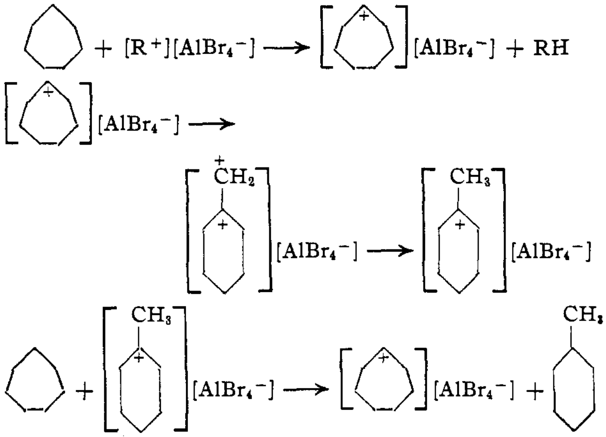

Oxygen and ultraviolet light cause the formation of a chain initiator, while benzene removes it and therefore causes the inhibition of the reaction.

It is important in the study of the isomerization of cycloheptane to keep the hydrocarbon in tightly covered bottles under an atmosphere of nitrogen or carbon dioxide. The presence of traces of peroxides or oxygenated hydrocarbons acts as a chain initiator; for that reason it is necessary that at frequent intervals a control experiment be made with aluminum bromide–hydrogen bromide as catalyst. If an isomerization occurs the cycloheptane should be passed over activated silica gel in order to remove any traces of oxygenated material that might have been formed.

Experimental

A. **Apparatus and Procedure.**—A high vacuum apparatus described previously[4] was used for the purification of the reactants and for charging and discharging the reaction tube. The technique of adding the chain initiators, such as *s*-butyl bromide or oxygen was the same as described previously.[1] In the experiments in which ultraviolet irradiation was involved, a round bulb of clear fused quartz was affixed through a graded seal to the Pyrex reaction tube; this permits a more effective transmission of light to the reaction zone. A Cenco quartz cadmium-mercury vapor arc lamp was used at a distance of 20 cm. from the reaction tube.

B. **Materials.** 1. **Cycloheptane.**—It was prepared by adding to 0.17 mole of cyclohexanone dissolved in one liter of ether, 0.17 mole of diazomethane[9] in 500 ml. of ether and 200 ml. of anhydrous methanol. After three days standing at room temperature the product was distilled on a three-plate column. The ketones boiled at 154–180°, n^{20}_{D} 1.4570.

The mixture of ketones was reduced by the Wolff–Kishner reaction as modified by Huang-Minlon.[10] The hydrocarbons thus obtained, 16 g., were distilled on a forty-plate column. The following fractions were separated: (a) b.p. 79.2°, 4 ml., n^{20}_{D} 1.4242 corresponding to cyclohexane and (b) b.p. 117°, 12.1 ml., n^{20}_{D} 1.4448, corresponding to cycloheptane.

The cycloheptane was passed through 200-mesh size activated silica gel in order to remove any traces of oxygenated material present.

C. **Analysis.**—The composition of the hydrocarbons obtained from the isomerization was determined by means of infrared spectral analysis. The spectra of methylcyclohexane and of cycloheptane, used as standards, were identical with those reported by the American Petroleum Institute Project 44.

The wave lengths used for calculating the composition of the samples were: 9.24, 10.40, 11.06, 11.56 and 12.44 μ.

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[9] E. Mosettig and A. Burger, This Journal, **52**, 3456 (1930).

[10] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

Lower Chlorides of Silicon

By Eugene G. Rochow and Rostislav Didtschenko

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The "inert pair" of *s* electrons in germanium, lead and tin, leads to well-defined monomeric bivalent compounds of these elements. However, compounds of bivalent silicon are represented only by the monoxide SiO (which sublimes only at red heat *in vacuo* and is polymeric) and a series of lower chlorides.[1–4] In the latter (and possible also in SiO) there are Si–Si bonds[4] and hence the silicon is not bivalent in the same sense as is tin in $SnCl_2$ or germanium in $GeCl_2$.

At the same time, the readiness with which $GeCl_2$ adds molecules like HCl[5] suggests that a dichloride of silicon would be very useful because it should absorb methyl chloride to form methylchlorosilanes. It was our intention to try to prepare $SiCl_2$ by methods similar to those used for the preparation of $GeCl_2$,[6] and then to investigate the addition of alkyl halides to such a dichloride.

