(1.0 g.-atom) of lithium clippings, and 200 ml. of tetrahydrofuran, after not reacting for 30 min. at room temperature, was heated to 53°. Within 4 min. the mixture turned olive-green, evolved a small amount of heat, and gave a strong positive Color Test I. After being stirred for 4 hr. the black mixture gave a very intense positive Color Test I. The mixture was filtered through glass wool and derivatives were prepared as described below.

Preparation of Trimethylsilyltri-*n*-butyltin.—To a stirred solution of tri-*n*-butyltinlithium prepared as described above from 0.1 mole of hexa-*n*-butylditin, was added a solution of 23.9 g. (0.22 mole) of chlorotrimethylsilane in 100 ml. of tetrahydrofuran slowly enough to enable maintaining the mixture below 0°. The black mixture gave a negative Color Test I and was filtered. After distilling the tetrahydrofuran and filtering the lithium chloride, the residue was vacuum distilled to give 56.6 g. (77.8%) of trimethylsilyltri-*n*-butyltin, b.p. 88° (0.2 mm.), $n^{20}\mathrm{D}$ 1.4873. The infrared spectrum shows peaks at 1250 cm.$^{-1}$ and 840 cm.$^{-1}$ characteristic of the trimethylsilyl group.

Anal. Calcd. for $C_{15}H_{36}SiSn$: C, 49.60; H, 9.99. Found: C, 49.40; 49.46; H, 9.73, 9.70.

Preparation of Tri-*n*-butyltin Hydride from Hexa-*n*-butylditin.—A solution of tri-*n*-butyltinlithium prepared as described above from 0.1 mole of hexa-*n*-butylditin was hydrolyzed with water. The organic layer was combined with ether extracts of the aqueous layer and dried over magnesium sulfate. Evaporation of solvents left a liquid residue which was distilled to give 39.1 g. (67%) of tri-*n*-butyltin hydride, b.p. 63–64° (0.41–0.48 mm.) (lit.,[7] b.p. 76–81° at 0.7–0.9 mm.), $n^{22}\mathrm{D}$ 1.4721.

Anal. Calcd. for $C_{12}H_{28}Sn$: C, 49.52; H, 9.69. Found: C, 49.56, 49.26; H, 9.35, 9.40.

Hexa-*n*-butylditin was also obtained (11.8 g., 20%); this was identified by comparison of its infrared spectrum with that of an authentic sample.[8]

Preparation of Tri-*n*-butyltinlithium from Tri-*n*-butyltin Chloride.—A mixture of 65.1 g. (0.2 mole) of tri-*n*-butyltin chloride and 15.0 g. (2.0 g.-atoms) of lithium clippings was stirred for 1 hr. Although the mixture turned dark, Color Test I was negative. When tetrahydrofuran (100 ml.) was slowly added the reaction became exothermic, the mixture turned dark green, and Color Test I became positive. After being stirred for 2 hr. the mixture was filtered through glass wool and a derivative was prepared as described below.

Preparation of Tri-*n*-butyltin Hydride from Tri-*n*-butyltin Chloride.—A solution of tri-*n*-butyltinlithium prepared as described above from 0.2 mole of tri-*n*-butyltin chloride was hydrolyzed with water. The mixture was treated in the same way as described above in the preparation of tri-*n*-butyltin hydride from hexa-*n*-butylditin. The yield of tri-*n*-butyltin hydride was 31.6 g. (54%), b.p. 46–49° (0.18 mm.), $n^{22}\mathrm{D}$ 1.4720. Hexa-*n*-butylditin was also obtained (16.5 g., 28%), $n^{22}\mathrm{D}$ 1.5089. The infrared spectrum of this material was identical with that of an authentic sample.[8]

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[7] J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Middlesex, England, 1958, p. 94.

[8] The hexa-*n*-butylditin was obtained from Metal and Thermit Corp., Rahway, N. J. The sample, $n^{25}\mathrm{D}$ 1.5090, was analytically pure.

