0 °C with an ice bath, and crystals of benzoic acid precipitated. The solid material was removed by filtration, and the filtrate was evaporated to dryness under vacuum. The residue was treated with 60 mL of acetone overnight, and the hygroscopic amine salt **21** solidified, collected by filtration, and washed with acetone. The yield of the white solid was 2.754 g (12.46 mmol, 92%): mp 150–151.5 °C; IR (Nujol) 3330, 2420, 1770, 1600 cm^{-1}; ^1H NMR (D_2O) δ 2.80 (s, 3, NCH_3), 4.20 (m, 1, CHOH), 5.25 (m, 1, CHOO); ^{13}C NMR δ 179.22 (C_2), 84.26 (C_{6a}), 73.80 (C_5), 42.07 (C_{3a}), 39.63, (C_6), 36.87 (C_3); mass spectrum, m/e 185 (M^+), 110, 44.

Conversion of the Lactone Amine Hydrochloride 21 into the Ene Aldehyde 1. A 50-mL, round-bottomed flask under nitrogen atmosphere was charged with the amine salt (1.0 g, 4.5 mmol) and 30 mL of methanol. Once the salt had dissolved, *tert*-butyl hypochlorite (550 mg, 9.2 mmol) was added, followed by solid sodium bicarbonate (375 mg, 4.46 mmol). After the mixture was stirred at room temperature for 1.5 h the solvent was removed under vacuum, and the product was isolated by chromatography on 100 g of silica gel (eluted with 3:7 acetone/hexane) to give **22** as a clear oil: 824 mg (3.76 mmol, 83.5% yield); IR (film) 3350, 2900, 1760, cm^{-1}; ^1H NMR δ 2.98 (s, 3, NCH_3), 4.07 (m, 1, CHOH), 5.04 (t, 1, CHOC).

To a solution of the *N*-chloro amine (825 mg, 3.77 mmol) in 20 mL of anhydrous ether was added a solution of sodium methoxide, made by solution of sodium (172 mg, 7.48 mmol) in 4 mL of methanol. There was an immediate precipitate, and the stirring was continued for 30 min at room temperature. An equal volume of 30% aqueous sulfuric acid was added, and the heterogeneous mixture was stirred overnight. The layers were separated, and the aqueous layer was extracted exhaustively with methylene chloride. The combined organic fractions were dried over sodium sulfate and evaporated to give the solid aldehyde **1** (234 mg, 1.54 mmol, 41%). Chromatography on silica gel (eluted with 40% acetone in hexane) gave the analytically pure sample: mp 49–51.5 °C; IR (CH_2Cl_2) 3700, 3050, 2740, 2840, 1780, 1680, 1170 cm^{-1}; ^1H NMR δ 2.75 (m, 2, CH_2CO), 2.95 (m, 2, $CH_2C{=}C$), 3.72 (br, 1, $CHC{=}C$), 5.21 (m, 1, CHOC), 6.89 (q, 1, $CH{=}$), 9.82 (s, 1, CHO); mass spectrum, m/e 152 (M^+), 124, 95, 79, 67. Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30; O, 31.55. Found: C, 63.39; H, 5.40.

This sample was compared with an authentic sample prepared according to the Corey route by thin-layer chromatography on silica gel (10% methanol in methylene chloride) as well as gas chromatography (6-ft column, 30% SE-30).

Acknowledgment. The authors thank Dr. L. Tokes, Ms. D. Chu, Mr. J. Smith, Dr. M. Maddox, Ms. J. Nelson, Ms. L. Kurz, and the Syntex Analytical Department for their expert help in obtaining the analytical data and Drs. J. Edwards, J. Moffat, and M. Marx for their suggestions and encouragement throughout the course of these research efforts.