Experimental

The apparatus shown in Fig. 1 was constructed in order to attempt the reduction of silicon tetrachloride with silicon at temperatures higher than those permitted by the apparatus of Troost and Hautefeuille.[1] Silicon tetrachloride, purified by stirring with dry sodium carbonate and then by distillation, was frozen in bulb A and the apparatus was evacuated. The silicon tetrachloride was then allowed to vaporize through the fused silica tube I, which contained 15 g. of pure silicon (99.8%) and was heated to 1000°. After 15 minutes a yellow viscous oil began to collect in the small bulbs at the rate of about 1 cc. per hour. The silicon tetrachloride was condensed in bulb B, distilled back into A through the by-pass, and so recirculated repeatedly.

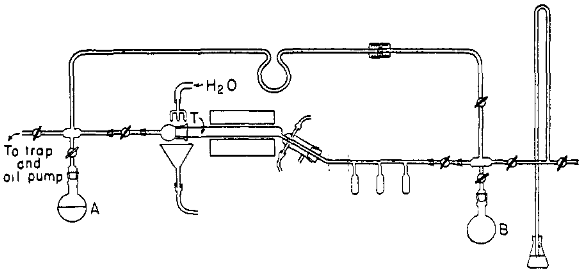

Fig. 1.

After 5 cc. of yellow oil had collected, it was transferred under dry nitrogen to a miniature still and distilled through a fractionating column 120 mm. long and 6 mm. in inside diameter, containing a nickel spiral wound around a coaxial glass rod. After some $SiCl_4$ and other volatile material had distilled up to 100° at atmospheric pressure, the pressure was reduced to 1 mm. and three fractions were collected at 70 to 120°, 120 to 170°, and 170 to 200°. Some decomposition in the distillation flask was evident, and a mirror of silicon formed on its walls. The products did not distil uniformly over the temperature ranges indicated, but appeared to be mixtures of relatively few components. However, the amounts were so small, and the heat capacity of the mercury-filled thermometer well so large, that more reliable boiling points could not be obtained. The fractions were sealed in the ampules in which they were collected.

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[1] Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 459 (1871).

[2] R. Schwartz, *Ber.*, **80**, 444 (1947).

[3] R. Silvers and N. Gregor, *Z. anorg. allgem. Chem.*, **241**, 395 (1939).

[4] K. A. Hertwig and E. Wiberg, *Z. Naturforsch.*, **6b**, 336 (1951).

[5] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.*, **31**, 1526 (1927); L. M. Dennis and H. L. Hunter, This Journal, **51**, 1151 (1929).

[6] L. M. Dennis and H. L. Hunter, *ibid.*, **51**, 1151 (1929).

Analyses for silicon and chlorine were complicated by the extreme sensitivity of the products to oxygen and moisture. Micropipets and other conventional apparatus could not be used because the adsorbed water on the glass caused immediate hydrolysis. Recourse was had to constricted sample tubes 6 × 60 mm. which were heated to 500°, cooled in a dry-box filled with nitrogen, filled with the samples from a drawn-out capillary (which also had been cooled in the dry-box), and then stoppered and sealed. To analyze for silicon the weighed tubes were broken in the middle and dropped into 5 ml. of absolute alcohol (in which all products were very soluble), and several drops of dilute ammonia water added. The solutions were boiled for one hour, and the resulting silica was filtered, dried and weighed in the usual manner, the empty sample tubes being reweighed afterward. To analyze for chlorine, the weighed sample tubes were broken into a known volume of standardized solution of sodium hydroxide in alcohol, and the excess base titrated against standard acid. After the titration was finished, the empty sample tubes were rinsed with dilute hydrofluoric acid to remove the adhering silica and then were weighed back. The results are given in Table I.

TABLE I

Fraction	Boiling range at 1 mm., °C.	Properties	Si, %	Cl, %
2	70–120	Colorless light oil	20.88 20.86	80.2
3	120–170	Viscous oil	23.2	67.5 66.8
4	170–200	Very viscous yellow oil	23.9	79.0

Fractions 2 and 3 appear to be composed of familiar chlorinated di-, tri-, and tetrasilanes and siloxanes, as reported by Troost and Hautefeuille.[1] However, fraction 4 appears to be identical with the "subchloride" of silicon richest in chlorine obtained by Hertwig and Wiberg[4] from the reduction of silicon tetrachloride with hydrogen in an electric discharge. On the basis of the silicon contents, their substance had the empirical composition $SiCl_{2.6}$ and ours $SiCl_{2.61}$.

