(dd, J = 5 Hz, J' = 10.5 Hz, 1 H, H-8 or H-9), 3.83 (dd, J = 7.5 Hz, J' = 10.5 Hz, 1 H, H-8 or H-9), 3.93 (m, 4 H, ethylenedioxy), 4.04 (dd, J = 7.5 Hz, J' = 5 Hz, 1 H, H-8 or H-9), 7.33 (m, 5 H, Ar); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.1 (CH$_3$), 16.0 (CH$_3$), 20.3, 23.1, 26.1, 26.8, 28.2, 31.4, 35.4, 37.0 (piperidine ring or side chain CH$_2$), 50.8 (C-6), 53.7 (C-2), 62.2 (C-8), 65.0 (ethylenedioxy), 65.5 (C-9), 111.9 (>C(-O-)-), 127.6, 128.4, 128.6, 130.0 (Ar); MS, *m/e* (relative intensity) 375 (M$^+$, 1), 360 (1), 344 (100), 318 (14), 218 (68), 144 (12), 129 (17), 98 (30), 91 (6). Anal. Calcd for C$_{23}$H$_{37}$NO$_3$: C, 73.54; H, 9.94; N, 3.73. Found: C, 73.17; H, 10.05; N, 3.83.

Preparation of (–)-Monomorine I (9 and 10a). A solution of alcohol **6** (75 mg, 0.2 mmol) in methanol (10 mL) containing HCl (0.1 mL, 1 M) was hydrogenated over 10% Pd/C at atmospheric pressure for 6 days. The reaction mixture was then filtered through a Celite bed and the filtrate evaporated in vacuo to give a white solid which was washed several times with ether to eliminate phenylethanol. The product was recrystallized from CH$_2$Cl$_2$ to give 43 mg (93%) of the epimeric mixture of **9·HCl** and **10a·HCl**. The mixture of bases was separated by a short column chromatography on alumina (hexane–ether, 9:1) which afforded monomorine I **9·HCl** (32 mg as hydrochloride, 70%) and the epimer **10a·HCl** (5 mg as hydrochloride, 10%).

9: $[\alpha]^{20}_D$ –35.8° (*n*-hexane, *c* 1.35);[10] ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.47 (t, J = 7 Hz, 3 H, CH$_3$), 1.69 (d, J = 6.5 Hz, 3 H, CH$_3$), 1.75–2.35 (m, 22 H, CH$_2$), 2.53 (m, 1 H, H-3 or H-9), 2.66 (m, 1

H, H-5), 2.9 (m, 1 H, H-3 or H-9); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.2 (CH$_3$), 22.9 (CH$_3$), 23.0, 25.1, 29.4, 29.8, 30.5, 31.1, 36.1, 39.8 (CH$_2$), 60.3 (C-5), 63.0 (C-3), 67.3 (C-9); MS, *m/e* (relative intensity) 195 (M$^+$, 3), 194 (2), 180 (3), 139 (11), 138 (100), 98 (15). Anal. Calcd for C$_{13}$H$_{25}$N·HCl: C, 67.35; H, 11.30; N, 6.04. Found: C, 66.89; H, 11.11; N, 6.34.

10a·HCl: $[\alpha]^{20}_D$ –69.2° (MeOH, *c* 0.55); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.91 (t, J = 7 Hz, 3 H, CH$_3$), 1.1–2.4 (m with d (J = 7 Hz) at 1.48, 22 H, CH$_2$ and CH$_3$), 2.97 (m, 2 H, H-5 and H-9), 3.83 (m, 1 H, H-3); MS, *m/e* (relative intensity) 195 (M$^+$, 3), 194 (2), 180 (6), 138 (100); exact mass 195.1986 (calcd for C$_{13}$H$_{25}$N 195.1980).

Registry No. **1**, 88056-92-2; **2**, 94458-71-6; **3**, 94458-72-7; **4** (isomer 1), 94458-73-8; **4** (isomer 2), 94535-29-2; **5**, 94458-74-9; **6**, 94458-75-0; **7**, 94535-26-9; **9**, 94535-27-0; **9·HCl**, 94595-24-1; **10a·HCl**, 94535-28-1; valeryl chloride, 638-29-9; ethylene, 74-85-1; 1-chloro-3-heptanone, 94458-76-1; 1-chloro-3-heptanone ethylene ketal, 94458-77-2; (+)-monomorine I, 53447-44-2; (–)-phenyl-glycinol, 56613-80-0; glutaraldehyde, 111-30-8.

