Anal. Calcd for $C_8H_4Br_2S_2$: 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 ($MgSO_4$). Evaporation of the ether left 2.9 g (88%) of a yellow oil. Further attempts of purification led to decomposition: nmr (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 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 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 ($MgSO_4$). Evaporation left a white solid which on recrystallization from ether–hexane yielded 1.65 g (90%) of the dithienothiophene **2**: mp 53–54°; nmr (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 $C_8H_4S_3$: 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 $NaHCO_3$ solution and water and dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue yielded 155 mg (75%) of **10** as colorless needles from ethanol: mp 234–235°; nmr (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 cm^{-1} (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 $C_8H_4S_3O_2$: 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 (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 cm^{-1} (SO_2); uv max (EtOH) 250 mμ (log ϵ 4.25), 342 (3.53).

Anal. Calcd for $C_8H_4S_3O_2$: 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

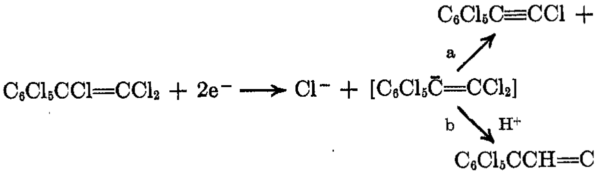
PRODUCT DISTRIBUTION AND YIELD FROM THE ELECTROLYTIC REDUCTION OF OCTACHLOROSTYRENE (**1**)[a]

Run	Electrolyte	Crude product, mol % by glc $C_6Cl_5C{\equiv}CH$ (**2**)	 $C_6Cl_5CH{=}CCl_2$ (**3**)	 $C_6HCl_4C{\equiv}CH$ (**4**)	Isolated yield of **2**, %
1 (Hg)	NH_4OAc	34.6	22.8	9.9	21
2 (Pb)	$NH_4OAc–NH_3$	69.8	7.9	22.4	60
3 (Pb)	$NH_4OAc–NH_3$	54.3	5.0	40.7	45
4 (Pb)	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


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

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

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

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

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[1] Department of Environmental Toxicology, University of California, Davis, Calif. 95616.

[2] S. Swann, Jr., in "Technique of Organic Chemistry," Vol. 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1948, p 171.

TABLE II

SUMMARY OF COMPOUND PROPERTIES

Compd[a]	Mp, °C	Ir, cm^{-1}	Nmr, ppm	C, % Calcd	C, % Found	H, % Calcd	H, % Found	Cl, % Calcd	Cl, % Found
$C_6Cl_5CH{=}CCl_2$ (**3**)	108–109	1600 (C=C)	6.66	27.8	27.9	0.3	0.5	71.9	71.5
$C_6HCl_4C{\equiv}CH$ (**4**)[b]	67–74	3220 (≡CH), 2250 (C≡C)	3.76 (≡CH), 7.49 (PhH)					60.4	59.2
$C_6HCl_4CH{=}CH_2$ (**5**)	46–49	1540 (C=C)	5.5–6.9 m (CH=CH$_2$) 7.47 (PhH)	40.0	39.4	1.7	1.6	58.5	85.6
2-$Cl_4PyC{\equiv}CH$ (**7a**)	108–111	3220 (≡CH), 2220 (C≡C)	3.55	34.9	35.1	0.4	0.6	58.8	59.0
3-$Cl_4PyC{\equiv}CH$ (**7b**)	85–88	3300 (≡CH), 2120 (C≡C)	3.86	34.9	34.7	0.4	0.5	58.8	59.0
trans-2-$Cl_4PyCH{=}CHCl$ (**8**)	117–121	1600 (C=C)	7.31 q (J = 12 cps)	30.3	30.4	0.7	0.7	63.9	63.8
trans-$C_6Cl_5CCl{=}CHCl$ (**9**)	109–110	1595 (C=C)	6.67	27.8	27.4	0.3	0.3	71.9	71.2
cis-$C_6Cl_5CCl{=}CHCl$ (**10**)	Oil	1590 (C=C)	6.50	27.8	27.3	0.3	0.4	71.9	71.4

