2-chloro-4-methyl-, 4-methoxy-, and 2,4-dimethoxypyrimidine to lithiate at C-5.[3] In the case of pyrazine, only the 2-chloro derivative has been lithiated at C-3,[4] and this reaction fails entirely for both *N*,*N*-diethyl-[5] and *N*-methylpyrazinamide.[6] No directed lithiations of pyridazines have been reported. We now report that methoxypyridazines, -pyrimidines, and -pyrazines ortho-lithiate cleanly and incorporate electrophiles in high yields.

The methoxypyrazine, -pyrimidine, -pyridazine starting materials (**1**–**7**, E = H) were easily prepared from the corresponding chloro heterocycles by refluxing with sodium methoxide in methanol. These methoxy heterocycles were then lithiated under standard conditions using LiTMP in THF at −78 °C for 15 min. To evaluate the utility of this reaction, TMS-Cl, MeI, PhCHO, and PhCOCl were added to the lithiated heterocycles to give the results shown in Table I. All yields are of purified products having consistent NMR, IR, and elemental analyses (Table II). TMS-Cl, MeI, and PhCHO incorporated into all the heterocycles in good yields, giving products **1A**–**7A**, **1B**–**7B**, and **1C**–**7C**, respectively. Some of the silated systems, such as **3A** and **6A**, show somewhat lower yields, which may reflect the loss of these volatile products upon chromatography and Kügelrohr distillation. However, 5-methoxypyrimidine (**2**, E = H) gives lower yields with all the electrophiles, perhaps indicating some problem with the lithiation of this material. In contrast with the other electrophiles, benzoyl chloride incorporates well into only 4,6-dimethoxy- and 2,4,6-trimethoxypyrimidine, this electrophile giving complex mixtures and low yields of the expected products with the other lithiated heterocycles.

Further work is now underway to investigate the utility of other ortho-directing groups in these heterocyclic systems.

Experimental Section

The methoxydiazine starting materials were prepared from the corresponding chlorodiazines and were Kügelrohr distilled before use. All IR spectra were recorded on a Perkin-Elmer Model 1800 FT-IR spectrometer. The 300-MHz NMR spectra were determined on a Bruker AM300 spectrometer using deuteriochloroform with 2% (v/v) tetramethylsilane as the internal reference. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. All products were purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent. All yields given are of purified material, and all compounds had NMR, MS, and IR spectra consistent with the assigned structures and satisfactory elemental analyses (±0.4%, except as noted in Table II).

General Procedure. *n*-Butyllithium (5.2 mL of a 2.5 M solution in hexanes, 13 mmol) was added to a solution of freshly distilled tetramethylpiperidine (2.19 mL, 13 mmol) in 250 mL of anhydrous THF at 0 °C. After stirring at 0 °C for 30 min, the pale yellow solution was cooled to −78 °C, and the methoxy heterocycle (10 mmol dissolved in 15 mL of THF) was added dropwise over 3 min. The solution was stirred at −78 °C for 15 min, the electrophile (15 mmol) was added, and the solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo, and the residue was partitioned between CH_2Cl_2 and water. The CH_2Cl_2 layer was separated, dried over Na_2SO_4, and concentrated in vacuo to give the crude product, which was purified by flash chromatography and Kügelrohr distillation.

Registry No. **1**, 4603-59-2; **1A**, 126327-65-9; **1B**, 89943-29-3; **1C**, 126327-66-0; **2**, 31458-33-0; **2A**, 126327-67-1; **2B**, 19175-07-6; **2C**, 126327-68-2; **3**, 3551-55-1; **3A**, 62803-27-4; **3B**, 5151-34-8; **3C**, 110821-05-1; **4**, 5270-94-0; **4A**, 126327-69-3; **4B**, 13566-63-7; **4C**, 126327-70-6; **4D**, 126327-71-7; **5**, 13106-85-9; **5A**, 126327-72-8; **5B**, 96494-12-1; **5C**, 126327-73-9; **5D**, 126327-74-0; **6**, 3149-28-8; **6A**, 126327-75-1; **6B**, 2847-30-5; **6C**, 91392-53-9; **7**, 4774-15-6; **7A**, 126327-76-2; **7B**, 90345-35-0; **7C**, 126327-77-3.