Electrochemical Reduction of Unsymmetrically Substituted Diphenyliodonium Salts at Mercury Cathodes in Dimethylformamide

Mohammad S. Mubarak and Dennis G. Peters*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received August 16, 1984

A study has been made of the electrochemistry of five unsymmetrically substituted diphenyliodonium salts at mercury cathodes in dimethylformamide containing tetramethylammonium perchlorate. Polarograms indicate that the iodonium cations undergo reduction in three stages: (1) one-electron reduction to yield either (a) iodobenzene and a substituted phenylmercury radical or (b) a substituted iodobenzene and a phenylmercury radical, (2) two-electron reduction of the iodobenzene or substituted iodobenzene, and (3) one-electron reduction of the substituted or unsubstituted phenylmercury radical. When electrolyses are performed at potentials corresponding to the first stage of reduction, electron-withdrawing substituents induce the production of more iodobenzene than substituted iodobenzene, whereas electron-releasing groups favor the formation of less iodobenzene than substituted iodobenzene; the other major products (diphenylmercury and symmetrically disubstituted diphenylmercury) arise via disproportionation of adsorbed phenylmercury radicals. At potentials corresponding to the second stage of reduction, electrolyses yield benzene, substituted benzene, and diorganomercury compounds; at potentials corresponding to the third stage of reduction, benzene and substituted benzene are formed.

In a recent investigation[1] we examined the polarographic and electrolytic behavior of diphenyliodonium bromide in dimethylformamide containing tetramethylammonium perchlorate. Depending on the concentrations of the supporting electrolyte and the diphenyliodonium cation, either three or four pulse polarographic waves are observed; for a solution containing 0.1 M tetramethylammonium perchlorate and greater than 0.74 mM diphenyliodonium bromide, four waves (Ia, Ib, II, and III) are seen. Large-scale controlled-potential electrolyses yield equal quantities of diphenylmercury and iodobenzene at potentials corresponding to either wave Ia or Ib, comparable amounts of benzene and diphenylmercury at potentials corresponding to wave II, and mostly benzene with some diphenylmercury at potentials corresponding to wave III.

Only two previous publications have dealt with the electrochemistry of unsymmetrically substituted iodonium salts. Colichman and Maffei[2] studied, as part of a larger survey, the polarography of (β-chlorovinyl)phenyliodonium chloride in an aqueous medium. In a later report Bachofner, Beringer, and Meites[3] probed the effects of size, electronegativity, charge, and reducibility of substituents on the polarographic waves for symmetric and unsymmetric diphenyliodonium compounds in an ethanol–water system. None of the preceding work concerned the behavior of unsymmetrically substituted diphenyliodonium salts in a nonaqueous solvent, nor were any results published pertaining to the influence of substituents on

(1) Mbarak, M. S.; Peters, D. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *152*, 183–196.

(2) Colichman, E. L.; Maffei, H. P. *J. Am. Chem. Soc.* **1952**, *74*, 2744–2748.

(3) Bachofner, H. E.; Beringer, F. M.; Meites, L. *J. Am. Chem. Soc.* **1958**, *80*, 4274–4278.

preparative-scale electrolyses of these compounds. In the present paper we describe the electrochemistry of five different unsymmetrically substituted diphenyliodonium bromides in dimethylformamide containing tetramethylammonium perchlorate, with particular emphasis on the relative extents of one-electron reductive cleavage of the two carbon–iodine bonds that is induced by an electron-withdrawing or electron-releasing substituent.

Experimental Section

Reagents. Dimethylformamide and tetramethylammonium perchlorate utilized as solvent and supporting electrolyte, respectively, were handled as described in our previous paper.[1] Mercury (Ventron, triply distilled) was used as received. Prepurified nitrogen (Matheson, 99.998%) was employed for the deaeration of all solutions. We purchased p-iodotoluene, m-iodotoluene, and m-chloroiodobenzene from Eastman Kodak Co., p-chloroiodobenzene from Aldrich Chemical Co., and p-bromochlorobenzene from the Dow Chemical Co.; all of these compounds were used without further purification. Five unsymmetrically substituted diphenyliodonium salts [(p-methoxyphenyl)-phenyliodonium bromide, (p-methylphenyl)phenyliodonium bromide, (m-methylphenyl)phenyliodonium bromide, (m-chlorophenyl)phenyliodonium bromide, and (p-chlorophenyl)-phenyliodonium bromide] were synthesized and purified according to published methods.[4-8] Diphenylmercury was obtained commercially (Alfa Products) and was used without additional purification; bis(p-chlorophenyl)mercury and bis(p-anisyl)mercury were prepared according to procedures described by Dessy and Kim.[9]

