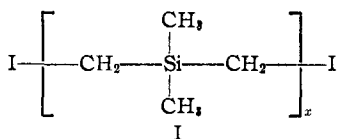


## Reactions of Bis-(halomethyl)-dimethylsilanes with Metals

BY JOHN D. ROBERTS AND SUKH DEV

In an attempt to synthesize 1,1-dimethylsilylo-cyclopropane, the reactions of bis-(chloromethyl)-dimethylsilane and bis-(iodomethyl)-dimethylsilane with zinc and magnesium have been investigated under conditions where 1,3-dihalopropanes give high yields of the corresponding cyclopropanes.

Treatment of bis-(chloromethyl)-dimethylsilane with zinc dust in aqueous ethanol in the presence of sodium iodide and sodium carbonate<sup>1</sup> gave chloromethyltrimethylsilane in good yield along with traces of tetramethylsilane. With magnesium in a mixture of dibutyl ether and xylene, the reaction proceeded slowly and only a polymeric material was obtained. Bis-(iodomethyl)-dimethylsilane reacted smoothly with zinc in absolute ethanol to give 87% of the theoretical amount of tetramethylsilane. With magnesium in diethyl ether, the iodo compound gave polymeric products which contained iodine and presumably some material having structures of the following type.



The part of the polymeric product which was volatile enough to be distilled had an iodine analysis corresponding roughly to I with an improbable value of  $x = 20$ . Consequently, the volatile material must have been a mixture containing a considerable fraction of non-iodine substituted cyclic organosilicon compounds of the formula  $(\text{C}_4\text{H}_{10}\text{Si})_n$ , as well as substances such as I with a low enough molecular weight to be distillable.

Our results indicate no tendency for bis-(halomethyl)-dimethylsilanes to undergo the Freund reaction with zinc and magnesium. This does not necessarily mean that silicocyclopropanes are unstable or incapable of existence since the ring closure reaction is always competitive with reduction in aqueous ethanol and intermolecular coupling in non-hydroxylic media and there is no assurance that ratios of rates which hold with 1,3-dihalopropanes will also be obtained with bis-(halomethyl)-silanes.

### Experimental

**Chlorination of Tetramethylsilane and Chloromethyltrimethylsilane.**—The chlorinations were carried out in the vapor phase using an apparatus and procedure similar to those described previously<sup>2</sup> except that the spiral reactor tube was surrounded by a jacket which permitted heating of the tube with vapors from boiling liquids.

In the chlorination of tetramethylsilane, the reaction zone was heated with boiling benzene and irradiated with a General Electric RS Sunlamp. From 44 g. (0.5 mole) of tetramethylsilane and 11.1 l. of chlorine gas (measured at 26° and 760 mm. over saturated salt solution) there was obtained 45 g. (74%) of chloromethyltrimethylsilane, b.p.

98–99°,  $n_D^{25}$  1.4145. The first 9.5 l. of chlorine was run in over 2 hours, the next 1.2 l. over one-half hour, and the final 0.4 l. over 40 minutes. The liquid-phase chlorination of tetramethylsilane has been reported to yield 33% of the monochlorination product.<sup>3</sup>

Chlorination of chloromethyltrimethylsilane was carried out in the same manner, using xylene vapor to heat the reaction tube. From 24.5 g. (0.2 mole) of chloromethyltrimethylsilane and 4.8 l. of chlorine gas (measured at 28° and 760 mm. over saturated salt solution) there was obtained 11 g. (35%) of dichloromethyltrimethylsilane, b.p. 130–135° and 14 g. (46%) of bis-(chloromethyl)-dimethylsilane, b.p. 155–160°. Intermediate fractions amounted to 3 g. The chlorine was added over 8 hours; the rate of addition being fastest at the start of the reaction and quite slow at the end to avoid carbon formation. After redistillation, the dichloromethyltrimethylsilane (b.p. 132–133°) had  $n_D^{25}$  1.4425 (lit.,<sup>4</sup> b.p. 135°,  $n_D^{25}$  1.4430). Redistillation of the bis-(chloromethyl)-dimethylsilane yielded camphoraceous-odored material of b.p. 159–160°,  $n_D^{25}$  1.4575 (lit.,<sup>4</sup> b.p. 160°,  $n_D^{25}$  1.4579).

Chlorination of tetramethylsilane with sulfuryl chloride and benzoyl peroxide in methylene chloride solution has been shown to give products resulting from cleavage of carbon-silicon bonds. No bis-(chloromethyl)-dimethylsilane could be isolated.<sup>5</sup>

**Bis-(iodomethyl)-dimethylsilane.**—A solution of 9.4 g. (0.060 mole) of bis-(chloromethyl)-dimethylsilane and 18.1 g. (0.12 mole) of sodium iodide in 75 ml. of acetone was refluxed for 10 hours. Most of the acetone was distilled and the residue was cooled, poured into water and extracted with ether. The ethereal extract was washed with water, sodium bisulfite solution and water. It was then dried over calcium sulfate and distilled. The yield of bis-(iodomethyl)-dimethylsilane of b.p. 97° (7 mm.) was 17 g. (83%).