(3) Kauffmann, T.; Greving, B.; König, J.; Mitschker, A.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 713.
(4) Turck, A.; Mojovic, L.; Quèguiner, G. *Synthesis* **1988**, 881.
(5) Personal communication B. I. Alo, V. Snieckus, University of Waterloo, Waterloo, Ontario, Canada.
(6) Personal communication G. Karageorge, CNS Chemistry, Bristol-Myers Squibb Company, Wallingford, CT.

Extensions of Bicycloalkyne Trimerizations

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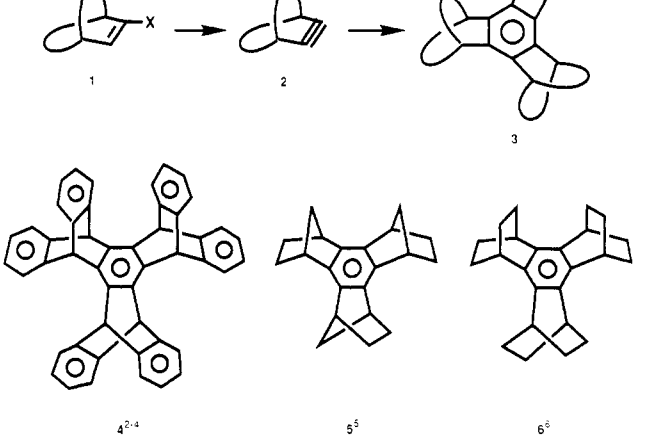
Received November 28, 1989

Bicyclic vinyl halides **1** can be "trimerized" to novel arenes **3** via bicycloalkyne intermediates **2**. Specific examples of arenes that have been made in this way are **4**-**6**.[7]



The mechanism by which **4** is formed is outlined in Scheme I.[4] Each intermediate depicted in the scheme was identified through trapping.

Although the overall yield of trimers in these reactions is rather low (~20%), the products are easily isolated and identified because of their symmetry and may form a take-off point for further chemistry. The starting material for **4**, the vinyl chloride **7**, is readily available from anthracene. We describe here our first extensions of this chemistry to analogues of **4** starting with substituted anthracenes.

Reaction of 2,3,6,7-tetramethylanthracene (**12**)[8] with *trans*-1,2-dichloroethene gave a 70% yield of adduct **13**,

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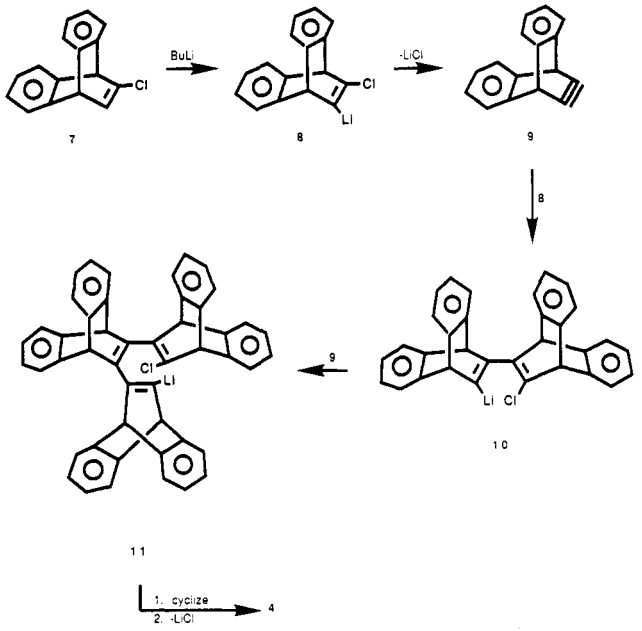
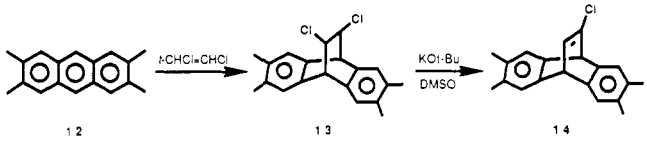
(2) Huebner, C. F.; Puckett, R. T.; Brezchfta, M.; Schwartz, S. L. *Tetrahedron Lett.* **1970**, 359–362.
(3) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432.
(4) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136–7140.
(5) Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6863–6864.
(6) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633–634. Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem. Lett.* **1988**, 2029–2032.
(7) Also known are syn-anti and all-syn bridgehead trimethyl-**4**[4] and *all-syn*-**5**.[5]
(8) Hinshaw, J. C. *Org. Prep. Proced. Int.* **1972**, *4*, 211-213.