Instrumentation and Procedures. Electrolysis cells, instrumentation, and procedures for conventional and pulse polarography and for controlled-potential electrolysis are discussed in an earlier publication.[10] All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride; this electrode has a potential of –0.75 V vs. the aqueous saturated calomel electrode.[11,12]

Gas chromatography and gas chromatography–mass spectrometry were used to separate, identify, and quantitate the electrolysis products; the instrumentation and columns used are described elsewhere.[1,10] All product yields are absolute percentages determined by means of gas chromatography with respect to an electroinactive internal standard (phenylcyclohexane or toluene) and are based on the quantity of starting material incorporated into a particular product.

Electrolytic Synthesis of Bis(p-tolyl)mercury. A 10 mM solution of bis(p-methylphenyl)iodonium bromide (synthesized and purified by means of published procedures[5,6,13]) in dimethylformamide containing 0.1 M tetramethylammonium perchlorate was electrolyzed in a cell with a mercury pool cathode at –0.1 V. Next, the electrolyzed solution was partitioned between water and diethyl ether, and the ether extract was washed with water, dried, and combined with the ether extract from another electrolysis. When the ether extract was concentrated, bis(p-tolyl)mercury precipitated; the solid was washed with ether to remove p-iodotoluene which is also a product of the reduction of bis(p-methylphenyl)iodonium bromide. Recrystallization from

(4) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.* **1976**, Part C, Symposium No. 56, 383–395.

(5) Sharefkin, J. G.; Saltzman, H. In "Organic Syntheses"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. V, pp 660–663.

(6) Saltzman, H.; Sharefkin, J. G. In "Organic Syntheses"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. V, pp 658–659.

(7) Lucas, H. J.; Kennedy, E. R. In "Organic Syntheses"; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. III, pp 482–483.

(8) Lucas, H. J.; Kennedy, E. R.; Formo, M. V. In "Organic Syntheses"; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. III, pp 483–485.

(9) Dessy, R. E.; Kim, J. Y. *J. Am. Chem. Soc.* **1960**, *82*, 686–689.

(10) La Perriere, D. M.; Carroll, W. F., Jr.; Willett, B. C.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 7561–7568.

(11) Marple, L. W. *Anal. Chem.* **1967**, *39*, 844–846.

(12) Hall, J. L.; Jennings, P. W. *Anal. Chem.* **1976**, *48*, 2026–2027.

(13) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, *81*, 342–351.

chloroform gave a white solid: mp 240 °C (lit.[14] 238 °C).

Product Identification. Benzene, toluene, chlorobenzene, anisole, iodobenzene, m-iodotoluene, p-iodotoluene, p-chloroiodobenzene, m-chloroiodobenzene, and p-iodoanisole were identified by comparison of their gas chromatographic retention times with those of commercially available authentic samples. Diphenylmercury, bis(p-chlorophenyl)mercury, bis(p-anisyl)mercury, and bis(p-tolyl)mercury were identified by comparison of their gas chromatographic retention times and mass spectra with those of purchased or synthesized samples. Symmetrical bis(m-tolyl)mercury and bis(m-chlorophenyl)mercury as well as trace amounts of unsymmetrically substituted diphenylmercury compounds were identified from their mass spectra. Due to the thermal instability of unsymmetrically substituted diphenylmercury compounds,[14,15] nothing more than trace amounts was detected; these substances decompose to symmetrical species according to the reaction

$$2PhHgPh' \rightarrow Ph_2Hg + Ph'_2Hg$$
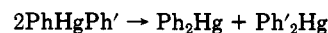
where Ph' denotes a substituted phenyl moiety.

