It may be objected that the peroxidase properties of charcoal are due solely to a combination of catalase and oxidase properties. This cannot be the case in the oxidation of uracil by hydrogen peroxide in the presence of charcoal[9] as shown in a previous paper.[1a] There we also stressed the fact that colloidal charcoal has definite peroxidase activity while lacking marked catalase activity. The latter property has now been investigated for a large number of charcoal sols. While 44 cc. of a 0.25 molar solution of hydrogen peroxide in a 100-cc. Pyrex flask liberated 3.0 cc. of oxygen in twenty minutes, when the water was replaced by a wide variety of charcoal sols, the yield of oxygen varied between 3.1 and 4.3 cc., a very small increase.

Experimental

Preparation of the Charcoals.—Approximately 190 g. of reagent-grade sucrose was suspended in 200 cc. of water in a porcelain vessel and heated until charring was complete. After grinding in an agate mortar, the product was activated for one hour in porcelain crucibles at 590 to 600°. Urea was added in the proportion of 5 parts to 95 of sucrose, while ferric chloride was added to the extent of 3%. The charcoals containing iron were washed repeatedly with distilled water until free from chloride before being activated.

Catalase Activity.—This was measured in a 100-cc. Pyrex flask, containing 100 mg. of the charcoal to be tested, 24 cc. of water, and 20 cc. of *p*H 7.5 citrate buffer. In a side-arm 1 cc. of superoxol was placed so that tilting the flask introduced it into the solution. The oxygen was measured in a 10-cc. gas buret while the flask was shaken 90 times per minute. In testing the charcoal hydrosols, the buffer and charcoal were omitted, and either 44 cc. of water or of charcoal hydrosol and 1 cc. of superoxol were used.

Preparation of the Charcoal Hydrosols.—Two general methods were used, the one described in the first paper of this series,[1a] and a new one involving the use of no diluent or foreign substance.[10] Some of the sols were stabilized with gelatin. In all cases the results were qualitatively the same as shown in Fig. 1, which represents the data for a gelatin protected sol obtained by the sodium chloride-grinding method. These sols contained in the neighborhood of 0.003 mg. of charcoal per cc.

Electrometric Measurements.—This work was performed as described originally[1a] except that only 4 cc. of 0.5% hydrogen peroxide was used. The results were duplicable within 3 mv. if one or more cc. of sol was present.

Summary

1. Several charcoals have been prepared and compared in catalase, peroxidase, oxidase and adsorptive properties.

2. The charcoals tested stand in the same order of activity for all three catalytic processes.

3. By electrometric means charcoal sols have been found to cause some activation of hydrogen peroxide and oxygen.

4. The catalase activity of the charcoal hydrosols prepared has been found to be very slight.

JERSEY CITY, N. J. RECEIVED MAY 9, 1938

---

[9] Schwob and Cerecedo, THIS JOURNAL, **56**, 2771 (1934).

[10] Schwob and Shea, unpublished research.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 69]

Studies in Organo-silicon Synthesis. I. The Wurtz Reaction with Silicon Chlorides

BY WALTER C. SCHUMB, JOSEPH ACKERMAN, JR., AND CHARLES M. SAFFER, JR.

Although numerous alkyl and aryl silanes have been prepared, and the field of organo-silicon chemistry has been explored extensively by Kipping and other investigators, it seemed worth while in the opinion of the writers to make a comparative study of compounds containing the linkages Si–C, Si–Si, and Si–X, leading to further knowledge of the stability of these bonds and of the reactivity of substituent groups as affected by the nature of the environment of the silicon atom.

The preparation of compounds of the type R_4Si and $R_3Si–SiR_3$, where R may be either alkyl or aryl, is generally effected by the Wurtz synthesis from SiX_4 and R_3SiX, where X is halogen. In some unpublished work[1] it had been determined that the Wurtz reaction, when applied to *p*-chlorobiphenyl and Si_2Cl_6, did not lead to the formation of hexaxenyldisilane but splitting of the Si–Si linkage occurred, and good yields of tetraxenylsilane were obtained. It was thought of interest, therefore, to determine whether this synthesis would be applicable to the preparation of other hexasubstituted disilanes, or whether cleavage of the Si–Si bond invariably would result.