Registry No. **1**, 75331-66-7; **3**, 26054-46-6; **5**, 75331-67-8; **5** disilyl ether, 75283-62-4; **6**, 75283-63-5; **6** benzoate, 75283-64-6; **7**, 75283-65-7; **8**, 75283-66-8; **9**, 75299-08-0; **11**, 75283-67-9; **11a**, 75331-68-9; **12**, 75283-68-0; **13a**, 75283-69-1; **13b**, 75283-70-4; **15a**, 75283-71-5; **15b**, 75283-72-6; **16**, 75283-73-7; **17a**, 75283-74-8; **17b**, 75283-75-9; **18**, 75283-76-0; **19**, 75331-69-0; **19** disilyl ether, 75363-08-5; **21**, 75283-77-1; **22**, 75283-78-2; chloro-*tert*-butyldimethylsilane, 18162-48-6; benzoyl chloride, 98-88-4; trimethyl orthoformate, 149-73-5; dimethoxymethane, 109-87-5; methylamine, 74-89-5; anisoyl chloride, 100-07-2; paraformaldehyde, 50-00-0; *n*-butylboronic acid, 4426-47-5; **17a** disilyl ether, 75283-79-3.

An Approach to the Synthesis of Unsymmetrically Substituted Chlorobiphenyls

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The Diels–Alder cycloaddition of *o*-chloranil with phenylacetylenes substituted with chlorine in the aryl ring can afford chlorobiphenyls upon photodecomposition of the bridged diketone adduct. Biphenyls derived from 3-chloro-, 4-chloro-, 2,4-dichloro-, and (2,5-dichlorophenyl)acetylene have been prepared by this route. These (chlorophenyl)acetylenes are available from the corresponding acetophenones. The applicability of this route suggests a general route to a number of biphenyls with 4–8 chlorines, which are not readily available by traditional biphenyl synthetic approaches. A further interest is the potential applicability of the route in providing specific homologues important in understanding the metabolic toxicology of chlorobiphenyls as a function of the distribution and number of chlorines present.

A central issue relating to the twin problems of chloro- and bromobiphenyls is to understand toxicological manifestations at the molecular level. Since toxicity varies with the number and pattern of halogen substitution, such understanding requires the use of pure compounds of diverse structural patterns, representing the 210 members each of the halobiphenyl series $C_{12}H_mX_n$ (m = 1 to 10, n = 10 − m). Very little work has been done in the bromo series. Except for some compounds in the chlorobiphenyl series which possess symmetry in substitution patterns in the two rings, studies have largely involved commercial mixtures or certain selected pure isomers.[1]

The synthesis of some of the symmetric chlorobiphenyl isomers is straightforward.[2] Approaches to unsymmetrically substituted analogues have not been widely pursued. Work described here illustrates the synthesis of five unsymmetrical congeners preparable unambiguously and in good yields without the presence of coproducts as impurities.

The method involves the photodecomposition of the Diels–Alder adduct **1**, formed from a (chlorophenyl)-acetylene and *o*-chloranil.[3] The preparation of dione adducts was accomplished by heating the appropriate chloro-substituted phenylacetylenes and *o*-chloranil at reflux in benzene solution for 12 h. Successful reactions were accomplished with (4-chlorophenyl)acetylene, (3-

(1) Conference Proceedings, National Conference on Polychlorinated Biphenyls, 1975 (published 1976), Environmental Protection Agency, Washington, DC, EPA 560/6-75-004; e.g., James D. McKinney "Toxicology of Selected Symmetrical Hexachlorobiphenyl Isomers: Correlating Biological Effects with Chemical Structure", pp 73–75. See also numerous contributions from "Health Effects of Halogenated Aromatic Hydrocarbons", W. J. Nicholson and J. A. Moore, Eds., *Ann. N.Y. Acad. Sci.* **320**, 0000 (1979).

(2) O. Hutzinger, S. Safe and V. Zitko, "The Chemistry of the PCB's", CRC Press, Cleveland, OH, 1974, Chapter 3, pp 41–71.

(3) (a) L. Horner and H. Merz, *Justus Liebigs Ann. Chem.*, **7**, 570 (1950); (b) J. L. Pyle, R. A. Lunsford, and J. S. Cantrell, *J. Org. Chem.*, **44**, 2391 (1979).