Mass Spectral Data for Diorganomercury Compounds at 70 eV. Though mercury has seven isotopes, the mass spectral data are based on the ^{202}Hg isotope;[16] the molecular ion and the mercury-containing fragments displayed the characteristic distribution of mercury isotopes. **Diphenylmercury:** mass spectrum, m/e 356, M$^+$ (4.9%); 279, $C_6H_5Hg^+$ (4.8%); 202, Hg$^+$ (1.6%); 154, $(C_6H_5)_2^+$ (9.3%); 77, $C_6H_5^+$ (100%). **Bis(m-chlorophenyl)mercury:** mass spectrum, m/e 424, M$^+$ (3.6%); 313, m-ClC$_6$H$_4$Hg$^+$ (7.3%); 226, $(m$-ClC$_6$H$_4)_2^+$ (0.9%); 224, $(m$-ClC$_6$H$_4)_2^+$ (4.5%); 222, $(m$-ClC$_6$H$_4)_2^+$ (6.5%); 202, Hg$^+$ (2.0%); 113, m-ClC$_6$H$_4^+$ (31.2%); 111, m-ClC$_6$H$_4^+$ (100%). **Bis(p-chlorophenyl)mercury:** mass spectrum, m/e 424, M$^+$ (4.8%); 313, p-ClC$_6$H$_4$Hg$^+$ (8.0%); 226, $(p$-ClC$_6$H$_4)_2^+$ (3.5%); 224, $(p$-ClC$_6$H$_4)_2^+$ (17.2%); 222, $(p$-ClC$_6$H$_4)_2^+$ (30.0%); 202, Hg$^+$ (10.2%); 113, p-ClC$_6$H$_4^+$ (30.0%); 111, p-ClC$_6$H$_4^+$ (100%). **Bis(m-tolyl)mercury:** mass spectrum, m/e 384, M$^+$ (5.5%); 293, m-CH$_3$C$_6$H$_4$Hg$^+$ (4.0%); 202, Hg$^+$ (1.2%); 182, $(m$-CH$_3$C$_6$H$_4)_2^+$ (10.2%); 91, m-CH$_3$C$_6$H$_4^+$ (100%). **Bis(p-tolyl)mercury:** mass spectrum, m/e 384, M$^+$ (4.5%); 293, p-CH$_3$C$_6$H$_4$Hg$^+$ (3.0%); 202, Hg$^+$ (2.2%); 182, $(p$-CH$_3$C$_6$H$_4)_2^+$ (5.5%); 91, p-CH$_3$C$_6$H$_4^+$ (100%). **Bis(p-anisyl)mercury:** mass spectrum, m/e 416, M$^+$ (6.2%); 214, $(p$-CH$_3$OC$_6$H$_4)_2^+$ (29.2%); 202, Hg$^+$ (29.2%); 107, p-CH$_3$OC$_6$H$_4^+$ (100%). **(p-Chlorophenyl)phenylmercury:** mass spectrum, m/e 390, M$^+$ (3.2%); 313, p-ClC$_6$H$_4$Hg$^+$ (1.1%); 279, $C_6H_5Hg^+$ (6.6%); 226, $(p$-ClC$_6$H$_4)_2^+$ (0.6%); 224, $(p$-ClC$_6$H$_4)_2^+$ (2.2%); 222, $(p$-ClC$_6$H$_4)_2^+$ (3.4%); 202, Hg$^+$ (12.0%); 154, $(C_6H_5)_2^+$ (18.9%); 113, p-ClC$_6$H$_4^+$ (7.9%); 111, p-ClC$_6$H$_4^+$ (22.5%); 77, $C_6H_5^+$ (100%). **(p-Methylphenyl)phenylmercury:** mass spectrum, m/e 370, M$^+$ (7.5%); 293, p-CH$_3$C$_6$H$_4$Hg$^+$ (5.4%); 279, $C_6H_5Hg^+$ (2.2%); 202, Hg$^+$ (3.2%); 91, p-CH$_3$C$_6$H$_4^+$ (100%); 77, $C_6H_5^+$ (15.0%).

Results and Discussion

Polarographic Characteristics of Unsymmetrically Substituted Diphenyliodonium Salts. Conventional dc polarograms for 1 mM solutions of (p-methoxyphenyl)phenyliodonium bromide, (p-methylphenyl)-phenyliodonium bromide, (m-methylphenyl)phenyliodonium bromide, (p-chlorophenyl)phenyliodonium bromide, and (m-chlorophenyl)phenyliodonium bromide in dimethylformamide containing 0.1 M tetramethylammonium perchlorate resemble those for unsubstituted diphenyliodonium bromide described in a previous publication.[1] Anodic waves with half-wave potentials of +0.54 V (corresponding to bromide-assisted oxidation of mercury) followed by cathodic waves with half-wave potentials

(14) Kharasch, M. S.; Marker, R. *J. Am. Chem. Soc.* **1926**, *48*, 3130–3143.

(15) Makarova, L. G.; Nesmeyanov, A. N. In "Methods of Elemento-Organic Chemistry"; Nesmeyanov, A. N., Kocheshkov, K. A., Eds.; North-Holland Publishing Co.: Amsterdam, 1967; Vol. 4, pp 289–302.