0022-3263/90/1955-3412$02.50/0

Scheme I

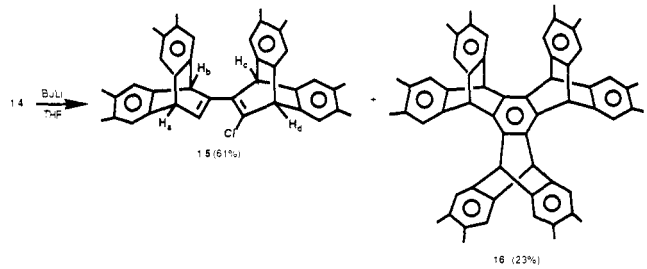


which was readily dehydrohalogenated to **14** (93%) with potassium *tert*-butoxide in DMSO. The C_2 symmetry of



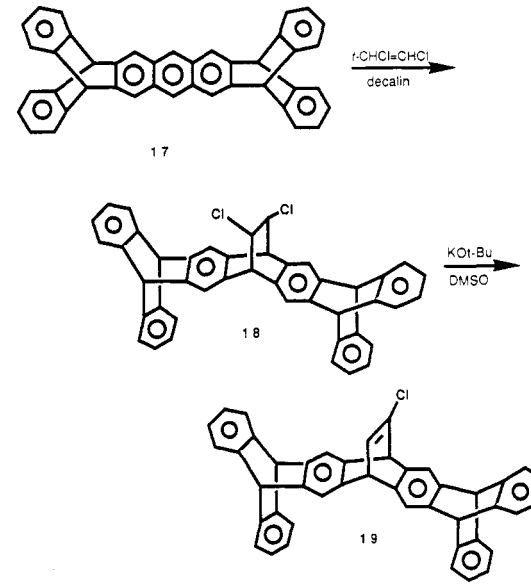
13 was clear from its ^{1}H NMR spectrum, with methyl singlets at δ 2.20 and 2.21 (6 H each) and aromatic singlets at δ 7.06 and 7.12 (2 H each). The bridgehead protons appeared at δ 4.14, and the protons adjacent to chlorine at δ 4.23, with only weak coupling between them (J = 1.2 Hz). In **14** the methyl and aryl protons again appeared as two sets of singlets (δ 2.16, 2.17 for the former, 6 H each, and δ 7.06, 7.15 for the latter, 2 H each), but the bridgehead protons were now no longer equivalent and appeared at δ 4.92 (d, J = 6.4 Hz) and δ 4.84 (d, J = 2.1 Hz), showing near and long range allylic coupling, respectively, with the vinyl proton (dd, δ 6.75, 6.77, J = 6.4, 2.1 Hz).

Treatment of **14** with 1.1 equiv of BuLi in THF gave, after a methanol quench, diene **15** (61%) and trimer **16** (23%). The pattern of the bridgehead protons in **15** was particularly revealing in structure determination. Two protons (H_c, H_d) appeared as singlets at δ 4.78 and 4.89, one (H_b) was a doublet (δ 5.68) with small allylic coupling with the vinyl proton (J = 1.87 Hz), and the remaining one (H_a) appeared at δ 4.98 with substantial coupling (J = 6.15 Hz) to the adjacent vinyl proton.



The D_{3h} symmetry of trimer **16** was apparent from its ^{1}H (three singlets at δ 2.06, 5.61, and 7.05, area ratio 6:1:2 for the methyl, bridgehead and aryl protons, respectively) and ^{13}C spectra [peaks at δ 19.38 (methyl), 49.09 (bridgehead), and only four aryl carbon signals]. We anticipate that, through bromination, the methyl groups in **16** will serve as a site for introducing a variety of functionality into these trimers.[9]

As a second starting point, we selected anthracene **17**,[10,11] a pentiptycene.[3,11] Heating with *trans*-1,2-dichloroethene in decalin at 200 °C for 6 days gave adduct **18** (76%) and recovered starting material. Dehydrohalogenation proceeded readily to give **19** (87%). The NMR spectra were entirely consistent with the assigned structures.