The Polarographic Reduction of *p*-Fluoroiodobenzene

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Received August 27, 1962

The polarographic reduction of *p*-fluoroiodobenzene was found to proceed normally to fluorobenzene contrary to the report of Colichman and Liu.[1] The early wave at −0.72 volt ascribed by these investigators to the reduction of the fluorine atom, is probably caused by the presence of *p*-nitrofluorobenzene as an impurity. The purified sample used in this study from vapor-phase chromatographic analysis still contained about 1% of this compound. *p*-Diiodobenzene which could arise in the preparation of *p*-fluoroiodobenzene from *p*-fluoroaniline was eliminated as another possible contributor to this early wave by its polarographic behavior.

TABLE I

POLAROGRAPHIC BEHAVIOR OF SUBSTITUTED BENZENES

Benzenes	$E^{1/2}$ (S.C.E.)	I_d
Iodobenzene	−1.73	2.86
p-Fluoroiodobenzene	−1.69	3.15
p-Nitrofluorobenzene	−0.74	5.40
p-Diiodobenzene	−1.61	2.96
	−1.79	2.96

The polarographic data for the various compounds and iodobenzene are reported in Table I. *p*-Diiodobenzene gave two waves of equal height close together. The half-wave potentials were calculated by using one-fourth and three-fourths of the total diffusion current.

The half-wave potentials for the first three compounds are slightly more negative than the values reported by Colichman.[1] The value for iodobenzene is, however, in good agreement with the data reported by others.[2]

Experimental

The current–voltage curves were obtained with a Sargent Model XXI Polarograph.

All measurements were made in a water thermostat at 25° ± 0.1° using an H cell fitted with a calomel electrode. The buffer solution used had a pH of 7 and contained 0.060 *M* lithium chloride, 0.024 *M* potassium acetate, and 0.013 *M* acetic acid in 90% alcohol. The composition was the same as that used by Colichman.[1]

The dropping mercury electrode at a pressure of 72 cm. had a drop time of 3.00 seconds (open circuit) in distilled water. The value of m was 1.97 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}$-$t^{1/6}$ of 1.90 mg.$^{2/3}$sec.$^{-1/2}$.

The iodobenzene was obtained from stock. *p*-Fluoronitrobenzene and *p*-diiodobenzene were obtained from the Eastman Kodak Co. *p*-Fluoroiodobenzene was obtained from the Pierce Chemical Co., Rockford, Ill. All samples were checked for purity by vapor-phase chromatography.

Gas chromatograms were obtained using a didecyl phthalate column at 171° with helium as the carrier gas at 20 p.s.i. The retention times of *p*-fluoroiodobenzene and *p*-nitrofluorobenzene were 12 min., and 16 min. and 45 sec., respectively, at a flow rate of 1 ml./sec.

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[1] E. L. Colichman and S. K. Liu, *J. Am. Chem. Soc.*, **76**, 913 (1954).

[2] C. S. Ramanathan and R. S. Subrahmanya, *Proc. Indian Acad. Sci.*, **47A**, 379 (1958).

The Reductive Cleavage of 2,5-Dimethyltetrahydrofuran Hydroperoxide in the Presence of Carbon Tetrachloride[1]

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Received July 30, 1962

The reductive cleavage of certain hydroperoxides has been reported in the literature.[3-5] The reaction in-

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[1] Taken from the Master's thesis of Donald F. Anderson.

[2] To whom inquiries should be sent.

[3] Jennings H. Jones and Merrell R. Fenske (to Esso Research and Engineering Co.), U. S. Patent 2,989,563 (June 20, 1961).

[4] J. Braunworth and G. W. Crosby, Abstracts of Papers presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, 13-O.

[5] W. Cooper and W. H. T. Davidson, *J. Chem. Soc.*, 1180 (1952).