The first synthesis tried was the preparation of hexaethyldisilane, $(C_2H_5)_3Si–Si(C_2H_5)_3$, which previously had been prepared by Friedel and Laden-

---

(1) J. Ackerman, Jr., S. B. Thesis, M. I. T. 1936.

burg[2] by the interaction of hexaiododisilane with diethylzinc in a sealed tube. Kraus and Nelson[3] also prepared it by the action of sodium on $(C_2H_5)_3SiBr$. By the reaction of sodium and hexachlorodisilane, Si_2Cl_6, with ethyl bromide the only product we obtained was tetraethylsilane, $(C_2H_5)_4Si$; no hexaethyldisilane could be isolated. With *n*-amyl chloride, Si_2Cl_6 and sodium, tetra-*n*-amylsilane was formed, a compound hitherto undescribed in the literature, which proved to be identical with the compound formed from $SiCl_4$, sodium and *n*-amyl chloride.

As aryl examples, the reaction of Si_2Cl_6 and sodium with chlorobenzene and with *p*-chlorobiphenyl gave tetraphenylsilane and tetraxenylsilane (a new compound), respectively, but no hexa-substituted disilanes. Hence it was concluded that hexaalkyl- and hexaaryldisilanes cannot be prepared from Si_2Cl_6 by this method of synthesis, since the Si–Si bond invariably is ruptured, leading to the formation of tetrasubstituted monosilanes. It may be argued that under gentler conditions of reaction, such as the avoidance of excess alkali metal, or lower temperatures, fission of the Si–Si bond might not occur; but we have observed no such cleavage when hexaphenyldisilane was treated with excess sodium in boiling xylene or benzene for ten hours with or without the addition of chlorobenzene, indicating that excess of sodium is not the cause of the splitting of the Si–Si linkage. At lower temperatures the reaction studied merely failed to proceed at a noticeable rate.

It seemed of considerable interest to determine the effect of employing a compound containing the more stable Si–O–Si configuration in the Wurtz synthesis. For this purpose, the reaction of Si_2OCl_6 with sodium and chlorobenzene was investigated. Somewhat unexpectedly, tetraphenylsilane was found to be the product formed. With ethyl bromide, Si_2OCl_6 and sodium, tetraethylsilane alone was isolated. Thus the Si–O–Si configuration likewise is broken up when it is subjected to the Wurtz reaction with alkyl or aryl halides.

Further studies in the synthesis of these compounds with the Grignard reagent are in progress.

Experimental

I. Reactions with $SiCl_4$. Tetraxenylsilane.—This substance was prepared according to the method employed in the preparation of tetraphenylsilane by Polis[4] from 45 g. of *p*-chlorobiphenyl, 10 g. of silicon tetrachloride and 12 g. of sodium wire in 250 cc. of anhydrous ether. A yield of about 90% of crude tetraxenylsilane was obtained when the ether was evaporated and the remaining solids extracted with hot benzene. The tetraxenylsilane was recrystallized several times from benzene in the form of long, glistening, colorless needles with 2 mols of benzene of crystallization. At 80° the needles lost benzene and became opaque. The benzene-free product melts at 274° (corr.). It is insoluble in water, alcohol, ether, and cold benzene. Its solubility in boiling benzene is 5 g. per liter, and it is more soluble in hot xylene. When rubbed in a mortar it becomes electrified.

Anal. Calcd. for $Si(C_{12}H_9)_4$: C, 89.9; H, 5.67; Si, 4.39; mol. wt., 640. Found: C, 90.0; H, 5.80; Si, 5.0; mol. wt. (camphor s. p.), 630.

Tetra-*n*-amylsilane.—This compound was prepared by the interaction of 85 g. of *n*-amyl chloride, 34 g. of silicon tetrachloride and 38 g. of sodium wire in 200 cc. of anhydrous ether. The general method followed was that employed by Taurke[5] in the preparation of tetraisoamylsilane. When the crude product was distilled, the largest fraction came over between 290 and 320°, corresponding to a yield of 80%, and after repeated distillation boiled at about 305°. The sample was washed with concentrated sulfuric acid to remove any silicols or silicones,[6] then with water, and finally dried with calcium chloride. It then boiled at 318° (corr.), $d^{32}_4 = 0.8252$, $n^{25}_D = 1.4510$. The purified material is a colorless, odorless oil, soluble in benzene, ether, absolute alcohol, cyclohexane, and xylene. It is practically insoluble in reagent alcohol and in water. It is not hydrolyzed in contact with water.