(16) Bryant, W. F.; Kinstle, T. H. *J. Organomet. Chem.* **1970**, *24*, 573–587.

substituent	half-wave potential, V[a]	
	wave I[b]	wave II
(a) 0.02 M Tetramethylammonium Perchlorate		
p-CH₃O	+0.30	-1.00
p-CH₃	+0.30	-0.98
m-CH₃	+0.29	-0.97
(none)	+0.30	-0.95
p-Cl	+0.30	-0.89
m-Cl	+0.31	-0.87
(b) 0.1 M Tetramethylammonium Perchlorate		
p-CH₃O	+0.33	-0.93
p-CH₃	+0.34	-0.92
m-CH₃	+0.33	-0.91
(none)	+0.34	-0.90
p-Cl	+0.34	-0.86
m-Cl	+0.34	-0.84

[a] The uncertainty in the half-wave potentials is ±0.01 V. [b] With 0.02 M tetramethylammonium perchlorate, only wave I is observed. With 0.1 M tetramethylammonium perchlorate, the meta-substituted compounds exhibit only wave I, but the para-substituted compounds exhibit both waves Ia and Ib (although just the half-wave potentials for wave Ia are tabulated).

of +0.34 V are observed for all five compounds; however, the polarograms are dominated by huge current maxima which render it impossible to determine the number of polarographic waves at more negative potentials. Maxima are pronounced even at lower (0.02 M) concentrations of supporting electrolyte.

Pulse polarograms for the above-mentioned unsymmetrically substituted diphenyliodonium bromides were recorded in dimethylformamide containing either 0.02 or 0.1 M tetramethylammonium perchlorate. As discussed in our earlier work,[1] the concentrations of supporting electrolyte and starting material affect the number of pulse polarographic waves as well as their half-wave potentials. For 1 mM solutions of any of the unsymmetrically substituted diphenyliodonium bromides in the presence of 0.02 M tetramethylammonium perchlorate, three waves are seen; wave I is attributed to one-electron reduction of the substituted or unsubstituted phenyl mercuric bromide arising from reaction of adsorbed starting material with the mercury cathode, wave II is postulated to correspond to two-electron reduction of a substituted or unsubstituted iodobenzene, and wave III is caused by one-electron reduction of an adsorbed, substituted or unsubstituted phenylmercury radical. For 0.1 M tetramethylammonium perchlorate, four pulse polarographic waves are observed for the para-substituted species as well as for the unsubstituted diphenyliodonium cation[1] because the first wave splits into wave Ia (caused by the same process that is responsible for wave I) and wave Ib (due to one-electron reduction of dissolved starting material). Interestingly, the first wave for each of the two meta-substituted compounds does not split when the concentration of supporting electrolyte is raised from 0.02 to 0.1 M.

Table I lists half-wave potentials for pulse polarographic waves I (or Ia) and II for the various substituted and unsubstituted diphenyliodonium salts in dimethylformamide containing 0.02 and 0.1 M tetramethylammonium perchlorate. Substituents have virtually no effect on half-wave potentials for the first pulse polarographic wave; analogous observations were made earlier by Bachofner, Beringer, and Meites[3] in their study of unsymmetrically substituted diphenyliodonium salts in an ethanol–water medium.

On the other hand, half-wave potentials for wave II (arising from reduction of a substituted or unsubstituted

iodobenzene) are significantly affected by the nature of the substituent on the benzene ring; electron-withdrawing groups (p-chloro and m-chloro) make addition of electrons easier as shown by the less negative half-wave potentials, whereas electron-releasing groups (p-methoxy, p-methyl, and m-methyl) make uptake of electrons more difficult as shown by more negative half-wave potentials. Our findings concerning the influence of substituents on the reducibility of iodobenzene parallel the results seen by Colichman and Liu,[17] by Bachofner, Beringer, and Meites,[3] and by Sease, Burton, and Nickol[18] (as well as other work cited in the last reference). Because reduction of iodobenzene probably proceeds via a transition state in which the carbon atom of the carbon–iodine bond acquires negative charge,[18] the effect on the half-wave potential caused by different substituents can be rationalized in terms of the relative stability of such a transition state; an electron-withdrawing group stabilizes the transition state through an inductive or resonance effect and makes the reduction more favorable, whereas an electron-releasing substituent destabilizes the transition state via the inductive effect or by resonance and makes the reduction more difficult. Even though, as described below, preparative-scale electrolysis of an unsymmetrically substituted diphenyliodonium cation results in production of a mixture of iodobenzene and a substituted iodobenzene, a polarogram for that diphenyliodonium cation does not exhibit a resolved pair of waves for the substituted and unsubstituted iodobenzenes because of the small difference in half-wave potentials for the two compounds.

