Experimental Section[15]

7,7-Dimethoxy-1,2,3,4-tetrachlorobenznorbornadiene (2).—A mixture of 24.3 g (0.092 mol) of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene,[4] 5.67 g (0.031 mol) of 2-carboxybenzenediazonium chloride, 250 ml of 1,2-dichloroethane, and 7 ml of propylene oxide was stirred at reflux for 2 hr. The solvent was removed on a rotary evaporator and the residue was chilled until crystalline. Recrystallization from isooctane gave 2.1 g of **2**, mp 121–123°; a second crop, 0.3 g, mp 110–114° was obtained. Distillation of the mother liquor at 85–92° (2–3 mm) afforded 6.93 g of starting material. Chromatography of the residue on standard alumina using 20% benzene–hexane followed by treatment as before gave 2.7 g of product (5.1 g overall, 49% based on diazonium salt) and 7.64 g of starting material. Three recrystallizations from isooctane gave analytically pure **2** as white crystals: mp 123–124°; nmr (CCl_4) τ 6.82 (3, s), 6.42 (3, s), 2.5–2.9 (4, m).

Anal. Calcd for $C_{13}H_{10}O_2Cl_4$: C, 45.89; H, 2.96; Cl, 41.73. Found: C, 46.12; H, 3.02; Cl, 41.75.

Thermal Fragmentation of 7,7-Dimethoxy-1,2,3,4-tetrachlorobenznorbornadiene (2). **A. Nonpolar Solvent.**—A quantity of **2** was dissolved in hexachlorobutadiene, placed in an nmr tube, and immersed in a constant-temperature bath. Periodic analysis revealed no change in the spectrum up to 14 hr at 100°. After 20 hr at 150–160°, *ca.* 25% of the starting ketal still remained. Immersion of the tube in boiling decalin (bp 193°) for 2 hr resulted in the formation of crystalline material which negated further nmr examination. On the preparative scale 0.300 g (0.882 mmol) of **2** and 4 ml of freshly distilled decalin (bp 193°) were refluxed for 2 hr. At the end of this time, the reaction was cooled to room temperature and 0.123 g of white needles, mp 195–197°, was collected by filtration and washed with hexane. Chromatography of the combined filtrate on silica gel using hexane afforded decalin and another component. Elution with benzene gave 0.030 g of a heavy yellow oil, the major portion of which (55%) consisted of methyl 2,3,4-trichloro-1-naphthoate (**7**): nmr (CCl_4) τ 6.00 (3, s), 2.40 (3, m), 1.75 (1, m); $\nu_{C=O}$ 1725 cm^{-1}. Elution with ether gave 0.023 g of a heavy yellow oil whose nmr suggested it contained products originating from the extruded dimethoxymethano bridge. Rechromatography of the hexane fraction on alumina to remove decalin gave on elution with benzene 0.097 g of white solid, identical with the initially isolated white needles and with authentic 1,2,3,4-tetrachloronaphthalene (**8**) prepared by the acid hydrolysis of **2**. The overall yield of **8** from thermolysis of **2** was 0.220 g (93.6%): nmr ($CDCl_3$) τ 2.4 (2, m) and 1.8 (2, m).

B. Polar Solvent.—A mixture of 75 mg of **2** (0.22 mmol) and 1 ml of acetonitrile was sealed in a nmr tube and immersed in a constant-temperature bath at 115°. Periodic analysis of the nmr spectrum revealed the formation of a new singlet at τ 6.00. Determination of the relative integral ratios of the original methyl absorptions of **2** and that of the new singlet with time provided an approximate rearrangement rate of 3×10^{-6} sec^{-1}. After 44 hr (0.7 half-lives), the contents of the nmr tube were sealed in a thick-walled Carius tube and heated in an oil bath at 145–155° for 14 hr. Removal of solvent gave 52 mg of yellow-white crystals whose nmr spectrum indicated that the material was predominantly methyl ester **7**. Chromatography on silica gel with hexane afforded 8 mg of white solid whose ir spectrum was identical with that of authentic **8**. Further elution with benzene afforded 41 mg of yellow-white crystals, mp 90–92°. Recrystallization from *n*-hexane gave mp 96.5–97.5°. Analysis of the nmr and ir spectra confirmed that the product was methyl 2,3,4-trichloro-1-naphthoate (**7**).