Anal. Calcd. for $Si(C_5H_{11})_4$: C, 76.8; H, 14.2; Si, 9.0; mol. wt., 312. Found: C, 76.4; H, 14.3; Si, 8.9; mol. wt. (cyclohexane s. p.), 309, 320.

II. Reactions with Si_2Cl_6.—These reactions were carried out in a dry atmosphere with 14 g. of Si_2Cl_6 and 20 g. of sodium wire in 300 cc. of anhydrous ether, together with the desired alkyl or aryl halide. The Si_2Cl_6 used boiled at 90° at 125 mm. and melted from −1 to 0°; the absence of any silicon tetrachloride was thus assured. In the case of the alkyl silanes the reaction product was extracted with ether and, after evaporation of the ether, the liquids were vacuum distilled to hinder formation of the corresponding silicones (trialkylsilicyl oxides).

Reaction with Ethyl Bromide.—Forty-nine grams of the alkyl halide was used with the reactants as described above. No reaction was noted even after several hours of refluxing. However, on addition of a few drops of ethyl acetate a gentle reaction ensued and was allowed to continue with warming for three days. (Kipping and Lloyd[7] report similar difficulty in the preparation of tetraethylsilane from silicon tetrachloride, by sodium and ethyl bromide, obtaining only a small yield.) The ether extract, after treatment with water to destroy excess hexachlorodisilane and evaporation of the ether, gave 2 cc. of a colorless oil. After two fractionations 0.8 cc. was obtained boil-

---

[2] Friedel and Ladenburg, *Ann.*, **203**, 251 (1880).

[3] Kraus and Nelson, THIS JOURNAL, **56**, 194 (1934).

[4] Polis, *Ber.*, **18**, 1540 (1885).

[5] Taurke, *ibid.*, **38**, 1661 (1905).

[6] Friedel and Crafts, *Ann. chim. phys.*, **19**, 337 (1870).

[7] Kipping and Lloyd, *J. Chem. Soc.*, **79**, 456 (1901).

ing at 150° (Emich method)[8] (b. p. of tetraethylsilane, 150–152°). Mol. weight, calcd., 144; found (cyclohexane s. p.), 135, 139. The substance therefore was concluded to be tetraethylsilane. No material boiling higher than 160° was observed, which excludes the formation of hexaethyldisilane, b. p. 250°.

Reaction with *n*-Amyl Chloride.—Thirty-five grams of *n*-amyl chloride was used, and a vigorous reaction gave a 60% yield of a crude oil. On purification this proved to be identical with the tetra-*n*-amylsilane prepared above from silicon tetrachloride and *n*-amyl chloride; b. p. 305–312°; mol. wt. calcd., 312; found (cyclohexane s. p.), 302.

Reaction with Chlorobenzene.—Thirty-five grams of chlorobenzene was used. The solid reaction products were extracted with xylene, the melting points of each crystallization fraction rising from 218 to 229 and 231° (corr.) for the highly purified product. The recorded melting point of tetraphenylsilane is 233° (corr.). A yield of about 60% was obtained. A mixed melting point of the product with some pure tetraphenylsilane gave no depression (231°), while known mixtures of tetraphenylsilane and hexaphenyldisilane gave marked depressions: mol. wt. calcd. for $Si(C_6H_5)_4$, 336; found (camphor s. p.), 340, 343.

Reaction with *p*-Chlorobiphenyl.—Eighty grams of *p*-chlorobiphenyl, used in a manner similar to the reaction of this substance with silicon tetrachloride, gave a 60% yield of tetraxenylsilane in the form of glistening needles, melting at 270° after repeated crystallization. A mixed melting point with a known sample of tetraxenylsilane gave no depression. The compound was, therefore, characterized as tetraxenylsilane.

Anal. Calcd. for $Si(C_{12}H_9)_4$: C, 89.9; H, 5.67. Found: C, 89.7, 89.9; H, 5.63, 5.87.