Treatment of **19** with BuLi in THF gave (in addition to recovered starting material) four products, of which the desired trimer constituted only 2%. Trimer **22**, with D_{3h} symmetry, has a beautiful structure best seen by examining models (Figure 1). The six added triptycene moieties that **22** has, compared with **4**, form two nearly enclosed spherelike cavities, one above and one below the plane of the central benzene ring. Each cavity has, at its bottom, one face of the central benzene ring; it is then lined with six more benzene rings, the three upper of which nearly touch one another at the cavity opening. In addition, three benzene rings lie in an equatorial plane outside each cavity.

Consistent with its symmetry, **22** (which has a molecular formula $C_{132}H_{78}$) showed only five sets of peaks in its ^{1}H NMR spectrum. The bridgehead protons appeared as sharp singlets at δ 5.50 (inner set of 6 H) and δ 5.17 (outer set of 12 H). The 12 isolated aromatic protons on the inner set of 6 aromatic rings appeared as a singlet at δ 7.24, whereas the 48 aromatic protons on the outer 12 aromatic rings appeared as two sets of multiplets, 24 H each, at δ 6.80 and 7.18. Similarly, the 132 carbons appeared as two peaks for the bridgehead carbons (δ 49.81, 53.79) and 8 (of a possible 10) aromatic signals.

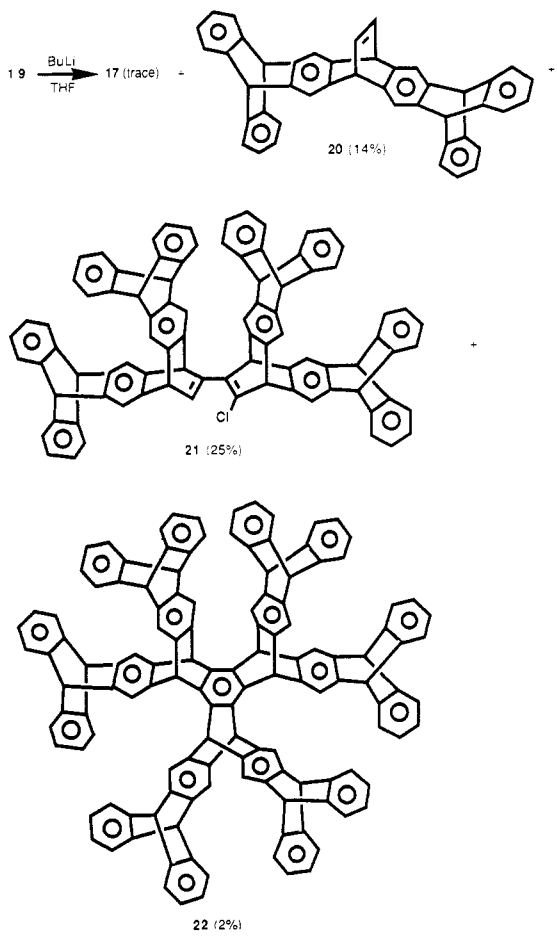
The formation of **17** in this reaction is rationalized as a retro-Diels-Alder product. Examples with analogous bicyclic vinyl chlorides have been described previously.[11]

Structures of **20** and **21** are assigned from their spectra and by analogy. The C_{2v} symmetry of **20** was apparent from its spectra, and the compound undoubtedly arises

(9) For conversion of analogous methyl groups to CH_2Br, CH_2SH, CHO and many other functionalities, see: Vinod, T. K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 6574–6575. Vinod, T. K.; Hart, H. *J. Org. Chem.* **1990**, *55*, 881–890.

(10) Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357–4360.

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



from some metalation at the C–Cl bond of **19**.

We are currently extending these studies to other substituted anthracenes, and to developing improved yields of the trimers.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution (except where mentioned otherwise) at 250 and 75 MHz, respectively. Mass spectra were recorded at 70 eV. High-resolution mass spectra were obtained at the Michigan State University mass spectrometry facility, which is supported in part by a grant (DRR-00480) from the Biotechnology Resources Branch, division of research resources, NIH. Melting points, taken on a Melt-Temp apparatus, are uncorrected. Silica gel for chromatography was 230–400 mesh. The drying agent throughout was anhydrous $MgSO_4$.