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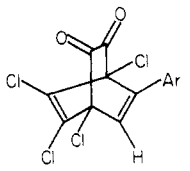
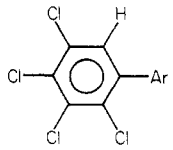


1a, Ar = C_6H_5
b, Ar = 4-chlorophenyl
c, Ar = 2,4-dichlorophenyl
d, Ar = 3-chlorophenyl
e, Ar = 2,5-dichlorophenyl

chlorophenyl)acetylene, (2,5-dichlorophenyl)acetylene, and (2,4-dichlorophenyl)acetylene. The yellow dione was isolated in each instance, by precipitation first as a hydrate or dihydrate, upon formation of which the color of the product turned white. The free dione may be regenerated by heating or by azeotropic removal of water in benzene solution. The crystalline diones showed infrared carbonyl absorptions (1773, 1754 cm^{-1}) and appropriate elemental analyses, with mass spectra identical with those of the analogous biphenyls, indicating facile loss of the bis CO bridge in the inlet of the mass spectrometer.

The preparation of the biphenyls (**2a–e**) was accom-



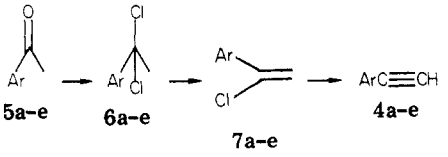
2a, Ar = C_6H_5
b, Ar = 4-chlorophenyl
c, Ar = 2,4-dichlorophenyl
d, Ar = 3-chlorophenyl
e, Ar = 2,5-dichlorophenyl

plished by irradiation of the diones in cyclohexane by a Coleman Model VII blue light source for 19 h. After solvent removal, purification of the product was carried out by column chromatography on silica gel, with CCl_4 as eluting solvent. This removed any traces of the unreacted dione. Beyond that reported previously[3] for **2a**, yields of recovered material for the chlorobiphenyls, after purification, from the dione were as follows: **2b**, 69%; **2c**, 55%; **2d**, 46%; **2e**, 62%. The products were identical with those prepared by alternate routes for **2b**,[4a] **2c**,[4b] and **2e**.[5]

In most instances the diones are prone to slow decomposition unless they are kept in the cold and dark. Hydrate formation is useful to avoid this problem and for facile workup.[3a] The formation of hydrates **3b–e** also proved beneficial in the purification of diones, by virtue of the fact that the hydrates are largely insoluble in nonpolar solvents (e.g., cyclohexane) and any unreacted *o*-chloranil could thereby be extracted. A purification cycle was so employed by adding water to the reaction product in refluxing benzene, giving a discolored hydrate (due to unreacted *o*-chloranil). The pure colorless hydrate could be obtained by washing out the impurities from the solid with cyclohexane. Azeotropic distillation, with removal of water via a Dean–Stark trap, then regenerated the dione.

The formation of the hydrates, **3**, appears to be quite sensitive to differences in nearby chlorine substitution patterns. Two hydrates were specifically examined in this respect. The dihydrate (**1b**·$2H_2O$) forms readily. The compound has complete absence of infrared absorptions in the carbonyl region—the precursor **1b** has two absorptions at 1773 and 1754 cm^{-1}—and evidence of intramolecular H-bonding in the form of a broad band centered at 3254 cm^{-1} exists. The elemental analysis confirms the dihydrate structure (see the Experimental Section).

Scheme I



5a–e **6a–e** **7a–e** **4a–e**

In the case of the dione **1c**, however, monohydrate formation is evidenced by the disappearance of one carbonyl band but not both (1770, 1754 cm^{-1} in the dione **1c**, but 1770 cm^{-1} only for **3c**). The elemental analysis of C, H, and Cl confirms the monohydrate in this instance. The structure of the monohydrate **3c** is on the basis that the more strained and more hindered carbonyl should be that cis to the phenyl substituent (see the Experimental Section).

The photodecomposition of the bridged diones was accomplished in benzene or cyclohexane solution by irradiation using various sources, of which the most effective was a General Electric Sunlamp (275 W), presumably owing to its stronger intensity, especially in the violet and near-UV region where the dione absorption maximum occurs (435 nm).