*Anal.* Calcd. for  $\text{C}_4\text{H}_{10}\text{I}_2\text{Si}$ : C, 14.11; H, 2.94. Found: C, 14.37; H, 3.05.

**Reaction of Bis-(chloromethyl)-dimethylsilane with Zinc and Magnesium.**—A mixture of 4.7 g. (0.030 mole) of the bis-chloro compound, 3.9 g. (0.060 g.-atom) of zinc dust, 1.1 g. of anhyd. sodium carbonate, 0.9 g. of sodium iodide, 15 ml. of ethanol, and 5 ml. of water was heated under reflux with an oil-bath at 90–95° for 6 hours. Throughout the reaction the reflux temperature was 69–70°. The top of the reflux condenser was connected to a Dry Ice-cooled trap in which about 0.2 ml. of a liquid boiling below 30° (apparently tetramethylsilane) collected during the reaction. The reaction mixture was distilled through a short column into an ice-cooled receiver until the head temperature reached 80°. The distillate was mixed with ice-water and the upper layer separated and dried over calcium chloride in a refrigerator. Distillation through an efficient center-tube type column gave a few drops of forerun b.p. 75–98° and 2.0 g. (55%) of chloromethyltrimethylsilane, b.p. 98–99°,  $n_D^{25}$  1.4135. The infrared spectrum of the product was identical with that of authentic chloromethyltrimethylsilane.

A mixture of 4.7 g. (0.030 mole) of bis-(chloromethyl)-dimethylsilane, 0.72 g. (0.030 g.-atom) of magnesium, 5 ml. of dibutyl ether and 10 ml. of xylene was heated under reflux in the same apparatus used for the zinc reaction. The reaction did not start until a crystal of iodine was added. After 20 hours, practically all of the magnesium had dissolved and the head temperature dropped from 135 to 120°. No material of b.p. below 120° was obtained. After removal of the dibutyl ether and xylene, there remained a high-boiling material which was not investigated further.

**Reaction of Bis-(iodomethyl)-dimethylsilane with Zinc and Magnesium.**—A mixture of 16 g. (0.046 mole) of bis-iodo compound, 6.1 g. (0.093 g.-atom) of zinc dust and 20 ml. of absolute ethanol was heated under a short glass-helix packed column. Distillate was taken off intermittently at 26–27° over a 4.5-hour period. The product amounted to 3.5 g. (87%) and, besides its b.p., was shown to be tetramethylsilane by its infrared spectrum which was identical with that of an authentic sample.

The reaction of 17 g. (0.050 mole) of the bis-iodo compound with 1.2 g. (0.050 g.-atom) of magnesium turnings in

(1) These reagents give crude cyclopropane in 95% yield from 1,3-dichloropropane, H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

(2) J. D. Roberts and R. H. Mazur, paper scheduled for publication in June, 1951.

(3) F. C. Whitmore and L. H. Sommer, *THIS JOURNAL*, **68**, 481 (1946).

(4) J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

(5) This work was carried out by Mr. Daniel Lundgren, B.S. Thesis, M. I. T., 1950.

60 ml. of dry ether proceeded readily without external heating. After one-half hour, the mixture was refluxed for 2 hours and then allowed to stand overnight. All of the magnesium dissolved and the mixture separated into two layers. The lower layer gave no Gilman test for Grignard reagent. The mixture was poured onto ice, the ether layer separated and washed with dilute hydrochloric acid and water. The ethereal solution was dried over calcium sulfate and the ether removed. The residue amounted to 4.2 g., contained iodine (by sodium fusion test) and was polymeric in nature. About 1.5 g. of material, b.p. 100–190° (6–7 mm.), was obtained on distillation before the residue began to decompose. The volatile product was purified by evaporative distillation for analysis.

*Anal.* Calcd. for  $(C_4H_{10}Si)_{20}I_2$ : C, 48.59; H, 10.19; I, 12.83. Found: C, 48.14; H, 10.41; I, 12.43.

The combustion analysis gave fair agreement for structure I with  $x = 20$ . Actually, the material is probably a mixture of  $(C_4H_{10}Si)_n$  and I with values of  $n$  and  $x$  small enough to give the observed b.p. range.

