(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}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}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}D 1.4720. Hexa-*n*-butylditin was also obtained (16.5 g., 28%), n^{22}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}D 1.5090, was analytically pure.

The Polarographic Reduction of *p*-Fluoroiodobenzene

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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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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.

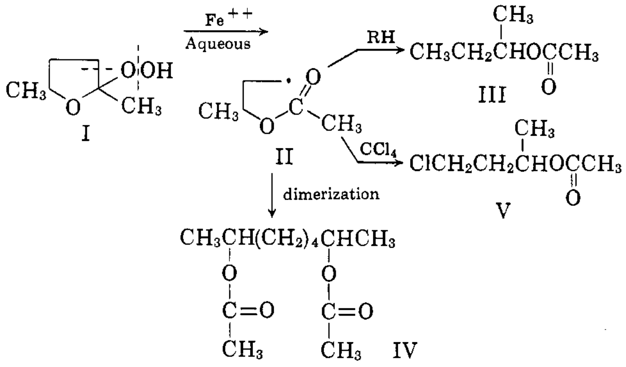
[2] To whom inquiries should be sent.

[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).

volving 2,5-dimethyltetrahydrofuran hydroperoxide[3] (I) apparently proceeds through free radical II, when aqueous ferrous ion is the reducing agent, to give *sec*-butyl acetate (III) by hydrogen abstraction from the solvent molecules, or 2,7-octanediol diacetate (IV) by dimerization of II as the principal products.



We have checked the work done by previous investigators on 2,5-dimethyltetrahydrofuran hydroperoxide with aqueous ferrous ion[3] and have extended this work by accomplishing the decomposition of I in the presence of carbon tetrachloride to produce 4-chloro-2-butyl acetate (V) along with IV. The production of V apparently proceeds by a reaction sequence similar to that for the formation of III except that in the presence of carbon tetrachloride the radical II reacts by extracting a chlorine atom to form V rather than by extracting a hydrogen atom from a solvent molecule as is the case with aqueous ferrous ion alone.

The extent of dimerization of II to produce IV when the reaction was done with aqueous ferrous ion along with carbon tetrachloride was comparable to that observed when the decomposition was done with aqueous ferrous ion alone (46 and 36%, respectively). In the experiment with carbon tetrachloride no III resulted but the yield of V with carbon tetrachloride approaches the yield of III in the absence of carbon tetrachloride (see Table I).

TABLE I

YIELD[a] OF VARIOUS ESTERS FROM DECOMPOSITION OF 2,5-DIMETHYLTETRAHYDROFURAN HYDROPEROXIDE

Compounds	Aqueous Fe^{++} only	Aqueous Fe^{++} with CCl_4
4-Chloro-2-butyl acetate	..	19
sec-Butyl acetate	32	..
2,7-Octanediol diacetate	46	36

[a] The yields given are in mole per cent in terms of the moles of hydroperoxide appearing as a particular product.

In addition to the ester-like material characterized in the reaction with carbon tetrachloride, a dark, viscous residue was recovered which amounted to 32 weight % of the starting hydroperoxide. This residue was not characterized.

Experimenta

Production of Hydroperoxide.—A sample of 2,5-dimethyltetrahydrofuran was allowed to stand in a glass reaction flask in contact with oxygen for a period of 6 weeks. Intermittent stirring was used to assure saturation with oxygen at all times. At the end of the 6-week period, analysis by the method of Wagner, Smith, and Peters[6] for hydroperoxide content indicated that the sample consisted of 38.6 g. of 2,5-dimethyltetrahydrofuran hydroperoxide and 139.4 g. of 2,5-dimethyltetrahydrofuran.

Decomposition of Hydroperoxide in the Presence of Carbon Tetrachloride.—The mixture described above was added, dropwise, to a mixture consisting of a saturated solution of ferrous sulfate heptahydrate, 1 l. of methanol, and 500 ml. of carbon tetrachloride. The methanol was added in an attempt to produce a homogeneous reaction medium but did not accomplish this end as two phases were present all during the reaction. The reaction mixture was contained in a 3-l., three-neck, round-bottom flask, equipped with an efficient stirrer, a condenser, and a dropping funnel from which the hydroperoxide was added. The reaction mixture was maintained at 30° by use of an ice bath as the reaction was quite exothermic. After the reaction was complete the resulting organic and water layers were separated and investigated individually.

The water layer contained no organic material boiling above 100°.

The organic layer was washed with three 100-ml. portions of potassium carbonate solution, then dried overnight with anhydrous magnesium sulfate. The dry organic layer was subjected to a simple distillation and separated into three large fractions. The first fraction boiled 59–78° and contained chloroform, methyl alcohol, carbon tetrachloride, 2,5-dimethyltetrahydrofuran, and water. The second fraction was collected at 78–81° was mainly carbon tetrachloride. The remaining material was charged to a fractionation column (about 30 theoretical plates, glass-packed) and fractionally distilled. Additional chloroform, methanol, carbon tetrachloride, 2,5-dimethyltetrahydrofuran, and water were obtained. After the material boiling below 100° was removed, the pressure was reduced and distillation was continued. Two significant fractions were subsequently distilled. One fraction, which was eventually found to be 4-chloro-2-butyl acetate, possessed the following properties: b.p. 59–64°/13 mm. (lit.,[7] 71–72°/16 mm.), $n^{20}{}_D$ 1.4280 (lit.,[7] 1.4273), m.p. of 3,5-dinitrobenzoate 113–114° (lit.,[7] 113–114°), sapon. equiv. 80.7 (corresponding to elimination of hydrogen chloride).

Anal. Calcd. for $C_6H_{11}ClO_2$: C, 48.6; H, 7.97; Cl, 23.5; O, 20.6. Found: C, 48.6; H, 7.55; Cl, 22.2; O, 21.7.

Qualitative infrared analysis indicated carbon–chlorine bonding in the material.

The other fraction, b.p. 71–115°/10 mm., $n^{20}{}_D$ 1.4285, sapon. equiv. 115, was water-white and did not contain chlorine. This fraction was not rigorously characterized but on the basis of work by previous investigators[3] plus the information cited above was assumed to be a diol diacetate, possibly 2,7-octanediol diacetate.

Decomposition of Hydroperoxide with Ferrous Ion Alone.—The decomposition and work-up of the hydroperoxide accomplished in the presence of aqueous ferrous ion alone was similar to that described for the carbon tetrachloride experiment. The principal products were *sec*-butyl acetate and 2,7-octanediol diacetate (see Table I) as had been established previously.[3]

Acknowledgment.—The authors are indebted to Dr. J. H. Jones of the Petroleum Refining Laboratory at The Pennsylvania State University for supplying the 2,5-dimethyltetrahydrofuran used in this investigation.

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(6) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

(7) S. Searles, K. A. Pollart, and F. Block, *J. Am. Chem. Soc.*, **79**, 952 (1957).

The Synthesis of the β-D-Glucoside of Medicagenic Acid, an Alfalfa Root Saponin[1]

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The β-D-glucoside of medicagenic acid has been synthesized by a four-step procedure. Crystalline

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