Recovery of crude product led to yields in the range of 90%. The biphenyls are readily purified by elution from a silica gel column with CCl_4 followed by sublimation, yielding pure product in good overall yields.

The (chlorophenyl)acetylenes **4a–e** used in this study were prepared from the corresponding chloroacetophenones **5a–e** according to the method described by Trompen and Huisman[6] (Scheme I). In this treatment, the acetophenone is converted to the α,α-dichloroethylbenzene (**6a–e**) by reaction with PCl_5. This product was converted, by double elimination of HCl, to the corresponding arylacetylene. This requires rigorous conditions in that the second elimination, from the α-chlorostyrenes (**7a–e**), is difficult, and the presence of the latter as an impurity in the final product is frequently encountered. This method is limited in yields. Additional problems potentially exist in the case of (halophenyl)acetylenes because of dehalogenation to benzynes and formation of α-styryl ethers arising from addition–elimination from the chlorostyrene **7b–e**.[7] Other approaches involving elimination processes may be applicable but have not yet been explored for (halophenyl)acetylenes.[8]

The synthesis of biphenyls from (halophenyl)acetylenes offers a facile alternative to other cycloaddition routes.[9] The opening of the dione ring by base with elimination of one chloride ion offers a route to congeners in the series A and B from the corresponding glyoxylates **8a** and **8b** by

(4) (a) E. T. McBee, W. R. Diveley, J. E. Burch, *J. Am. Chem. Soc.*, 77, 385 (1955); (b) S. Safe and O. Hutzinger, *J. Chem. Soc., Perkin Trans. 1*, 686 (1972).

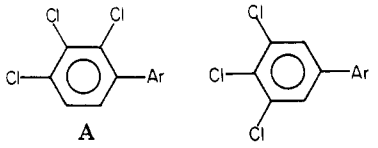
(5) M. Bolger, "Progress Reports on PCB Isomers", in Analabs Inc., Research Notes, Vol. 13, no. 3, Analabs Inc., North Haven, CT, 1973, p 18.

(6) W. P. Trompen and H. O. Huisman, *Recl. Trav. Chim. Pays-Bas*, 85, 167 (1966).

(7) G. Kobrich and P. Buck, "Synthesis of Acetylenes and Polyacetylenes by Elimination Reactions", in H. G. Viehe, "The Chemistry of Acetylenes", Marcel Dekker, New York, 1969.

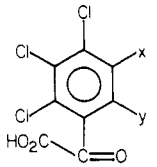
(8) (a) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972); (b) L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier Publishing Co., Amsterdam and New York, 1971, Chapter VI; (c) M. Yalpani, *Tetrahedron Lett.*, 1505 (1964); (d) I. Lalezari, A. Shatiee, and M. Yalpani, *Angew. Chem., Int. Ed. Engl.*, 9, 464 (1970).

(9) R. W. Hoffman and H. Hauser, *Tetrahedron Lett.*, 197 (1964); E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, 77, 6674 (1955).



A B

removal of the α-oxoglyoxylate moiety.[3b] The capabilities



8a, x = H; y = Ar
b, x = Ar; y = H

of the method could be further enhanced by the use of other orthoquinones containing dichloro and trichloro substitution, extending the scope further, provided that regioselectivity in the cycloaddition could be achieved. An obvious further example is that of *o*-bromanil, offering applicability of the approach to the synthesis of bromobiphenyls. Further, the synthesis of halonaphthalenes, fluorenones, and benzofurans may be envisaged from this route.