Anal. Calcd for $C_{12}H_7O_2Cl_3$: C, 49.78; H, 2.42. Found: C, 49.99; H, 2.51.

Thermal Fragmentation of 7,7-Dimethoxy-1,2,3,4-tetrachloronorbornadiene (4a).—A quantity of **4a**[6] was dissolved in hexachlorobutadiene, placed in an nmr tube, and immersed in a constant-temperature bath at 100°. Analysis of the spectrum after 3 hr revealed complete disappearance of the vinylic protons for **4a**.

Dechlorination of 2.—To a vigorously stirred mixture of 6.0 g (0.018 mol) of **2**, 14.7 g of *tert*-butyl alcohol (distilled from sodium) and 105 ml of tetrahydrofuran (distilled from lithium aluminum hydride), there was added, in an argon atmosphere, 10.9 g (0.471 g-atom) of freshly cut sodium metal. The mixture was stirred at reflux for 8.5 hr and methanol then added cautiously to destroy excess sodium. The reaction was poured onto 200 g of ice and the reaction flask was washed with 200 ml of water. The mixture was extracted with three 100-ml portions of ether and the combined extracts were washed with three portions of water and one portion of saturated NaCl solution. The ethereal solution was dried over $MgSO_4$ and filtered. Removal of solvent on a rotary evaporator gave a yellow oil which, upon chilling, gave 0.4 g of white crystals, mp 43–45°, after thorough washing with hexane. Distillation of the mother liquor at 83–86° (1.5–2.0 mm) gave 2.6 g (3.0 g overall, 84%) of a colorless oil whose nmr spectrum was identical with that of the white crystals. Glpc analysis at 150° (5 ft × $^1/_8$ in. 5% SE-30 column) indicated the presence of two components in *ca.* equal proportions, data consistent with nmr integral ratios. Attempted separations by column chromatography and $AgNO_3$ partition extraction were only partially successful. The nmr (CCl_4) spectrum of 7,7-dimethoxybenznorbornadiene showed the methoxy protons as singlets at τ 7.08 and 6.88, two bridgehead protons as a triplet at 6.17, two olefinic protons as a triplet at 3.45, and four aromatic protons as an A_2B_2 multiplet at 3.01.

7,7-Dimethoxybenznorbornene (9).—A 3.28-g sample of the dechlorinated ketal mixture (estimated to contain 1.64 g, 8.1 mmol, of unsaturated ketal) in 30 ml of methanol was hydrogenated at room temperature with 150 mg of 10% Pd/C as catalyst. Hydrogenation was complete in about 35 min with an uptake of about 225 ml (*ca.* 10 mmol) of hydrogen. The solution was filtered through a pad of Celite, and, on removal of solvent, a brownish oil was obtained. Chromatography on standard alumina with hexane gave 2.5 g (76%) of a colorless oil which solidified upon standing, mp 45–48°. Two recrystallizations from petroleum ether (bp 20–40°) gave 7,7-dimethoxybenznorbornene (**9**): mp 54–54.8°; nmr ($CDCl_3$) τ 8.86 (2, m), 7.90 (2, m), 6.91 (3, s), 6.81 (5, broad singlet), 2.96 (4, s).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.54; H, 7.98.