[a] The elemental formulas were supported by analysis of the parent and isotope peaks, clearly visible in all cases, in the mass spectra.
[b] This compound was only 85% pure (by nmr and mass spectrometry); the impurity could not be removed by recrystallization or preparative gas chromatography.

in the reduction. Initial cleavage of the α C–Cl bond leads to an anion (step 1) which, upon subsequent elimination of chloride from the β position (step 1a), gives a chloroacetylene analogous to the primary product proposed in the electrolytic reduction of hexachlorobutadiene.[3] The chloroacetylene was not observed, apparently because the potential at which it is reduced to the major product 2 (step 2) is more positive than the potential at which the reaction was carried out. Addition of a proton to the initially formed anion (step 1b) results in the formation of the heptachlorostyrene **3**. The lower percentage of **3** formed in runs conducted at higher pH is thus explained. Further reduction of **3** was not observed, though reductive dechlorination at the β position is expected at a sufficiently negative cathode potential.[4,5] That reductive dechlorination did not occur at the β position of **1** points to exclusive formation of an anion adjacent to the pentachlorophenyl group in the initial step of the reduction. The important role of the pentachlorophenyl group in anion stabilization, inferred from chemical reactivity data,[6] is thus supported in the electrolytic reduction. The results are also in accord with the reactivity of octafluorostyrene in hydride reduction which proceeds, presumably through formation of $C_6H_5\bar{C}FCHF_2$, with exclusive substitution at the β position.[7]

Step 3 involves reductive dechlorination at the ring 4 position to give the tetrachloroethynylbenzene **4**, not unexpected in view of the reactivity of this position demonstrated previously with various pentafluorophenyl compounds.[7,8] This step could be minimized by keeping the solution acidic to favor discharge of hydrogen at the cathode. Finally, reduction of **4** (step 4) leads to the tetrachlorostyrene **5**, a major product of deliberate overreduction. Further reduction of **5** was not observed although this might have reasonably been expected. The ease of reduction observed for styrene *vs.* ethynylbenzene[9] is thus reversed for the tetrachloroethynylbenzene **4** and the tetrachlorostyrene **5**. The explanation for this may lie in the steric opposition to further saturation in the side chain from chlorine substituents at the 2 and 6 positions in the pentachlorophenyl ring.[10]

Reduction of heptachloro-2- and -3-vinylpyridines (**6**) followed a course similar to that of **1**, yielding as major product the corresponding tetrachloro-2- and 3-ethynylpyridines (**7**). Both reactions were carried out in 1:1

$$\underset{\textbf{6a}}{2\text{-}Cl_4PyCCl{=}CCl_2} \longrightarrow \underset{\textbf{7a}}{2\text{-}Cl_4PyC{\equiv}CH} + \underset{\textbf{8}}{trans\text{-}2\text{-}Cl_4PyCH{=}CHCl} + 1 \text{ other}$$

$$\underset{\textbf{6b}}{3\text{-}Cl_4PyCCl{=}CCl_2} \longrightarrow \underset{\textbf{7b}}{3\text{-}Cl_4PyC{\equiv}CH} + 2 \text{ others}$$

methanol–dimethoxyethane containing ammonium acetate and aqueous ammonia at a lead cathode, and the products were obtained in crude yields of 63% (**7a**) and 69% (**7b**). Along with **7a** there was isolated small amounts of *trans*-β-3,4,5,6-pentachloro-2-vinylpyridine (**8**) and another unidentified product. The occurrence of **8**, rather than the hexachloro derivative analogous to **3**, suggests a greater reactivity of a β *vs.* a ring chlorine atom in the presumed intermediate 2-$Cl_4PyCH{=}CCl_2$. Insufficient amounts of the two minor products from **6b** were available for identification, but their glc retention times indicate that they are analogous to those from **6a**.