Experimental Section

o-Chloranil was prepared from pentachlorophenol according to established procedures.[10] Starting acetophenones (**5b–e**) were obtained from commercial sources (Eastman). Gas chromatography (GC) was performed on a Hewlett-Packard Model 700 chromatograph equipped with a thermal-conductivity detector. Infrared spectra (IR) were obtained with a Perkin-Elmer Model 237B infrared spectrophotometer. Liquid samples were run as thin films between CsI plates, and solid samples were taken both in Nujol mulls and in hexachlorobutadiene for complete coverage. Some low-melting solids were run neat as liquid melts. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6B spectrometer at 70 eV by using the direct inlet (DI). Nuclear magnetic resonance spectra (NMR) were obtained on a JEOL-C-60H spectrometer. Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1,4,5,6-Tetrachloro-2,2,3,3-tetrahydroxy-7-(4-chlorophenyl)bicyclo[2.2.2]octa-5,7-diene, 3b. A solution of (4-chlorophenyl)acetylene (**4b**; 5.0 g, 0.04 mol) and *o*-chloranil (9.7 g, 0.04 mol) in 150 mL of benzene was heated at reflux for 12 h. After volume reduction to 50 mL, an orange-red precipitate formed after 90 min at 60–65 °C. After the precipitate was washed with cyclohexane to remove *o*-chloranil, the impure adduct **1b** was purified by formation of the dihydrate **3b**, by adding 60 mL of benzene and 30 mL of water and heating at 65–75 °C for 2 h, giving a discolored orange solid. Further washing with cyclohexane gave, after air drying, a white amorphous powder. Additional hydrate was formed from overnight crystallization from the wet cyclohexane filtrates, giving a total yield of **3b** of 11.60 g, 76%. Above 100 °C, **3b** became yellow, indicating loss of water and regeneration of the dione **1b**, with melting of the yellow solid occurring at 129.5–131 °C. For **3b**: IR (Nujol or hexachlorobutadiene) 647, 679, 733, 1597, 3300 cm^{-1}; NMR (acetone-d_6) δ 7.46 (m, 4 H), 6.56 (d, J = 7.2 Hz, 1 H); mass spectrum, m/e (relative intensity) 334 (2), 332 (4), 330 (20), 328 (65), 326 (100), 324 (65).

Anal. Calcd for $C_{14}H_9Cl_5O_4$: C, 40.18; H, 2.16; Cl, 42.36. Found: C, 40.16; H, 1.99; Cl, 42.36.

1,4,5,7-Tetrachloro-7-(4-chlorophenyl)bicyclo[2.2.2]octa-5,7-diene-2,3-dione, 1b. The dihydrate **3b** in 200 mL of cyclohexane was azeotropically dehydrated. Crystallization under nitrogen gave a small quantity of solid dione: mp 129–130 °C; IR (Nujol or hexachlorobutadiene) 644, 751, 774, 1617, 1754, 1773, 3106 cm^{-1}; NMR (acetone-d_6) δ 7.55 (m, 4 H), 6.55 (d, J = 7.8 Hz, 1 H).

1,4,5,6-Tetrachloro-3,3-dihydroxy-7-(2,4-dichlorophenyl)bicyclo[2.2.2]octa-5,7-dien-2-one, 3c. A 60-mL combined benzene solution of (2,4-dichlorophenyl)acetylene (**4c**; 2.00 g, 0.01 mol) and *o*-chloranil (2.85 g, 0.01 mol) was heated at reflux for 12 h. After volume reduction to 20 mL, 10 mL of water was added and heating for 2 h at 80–85 °C produced a brittle red solid. This was mixed with 150 mL of cyclohexane and azeotropically dehydrated. Overnight crystallization gave 0.91 g of a white solid. The filtrate stood overnight with a small quantity of water, from which 2.91 g of additional crystalline hydrate was obtained. Total yield was 3.82 g (75.8% based on monohydrate formation). Heating above 110 °C produced a yellow solid: mp 169–170 °C; IR (Nujol or hexachlorobutadiene) 625–714, 1770, 3106, 3509 cm^{-1}; NMR (acetone-d_6) δ 7.40–7.72 (m, 3 H), 6.69 (d, J = 6.0 Hz, 1 H); mass spectrum, m/e (relative intensity) 366 (1.9), 364 (34), 362 (80), 360 (100), 358 (53).