7-Benznorbornenone (10).—A mixture of 150 mg (0.735 mmol) of ketal **9**, 4 ml of tetrahydrofuran, and 2 ml of concentrated H_2SO_4 was stirred at room temperature for 2 hr. At the end of this time, the dark red solution was poured into water and the aqueous mixture was extracted three times with ether. The combined extracts were dried and filtered, and the solvent was removed on a rotary evaporator to give a dark yellow oil which was percolated through a column of standard alumina with ether. Removal of solvent gave 0.101 g (87%) of 7-benznorbornenone (**10**) [nmr (CCl_4) τ 2.83 (4, s), 6.75 (2, t), 7.87 (2, m), 8.68 (2, m)], identical with an authentic sample prepared by chromium trioxide oxidation of *anti*-7-benznorbornenol, mp 101–103° (lit.[13] mp 103–104°), obtained from catalytic hydrogenation of *anti*-7-benznorbornadienol.[3] The 2,4-dinitrophenylhydrazone of **10** gave yellow crystals from ethanol, mp 152–152.5° (lit.[13] mp 143.6–146.4°).

Registry No.—**2**, 24472-15-9; **7**, 29261-09-4; **9**, 29370-70-5; **10**, 6165-88-4.

Acknowledgment.—Support of this work by the National Science Foundation (GP-9412) is gratefully acknowledged.

(15) Melting points were determined with a Thomas-Hoover apparatus. All melting and boiling points were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Atlantic Microlab, Inc., Atlanta, Ga. Vapor phase chromatographic analyses were performed with an Aerograph Model 600-D instrument equipped with a hydrogen flame ionization detector. Infrared spectra were recorded on either a Perkin-Elmer 137 or Beckman IR-10 instrument. Solid samples were examined as Nujol mulls while liquid samples were examined neat on sodium chloride plates. Nmr spectra were obtained on a Varian A-60A instrument using tetramethylsilane as an internal reference. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E instrument.

Synthesis of Dithienothiophenes

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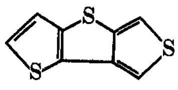
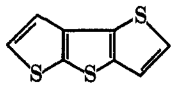
Recently we reported the synthesis of four of the six possible dithienothiophene isomers.[1] The two remain-

(1) F. de Jong and M. J. Janssen, *J. Org. Chem.*, **36**, 1645 (1971).

ing compounds **1** and **2** could not be prepared by the same procedure because of the instability of 2-bromo-3-thienyllithium.[2] Selective bromination reactions have been used now to prepare dithieno[3,2-*b*:3′,4′-*d*]thiophene (**1**) and dithieno[2,3-*b*:2′,3′-d]thiophene (**2**).

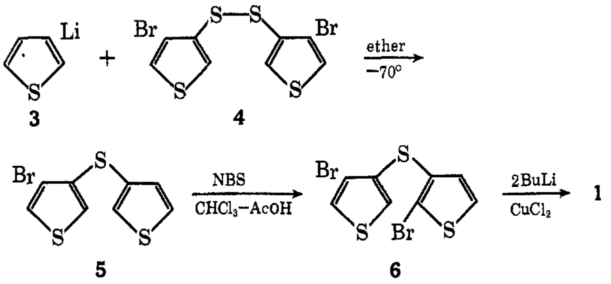


1

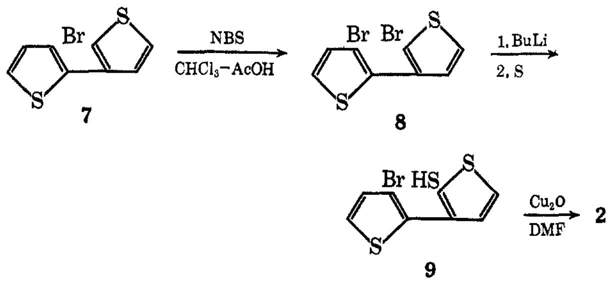


2

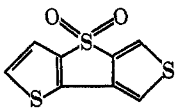
From the reaction of 3-thienyllithium[3] (**3**) with 4,4′-dibromo-3,3′-dithienyl disulfide[1] (**4**) in ether at −70°, 4-bromo-3,3′-dithienyl sulfide (**5**) was isolated. Treatment of sulfide **5** with *N*-bromosuccinimide (NBS) in a chloroform–acetic acid mixture[4] afforded 2,4′-dibromo-3,3′-dithienyl sulfide (**6**). The nmr spectrum confirmed that bromination had occurred in the 2 position, since two pairs of doublets were observed with J = 3.4 Hz (2,5 coupling) and J = 5.6 Hz (2,3 coupling). Dilithiation of **6** followed by oxidative ring closure gave the dithienothiophene **1** in 13% overall yield. The compound was characterized by elementary analysis and the nmr spectrum showed the correct coupling constants ($J_{2,3}$ = 5.1 and $J_{2,5}$ = 2.5 Hz).



