}.

Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34. Found: C, 88.25; H, 5.36.

6,13-Dihydroxy-5,7,12,14-tetrahydro-5,14[1′,2′]:7,12-[1″,2″]-dibenzenopentacene (2, R = OH). A solution containing 100 mg (0.20 mmol) of **2** (R = OCH_3) in 30 mL of glacial acetic acid and 10 mL of 47% hydrogen iodide was heated at reflux for 2 h. The cooled solution was extracted with chloroform, and the combined organic layers were washed successively with water, aqueous sodium bisulfite, aqueous sodium bicarbonate, and water and dried ($MgSO_4$). Removal of the solvent (rotoevaporator) left 90 mg (97%) of **2** (R = OH) as a white solid which becomes gray at about 300 °C and melts with decomposition at 427–430 °C: ^1H NMR ($CDCl_3$) δ 4.40 (br s, 2 H), 5.50 (s, 4 H), 6.76 (m, 8 H), 7.20 (m, 8 H); ^1H NMR (Me_2SO-d_6) δ 5.63 (s, 4 H), 6.66 (m, 8 H), 7.06 (m, 8 H), 8.40 (s, 2 H); UV (CH_3OH) λ_{max} 398 nm (log ε 4.61), 278 (4.82), 262 (4.92); mass spectrum, *m/e* (relative intensity) 462 (74), 445 (39), 284 (32), 230 (42), 202 (100), 178 (80); IR (KBr) 3500, 1470, 1460, 1220, 750 cm^{-1}. The compound is not very stable in air and oxidizes slowly to the corresponding quinone.

5,7,12,14-Tetrahydro-5,14[1′,2′]:7,12[1″,2″]-dibenzenopentacene-6,13-dione (6). A solution containing 36 mg (0.078 mmol) of hydroquinone **2** (R = OH) and 0.5 g of ceric ammonium nitrate in 100 mL of acetonitrile was stirred at room temperature for 2 h. The solvent was removed (rotoevaporator). The residue was extracted with chloroform, and the organic layers were washed with water (three times) and dried ($MgSO_4$). Removal of the chloroform and recrystallization from the same solvent gave 31 mg (86%) of **6** which, on heating, became gray at about 270 °C and slowly turned black but did not melt up to 510 °C: ^1H NMR ($CDCl_3$) δ 5.60 (s, 4 H), 6.76 (m, 8 H), 7.16 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 47.47, 124.31, 125.52, 143.77, 151.06, 180.02; UV (CH_3CN) λ_{max} 270 nm (log ε 4.76), 279 (4.73); mass spectrum, *m/e* (relative intensity) 460 (11), 230 (48), 202 (100), 178 (92); IR (KBr) 1650, 1475, 1460, 765, 755, 745 cm^{-1}.

Anal. Calcd for $C_{34}H_{20}O_2$: C, 88.67; H, 4.38. Found: C, 88.57; H, 4.49.

5,7,12,14-Tetramethoxy-5,7,12,14-tetrahydro-5,14-[1′,2′]:7,12[1″,2″]-dibenzopentacene (11). The procedure was the same as in the preparation of **2** (R = H), but 9,10-dimethoxyanthracene (2.38 g, 10 mmol) and 10 mmol of **7** (R = H) were used. Flash chromatography gave no recovered 9,10-dimethoxyanthracene and 0.55 g (1.0 mmol, 10%) of **11**, recrystallized from methylene chloride, as colorless prisms: mp 472–475 °C; ^1H NMR ($CDCl_3$) δ 4.30 (s, 12 H, methoxyls), 6.87–7.07 (m, 8 H), 7.27–7.53 (m, 8 H), 7.77 (s, 2 H); UV (CH_2Cl_2) λ_{max} 273 nm (sh, ε 7600), 280 (9300), 288 (9100); mass spectrum, *m/e* (relative intensity) 550 (M^+, 100), 504 (27), 489 (16), 473 (41), 458 (25), 442 (37).

Anal. Calcd for $C_{38}H_{30}O_4$: C, 82.88; H, 5.49. Found: C, 82.75; H, 5.56.