Anal. Calcd for $C_{14}H_6Cl_6O_3$: C, 38.66; H, 1.39; Cl, 48.91. Found: C, 38.80; H, 1.41; Cl, 49.17.

1,4,5,6-Tetrachloro-7-(2,4-dichlorophenyl)bicyclo[2.2.2]octa-5,7-diene-2,3-dione, 1c. The dione **1c** was prepared by dehydration by mixing **3c** with 150 mL of cyclohexane and azeotropic distillation. Crystallization gave a bright yellow product (5.15 g, 70.5%). The melting point (170–171 °C) matched that of the hydrate: IR (Nujol) 647–787 (br) 1582, 1742, 1754, 1770 cm^{-1}; NMR (acetone-d_6) δ 7.45–7.85 (m, 3 H), 6.71 (d, J = 6.7 Hz, 1 H).

Anal. Calcd for $C_{14}H_4Cl_6O_2$: C, 40.33; H, 0.97. Found: C, 39.94; H, 1.02.

1,4,5,6-Tetrachloro-7-(3-chlorophenyl)bicyclo[2.2.2]octa-5,7-diene-2,3-dione, 1d. A solution of (3-chlorophenyl)acetylene (**4d**; 2.00 g, 0.01 mol) and *o*-chloranil (3.9 g, 0.15 mol) in 70 mL of benzene was reacted as for the adduct **1c**. The residue was dried under vacuum (0.3 torr), giving an impure golden-yellow product which was carried forward without further purification: mp 45–60 °C; 4.49 g (80.6%); IR 1757, 3460 cm^{-1}; mass spectrum, m/e (relative intensity) 332 (5.7), 330 (21), 328 (65), 326 (100), 324 (63).

1,4,5,6-Tetrachloro-7-(2,5-dichlorophenyl)bicyclo[2.2.2]octa-5,7-diene-2,3-dione, 1e. Benzene solutions (20 mL) of (2,5-dichlorophenyl)acetylene (**4e**; 1.1 g, 0.006 mol) and *o*-chloranil (1.6 g, 0.006 mol) were reacted as for the adduct **1c**. The residue was recrystallized from cyclohexane: 1.00 g (37.3%); mp 187–189 °C; IR (Nujol or hexachlorobutadiene) 621–778 (br), 1799, 3076 cm^{-1}; NMR (acetone-d_6) δ 7.61 (m, 3 H), 6.72 (d, J = 6 Hz, 1 H); mass spectrum, m/e (relative intensity) 368 (1.4), 366 (8.6), 364 (35), 362 (80), 360 (100), 358 (53).

Anal. Calcd for $C_{14}H_4Cl_6O_2$: C, 40.33; H, 0.97; Cl, 51.02. Found: C, 40.37; H, 0.84; Cl, 51.02.

2,3,4,4′,5-Pentachlorobiphenyl, 2b. Compound **1b** (7.11 g, 0.019 mol), generated by azeotropic dehydration of 7.79 g of the dihydrate **3b**, was photolyzed, in a quartz irradiation vessel for 24 h under a nitrogen atmosphere with stirring in 200 mL of cyclohexane, with a General Electric visible flood lamp. Removal of the solvent gave a brown solid, mp 93–97 °C. Column chromatography using silica gel and CCl_4 as the eluting solvent gave good separation of the biphenyl product: 4.19 g (69.4%); mp 98.5–99.5 °C (lit.[4a] mp 98–99 °C); IR (neat) 650, 713, 729, 737, 2924, 3067 cm^{-1}; NMR (CCl_4) δ 7.39–7.48 (m); mass spectrum, m/e (relative intensity) 334 (2.1), 332 (4.0), 330 (19), 328 (64), 326 (100), 324 (64).

Anal. Calcd for $C_{12}H_5Cl_5$: C, 44.15, H, 1.54; Cl, 54.30. Found: C, 44.19; H, 1.47; Cl, 54.15.