***trans*-11,12-Dichloro-2,3,6,7-tetramethyl-9,10-dihydro-9,10-ethanoanthracene (13).** A mixture of 2,3,6,7-tetramethylanthracene[8] (3.5 g, 15 mmol) and 25 mL of *trans*-1,2-dichloroethene[12] in a sealed tube was heated at 200 °C for 2 days. The mixture was cooled and excess dichloroethene was removed (rotavap) to leave a dark residue. The residue from two such runs were combined and chromatographed over silica gel using hexanes:CH_2Cl_2 (19:1) as eluent to give a white solid which, on recrystallization from the same solvent mixture, gave 6.93 g (70%) of **13**: mp 180–181 °C; ^1H NMR δ 2.20 (s, 6 H), 2.21 (s, 6 H), 4.14 (dd merged to a triplet, J = 1.2 Hz, 2 H), 4.23 (d, J = 1.2 Hz, 2 H), 7.06 (s, 2 H), 7.12 (s, 2 H); ^{13}C NMR δ 19.61, 51.41, 66.03, 125.50, 127.59, 135.03, 135.84, 137.37 (one aromatic peak overlapped); mass spectrum, m/e (relative intensity) 235 (20), 234 (100, M^+ – CHCl=CHCl), 117 (15), 115 (5), 114 (7), 109 (8), 108 (17), 102 (9), 101 (10), 96 (10), 57 (10), 56 (5), 55 (6), 43 (12), 41 (13). Anal. Calcd for $C_{20}H_{20}Cl_2$: C, 72.51; H, 6.08. Found: C, 72.36; H, 5.98.

(12) Hart, H.; Shahlai, K. *Tetrahedron Lett.* **1987**, *28*, 5437–5440.
(13) Aldrich Chemical Co., Cat. No. D6220-9.

11-Chloro-2,3,6,7-tetramethyl-9,10-dihydro-9,10-ethenoanthracene (14). To a stirred solution of **13** (6.62 g, 20 mmol) in 125 mL of a 4:1 mixture of DMSO/THF was added 2.45 g (21.9 mmol) of potassium *tert*-butoxide at room temperature. The color of the reaction mixture immediately turned brown. The mixture was stirred overnight at room temperature, quenched with water (500 mL), and extracted with CH_2Cl_2. The organic layer was washed with water and saturated aqueous sodium chloride and dried. Removal of the solvent (rotavap) and chromatography over silica gel with hexanes as the eluent gave a white solid, which, on recrystallization from hexane/CH_2Cl_2, gave 5.49 g (93%) of **14**: mp 154–155 °C; ^1H NMR δ 2.16 (s, 6 H), 2.17 (s, 6 H), 4.84 (d, J = 2.12 Hz, 1 H), 4.92 (d, J = 6.4 Hz, 1 H), 6.75, 6.77 (dd, J = 6.4, 2.12 Hz, 1 H), 7.06 (s, 2 H), 7.15 (s, 2 H); ^{13}C nMR δ 19.37, 19.44, 50.53, 57.75, 124.45, 124.73, 132.26, 132.78, 142.73, 143.08, 144.95 (one peak overlapped); mass spectrum, m/e (relative intensity) 296 (5, M^+), 295 (4), 294 (17, M^+), 260 (22), 259 (100, M^+ – Cl), 258 (12), 245 (7), 244 (33), 243 (13), 229 (14), 228 (9), 129 (14), 122 (32), 119 (12), 114 (38), 113 (15), 107 (29), 101 (16), 95 (18), 83 (11), 71 (16), 69 (15), 57 (33), 55 (24), 44 (32), 43 (40), 41 (32). Anal. Calcd for $C_{20}H_{19}Cl$: C, 81.48; H, 6.50. Found: C, 81.54; H, 6.46.