The structure of the heptachlorostyrene by-product **3** rests on the following evidence. Chlorination of pentachloroethynylbenzene (**2**) at room temperature in carbon tetrachloride resulted in the formation of two products, **9** and **10**, both C_8HCl_7 from elemental and mass spectroscopic analysis, in the ratio of 2.5:1. The major product, mp 109–110°, had a single nmr absorption at 6.67 ppm and the minor product, an oil, had a single nmr absorption at 6.50 ppm. They are thus geometric isomers, with the assignment of **9** as *trans*- and **10** as *cis*-α,β,2,3,4,5,6-heptachlorostyrene being favored on their formation ratio and melting point difference. The addition of chlorine to pentafluoroethynylbenzene to give 90% *trans*- and 10% *cis*-1,2-dichloro-1-pentafluoroethylene[11] may be cited to support this argument. Compound **3**, the electrolytic reduction by-product, also C_8HCl_7 by elemental and mass spectroscopic analysis, had mp 108–109° and

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(11) P. L. Coe, R. G. Plevey, and J. C. Tatlow, *J. Chem. Soc. C*, 597 (1966).

a single nmr absorption, at 6.66 ppm, but was differentiated from **9** by its infrared spectrum and glc retention time. The structure of **3** then corresponds, by elimination of possibilities, to α,β,2,3,4,5,6-heptachlorostyrene.

Experimental Section

General.—Melting points were taken in glass capillaries and are uncorrected. The ir spectra were determined in carbon tetrachloride solution using a Beckman IR-4 spectrophotometer. The nmr spectra were determined in deuteriochloroform using a Varian A-60 spectrophotometer, with TMS as the internal standard. Gas chromatography was carried out using a Varian Aerograph A-90P instrument equipped with a thermal conductivity detector, on a 5 ft × 0.25 in. stainless steel column containing 20% SE-30 on Chromosorb W, at 230°. Perchlorinated styrene and vinylpyridine starting materials were prepared according to a published vapor phase chlorination procedure.[12]

An undivided cell containing as electrodes either alternating plates of sheet lead and graphite or a pool of mercury stirred by a magnetic bar and faced by a graphite disk was used with a calomel reference electrode and an NJE Model RVC-36-25 M potentiostat. In all experiments, oxidation of methanol was the principal anode reaction. Reactant concentrations were 0.1–0.15 mol/l., and electrolyte concentrations were 0.1, 0.5, and 1.0 *M* for hydrochloric acid, ammonium chloride, and ammonium acetate, respectively. Cathode current densities were 0.005–0.02 A/cm^2 and current efficiencies ranged from 50 to 80% based on a transfer of four electrons per molecule. The cathode potentials were maintained at values corresponding to the least amount of overreduction for a given reaction, as determined by following the course of reaction by glc, and were within the range -0.7 to -1.5 V (*vs.* sce). The cathode was generally partly covered at the end of the reaction by a yellow amorphous film which was not identified.

Reduction of Octachlorostyrene (1).—The following example, corresponding to run 2 of Table I, is illustrative. A mixture of 70.0 g (0.185 mol) of octachlorostyrene, 1 l. of methanol, 1.2 l. of dimethoxyethane, 20 ml of concentrated aqueous ammonia, 150 g of ammonium acetate, and 100 ml of water was warmed to 60° until complete solution was effected and then placed in a cell equipped with alternating plates, three each, of sheet lead (0.2-cm thickness) and graphite (0.5-cm thickness). The gross working lead cathode surface was 470 cm^2. Electrolysis was carried out with vigorous stirring at a cathode potential of -1.2 V (*vs.* sce) resulting in an average flow of 10-A current, or an average current density of 0.021 A/cm^2. After 2 hr, glc analysis indicated a conversion of 86% and product distribution as shown in Table I. The reaction solution was drained from the cell and 250 ml of water was added. Overnight cooling resulted in the separation of 26.4 g of pentachloroethynylbenzene (**2**): ir 3280 ($\equiv$CH) and 2200 cm^{-1} (C$\equiv$C), mp 180–182° (lit.[6] mp 185–186°). The mother liquor was further diluted with water (3 l.) and extracted with dichloromethane (three 500-ml) portions. Preparative glc of the concentrated extract resulted in the isolation of β,β-2,3,4,5,6-heptachlorostyrene (**3**) and 2,3,5,6-tetrachloroethynylbenzene (**4**). The properties of these and subsequent products are given in Table II (p 2001).