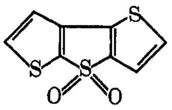
Dithieno[2,3-*b*:2′,3′-*d*]thiophene (**2**) was prepared starting from 3-bromo-2,3′-dithienyl (**7**).[5] On treatment with *N*-bromosuccinimide **7** was almost quantitatively converted to 2,3′-dibromo-3,2′-dithienyl (**8**), which on monolithiation followed by reaction with sulfur yielded the intermediate thiol, presumably **9**. Because of thermal instability, the thiol was not isolated but directly treated with cuprous oxide in dimethylformamide[6] to give dithienothiophene **2** in 65% overall yield. The structure of **2** was supported by elementary analysis and its nmr spectrum, showing two AB systems with J = 5.0 Hz (2,3 coupling).



In the case of the other four dithienothiophenes, the sulfur atom of the central ring has been proved[1] to be the most reactive toward oxidizing agents. In accordance with these results, compounds **1** and **3** were oxidized by *m*-chloroperbenzoic acid to the corresponding sulfones **10** and **11**, as was indicated by the ir spectra (SO_2 absorptions at 1130 and 1300 cm^{-1}) and the nmr spectra ($J_{2,3}$ and $J_{2,5}$ do not change significantly upon oxidation).



10



11

Experimental Section

All experiments with lithio compounds were conducted in a dry N_2 atmosphere. Melting points are uncorrected. Nmr spectra were recorded on a Varian A-60 instrument with TMS as internal standard. Uv spectra were determined with a Zeiss PMQ II and infrared spectra were run on a Unicam SP 200. The microanalyses were carried out in the analytical section of this department under direction of Mr. W. M. Hazenberg.

4-Bromo-3,3′-dithienyl Sulfide (5).—A solution of 3-thienyllithium was prepared at −70° from 21.3 g (0.13 mol) of 3-bromothiophene[7] in 250 ml of absolute ether and 100 ml of 1.3 *N* ethereal *n*-BuLi (0.13 mol). The mixture was transferred to an externally cooled dropping funnel and added during 30 min to a stirred suspension of 50.0 g (0.13 mol) of the disulfide **4** cooled to −70°. After stirring at −70° for 2.5 hr, the mixture was allowed to warm and 200 ml of water was added. The ether layer was separated, washed with water, dried ($MgSO_4$), and concentrated. Distillation of the residue yielded 29.0 g (80%) of **5**: bp 132–134° (0.04 mm); $n^{20}D$ 1.6930; nmr (CD_3COCD_3) δ 7.0–7.5 (m); uv max (EtOH) 265 mμ (log ε 3.67).

Anal. Calcd for $C_8H_5S_3Br$: C, 34.66; H, 1.82; S, 34.70; Br, 28.83. Found: C, 34.96; H, 2.00; S, 34.50; Br, 29.19.

2,4′-Dibromo-3,3′-dithienyl Sulfide (6).—To a stirred solution of 15.0 g (0.054 mol) of **5** in 500 ml of a mixture of chloroform–acetic acid (1:1) was added in small portions 9.8 g (0.055 mol) of *N*-bromosuccinimide. The mixture was stirred at room temperature for 3 hr, then water was added, and the chloroform layer separated, washed with aqueous KOH solution, again with water, and dried ($MgSO_4$). Evaporation of the solvent left a solid residue which was recrystallized from ether–pentane (1:1) yielding 16 g (84%) of **6**: mp 33–34°; nmr (CD_3COCD_3) δ 7.63 (d, 1, J = 5.8 Hz), 7.37 (d, 1, J = 5.8 Hz), 7.50 (d, 1, J = 3.4 Hz), 6.78 (d, 1, J = 3.4 Hz); uv max (EtOH) 234 mμ (log ε 3.96), 278 (3.72).