Trimerization of 14. To a stirred solution of **14** (2.95 g, 10 mmol) in THF (50 mL) at –78 °C under argon was added dropwise a hexane solution of butyllithium (1.1 equiv; 3.6 mL of a 2.5 M solution). After addition was complete, the mixture was allowed to slowly warm to room temperature, during which time the yellow solution turned green and then brown. After 10 min at room temperature, the mixture was heated at gentle reflux for 15 min, during which the color became violet. After cooling, the mixture was quenched with methanol (1 mL). Solvents were removed (rotavap) to give a red residue, which was taken up in CH_2Cl_2, washed with water and saturated aqueous sodium chloride, and dried. A proton NMR spectrum on the crude product showed only peaks due to **15** and **16**. Removal of the solvent and chromatography of the red residue over silica gel using CH_2Cl_2–hexane (1:9) as eluent gave 1.69 g (61%) of **15** and 0.58 g (23%) of **16**. For 12-chloro-2,2′,3,3′,6,6′,7,7′-octamethyl-9,9′,10,10′-tetrahydro-11,11′-bi(9,10-ethenoanthracene) (**15**): mp 325 °C dec; ^1H NMR δ 2.10 (m, 24 H), 4.78 (s, 1 H), 4.89 (s, 1 H), 4.98 (d, J = 6.15 Hz, 1 H), 5.68 (d, J = 1.87 Hz, 1 H), 6.95 (s, 2 H), 6.99 (s, 4 H), 7.04 (s, 3 H, 2 aryl and 1 vinyl); ^{13}C NMR δ 19.37, 50.21, 51.18, 54.85, 59.36, 124.17, 124.26, 125.25, 131.95, 132.44, 132.71, 135.42, 139.54, 142.29, 142.37, 143.62, 144.08, 148.98; mass spectrum, m/e (relative intensity) 552 (22, M^+), 519 (4), 518 (17), 517 (41), 516 (38), 502 (7), 501 (10), 487 (4), 398 (8), 393 (4), 284 (6), 283 (6), 281 (4), 268 (5), 259 (9), 258 (8), 251 (5), 244 (6), 243 (7), 236 (8), 235 (26), 234 (100), 233 (8), 228 (4), 203 (7), 202 (4). Anal. Calcd for $C_{40}H_{37}Cl$: C, 86.95; H, 6.74. Found: C, 86.61; H, 6.63.

For 2,3,8,9,14,15,22,23,28,29,34,35-dodecamethyl-5,6,11,12,17,18-hexahydro-5,18[1′,2′]:6,11[1″,2″]:12,17[1‴,2‴]-tribenzenotrinaphthylene (**16**): mp >400 °C; ^1H NMR δ 2.06 (s, 36 H, CH_3's), 5.61 (s, 6 H, bridgehead), 7.05 (s, 12 H, arom); ^{13}C NMR δ 19.38, 49.09, 124.64, 132.49, 134.87, 143.17; mass spectrum, m/e (relative intensity) 774 (100, M^+), 759 (26), 540 (33), 510 (30), 387 (41), 334 (41), 319 (33), 235 (30), 234 (67), 73 (41), 57 (60), 55 (82). Anal. Calcd for $C_{60}H_{54}$: C, 92.98; H, 7.02. Found: C, 92.87; H, 6.98.

***trans*-19,20-Dichloro-5,18:9,14-*o*-dibenzeno-5,7,9,14,16,18-hexahydro-7,16-ethanoheptacene (18).** A solution of pentiptycene 17[10,11] (0.53 g, 1 mmol) in 30 mL of a 1:1 mixture of *trans*-1,2-dichloroethene and decalin was heated in a sealed glass tube at 200 °C for 6 days. Removal of excess dichloroethene and decalin solvent (rotavap) and chromatography of the residue over silica gel using hexanes–CH_2Cl_2 (4:1) as eluent gave 0.13 g (24%) of recovered 17 and 0.36 g (76%) of **18**: mp 349–350 °C dec; ^1H NMR δ 3.97 (s, 2 H), 4.15 (s, 2 H), 5.30 (s, 2 H), 5.31 (s, 2 H), 6.82 (m, 4 H), 6.99 (m, 4 H), 7.21 (m, 4 H), 7.24 (s, 2 H), 7.30 (s, 2 H), 7.37 (m, 4 H); ^{13}C NMR δ 52.12, 53.89, 65.31, 119.83, 122.02, 123.37, 123.48, 123.73, 125.01, 125.12, 135.06, 136.95, 144.20, 144.37, 145.12. Anal. Calcd for $C_{44}H_{28}Cl_2$: C, 84.21; H, 4.50. Found: C, 84.05; H, 4.37.

9-Chloro-5,18:9,14-*o*-dibenzeno-5,7,9,14,16,18-hexahydro-7,16-ethenoheptacene (19). To a stirred solution of dichloride **18**, (1.26 g, 2 mmol) in 125 mL of DMSO/THF (4:1) was added 0.34 g (3 mmol) of potassium *tert*-butoxide at room temperature.