Large-Scale Controlled-Potential Electrolyses. Compiled in Tables II–VI are coulometric n values and product distributions for electrolyses at mercury pool cathodes of 5 mM solutions of each of the five unsymmetrically substituted diphenyliodonium bromides in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. To clarify the significance of the percentage yield of each electrolysis product, the following example can be considered. Each mole of diphenyliodonium cation contains 2 mol of the phenyl moiety, and, in the first entry of Table II, we see that an electrolysis of 1 mol of (p-methoxyphenyl)phenyliodonium bromide would give 0.16 mol of iodobenzene, 0.77 mol of p-iodoanisole, approximately 0.01 mol of benzene, 0.09 mol of anisole, 0.375 mol of diphenylmercury, and 0.04 mol of bis(p-anisyl)mercury; the total number of moles (1.86) of phenyl moiety among all products agrees well with the theoretical value of 2.

At potentials corresponding to the first pulse polarographic wave (+0.3 V lies on the rising portion of wave I for the meta-substituted species and on the rising portion of wave Ia for the para-substituted species, whereas -0.4 V is on the plateau of the first pulse polarographic wave for all compounds), a coulometric n value of 1 is obtained, and the electrolysis products include iodobenzene, substituted iodobenzene, diphenylmercury, and symmetrically disubstituted diphenylmercury (diphenylmercury and disubstituted diphenylmercury will be referred to collectively hereafter as organomercury compounds) as well as small amounts of benzene and monosubstituted benzene. For a potential (-1.0 V) at the top of the second pulse polarographic wave, at which iodobenzenes (but neither organomercury compounds nor organomercury radicals) are electroactive, an n value of 3 is observed, and benzene, substituted benzene, and organomercury compounds are the products. In agreement with our earlier study[1] of the

(17) Colichman, E. L.; Liu, S. K. *J. Am. Chem. Soc.* **1954**, *76*, 913–915.
(18) Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595–2598.

Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 5 mM (p-Methoxyphenyl)phenyliodonium Bromide at Mercury Cathodes in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n	prod distributn, %					
		iodobenzene	p-iodoanisole	benzene	anisole	Ph_2Hg	Ph'_2Hg^a
+0.3	0.94	16	77	<1	9	75	8
-0.4	0.92	18	77	<1	12	69	11
-1.0	2.88			24	84	72	16
-1.3	3.04			24	83	73	11
-1.8	3.92			78	97		

[a] Ph'_2Hg = bis(p-anisyl)mercury [$(p-CH_3OC_6H_4)_2Hg$].

Table III. Coulometric Data and Product Distributions for Electrolytic Reduction of 5 mM (p-Methylphenyl)phenyliodonium Bromide at Mercury Cathodes in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n	prod distributn, %						
		iodobenzene	p-iodotoluene	benzene	toluene	Ph_2Hg	Ph'_2Hg^a	other[b]
+0.3	0.98	33	66	2	3	64	27	<0.5
-0.4	0.97	39	59	<1	3	60	31	<0.5
-1.0	2.81			33	50	58	37	
-1.3	3.00			33	52	53	32	
-1.8	3.81			72	93			

[a] Ph'_2Hg = bis(p-tolyl)mercury [$(p-CH_3C_6H_4)_2Hg$]. [b] A very small amount of (p-methylphenyl)phenylmercury ($p-CH_3C_6H_4HgC_6H_5$) was detected.

Table IV. Coulometric Data and Product Distributions for Electrolytic Reduction of 5 mM (m-Methylphenyl)phenyliodonium Bromide at Mercury Cathodes in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n	prod distributn, %						
		iodobenzene	m-iodotoluene	benzene	toluene	Ph_2Hg	Ph'_2Hg^a	other[b]
+0.3	0.95	40	57	<1	<1	52	43	<0.5
-0.4	0.96	40	58	<1	2	47	38	<0.5
-1.0	2.81			31	47	52	40	
-1.3	2.99			33	50	50	35	
-1.8	3.90			78	92			

[a] Ph'_2Hg = bis(m-tolyl)mercury [$(m-CH_3C_6H_4)_2Hg$]. [b] Traces of (m-methylphenyl)phenylmercury ($m-CH_3C_6H_4HgC_6H_5$) were detected.