Anal. Calcd for $C_8H_4S_3Br_2$: C, 26.98; H, 1.13; S, 27.01; Br, 44.88. Found: C, 27.02; H, 1.27; S, 26.74; Br, 45.03.

Dithieno[3,2-*b*:3′,4′-*d*]thiophene (1).—To a solution of 16.0 g (0.045 mol) of sulfide **6** in 150 ml of absolute ether cooled to −70° was added 70 ml of a 1.3 *N* ethereal *n*-BuLi solution (0.091 mol). After stirring at −70° for 30 min, the mixture was transferred to an externally cooled (−70°) dropping funnel and added in a slow stream to a vigorously stirred suspension of 17 g (0.10 mol) of anhydrous $CuCl_2$ in 250 ml of absolute ether cooled to −30°. The mixture was stirred overnight, water was added, and the Cu_2Cl_2 precipitation was filtered. The ether layer was separated, washed with 2 *N* HCl and then water, and dried ($MgSO_4$). After evaporation of the ether, the residual oil was purified through the picrate yielding 1.7 g (19%) of **1** as colorless needles from methanol: mp 55–55.5°; nmr (CD_3COCD_3) δ 7.63 (d, 1, J = 2.5 Hz), 7.52 (d, 1, J = 2.5 Hz), 7.58 (d, 1, J = 5.1 Hz), 7.22 (d, 1, J = 5.1 Hz); uv max (EtOH) 223 mμ (log ε 3.95), 250 (4.02), 265 (3.96), 285 (4.11), 296 (4.16), 315 (3.69).

Anal. Calcd for $C_8H_4S_3$: C, 48.95; H, 2.06; S, 49.00. Found: C, 49.13; H, 2.08; S, 48.98.

2,3′-Dibromo-3,2′-dithienyl (8).—From 4.40 g (0.018 mol) of 3-bromo-2,3′-dithienyl[5] and 3.2 g (0.018 mol) of *N*-bromosuccinimide, the procedure described for the synthesis of **6** yielded 4.8 g (83%) of **8**: mp 54–55° (from methanol); nmr ($CDCl_3$) δ 7.28 (d, 1, J = 5.2 Hz), 7.08 (d, 1, J = 5.2 Hz), 7.33 (d, 1, J = 5.5 Hz), 7.03 (d, 1, J = 5.5 Hz); uv max (EtOH) 242 mμ (log ε 4.10), 285 (3.59).

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(6) E. Jones and I. M. Moodie, *Tetrahedron*, **21**, 2413 (1965).

(7) S. Gronowitz, *Acta Chem. Scand.*, **13**, 1045 (1959).

Anal. Calcd for $\mathrm{C_8H_4Br_2S_2}$: C, 29.65; H, 1.24; S, 19.79; Br, 49.32. Found: C, 29.89; H, 1.40; S, 19.78; Br, 49.40.

2-Mercapto-3′-bromo-2′,3-dithienyl (9).—To a solution of 3.89 g (0.012 mol) of dithienyl **8** in 125 ml of absolute ether cooled to −70° was added 7.5 ml of a 1.6 *N* ethereal *n*-BuLi solution (0.012 mol). The mixture was stirred for 45 min and then 0.42 g (0.013 mol) of dry sulfur was added and stirred for another 45 min at −30°. After addition of water, the ether layer was extracted with 100 ml of 2 *N* NaOH solution. The combined aqueous layers were acidified and extracted with ether; the ether layer was washed with water and dried ($\mathrm{MgSO_4}$). Evaporation of the ether left 2.9 g (88%) of a yellow oil. Further attempts of purification led to decomposition: nmr ($\mathrm{CD_3COCD_3}$) δ 7.65 (d, 1, J = 5.3 Hz), 7.11 (d, 1, J = 5.3 Hz), 7.17 (d, 1, J = 5.3 Hz), 7.57 (d, 1, J = 5.3 Hz), 3.08 (s, 1, SH); ir (liquid) 2550 $\mathrm{cm^{-1}}$ (SH).

