

## Synthesis of a Silicone Derivative of Sucrose

CLARENCE D. CHANG<sup>1</sup> AND H. B. HASS<sup>2</sup>

Received December 30, 1957

We wish to report the synthesis of a silicone derivative of sucrose. The compound, the octakis(trimethylsilyl) ether of sucrose, was prepared by treating sucrose in pyridine solution with trimethylchlorosilane (General Electric Silicone SC-01). Schwarz, Baronetsky, and Schoeller<sup>3</sup> have reported the preparation of glucose derivatives.

The sucrose used was commercial grade material which was purified by recrystallization from aqueous ethanol and dried *in vacuo*; the silylating agent, assaying 85% minimum trimethylchlorosilane, was used without preliminary purification.

Trimethylchlorosilane (250 g., 2.3 mole) was added dropwise into a mechanically stirred solution of 85.6 g. (0.25 mole) sucrose in 1.5 l. of anhydrous pyridine, after which the reaction mixture was heated at 80°–85° for two hours. Upon completion of the reaction the excess pyridine was distilled off *in vacuo* and the residual slurry extracted thoroughly with petroleum ether. The ether extract was concentrated *in vacuo* and the viscous concentrate distilled in a Hickman alembic still at 0.02–0.05 mm. at 190°–200°.

The product was a clear, almost colorless oil with high viscosity, soluble in benzene, methanol, acetone, petroleum ether, diethyl ether, and chlorinated hydrocarbons, and insoluble in water.  $[\alpha]_D^{20} + 3.47^\circ$  (50 wt. % in benzene);  $n_D^{20}$  1.4434.

*Anal.*: Calcd. for  $C_{36}H_{86}O_{11}Si_8$ : mol. wt., 918. Found: Si, 23.3; mol. wt. (Rast), 933.

The data suggest that the compound may be a mixture containing some hepta or lower silicated derivatives. However, it is believed that these very possibly have higher boiling points or even would tend to polymerize without distillation.

The compound exhibited a marked tendency to hydrolyze in the presence of water. A sample, refluxed with water and chromatographed, showed a single spot which was identified as sucrose. Since the compound is volatile and can readily be hydrolyzed, yielding sucrose, it offers a good means for the analytical separation of sucrose by vapor phase chromatography and its identification.

*Acknowledgment.* This work was part of Project #82 granted by Sugar Research Foundation, Inc.

NEW YORK, N. Y.

(1) Herstein Laboratories, Inc.

(2) Sugar Research Foundation, Inc.

(3) R. Schwarz, E. Baronetsky, and K. Schoeller, *Angew. Chem.*, **63**, 335 (1956).

## Reduction of Chlorobenzene at the Dropping Mercury Electrode

FRANK L. LAMBERT AND KUNIO KOBAYASHI

Received February 17, 1958

Although there have been several attempts to reduce chlorobenzene and its derivatives at the dropping mercury electrode,<sup>1–3</sup> they were not successful, ostensibly because of the extreme potentials involved. We wish to report the reduction of chlorobenzene and to suggest that other difficultly reducible organic substances will be accessible by the technique employed. Because our work lies primarily in the area of aliphatic halogen compounds, we do not intend to pursue further investigations of chlorobenzenes or unsaturated compounds which might now be reducible by others according to the procedure described herein.

Tetrabutylammonium iodide (TBI) has been shown to be the supporting electrolyte with the most negative decomposition potential of the substances tested in dioxane-water.<sup>4</sup> Kolthoff and Coetzee<sup>5</sup> found that several supporting electrolytes had the same decomposition potential in anhydrous acetonitrile. As might be expected, our work in anhydrous *N,N*-dimethylformamide (DMF) has shown that 0.05*M* TBI has an apparent decomposition potential of approximately –2.85 volts *vs.* the saturated calomel electrode (S.C.E.) and 0.05*M* tetraethylammonium bromide (TEB) “discharges” at –2.76 volts. Yet, contrary to obvious deduction, chlorobenzene in DMF solution with TBI as the supporting electrolyte yields only a marked rise in current just prior to the cathodic discharge, whereas with TEB as the supporting electrolyte chlorobenzene gives a clear wave with a flat plateau. The half-wave potential in 0.05*M* TEB is –2.58 volts *vs.* the S.C.E.

The reduction of chlorobenzene is influenced by the cation of the supporting electrolyte because no polarographic wave is observed when tetrabutylammonium bromide (or TBI) is used but waves are present with 0.05*M* tetraethylammonium iodide or perchlorate (or TEB) as supporting electrolytes. (The half-wave potentials are –2.58 for chlorobenzene in tetraethylammonium iodide and –2.60 in tetraethylammonium perchlorate.) With tetramethylammonium bromide a rise in current is discernible before cathodic discharge but the wave

(1) H. Keller, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **29**, 761 (1946).

(2) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(3) E. S. Levin and Z. I. Fodiman, *Zhur. Fiz. Khim.*, **28**, 601 (1954). *Chem. Abstr.*, **48**, 11218 (1954).

(4) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942).

(5) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).