

Electrochemical Reactions. Part VII.¹ Reduction of Diphenyliodonium Salts

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Electrochemical reduction of diphenyliodonium hydroxide and its 4,4'-dimethyl- and 4,4'-dimethoxy-derivatives at a mercury cathode controlled at -1.6V vs. a saturated calomel electrode gives the corresponding diphenylmercury.

BACHOFNER, BERINGER, AND MEITES² investigated the electroreduction of diphenyliodonium salts by polarography and coulometry at controlled potential, but failed to isolate the products. Zappi and Mastropaolo,³ however, isolated iodobenzene and biphenyl from the electrolysis of aqueous diphenyliodonium hydroxide; 2,2'- and 4,4'-dimethoxy-diphenyliodonium hydroxides were found to undergo a similar reaction. Schwab and Pechlivanidis⁴ isolated an unidentified crystalline product, m.p. 118–119°, from the electrolysis of aqueous diphenyliodonium nitrate and iodide at a mercury cathode; we have shown that the compound was almost certainly diphenylmercury.

We re-examined the electroreduction of diphenyliodonium salts at a mercury cathode at potentials in the region of the polarographic waves I and II.² Solubility difficulties made it necessary to use solutions of the diphenyliodonium hydroxide in aqueous sodium hydroxide as the electrolyte. No current passed through the electrolyte during attempted reduction of diphenyliodonium hydroxide at cathode potentials between -0.2 and -0.6V vs. a saturated calomel electrode. Current began to flow only at potentials of ca. -0.8V ; the electrochemical reaction was rapid at a potential of -1.6V and the product was identified as diphenylmercury.

meta- and *para*-Substituents in the diphenyliodonium salts exerted only a very small effect on the half-wave potentials for waves I and II,² and we found that on controlled potential electrolysis they afforded the corresponding diphenylmercury derivative. Although this reaction is of preparative use its general application is limited because of competing nucleophilic attack on the iodonium cation by hydroxide ions.⁵ Iodonium ions bearing electron-withdrawing substituents are decomposed too rapidly at room temperature for satisfactory electrolysis.

We have been unable to isolate biphenyl, as reported by Zappi and Mastropaolo, from the reduction of diphenyliodonium hydroxide at 0°. Biphenyl and diphenylmercury can both be formed by reactions of phenyl radicals. In a similar electrochemical situation

benzyl radicals generated by reduction of benzyl bromides give either bibenzyl or dibenzylmercury the proportion of each being dependent upon the experimental conditions.⁶ Alternatively, biphenyl may have been formed during work up and steam distillation of the reaction mixture. Although diphenylmercury is known⁷ to decompose to mercury and biphenyl when heated, we found that diphenylmercury could be steam-distilled unchanged.

Diphenyliodonium salts react with finely divided mercury at 56° to give iodobenzene and the phenylmercuric salt⁸ and electrolytic reduction is known to be a suitable method for the conversion of some alkylmercuric salts into the dialkylmercury.⁹ Under conditions similar to those used in the electrolysis, diphenyliodonium bromide or hydroxide showed no significant reaction with a pool of mercury at room temperature.

EXPERIMENTAL

For general directions on the technique of electrochemical reduction see Part I.¹⁰ The potentiostat used has been described previously.¹¹

Preparation of Diphenyliodonium Bromides.—The appropriate benzene derivative was treated with potassium iodate and sulphuric acid in acetic anhydride and the resulting iodonium ion was precipitated as the bromide with an excess of sodium bromide solution. Diphenyliodonium bromide had m.p. 208–209° (lit.,¹² m.p. 208–209°); 4,4'-dimethoxydiphenyliodonium bromide had m.p. 197–198° (lit.,¹³ m.p. 195–197°); 4,4'-dimethyldiphenyliodonium bromide had m.p. 205–206° (lit.,¹² m.p. 205–207°); 4,4'-dichlorodiphenyliodonium bromide had m.p. 215–218° (decomp.) (lit.,¹⁴ m.p. 204–205°).

Reduction of Diphenyliodonium Hydroxides.—A stirred suspension of the iodonium bromide (5 g.) in aqueous sodium hydroxide (100 ml.; 2*N*) was treated with an equivalent amount of freshly precipitated silver oxide for 2–5 hr. The inorganic salts were filtered off and washed with 2*N*-sodium hydroxide; the combined filtrate and washings were reduced electrolytically. Reductions were carried out in a two-compartment cell similar to that described by Pasternak with a mercury cathode (area 38 cm.²) and a lead anode; lead dioxide was precipitated at the anode.

⁷ F. C. Whitmore, 'Organic Compounds of Mercury,' Chemical Catalog Co., New York, 1921, p. 163.

⁸ O. A. Ptitsyna, S. I. Orlov, and O. A. Reutor, *Vestnik Mosk. Univ. Ser. II, Khim.*, 1966, **21**, 105 (*Chem. Abs.*, 1966, **65**, 13,755).

⁹ J. L. Maynard and H. C. Howard, *J. Chem. Soc.*, 1923, 960.