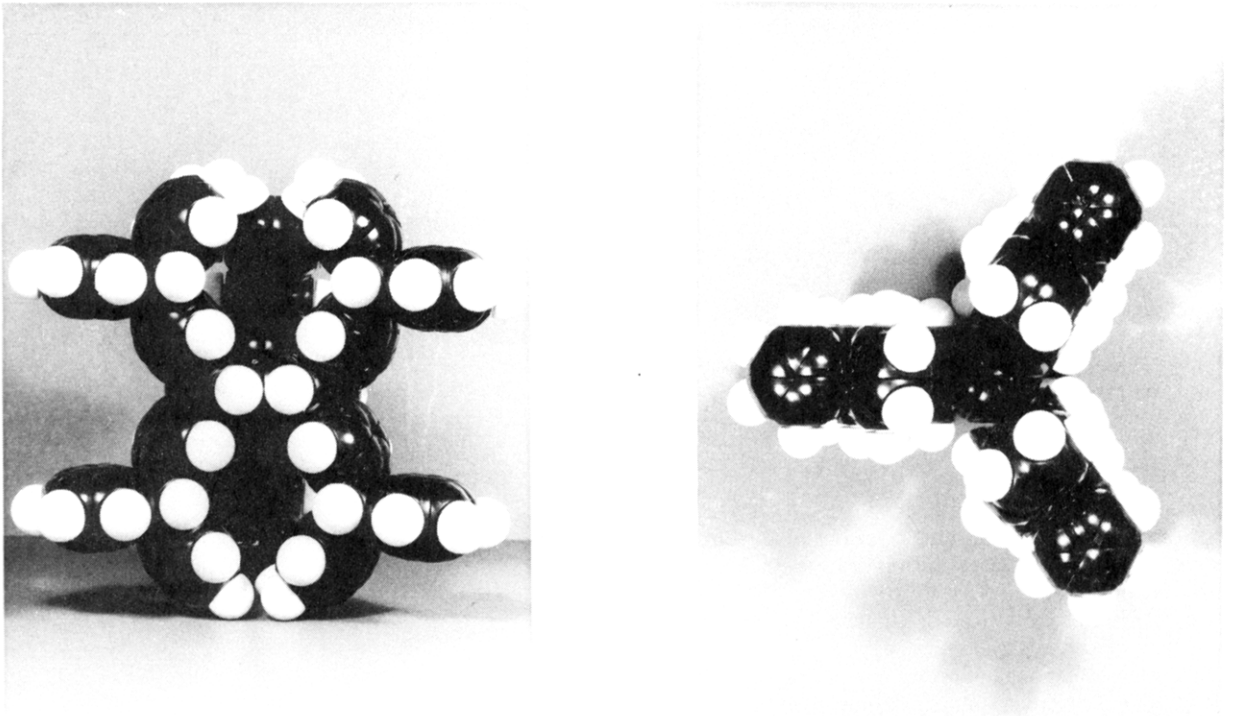


Figure 1. CPK model of **22**: side view showing cavities above and below the central benzene ring (left), and top view looking into one of the cavities, with the central benzene ring at the bottom of the cavity (right).

The mixture, which immediately turned brown, was stirred overnight, quenched with water (100 mL), and extracted with CH_2Cl_2. The organic layer was washed with water and saturated aqueous sodium chloride and dried. Removal of the solvent (rotavap) and recrystallization of the residue from hexanes–CH_2Cl_2 gave 1.03 g (87%) of **19**: mp 340 °C dec; ^{1}H NMR δ 4.72 (d, J = 2.18 Hz, 1 H), 4.82 (d, J = 6.4 Hz, 1 H), 5.24 (s, 2 H), 5.25 (s, 2 H), 6.59 and 6.61 (dd, J = 6.4, 2.18 Hz, 1 H), 6.83 (m, 4 H), 6.93 (m, 4 H), 7.21 (m, 4 H), 7.23 (s, 2 H), 7.28 (s, 2 H), 7.32 (m, 4 H); ^{13}C NMR δ 51.09, 53.88, 53.93, 58.33, 119.10, 119.35, 123.41, 124.97, 125.05, 132.85, 142.17, 142.70, 145.27, 145.67. Anal. Calcd for $C_{44}H_{27}Cl$: C, 89.40; H, 4.60. Found: C, 89.30; H, 4.55.