2,2′,3,4,4′,5-Hexachlorobiphenyl, 2c. Compound **1c** (3.93 g, 9.42 mmol) in 150 mL of benzene was irradiated by a General Electric sunlamp for 5.5 h. The result was treated as for **1b** above, yielding a light yellow solid, mp 67–71 °C, which was sublimed to give **2c**: 3.14 g (92.4%); mp 77–79 °C (lit.[4b] mp 77–78 °C); IR (neat) 656, 685, 786, 3077 cm^{-1}; NMR (CCl_4) δ 7.30 (m); mass spectrum, m/e (relative intensity) 366 (7.6), 364 (32), 362 (81), 360 (100), 358 (56).

2,3,3′,4,5-Pentachlorobiphenyl, 2d. Compound **1d** was carried forward from the cycloaddition reaction (vide supra) and 354.9 mg (9.28 × 10^{-4} mol) in 20 mL of cyclohexane was irradiated in

(10) A. Rocklin, U.S. Patent 2920082 ("Halo-*o*-quinones"), 1960; *Chem. Abstr.*, **54**, 10959*i* (1960).

a quartz vessel with a Coleman Model VII M blue light source for 19 h. Workup as previously indicated gave a clear slightly yellow mobile oil. Overnight drying under vacuum (0.3 torr) gave an off-white solid (139.5 mg), of which 106.7 mg was sublimed, giving 103.6 mg of **2d** (44.7%): mp 85–87 °C; IR (neat) 677, 697, 722, 750, 788, 2874, 2933, 3067 cm^{-1}.

Anal. Calcd for $C_{12}H_5Cl_5$: C, 44.15; H, 1.54; Cl, 54.30. Found: C, 44.30; H, 1.61; Cl, 54.30.

2,2',3,4,5,5'-Hexachlorobiphenyl, 2e. Compound **1e** (122.2 mg, 2.9×10^{-4} mol) was irradiated in 5 mL of benzene solution with a Coleman Model VII M blue light for 12 h. Solvent removal gave a crude residue, mp 85–88 °C, which upon sublimation of 115.9 mg gave 65.5 mg (62%) of **2e**: mp 88–89.5 °C (lit.[5] mp 89–91 °C); IR (neat) 645, 687, 722, 769, 3096 cm^{-1}; NMR (CCl_4) δ 7.42 (m); mass spectrum, *m/e* (relative intensity) 366 (8.9), 364 (35), 362 (80), 360 (100), 358 (53).

Anal. Calcd for $C_{12}H_4Cl_6$: C, 39.94; H, 1.12; Cl, 58.94. Found: C, 39.86; H, 1.19; Cl, 59.02.

(4-Chlorophenyl)acetylene, 4b. Compound **4b** was prepared according to Scheme I. A solution of **5b** (50 g, 0.32 mol) and hydroquinone (0.35 g, 0.003 mol) was frozen in an ice–salt water bath, and PCl_5 (72 g, 0.35 mol) was added to the solid mixture. When the mixture was warmed to 25 °C under a reflux condenser equipped with a $CaCl_2$ tube, evolution of HCl commenced. The reaction mixture was maintained with stirring at 63–75 °C for 75 min, filtered, and distilled in vacuo, giving $POCl_3$ [bp 30–38 °C (17 torr)] and a fraction, bp 121–124 °C (17 torr), which was mixed with a solution of KOH (75 g, 1.34 mol) in 300 mL of 95% ethanol, heated to reflux for 12 h, and steam distilled into ice. Suction filtration and air drying gave crystalline **4b**: 10.6 g (24%); mp 44–45 °C (lit.[6] mp 41–43 °C); IR (neat) 625–700 (br), 780, 825, 2288, 3278 cm^{-1}; mass spectrum, *m/e* (relative intensity) 138 (33), 136 (100), 101.