Table V. Coulometric Data and Product Distributions for Electrolytic Reduction of 5 mM (p-Chlorophenyl)phenyliodonium Bromide at Mercury Cathodes in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n	prod distributn, %						
		iodobenzene	p-chloro-iodobenzene	benzene	chlorobenzene[a]	Ph_2Hg	Ph'_2Hg^b	other[c]
+0.3	0.94	61	40	<1	5	36	47	<0.5
-0.4	1.00	52	48	<1	7	44	48	
-1.0	2.88			42	57	45	42	
-1.3	3.01			42	68	35	29	

[a] Because chlorobenzene is reducible at potentials more negative than -1.5 V, reduction at -1.8 V was not carried out. [b] Ph'_2Hg = bis(p-chlorophenyl)mercury [$(p-ClC_6H_4)_2Hg$]. [c] Small amounts of (p-chlorophenyl)phenylmercury ($p-ClC_6H_4HgC_6H_5$) were detected.

Table VI. Coulometric Data and Product Distributions for Electrolytic Reduction of 5 mM (m-Chlorophenyl)phenyliodonium Bromide at Mercury Cathodes in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate

potential, V	n	prod distributn, %					
		iodobenzene	m-chloroiodobenzene	benzene	chlorobenzene	Ph_2Hg	Ph'_2Hg^b
+0.3	0.77[a]	74	25	2	5	18	68
-0.4	1.01	61	40	1	14	31	45
-1.0	2.81			53	50	33	49
-1.3	3.06			53	63	34	36

[a] (m-Chlorophenyl)phenyliodonium bromide undergoes chemical decomposition at mercury. [b] Ph'_2Hg = bis(m-chlorophenyl)mercury [$(m-ClC_6H_4)_2Hg$].

diphenyliodonium cation, an electrolysis of any of the unsymmetrically substituted diphenyliodonium salts at a potential of -1.3 V results in a slightly larger n value and the yields of benzenes and organomercury compounds are somewhat higher and lower, respectively. Finally, at a very negative potential (e.g., -1.8 V, at which organomercury compounds are reducible), a coulometric n value of 4 is obtained, with benzene and substituted benzenes being the only products. It should be noted that aromatic chlorides are reducible at potentials more negative than -1.5 V, so no entries appear in Tables V and VI for -1.8 V.

Substituents have virtually no influence on half-wave potentials for the first pulse polarographic wave. However, by controlling which of the two carbon–iodine bonds will

Table VII. Distribution of Iodobenzene and Substituted Iodobenzene for Electrolysis of 5 mM Unsymmetrically Substituted Diphenyliodonium Bromide at +0.30 V in Dimethylformamide Containing 0.1 M Tetramethylammonium Perchlorate
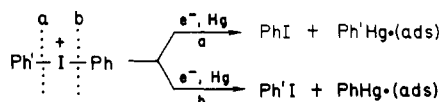
substituent	iodobenzene, %	substituted iodobenzene, %	ratio of iodobenzene to substituted iodobenzene
p-CH$_3$O	16	77	0.21
p-CH$_3$	33	66	0.50
m-CH$_3$	40	57	0.70
p-Cl	61	40	1.53
m-Cl	74	25	2.96

undergo preferential cleavage, substituents have a profound and tangible effect on the ratio of yields of substituted and unsubstituted iodobenzene. Table VII compares the yields of substituted and unsubstituted iodobenzene obtained from electrolyses at +0.3 V of 5 mM solutions of the previously mentioned diphenyliodonium bromides in dimethylformamide containing 0.1 M tetramethylammonium perchlorate. From the data in Table VII, it is apparent that electron-withdrawing substituents favor breakage of the carbon–iodine bond leading to more iodobenzene whereas electron-releasing groups promote scission of the carbon–iodine bond leading to more of the substituted iodobenzene.