Trimerization of 19. To a stirred solution of **19** (0.60 g, 1 mmol) in 20 mL of THF under argon at −78 °C was added dropwise a hexane solution of butyllithium (1.1 equiv; 0.3 mL of a 2.5 M solution). After addition was complete, the mixture was allowed to slowly warm to room temperature, stirred for 2 h, and then heated at reflux for 30 min. The reaction was quenched with 1 mL of methanol. Solvent was removed (rotavap), the residue was extracted with CH_2Cl_2, and the extract was washed with water and saturated aqueous sodium chloride and dried. Removal of the solvent and chromatography of the residue over silica gel with CH_2Cl_2–hexanes (3:7) as eluent gave 0.13 g (22%) of recovered **19**, a trace of **17**,[10,11] 0.059 g (14%) of **20**, 0.11 g (25%) of **21**, and 0.009 g (2%) of **22**. For 5,18[1′,2′]:9,14[1″,2″]dibenzeno-7,16-etheno-5,7,9,14,16,18-hexahydroheptacene (**20**): mp 362 °C dec; ^{1}H NMR δ 4.91 (dd merged to a t, J = 3.2 Hz, 2 H), 5.23 (s, 4 H), 7.25 (s, 4 H), 6.82 (m, 6 H, 4 arom and 2 vinyl), 6.90 (m, 4 H), 7.21 (m, 4 H), 7.28 (m, 4 H); ^{13}C NMR δ 50.89, 53.85, 119.05, 123.27, 124.84, 139.79, 141.74, 143.52, 145.36, 145.63 (two arom overlapped); high-resolution mass spectrum calcd for $C_{44}H_{28}$ 556.30, found 556.22. For 20-chloro-5,5′,7,7′,9,9′,14,14′,16,16′,18,18′-dodecahydro-5,18[1′,2′]:9,14[1″,2″]:5′,18′[1‴,2‴]:9′,14′[1⁗,2⁗]tetrabenzeno-19,19′-bi(7,16-ethenoheptacene) (**21**); mp 358 °C dec; ^{1}H NMR δ 4.65 (s, 2 H), 4.84 (d, J = 6.1 Hz, 1 H), 5.10 (s, 2 H), 5.11 (s, 2 H), 5.17 (s, 2 H), 5.18 (s, 2 H), 5.48 (d, J = 1.4 Hz, 1 H), 6.78 (m, 8 arom H and 1 vinyl H), 6.80 (m, 8 H), 7.18 (m, 24 H); ^{13}C NMR δ 50.52, 51.42, 53.60, 55.35, 59.60, 118.56, 118.67, 119.02, 119.81, 123.08, 123.31, 124.69, 135.13, 139.05, 141.39, 141.56, 141.79, 141.91, 142.18, 142.76, 143.31, 145.10, 145.31, 145.41, 148.74. Anal. Calcd for $C_{88}H_{53}Cl$: C, 92.24; H, 4.66. Found: C, 92.16; H, 4.60. For 2,3:8,9:14,15:22,23:28,29:34,35-hexakis(9,10-dihydro-9,10-anthraceno)-5,6,11,12,17,18-hexahydro-5,18[1′,2′]:6,11-[1″,2″]:12,17[1‴,2‴]tribenzenotrinaphthylene (**22**): mp >400 °C; ^{1}H NMR (CD_2Cl_2) δ 5.17 (s, 12 H), 5.50 (s, 6 H), 6.80 (m, 24 H), 7.18 (m, 24 H), 7.24 (s, 12 H); ^{13}C NMR (CD_2Cl_2) δ 49.81, 53.79, 119.48, 123.45, 125.00, 134.86, 142.59, 142.96, 145.27, 146.01; high-resolution mass spectrum calcd for $C_{132}H_{78}$ 1662.61, found 1662.98.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE-87-12118) for a grant in support of this research.

Preparation of Aryl Chlorides from Phenols

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Received March 3, 1988

Very few methods have been reported in the literature for converting phenols directly into arylhalides. To our knowledge, only two such processes are available to accomplish this transformation. Bestmann and Schnabel[1] have found that chlorobenzene can be prepared from phenol via a phenylchloroformate intermediate produced by reaction with phosgene. This material can then be treated with triphenylphosphine, producing chlorobenzene in 67% yield by elimination of carbon dioxide. Unfortunately, triphenylphosphine remains with the product and must be deliberately removed.

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0022-3263/90/1955-3415$02.50/0