(3-Chlorophenyl)acetylene, 4d. Compound **4d** was prepared from the corresponding acetophenone **5d** (30 g, 0.19 mol) and hydroquinone (0.40 g, 0.009 mol), as for **4b** above, according to the method of Trompen and Huisman.[6] After steam distillation into ice, the organic distillate separated as a second liquid phase. The entire volume was extracted with ether, and the ethereal solution dried over Na_2SO_4. Fractional distillation of the residue under vacuum gave **4d**, bp 77–79 °C (19 torr) [lit.[11] bp 64–65 °C (12 torr)], pure by gas chromatography: 2.17 g (8.2%); IR (neat) 625–775 (br), 680, 748, 2985, 3400 cm^{-1}; NMR (CCl_4) δ 3.16 (s, 1 H), 7.29–7.58 (m, 4 H); mass spectrum, *m/e* (relative intensity) 138 (40), 136 (100), 101.

(2,4-Dichlorophenyl)acetylene, 4c. Compound **5c** (11.5 g, 0.06 mol), hydroquinone (0.13 g, 0.001 mol), and PCl_5 (12.7 g, 0.06 mol) were reacted as for **4b** above. After treatment with KOH, the reaction mixture was poured over ice with stirring, suction filtered, and washed with water, giving an orange solid. Sublimation gave 3.4 g of white crystalline **4c** (33%): mp 52–55 °C; IR (neat) 676, 698, 707, 824, 862, 2299, 3086, 3300 cm^{-1}; NMR (CCl_4) δ 3.37 (s, 1 H), 7.37 (m, 3 H); mass spectrum, *m/e* (relative intensity) 174 (100), 172 (66), 170 (11), 135, 100.

(2,5-Dichlorophenyl)acetylene, 4e. A solution of **5e** (10.0 g, 0.05 mol) and hydroquinone (0.10 g, 0.009 mol) was reacted as for the preparation of **4b**. Upon steam distillation into ice, the product crystallized. Suction filtration and air drying gave **4e**: 1.22 g (13%); mp 38–41 °C (lit.[12] 40 °C); IR (neat) 625–700 (br), 633, 680, 694, 708, 2262, 3021, 3096, 3300 cm^{-1}; mass spectrum, *m/e* (relative intensity) 174 (100), 172 (47), 170 (11), 135, 100.

Registry No. **1a**, 22612-94-8; **1b**, 75717-71-4; **1c**, 75717-72-5; **1d**, 75717-73-6; **1e**, 75717-74-7; **2a**, 33284-53-6; **2b**, 74472-37-0; **2c**, 35694-06-5; **2d**, 70424-69-0; **2e**, 52712-04-6; **3b**, 75717-75-8; **3c**, 75731-92-9; **3d**, 75717-76-9; **3e**, 75731-93-0; **4a**, 536-74-3; **4b**, 873-73-4; **4c**, 75717-77-0; **4d**, 766-83-6; **4e**, 38417-89-9; **5a**, 1334-78-7; **5b**, 99-91-2; **5c**, 2234-16-4; **5d**, 99-02-5; **5e**, 2476-37-1; *o*-chloranil, 2435-53-2; pentachlorophenol, 87-86-5.

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Six-Membered-Ring Annulation via a Conjugate Addition/Alkylation Sequence Using Functionalized Aryllithium Reagents and Vinyl Sulfones[1]

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A new method, which is a one-flask procedure involving addition of substituted aryllithium reagents **6** to vinyl sulfones **8** and **9** followed by spontaneous intramolecular alkylation of the resulting α-lithio sulfones, has been developed for the annulation of tetrahydronaphthalene moieties onto preexisting carbon frameworks. The aryllithium reagents employed in this study are the previously investigated intermediates obtained by the chemoselective lithium–halogen exchange reactions of simple as well as oxygenated *o*-halo-β-phenethyl halides **5**. The annulation products **11** and **12** may be subjected to various further transformations which should make the overall sequences of considerable utility in the synthesis of steroids and other polycyclic systems.

Because of the widespread occurrence of six-membered carbocyclic rings as structural units of several classes of important natural products, we have been investigating new methods to complement the presently available procedures for the construction of cyclohexane-containing systems.[2] In particular, we have been interested in developing pathways for the annulation of six-membered rings onto preexisting ring systems that would be appli-

(1) This work was described in part at the 179th National Meeting of the American Chemical Society, Houston, TX, Mar 1980, Abstract No. ORGN 128.

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