Mechanistic Implications. As discussed in our previous paper[1] and as mentioned earlier in this report, the first pulse polarographic wave (I or Ia) can be attributed to reduction of the substituted (Ph'HgBr) or unsubstituted (PhHgBr) phenyl mercuric bromide which is formed chemically by the reaction between the adsorbed iodonium salt and the mercury electrode:
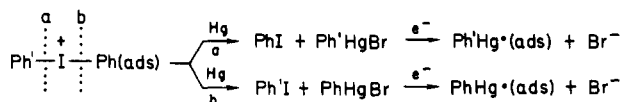
Under suitable conditions, the first pulse polarographic wave is split into two waves, the second one (Ib) arising from direct reduction of the dissolved iodonium salt:


Regardless of which of the above pathways is followed, the net result is the production of either (i) iodobenzene and a substituted phenylmercury radical or (ii) a substituted iodobenzene and a phenylmercury radical. Once formed, the adsorbed organomercury radicals disproportionate quickly (0.2 ms) to give diorganomercury compounds. Large amounts of diphenylmercury and the symmetrically disubstituted diphenylmercury species are obtained at potentials (e.g., +0.3 V) corresponding to the first pulse polarographic wave; however, very little, if any, of the unsymmetrical diphenylmercury compound is detected, because of the pronounced tendency for these substances to decompose into symmetrical diphenylmercury compounds.[14,15]

An electron-withdrawing group weakens the carbon–iodine bond (a) closer to the substituent, relative to the more distant carbon–iodine bond (b); this effect appears to explain the high ratio of iodobenzene to substituted iodobenzene (Table VII). However, an electron-releasing group strengthens the carbon–iodine bond (a) closer to the substituent, relative to the more distant carbon–iodine
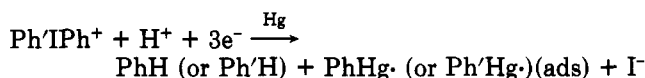
bond (b), by increasing the electron density around the closer bond and, as a result, that bond is comparatively harder to break; this phenomenon seems to account for the low ratio of iodobenzene to substituted iodobenzene (Table VII).

Because phenylmercury radicals are products at potentials corresponding to the first polarographic wave and because radicals are not as sensitive to substituent effects as carbanions—carbanions are stabilized by electron-withdrawing groups and destabilized by electron-releasing groups—the half-wave potentials for the first polarographic wave are unaffected by changes in the substituents.

Reduction of iodobenzene or substituted iodobenzene is responsible for the second pulse polarographic wave. Reed[19] has shown that a large-scale controlled-potential electrolysis of iodobenzene in dimethylformamide containing 0.1 M tetraethylammonium bromide is a two-electron process resulting in quantitative production of benzene:

$$\text{PhI (or Ph'I)} + \text{H}^+ + 2e^- \rightarrow \text{PhH (or Ph'H)} + \text{I}^-$$
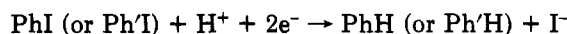
Water, present as an impurity in dimethylformamide at concentrations ranging from 10 to 50 mM, is the most probable source of protons for the phenyl carbanion intermediate, although the supporting-electrolyte cation (tetramethylammonium ion) can function as a proton donor.[20] At potentials corresponding to the second pulse polarographic wave, the net reduction of an unsymmetrically substituted diphenyliodonium bromide can be represented as the three-electron reaction

$$\text{Ph'IPh}^+ + \text{H}^+ + 3e^- \xrightarrow{\text{Hg}}$$
$$\text{PhH (or Ph'H)} + \text{PhHg} \cdot \text{ (or Ph'Hg} \cdot)\text{(ads)} + \text{I}^-$$
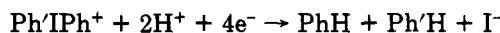
with the adsorbed phenylmercury radicals subsequently undergoing disproportionation to yield organomercury compounds.

Finally, as demonstrated in our earlier work,[1] the third pulse polarographic wave is attributable to one-electron reduction of an adsorbed phenylmercury radical:

$$\text{PhHg} \cdot \text{ (or Ph'Hg} \cdot)\text{(ads)} + \text{H}^+ + e^- \rightarrow$$
$$\text{PhH (or Ph'H)} + \text{Hg}$$
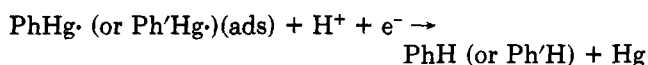
Thus, when an unsymmetrically substituted diphenyliodonium bromide is electrolyzed at potentials so negative (−1.8 V) that organomercury radicals and even diorganomercury compounds are reducible, an overall four-electron process occurs

$$\text{Ph'IPh}^+ + 2\text{H}^+ + 4e^- \rightarrow \text{PhH} + \text{Ph'H} + \text{I}^-$$

and benzene and substituted benzene are the only products.

(19) Reed, R. C. Ph.D. Dissertation, Wesleyan University, Middletown, CT, 1971.
(20) Vieira, K. L.; Mubarak, M. S.; Peters, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5372-5373.