6,7,14,15-Tetramethyl-5,8,13,16-tetrahydro-5,16[1′,2′]:8,13-[1″,2″]-dibenzenohexacene (13). The procedure and scale were as with **2** (R = CH_3). Chromatography over silica gel and elution with hexane gave 0.41 g (2.08 mmol) of recovered anthracene. Further elution with 4:1 hexane–methylene chloride gave 1.607 g (3.0 mmol, 75%) of **13** which was recrystallized from methanol/chloroform: mp 358–360 °C; ^1H NMR ($CDCl_3$) δ 2.66 (s, 12 H), 5.60 (s, 4 H), 6.76 (m, 8 H), 7.16 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 20.41, 50.57, 123.52, 125.25, 132.95, 140.69, 145.00 (2 C's); mass spectrum, *m/e* (relative intensity) 536 (12), 253 (22), 246 (23), 238 (8), 83 (62), 57 (50), 44 (100); UV (CH_3CN) λ_{max} 277 nm (log ε 5.09), 273 (5.06), 259 (4.89); IR (KBr) 3000, 2900, 1460, 770, 750, 720 cm^{-1}; high-resolution mass spectrum calcd for $C_{42}H_{32}$ *m/e* 536.248 55, found 536.250 41.

4,5-Dibromo-3,6-diiodo-*o*-xylene (15). A solution of 16 g (0.0606 mol) of 4,5-dibromo-*o*-xylene[26] and 42 g of mercuric oxide in 160 mL of trifluoroacetic acid was heated at reflux for 4 h (a white precipitate formed after about 2 h).[30] The solution was cooled, and the white solid was filtered and subjected directly to iodination without purification. A mixture of iodine (60 g), potassium iodide (40 g), and the crude 4,5-dibromo-3,6-bis[(trifluoroacetato)mercuri]-*o*-xylene in 200 mL water was heated at 70–75 °C with stirring for 8 h, cooled, and filtered. The solid product was dissolved in chloroform, washed successively with 10% aqueous sodium bisulfite, sodium bicarbonate, and water, and then dried ($MgSO_4$). Removal of the solvent (rotavap) and recrystallization from chloroform gave 25.5 g (81%) of **15**: mp 239–240 °C; ^1H NMR ($CDCl_3$) δ 2.66 (s); mass spectrum, *m/e* (relative intensity) 516 (2), 390 (17), 263 (15), 182 (20), 102 (100), 71 (61), 51 (64).

Anal. Calcd for $C_8H_6Br_2I_2$: C, 18.62; H, 1.17. Found: C, 18.72; H, 1.19.

6,7-Dimethyl-5,8,13,14-tetrahydro-5,14[1′,2′]:8,13[1″,2″]-dibenzenopentaphene (3, R = CH_3). The procedure and scale were as with **2** (R = CH_3) except that the reaction was carried out at −23 °C. Chromatography on silica gel and elution with hexane gave 1.13 g (6.34 mmol) of recovered anthracene. Further elution with 4:1 hexane–methylene chloride gave 0.322 g (0.70 mmol, 38%) of **3** (R = CH_3) which was recrystallized from methanol/chloroform: mp 382–384 °C; ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H), 5.50 (s, 2 H), 5.83 (s, 2 H), 6.83 (m, 8 H), 7.23 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 15.32, 50.18, 50.93, 123.42, 123.61, 125.15, 125.21, 127.20, 136.31, 139.53, 145.52, 145.53; mass spectrum, *m/e* (relative intensity) 458 (97), 443 (5), 280 (100), 178 (52); IR (KBr) 2900–3050, 1445, 1380, 750, 720, 690, 620, 610 cm^{-1}; UV (CH_3CN) λ_{max} 227 nm (log ε 4.70) 262 (sh, 3.91), 269 (sh, 3.89), 277 (sh, 3.83); high-resolution mass spectrum calcd for $C_{36}H_{26}$ *m/e* 458.203 18, found 458.203 46.

11-Chloro-9,10-dihydro-9,10-ethenoanthracene (7).[31] To a solution of potassium *tert*-butoxide, prepared from 3.9 g (0.1 mol) of potassium in 200 mL of *tert*-butyl alcohol, under argon was added 6.5 g (0.023 mol) of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene,[31] and the mixture was refluxed for 1 h. After the mixture cooled to room temperature, 20 mL of water was added, and the solvent was removed under reduced pressure (rotoevaporator). The remaining solid was dissolved in 200 mL of ether, washed with water (3 × 50 mL), and dried ($MgSO_4$). Removal of the ether left 5.0 g (88%) of **7** which was recrystallized from methanol; mp 128 °C (lit.[31] mp 127.5–129 °C).

Metalation of 7. To a solution of **7** (0.5 g, 2.1 mmol) in anhydrous THF (50 mL) at −42 °C under argon was added 2 mL (2.5 mmol) of *tert*-butyllithium (1.3 M in pentane). The mixture was stirred for 2 h and then warmed to 0 °C. CH_3OD (1 mL) was

(29) Klanderman, B. H.; Criswell, T. R. *J. Org. Chem.* **1969**, *34*, 3426.

