165. *The Reaction of Silicon with Dihydric Phenols: The Direct Synthesis of Silicon-containing Heterocycles.*

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Two dihydric phenols react with elemental silicon at elevated temperatures in the presence of metallic copper, producing heterocyclic compounds with silicon as a spiro-atom. The mechanism of the reaction is discussed.

Rochow [1] discovered that organic halides react with silicon in the presence of metallic catalysts, producing a mixture of alkyl- or aryl-halogenosilanes: $2RX + Si \longrightarrow R_2SiX_2$. Although alcohols would be expected to produce organosilanols in a similar fashion, the action of methanol on silicon yields only tetramethoxysilane: [2] $4MeOH + Si \longrightarrow Si(OMe)_4 + 2H_2$. Higher alcohols react sluggishly. Phenol reacts in a similar manner with silicon–copper at 300—350° in a flow system or in an autoclave under hydrogen, giving tetraphenoxysilane in up to 79% yield. [3]

This paper describes an investigation of the action of dihydric phenols on silicon. Catechol reacts with freshly sintered 9 : 1 w/w silicon–copper at 265° under a high pressure of hydrogen, producing a hard, brown solid which becomes covered with small white crystals of catechol when kept in air. Vacuum-distillation and sublimation at 237° *in vacuo* gave a nearly quantitative amount of a transparent, water-white, moisture-sensitive glass, softening at ~360° and insoluble in organic solvents. It decomposed in pyridine and dimethylformamide at room temperature, and in boiling nitrobenzene. It is very sensitive to moisture, but the transparent glass soon becomes coated with a layer of white
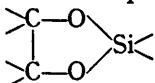
[1] Rochow, *J. Amer. Chem. Soc.*, 1945, **67**, 963.
[2] Rochow, *J. Amer. Chem. Soc.*, 1948, **70**, 2170.
[3] Kuis and Waterman, *Research*, 1955, **8**, S2; Zuckerman, Thesis, Harvard, 1960.

solid which hinders further hydrolysis. Hydrolysis regenerates catechol. The empirical formula is $Si(O_2C_6H_4)_2$ and infrared spectra are consistent with its formulation as di-(*o*-phenylenedioxy)silane. *X*-Ray photographs show the material to be amorphous.

A molecular-weight determination on a freshly sublimed sample by the Rast method indicates that the compound is monomeric. However, a reaction (presumably trans-esterification) takes place at the melting point of the camphor mixture which converts the entire mass into a glass. Thus only one melting point could be determined on each sample.

Models show the five-membered spiro-ring system to be sterically feasible: many simple systems of the type [structure] are known.[4] The preference, however, for the formation of the dimer or tetramer in reaction has been noted.[5]

Two reactions which can result in the formation of this ester have previously been carried out: thermal decomposition of di-(*o*-methoxyphenoxy)silane (the products were not characterized),[6] and reaction of catechol with silicon tetrachloride which gave an ester in 60% yield.[7] This ester, unlike our compound, dissolved in hot chloroform and was shown to be tetrameric.

2,2′-Dihydroxybiphenyl reacts similarly at as low a temperature as 130°, giving di-(2,2′-biphenylenedioxy)silane. At 230° a good yield is obtained of a monomeric white ester, m. p. 315°, only slightly soluble in organic solvents and much more stable to hydro-lysis than the catechol analogue. Hydrolysis regenerates 2,2′-dihydroxybiphenyl. This ester was earlier prepared from silicon tetrachloride and 2,2′-dihydroxybiphenyl in ether.[8]
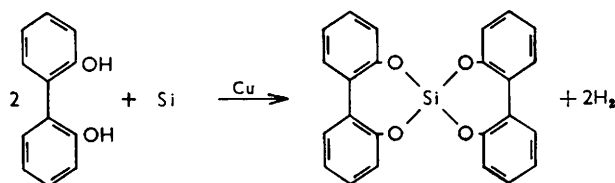
A study of further examples indicated that the method is limited by the thermal stability of the organic starting material. Ethylene glycol and diethylene glycol underwent pyrolysis when treated with silicon–copper under similar conditions. 2,3-Dihydroxy-naphthalene and 2,2′-dihydroxy-1,1′-binaphthyl decompose to β-naphthol, and 3-methyl-quinol and 2,3-dihydroxyquinoxaline give a variety or organic products, but no volatile silicon-containing compounds.