The publication by Hertwig and Wiberg[4] appeared while this investigation was in progress, and since Hertwig showed at once that their subchloride would absorb methyl chloride to produce methylchlorosilanes,[7] it seemed unnecessary to continue our work. We have shown that under appropriate conditions silicon tetrachloride can be reduced by silicon to form a lower chloride similar to that produced by reduction with hydrogen in an electric discharge.

Acknowledgment.—The authors are grateful for assistance provided by a fund given by the Mallinckrodt Chemical Works.

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[7] K. A. Hertwig, *Z. Naturforsch.*, **6b**, 337 (1951).

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Formylation of the Dimethoxybenzenes Using Phosphorus Oxychloride and N-Methylformanilide

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An indication[1] in the literature that formylation of 1,3-dimethoxybenzene with phosphorus oxychloride and N-methylformanilide gives 2,6-dimethoxybenzaldehyde instead of the expected 2,4-dimethoxybenzaldehyde prompted an investigation of this reaction. The same reagents were combined with veratrole and 1,4-dimethoxybenzene for comparative purposes.

Treatment of 1,3-dimethoxybenzene with phosphorus oxychloride and N-methylformanilide mixture by a procedure described earlier[2] gave an 85% yield of 2,4-dimethoxybenzaldehyde. More vigorous conditions were required to convert veratrole and 1,4-dimethoxybenzene to veratraldehyde and 2,5-dimethoxybenzaldehyde, and the yields were lower than with the meta isomer. Veratraldehyde has been synthesized[3] by the analogous reaction of veratrole with formylpiperidine and phosphorus oxychloride in a yield comparable to that reported here. However, condensation of 1,3-dimethoxybenzene with a mixture of formyldiethylamine and phosphorus trichloride yielded only 40% of 2,4-dimethoxybenzaldehyde. The following procedure appears to be superior to previously described methods for synthesizing this aldehyde.

Experimental

2,4-Dimethoxybenzaldehyde.—Equimolar quantities of phosphorus oxychloride (153 g., 1 mole) of N-methylformanilide (135 g., 1 mole) were placed in a 1-l., 3-neck flask and allowed to stand for 45 minutes. To this mixture was added, during 70 minutes with stirring, 138 g. (1 mole) of 1,3-dimethoxybenzene while the internal temperature was held at 25° by a cold water-bath. When addition was complete the bath was removed and the mixture was stirred for 3 hours longer during which time the temperature rose to 34°. The sirupy red mixture was allowed to stand overnight and was then poured slowly with good stirring into 2.5 l. of cold water. The resulting solid was collected and washed well with water on the filter. The wet cake was dissolved in 250 ml. of warm benzene, and the aqueous layer was separated and shaken with 50 ml. of benzene. The combined extracts were concentrated and distilled from a Claisen flask, yielding 141 g. (85%) of aldehyde, b.p. 110° (0.1 mm.), m.p. 68-70°. The **oxime** melts at 105-106° (lit.[4] 106°). The **semicarbazone**, from alcohol, melts at 203°.

Anal. Calcd. for $C_{10}H_{13}N_3O_3$: N, 18.82. Found: N, 18.78.

Veratraldehyde.—Veratrole (27.6 g., 0.2 mole) was added to an equimolar amount of the formylating mixture prepared as described above and the mixture was stirred at 70° for 18 hours. It was poured into water and ice and the product extracted with ether. The extract was shaken with sodium bicarbonate solution, dried and distilled. This gave 15.3 g. of product, b.p. 167-170° (21 mm.), m.p. 39-42°. It was recrystallized from cyclohexane and 12.5 g. (38%) of aldehyde, m.p. 44-45°, was obtained.

2,5-Dimethoxybenzaldehyde.—By the procedure described for veratraldehyde there was obtained a 16% yield of this aldehyde, m.p. 51°. The ***p*-nitrophenylhydrazone** melts at 216°.[5]

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[1] L. N. Ferguson, *Chem. Revs.*, **38**, 231 (1946).

[2] A. W. Weston and R. J. Michaels, Jr., *Org. Syntheses*, **31**, 108 (1951).

[3] S. Akabori and Y. Senoh, *Bull. Chem. Soc. Japan*, **14**, 166 (1939); *C. A.*, **33**, 6270 (1939).

[4] L. Gattermann, *Ann.*, **357**, 369 (1907).

[5] H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, 2339 (1927).

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NEW COMPOUNDS

Dimercaptols of Acetonylacetone

The *n*-tetradecyl- and *n*-octadecyl dimercaptols of acetonylacetone were prepared in approximately 60% yield by