(30) This procedure is analogous to that described by: Yagupol'skii, L. M.; Popov, V. I.; Kondratenko, N. V. *Zh. Org. Khim.* **1976**, *12*, 916; *J. Org. Chem. USSR (Engl. Transl.)* **1966**, *12*, 923.

(31) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193.

added. The solvent was removed on a rotary evaporator, and the residue was taken up in ether, washed with water, and dried ($MgSO_4$). The ether solution was concentrated to give 0.5 g of **18**: mp 128–129 °C (from methanol); NMR (CCl_4) δ 4.86 (s, C-10 H), 4.93 (s, C-9 H), 6.60–7.33 (m, 8 H); mass spectrum, *m/e* (relative intensity) 241 (10), 239 (32), 204 (100).

Metalation of **7** in a similar manner and on the same scale, followed by pouring the resulting **16** over a slush of dry ice and 100 mL of anhydrous ether, gave, on workup by extraction with 10% sodium hydroxide and acidification to pH 2, 0.3 g (50%) of the known chloro acid **17**, mp 259–260 °C (lit.[16,32] mp 260–261 °C).

Metalation of **7** as above was followed by cooling of the resulting solution of **16** to −78 °C and addition of methyl iodide (1 mL). After 1 h the mixture was quickly warmed to room temperature. The solvent was removed (rotoevaporator), and the residue was taken up in ether, washed with water, and dried ($MgSO_4$). The ether solution was concentrated to give 0.53 g (100%) of **19** which was recrystallized from methanol: mp 204–205 °C (lit.[33] mp 206–208 °C); NMR (CCl_4) δ 1.90 (s, 3 H, methyl), 4.63 (s, 1 H, bridgehead), 4.76 (s, 1 H, bridgehead), 6.66–7.20 (m, 8 H, arom); mass spectrum, *m/e* (relative intensity) 252 (32), 217 (100), 202 (33).

The procedure described for **19** was followed, but with 1 mL of 1,2-dibromoethane in place of methyl iodide, to give after a similar workup 0.48 g (72%) of **20** after recrystallization from methanol: mp 173–175 °C; NMR (CCl_4) δ 4.86 (s, 1 H), 4.90 (s, 1 H), 6.60–7.23 (m, 8 H); mass spectrum, *m/e* (relative intensity) 318 (2), 281 (10), 237 (66), 202 (100); high-resolution mass spectrum calcd for $C_{16}H_{10}BrCl$ *m/e* 315.967 15, found 315.965 50.

5,6,11,12,17,18-Hexahydro-5,18[1′,2′]:6,11[1″,2″]:12,17-[1‴,2‴]-tribenzenotrinaphthylene (4). To a solution of **7** (1.0 g, 4.2 mmol) in anhydrous THF (70 mL) at −42 °C under argon was added 4 mL (5 mmol) of *tert*-butyllithium (1.3 M in pentane). The mixture was stirred at −42 °C for 2 h, quickly warmed to room temperature, and heated at reflux for 2 h. The mixture was cooled to room temperature and quenched with methanol (2 mL). The resulting white precipitate was filtered, washed with water, and dried to give 0.169 g (20%) of **4**: ^1H NMR ($CDCl_3$) δ 6.18 (s, 6 H, bridgehead protons), 6.92 (m, 12 H), 7.45 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 48.64, 123.42, 125.01, 135.33, 145.36; mass spectrum, *m/e* (relative intensity) 606 (100), 428 (82), 256 (4), 178 (19).

The filtrate after removal of **4** was concentrated on a rotary evaporator. The resulting brown solid was taken up in chloroform, washed with water, and dried ($MgSO_4$). The residue which remained after removal of the chloroform was chromatographed on alumina with a 3:1 hexane–chloroform eluant to give 0.36 g (39%) of **21**, mp 266–268 °C (lit.[16] mp 268 °C).

Trapping Experiments for Cycloalkyne 22. To a solution of **7** (1.0 g, 4.2 mmol) in anhydrous THF (50 mL) at −42 °C under argon was added 4 mL (5 mmol) of *tert*-butyllithium (1.3 M in pentane), and the mixture was stirred for 2 h. This solution was transferred by syringe to a dropping funnel equipped with a cooling jacket (at −42 °C) and was added dropwise over 1 h under argon to a refluxing solution containing 5 g of 2,5-dimethylfuran in 100 mL of anhydrous THF. After 1 h of additional reflux, the solution was cooled and quenched with methanol (2 mL). The solvent was removed on the rotary evaporator, and the residue was taken up in ether, washed with water, and dried ($MgSO_4$). The ether was removed to give a yellow solid which was chromatographed over alumina (first with hexane and then with 4:1 hexane–chloroform as eluant) to give 0.50 g (40%) of **23**: mp 179–180 °C; ^1H NMR (CCl_4) δ 1.63 (s, 6 H, methyls), 4.70 (s, 2 H, bridgehead), 6.00 (s, 2 H, vinyl), 6.40–7.16 (m, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 15.84, 50.93, 91.74, 123.03, 123.32, 124.34, 124.86, 145.01, 145.25, 145.57, 168.59; mass spectrum, *m/e* (relative intensity) 298 (100), 283 (68), 272 (36), 255 (87), 239 (67), 229 (36), 215 (23), 202 (40), 178 (50); high-resolution mass spectrum, calcd for $C_{22}H_{18}O$ *m/e* 298.135 77, found 298.136 30.