¹⁰ J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. (C)*, 1966, 653.

¹¹ J. Grimshaw and R. K. Quigg, *Analyst*, 1966, 667.

¹² F. M. Beringer, M. Drexler, E. M. Grindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

¹³ J. T. Plati, U.S.P. 2,839,583 (*Chem. Abs.*, 1958, **52**, 16,288).

¹⁴ F. M. Beringer, R. A. Falk, M. Karilyn, I. Lillier, G. Masulla, M. Mausner, and E. Sommer, *J. Amer. Chem. Soc.*, 1959, **81**, 342.

¹ Part VI, J. F. Archer and J. Grimshaw, *J. Chem. Soc. (B)*, 1969, 266.

² H. E. Bachofner, F. M. Beringer, and L. Meites, *J. Amer. Chem. Soc.*, 1958, **80**, 4269, 4274.

³ E. V. Zappi and R. F. Mastropaolo, *Anales Asoc. quim. argentina*, 1941, **29**, 88 (*Chem. Abs.*, 1941, **35**, 6516).

⁴ G.-M. Schwab and J. Pechlivanidis, *Svensk. Kem. Tidsk.*, 1947, **59**, 130.

⁵ F. M. Beringer, A. Brierley, M. Drexler, E. M. Grindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.

⁶ J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. (B)*, 1968, 60.

The cathode compartment contained the diphenyliodonium hydroxide solution and the anode compartment aqueous 2*N*-sodium hydroxide. Electrolysis was continued with stirring under nitrogen at a cathode potential of -1.6 v *vs.* a saturated calomel half-cell until the current across the working electrodes had fallen from *ca.* 2 A to a negligible value. A white suspension appeared in the cathode chamber. The contents of this chamber were extracted with benzene when the benzene layer was washed with water, dried (MgSO_4), and the solvent removed under reduced pressure. The residue of crystals and oil was diluted with light petroleum (b.p. $60-80^\circ$) and the insoluble diphenylmercury was filtered off. Diphenylmercury (1.24 g., 51%) * crystallised from ethanol as needles, m.p. $124-125^\circ$ (lit.,¹⁵ m.p. $124-125^\circ$) (Found: C, 40.6; H, 3.0. Calc. for $\text{C}_{12}\text{H}_{10}\text{Hg}$; C, 40.6; H, 2.8%) undepressed on admixture with authentic material prepared by reduction of phenylmercuric acetate with sodium stannite.¹⁵ 4,4'-Dimethyldiphenylmercury (1.00 g., 41%) crystallised from chloroform as needles, m.p. $240-242^\circ$ (lit.,¹⁶ m.p. $241-242^\circ$) (Found: C, 44.0; H, 3.9. Calc. for $\text{C}_{14}\text{H}_{14}\text{Hg}$: C, 43.9; H, 3.7%). 4,4'-Dimethoxydiphenylmercury (1.44 g., 58%) crystallised from benzene as needles, m.p. $201-202^\circ$ (lit.,¹⁶ m.p. 202°) (Found: C, 40.1; H, 3.65. Calc. for $\text{C}_{14}\text{H}_{14}\text{HgO}_2$: C, 40.5; H, 3.4%).

The yield for conversion of the iodonium bromides into the hydroxide by an aqueous suspension of silver oxide was determined by titration of the filtrate with *N*-hydrochloric

* Yield based on the amount of Ph_2IBr taken and reaction: $2\text{Ph}_2\text{I}^+ + 2e + \text{Hg} \rightarrow \text{Ph}_2\text{Hg} + 2\text{PhI}$.

acid with Methyl Orange as indicator; yields were in the range 50–75%. When 4,4'-dichloridiphenyliodonium bromide was stirred with silver oxide and sodium hydroxide it was converted into a viscous solid which smelt of 4-chlorophenol. The filtrate from this experiment gave no precipitate of the iodonium iodide with sodium iodide solution.

Reaction of Diphenyliodonium Hydroxide with Mercury.—Diphenyliodonium bromide (2.50 g.) was stirred with freshly precipitated silver oxide in water (50 ml.) for 2.5 hr. The inorganic salts were then filtered off and washed with water; the total filtrate and washings were adjusted to 100 ml. Half the solution was stirred over a pool of mercury (area *ca.* 10 sq. cm.) for 45 min. No precipitate resulted. The aqueous layer was separated, neutralised with hydrobromic acid, and a concentrated solution of sodium bromide was added to it. The precipitated iodonium bromide was collected and dried, m.p. $207-209^\circ$ (1.10 g., 88%); it was identified by i.r. spectroscopy. The second portion of iodonium hydroxide solution was precipitated with sodium bromide to give the iodonium bromide (1.25 g., 100%).

Diphenyliodonium bromide was recovered unchanged after being stirred with mercury under similar conditions.

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¹⁵ O. Dimroth, *Ber.*, 1902, **35**, 2853.

¹⁶ D. Spinelli and A. Salvemini, *Ann. Chim. (Rome)*, 1960, **50**, 1423.