III. Reactions with Si_2OCl_6.—The Si_2OCl_6 had been prepared by Mr. A. B. Levine in this Laboratory by the simultaneous action of chlorine and oxygen upon heated silicon, followed by a series of careful fractional distillations. The purified substance, melting at −35°, was analyzed for chlorine and silicon, the results being in good agreement with the theory. 16.5 g. of Si_2OCl_6 and 20 g. of sodium wire were used in each of the following experiments.

Reaction with Chlorobenzene.—Forty-five grams of chlorobenzene was used. The purified needles obtained by repeated crystallization from xylene and benzene gave a product melting at 227° (uncorr.). A yield of approximately 60% was obtained. A mixed melting point (227°) with tetraphenylsilane, m. p. 228° (uncorr.), gave no depression.

Anal. Calcd. for $Si(C_6H_5)_4$: C, 85.71; H, 6.01; mol. wt., 336. Found: C, 85.74; H, 6.17; mol. wt. (camphor s. p.), 339, 346, 330.

Thus it is to be concluded that the main product of the reaction is tetraphenylsilane. A small amount of material from the ether washings of the product gave a melting point of 148°, corresponding exactly with the recorded melting point of triphenylsilicol, $(C_6H_5)_3SiOH$.

Reaction with Ethyl Bromide.—The same sluggish reaction was observed as in the case of hexachlorodisilane and with silicon tetrachloride. Fifty grams of ethyl bromide was used. One cc. of an oil, boiling between 150 and 158° (Emich method),[8] was obtained. No material boiling above 165° was found. Molecular weight, calcd. for $Si(C_2H_5)_4$, 144; found, 150, 154. The compound therefore was characterized as tetraethylsilane.

IV. Molecular Weight Determinations with Cyclohexane and Camphor.—Cyclohexane, because of its large cryoscopic constant and miscibility with alkyl silanes, was used in the usual Beckmann freezing point apparatus. The molecular weights of the solid compounds (aryl silanes) were determined using camphor, in a modification of the Rast method.[9] A few milligrams of the compound was mixed with ten times as much camphor in a small Pyrex test-tube. The tube was then sealed off and the substances melted together in an oil-bath. The solidification point can be determined directly, *i. e.*, by observing the mixture in the original oil-bath, or by observing the solidification point of the substance in a melting point tube. The second method was checked to determine whether or not sublimation of a small amount of camphor from the melting point tube affected the results. The same results were obtained in both cases.

V. Silicon Analysis.—The percentage of silicon in the compounds was determined by a modification of the method described by Marvin and Schumb:[10] 0.5 gram of the sample was introduced from a weighed pipet into a nickel crucible half full of a fusion mixture, consisting of sodium peroxide and sugar charcoal. More of the mixture was added and, after ignition in the usual manner, the sodium silicate present in the fusion product was then analyzed, the silicon being determined as silicon dioxide.

Summary

1. Hexasubstituted alkyl and aryl disilanes and hexasubstituted silicyl oxides could not be prepared from hexachlorodisilane and trichlorosilicyl oxide, respectively, by the Wurtz synthesis. Instead, the Si-Si linkage invariably was broken, leading to the formation of tetrasubstituted monosilanes.

2. The Wurtz reaction was carried out with hexachlorodisilane and ethyl bromide, *n*-amyl chloride, chlorobenzene and *p*-chlorobiphenyl yielding, respectively, the tetrasubstituted silanes, $Si(C_2H_5)_4$, $Si(n\text{-}C_5H_{11})_4$, $Si(C_6H_5)_4$ and $Si(C_{12}H_9)_4$. No substituted disilanes could be detected.

3. Likewise the Wurtz reaction, applied to trichlorosilicyl oxide and ethyl bromide or chlorobenzene, resulted in the breaking of the Si–O–Si linkage, giving tetrasubstituted silanes.

4. Tetraxenylsilane and tetra-*n*-amylsilane were prepared from both tetrachlorosilane and hexachlorodisilane.

CAMBRIDGE, MASS. RECEIVED JULY 22, 1938

---

(8) Emich, *Monatsh.*, **38**, 219 (1917).

(9) Rast, *Ber.*, **55**, 1051, 3727 (1922).

(10) Marvin and Schumb, THIS JOURNAL, **52**, 574 (1930).