The same procedure was followed but with 1,3-diphenylisobenzofuran (1.13 g, 4.2 mmol) as the trapping agent. Chromatography of the crude product on alumina with hexane as eluant gave 0.32 g of unreacted 1,3-diphenylisobenzofuran. Further elution with 3:1 hexane–chloroform gave 1.21 g (61%) of **24**: mp 208–209 °C; ^1H NMR (CCl_4) δ 5.00 (s, 2 H, bridgehead), 6.20–7.60 (m, 22 H, arom); ^{13}C NMR ($CDCl_3$) δ 51.86, 94.35, 120.82, 123.06, 123.42, 124.44, 125.08, 128.82, 128.97, 134.53, 144.65, 145.43, 150.46, 167.75 (four peaks are overlapped); mass spectrum, *m/e* (relative intensity) 472 (100), 395 (15), 265 (20), 178 (21); high-resolution mass spectrum calcd for $C_{36}H_{24}O$ *m/e* 472.182 72, found 472.179 13.

The same procedure was followed but with 5,5-dimethoxytetrachlorocyclopentadiene (1.10 g, 4.2 mmol) as the trapping agent. Chromatography of the crude product on alumina with hexane as eluant removed the unreacted diene (0.2 g). Further elution with 3:1 hexane–chloroform gave 0.82 g (42%) of **25** as a yellow oil. Further purification by preparative TLC on alumina gave pure **25**: mp 141–142 °C; ^1H NMR (CCl_4) δ 3.16 (s, 3 H, methoxyl), 3.36 (s, 3 H, methoxyl), 4.95 (s, 2 H, bridgehead), 6.66–7.30 (m, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 51.65, 55.28, 59.38, 105.39, 123.40, 123.68, 125.16, 125.57, 134.23, 143.73, 144.39, 146.50; mass spectrum, *m/e* (relative intensity) 466 (6), 429 (2), 393 (2), 264 (15), 229 (35), 203 (70), 178 (100), 101 (15); high-resolution mass spectrum calcd for $C_{23}H_{16}Cl_4O_2$ *m/e* 463.991 35, found 463.990 45.

Acknowledgment. We are indebted to the National Institutes of Health (Grant No. GM 15997) and to the National Science Foundation (Grant No. CHE 80-17746) for financial support of this research.

Registry No. 2 (R = H), 52776-07-5; **2** (R = CH_3), 78823-43-5; **2** (R = OCH_3), 78823-44-6; **2** (R = OH), 78823-45-7; **3** (R = CH_3), 78823-46-8; **4**, 25911-58-4; **6**, 6932-41-8; **7**, 6226-22-8; **8** (R = H), 636-28-2; **8** (R = CH_3), 23488-38-2; **8** (R = OCH_3), 19403-94-2; **9**, 21372-93-0; **10**, 2395-97-3; **11**, 78823-47-9; **12**, 68185-77-3; **13**, 78823-48-0; **14**, 24932-48-7; **15**, 78823-49-1; **16**, 78823-50-4; **17**, 25911-55-1; **18**, 78823-51-5; **19**, 78823-52-6; **20**, 78823-53-7; **21**, 25911-56-2; **23**, 78837-41-9; **24**, 78823-54-8; **25**, 78837-42-0; anthracene, 120-12-7; 4,5-dibromo-3,6-bis[(trifluoroacetato)mercuri]-*o*-xylene, 78823-55-9; *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene, 6476-15-9; 2,5-dimethylfuran, 625-86-5; 1,3-diphenylisobenzofuran, 5471-63-6; 5,5-dimethoxytetrachlorocyclopentadiene, 2207-27-4.

(32) Miettinen, T. *Acta Chem. Scand., Ser. B* **1979**, *33B*, 157.
(33) Noland, W. E., Libers, R. *Tetrahedron* **1963**, *19* (Suppl 1), 23.