From a reaction similar to the above, but electrolyzed 4 hr at -1.4 V (*vs.* sce) to favor overreduction, preparative glc of the crude product resulted in the isolation of 2,3,5,6-tetrachlorostyrene (**5**), the major product.

Reduction of Heptachloro-2-vinylpyridine (6a) and Heptachloro-3-vinylpyridine (6b).—Reduction was carried out in essentially the same fashion as described above. The crude product from **6a** contained 50.6% tetrachloro-2-ethynylpyridine (**7a**), isolated in pure form by crystallization from ethanol, 13.0% *trans*-β,3,4,5,6-pentachloro-2-vinylpyridine (**8**), isolated in pure form by preparative glc, 17.6% a third product which was not identified, and 18.8% unreacted **6a**.

The crude product from **6b** contained 50.7% tetrachloro-3-ethynylpyridine (**7b**), isolated in pure form by crystallization from ethanol, 22.4% two other products which were not identified, and 26.9% unreacted **6b**.

Addition of Chlorine to Pentachloroethynylbenzene (2).—Chlorine gas was bubbled through a stirred solution of 10 g (0.04 mol) of **2** in 150 ml of carbon tetrachloride at the rate of *ca.* 10 ml/min. After 30 hr, most of the **2** disappeared and two major products were formed in the ratio of 2.5:1. Evaporation of the solvent gave 14.4 g of an oil which partially solidified on standing. Two recrystallizations from acetone gave 1.5 g of the major component (**9**) as tan crystals. From the concentrated mother liquors, the minor component (**10**) was obtained as a colorless oil by preparative glc.

Registry No.—**1**, 29082-74-4; **3**, 29082-75-5; **4**, 29082-76-6; **5**, 29082-77-7; **6a**, 22652-20-6; **6b**, 29086-34-8; **7a**, 29086-35-9; **7b**, 29086-36-0; **8**, 29086-37-1; **9**, 29086-38-2; **10**, 29086-39-3.

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[12] W. H. Taplin (Dow Chemical Co.), U. S. Patent 3,420,833 (1969).

The Hammick Reaction of Methoxypyridine-2-carboxylic Acids with Benzaldehyde. Preparation of Methoxy-2-pyridyl Phenyl Ketones

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The Hammick reaction,[1,2] synthesis of carbinols by thermal decarboxylation of certain heterocyclic carboxylic acids in the presence of carbonyl compounds, has been widely used in the preparation of a number of 2-pyridyl carbinols.[3,4] Thus far the only substituted pyridine-2-carboxylic acids used as substrates in the Hammick reaction have been the methylpyridine acids.[4] The corresponding carbinols have been obtained by thermal decomposition of these acids in benzaldehyde and anisaldehyde in yields ranging from 35 to 53%. In the present study, synthesis of the methoxypyridine-2-carboxylic acids and their thermal decomposition in benzaldehyde are described. In each case two products, the corresponding methoxy-2-pyridyl phenyl carbinol and the methoxypyridine, were obtained. The carbinols were oxidized to the corresponding ketones by chromic acid solution.

Reaction Medium.—In each case, 1 g of the acid was heated with 6 g of benzaldehyde and 6 g of *p*-cymene. The use of *p*-cymene has been found to increase the yield of the Hammick product.[3,4] All the methoxy acids are soluble in this reaction medium above 90° and insoluble at 25°. The highest temperature for the reaction was 175°, the reflux temperature.

General Procedure.—The finely divided acid was added in one portion to the reaction medium. The mixture was stirred under nitrogen and heated below the decarboxylation temperature until a clear solution was obtained. It was then brought up to the reaction temperature and maintained there for the desired period. On cooling overnight, the unreacted acid, if any, was removed by filtration. The solution was then extracted three times with hydrochloric acid (15%) and the acid extracts were washed with petroleum ether.

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