Dithieno[2,3-*b*:2′,3′-*d*]thiophene (2).—To a suspension of 0.54 g (9.5 mmol) of KOH and 0.62 g (4.8 mmol) of $\mathrm{Cu_2O}$ in 300 ml of dry dimethylformamide (DMF) was added during 1 hr a solution of 2.60 g (9.4 mmol) of freshly prepared thiol **8** in 20 ml of dry DMF. The mixture was heated under reflux for 45 hr. Most of the DMF was removed *in vacuo* and the residue dissolved in a benzene–pentane (1:1) mixture. The solution was washed with 4 *N* HCl solution and water and dried ($\mathrm{MgSO_4}$). Evaporation left a white solid which on recrystallization from ether–hexane yielded 1.65 g (90%) of the dithienothiophene **2**: mp 53–54°; nmr ($\mathrm{CD_3COCD_3}$) δ 7.42 (d, 1, J = 5.0 Hz), 7.60 (d, 1, J = 5.0 Hz), 7.36 (d, 1, J = 5.0 Hz), 7.52 (d, 1, J = 5.0 Hz); uv max (EtOH) 253 mμ (log ϵ 4.30), 266 (4.23), 278 (4.06).

Anal. Calcd for $\mathrm{C_8H_4S_3}$: C, 48.95; H, 2.06; S, 49.00. Found: C, 48.91; H, 2.12; S, 48.70.

Dithieno[3,2-*b*:3′,4′-*d*]thiophene 4,4-Dioxide (10).—A solution of 175 mg (0.9 mmol) of dithienothiophene **1** and 350 mg (2.0 mmol) of *m*-chloroperbenzoic acid in 50 ml of dry dichloromethane was allowed to stand 14 hr at −15°. The solution was washed with 25 ml of a saturated $\mathrm{NaHCO_3}$ solution and water and dried ($\mathrm{MgSO_4}$). Evaporation of the solvent and recrystallization of the residue yielded 155 mg (75%) of **10** as colorless needles from ethanol: mp 234–235°; nmr ($\mathrm{CD_3COCD_3}$) δ 7.75 (d, 1, J = 2.4 Hz), 8.16 (d, 1, J = 2.4 Hz), 7.35 (d, 1, J = 5.4 Hz), 7.72 (d, 1, J = 5.4 Hz); ir (KBr) 1130, 1290 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); uv max (EtOH) 225 mμ (log ϵ 4.24), 250 (sh), 284 (3.97), 294 (4.00), 315 (3.65).

Anal. Calcd for $\mathrm{C_8H_4S_3O_2}$: C, 42.08; H, 1.76; S, 42.13. Found: C, 42.14; H, 1.72; S, 42.28.

Dithieno[2,3-*b*:2′,3′-*d*]thiophene 4,4-Dioxide (11).—From 196 mg (1 mmol) of **2** and 400 mg (2.2 mmol) of *m*-chloroperbenzoic acid, the procedure described above yielded 150 mg (65%) of the sulfone **11**: mp 185–186°; nmr ($\mathrm{CD_3COCD_3}$) δ 8.02 (d, 1, J = 5.0 Hz), 7.42 (d, 1, J = 5.0 Hz), 7.73 (d, 1, J = 5.2 Hz), 7.40 (d, 1, J = 5.2 Hz); ir (KBr) 1140, 1280 $\mathrm{cm^{-1}}$ ($\mathrm{SO_2}$); uv max (EtOH) 250 mμ (log ϵ 4.25), 342 (3.53).

Anal. Calcd for $\mathrm{C_8H_4S_3O_2}$: C, 42.08; H, 1.76; S, 42.13. Found: C, 42.06; H, 1.86; S, 41.90.

Registry No.—**1**, 29127-68-2; **2**, 236-65-7; **5**, 29127-70-6; **6**, 29127-71-7; **8**, 29127-72-8; **9**, 29127-73-9; **10**, 29127-74-0; **11**, 29127-75-1.