DEPARTMENT OF CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
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## Polarographic Behavior of Organic Compounds. VIII. The System *meso*- $\alpha,\alpha'$ -Dibromosuccinic Acid–Fumaric Acid

BY ISADORE ROSENTHAL AND PHILIP J. ELVING

Previous work on the  $\alpha$ -halogenated acids<sup>1,2</sup> has shown that the polarographic reduction of these compounds involves the fission of the carbon-halogen bond and the formation of the saturated acid. This behavior is in accord with the chemical reduction of carbon-halogen linkages. In the case of  $\alpha,\beta$ -dibromides both chemical reduction<sup>3,4</sup> and polarographic reduction<sup>5</sup> result in formation of the olefin. The polarographic work<sup>5</sup> on 1,2-dibromoethane and the preparative electrolysis<sup>5</sup> on 2,3-dibromobutane, unfortunately, was done at only one set of conditions in unbuffered solution. No attempt was made to identify the configuration of the olefin produced, which is of primary interest with regard to any mechanism proposed for the reduction. It was therefore felt to be of interest to study this phenomenon under suitable conditions, with a view to investigating the nature of the process and to see if the isomers formed as reduction products were analogous to those formed chemically. The compound chosen for study was *meso*- $\alpha,\alpha'$ -dibromosuccinic acid whose olefinic reduction product would be either fumaric or maleic acid, either of which could be identified polarographically. In addition, the dibromosuccinic acid with its two equivalent carbon-halogen bonds held promise of shedding additional light on the mechanism of polarographic reduction of symmetrical linkages and of carbon-halogen bonds.

The work done on fumaric acid was primarily to aid in identifying the second polarographic wave obtained with the dibromosuccinic acid. At the

same time it was possible to extend previous work on fumaric acid.<sup>6</sup>

### Experimental

The experimental conditions, procedures and apparatus are the same as elsewhere described<sup>2</sup> except that a new capillary was used, whose  $m$  value was 1.027 mg./sec. at open circuit, into distilled water, with a head of 50 cm. and a drop-time of 6.0 seconds. The buffers used are given in Table I and are analogous to those previously used in the fumaric acid study.<sup>6</sup> All measurements were made at  $25.0 \pm 0.1^\circ$ .

TABLE I  
BUFFER SOLUTIONS

Range	Concentration of components
0 to 2	0.9 M in KCl with added HCl
4 to 6	0.9 M in NAOAc with added HOAc
8 to 9	0.9 M in $NH_4Cl$ with added $NH_4OH$

Fumaric acid (Eastman Kodak Co. practical grade) was recrystallized three times from 1 *N* hydrochloric acid. *meso*- $\alpha,\alpha'$ -Dibromosuccinic acid, prepared according to "Organic Syntheses,"<sup>7</sup> was purified by repeated washing with water and by recrystallization from ethyl ether. By means of solubility tests in ethyl ether it was shown that the amount of fumaric acid present as impurity was less than 3 mole %.

### Discussion and Conclusions<sup>8</sup>

The polarographic data for dibromosuccinic acid, fumaric acid, and mixtures of the two are given in Table II. Two well-defined cathodic waves were obtained for dibromosuccinic acid over the pH range 2 to 9 except at pH 5.9 where three waves were obtained. The first of these waves marks the reduction of the dibromosuccinic acid to fumaric acid and the remaining wave (two waves at pH 5.9) is due to the reduction of the fumaric acid thus formed to succinic acid (no. 4 to 6 and 8 to 11). The identity of the second wave is shown by comparing the curves of dibromosuccinic acid with the waves produced with fumaric acid and fumaric-dibromosuccinic acid mixtures (no. 3 and 4; 5 and 6; 7 and 8; 9 and 10); in all cases the  $E_{0.5}$  and  $i_a/c$  values agree. In calculating the  $i_a/c$  values for the second waves of the fumaric acid-dibromosuccinic acid mixture, the concentration values used were the sum of the fumaric acid and the dibromosuccinic acid concentrations. At pH 5.9 the reduction of fumaric acid involves two waves and, consequently, the reduction of dibromosuccinic acid at this pH results in three waves (no. 7 and 8). While the diffusion current constants for the reduction of the two acids are similar at any one pH, they vary considerably among themselves at different pH values. This behavior in the diffusion currents has been previously noted.<sup>6</sup>

A plot of  $E_{0.5}$  vs. pH for the dibromosuccinic acid

(1) P. J. Elving and C. S. Tang, *THIS JOURNAL*, **72**, 3244 (1950).  
(2) P. J. Elving, I. Rosenthal and M. K. Kramer, *ibid.*, **73**, 1717 (1951).  
(3) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 86.  
(4) S. Winstein, D. Pressman and W. G. Young, *THIS JOURNAL*, **61**, 1645 (1939).  
(5) M. v. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(6) P. J. Elving and C. Teitelbaum, *THIS JOURNAL*, **71**, 3916 (1949).  
(7) H. S. Rhinesmith, in "Organic Syntheses," Vol. 18, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 17.  
(8) Although reference is made to the acids throughout the paper, it should be remembered that the behavior of the anions was being observed under many of the conditions used.