Electrolytic Dechlorination of Perchlorinated Styrene and Vinylpyridines

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Our interest in the selective dehalogenation of perhalogenated aromatic compounds has prompted us to investigate the electrochemical reduction of a number of such compounds. Results with the reduction of perchlorinated styrene and vinylpyridines, which we report here, have led to a simple method for making chloroaromatic acetylene derivatives in good yield and, in addition, demonstrate the probable order of occurrence of multiple reduction steps in compounds substituted in both the ring and side chain with chlorine.

The electrolytic reduction of octachlorostyrene (**1**) at a moving mercury cathode, carried out in 1:1 methanol–dimethoxyethane containing 5% water and ammonium acetate electrolyte, resulted in the isolation of pentachloroethynylbenzene (**2**) in 21% yield. There was also isolated from the crude product small amounts of β,β,2,3,4,5,6-heptachlorostyrene (**3**) and 2,3,5,6-tetrachloroethynylbenzene (**4**). Table I lists the improved results and product distributions obtained under different conditions (but all run in 1:1 methanol–dimethoxyethane solvent). Use of a lead cathode clearly increased the yield of the ethynylbenzene **2** and the cleanness of the reaction. The data also indicate that the yield of the by-product **3** is minimized by using buffered basic conditions (runs 2 and 3) while the amount of overreduction leading to **4** is minimized by using nearly neutral or slightly acidic conditions (runs 4 and 5).

TABLE I

PRODUCT DISTRIBUTION AND YIELD FROM THE ELECTROLYTIC REDUCTION OF OCTACHLOROSTYRENE (1)[a]

		Crude product, mol % by glc			
Run	Electrolyte	$\mathrm{C_6Cl_5C{\equiv}CH}$ (**2**)	$\mathrm{C_6Cl_5CH{=}CCl_2}$ (**3**)	$\mathrm{C_6HCl_4C{\equiv}CH}$ (**4**)	Isolated yield of **2**, %
1 (Hg)	$\mathrm{NH_4OAc}$	34.6	22.8	9.9	21
2 (Pb)	$\mathrm{NH_4OAc{-}NH_3}$	69.8	7.9	22.4	60
3 (Pb)	$\mathrm{NH_4OAc{-}NH_3}$	54.3	5.0	40.7	45
4 (Pb)	$\mathrm{NH_4Cl}$	80.2	17.5	2.2	77
5 (Pb)	HCl	69.2	23.6	7.1	. . .[b]

[a] Figures are corrected for unreacted octachlorostyrene (~20% in all cases). [b] Product was not isolated.

In a few cases (illustrated by run 3) a greater amount of the overreduced product **4** was obtained at the same conversion level. This lack of reproducibility was partially alleviated by use of a spongy lead cathode,[2] which offers a greater surface area for the same size cathode. When the reaction was deliberately carried to overreduction, the resulting product was a mixture of the tetrachloroethynylbenzene **4** and 2,3,5,6-tetrachlorostyrene (**5**).

The results indicate that the following steps occur

$$\begin{tikzcd} & & \mathrm{C_6Cl_5C{\equiv}CCl + Cl^-} \\ \mathrm{C_6Cl_5CCl{=}CCl_2 + 2e^-} \arrow[r] & \mathrm{Cl^- + [C_6Cl_5\bar{C}{=}CCl_2]} \arrow[ur, "a"] \arrow[dr, "b"', "H^+"] & \\ & & \mathrm{C_6Cl_5CCH{=}CCl_2} \end{tikzcd} \qquad (1)$$

$$\mathrm{C_6Cl_5C{\equiv}CCl + 2e^- + H^+ \longrightarrow C_6Cl_5C{\equiv}CH + Cl^-} \qquad (2)$$

$$\mathrm{C_6Cl_5C{\equiv}CH + 2e^- + H^+ \longrightarrow C_6HCl_4C{\equiv}CH + Cl^-} \qquad (3)$$

$$\mathrm{C_6HCl_4C{\equiv}CH + 2e^- + 2H^+ \longrightarrow C_6HCl_4CH{=}CH_2} \qquad (4)$$

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