The reactions between methanethiol or thiophenol and sintered silicon–copper were investigated in a flow system. At a wide range of flow rates and temperatures, extensive pyrolysis took place in both cases, there was transport of the copper catalyst in the reaction tubes, and silicon sulphides were found in the contact mass. No volatile silicon-containing products were isolated. The reaction of 3-methylbenzene-1,2-dithiol in an autoclave also failed to give volatile silicon-containing products.

Mechanism.—The first step in the reaction of organic halides with silicon is the form-ation of a halogenosilane (not necessarily a definite compound, but a surface or crystal-lattice phenomenon).[9] This species is then alkylated and halogenated by added organic halide to form organo-halogenosilanes.

[4] Vol'nov and Dolgov, *Zhur. obshchei Khim.*, 1940, **10**, 550; Kipping and Abrams, *J.*, 1944, 81; Vol'nov, *Zhur. obshchei Khim.*, 1947, **17**, 1428; Hahn, *Makromol. Chem.*, 1953, **11**, 57.

[5] Krieble and Burkhard, *J. Amer. Chem. Soc.*, 1947, **69**, 2689; Schwartz and Kuchen, *Chem. Ber.*, 1953, **86**, 1144; Jacovic, *Z. anorg. Chem.*, 1956, **288**, 324; Voronkov, Davydova, and Dolgov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 677; Sprung, *J. Org. Chem.*, 1958, **23**, 58.

[6] Vol'nov and Michelevich, *Zhur. obshchei Khim.*, 1943, **13**, 213.

[7] Schwartz and Kuchen, *Z. anorg. Chem.*, 1951, **266**, 185.

[8] Schwartz and Kuchen, *Z. anorg. Chem.*, 1955, **279**, 84.

[9] Hurd and Rochow, *J. Amer. Chem. Soc.*, 1945, **67**, 1057 (1945).

It is possible that in the reaction of alcohols and phenols with silicon there is a similar intermediate. An alternative explanation is that alcohols and phenols act on silicon as do acids on a metal, hydrogen being evolved. The carbon–oxygen bond then remains intact. What role the copper catalyst would play in such a reaction is not clear.

Initiation of the phenol–silicon reaction depends on the use of water-free phenol and proper preparation of the contact mass. The latter had to be freshly sintered in a stream of hydrogen a high temperature. This process removes the coating of vitreous oxide which is known to form on the surface of elemental silicon, thereby providing a " clean " site for initiation of the reaction.

The abnormally high vapour pressure of silicon in hydrogen at high temperatures has been attributed to the formation of volatile silicon subhydrides.[10] Possibly the sintering of silicon–copper in hydrogen at high temperatures also introduces hydrogen into the silicon lattice.[11] The infrared spectrum of a sample of silicon powder (heated in hydrogen at *ca.* 1000°) was examined in a potassium bromide disc from 4000 to 2000 cm.$^{-1}$ (elemental silicon is relatively transparent in this region [12]). A sharp peak is observed which is in the region reported for silicon–hydrogen stretching vibrations.[13] Thus it is likely that surface hydride is an active intermediate in the reaction with copper–silicon.

It is then easy to explain the reactivity of alcohols and phenols, and the formation of esters from these reactions. The copper–catalyzed reaction of these compounds with silanes has been thoroughly investigated.[14] The rate of the methanol–monosilane reaction (which is strongly copper-catalyzed) increases markedly after the introduction of the first methoxy-group, and rapidly leads to tetramethoxysilane.[15] The formation of a silicon hydride intermediate in the reaction of elemental silicon would explain the production of tetra-alkoxy- and tetra-aryloxy-silanes.

In the reaction of the thiols the extensive transport of the copper catalyst in the flow system, presumably due to the intermediate formation of volatile, unstable copper alkyls and aryls,[9] indicates that these compounds have undergone carbon–sulphur bond cleavage. Therefore, the products are expected to be those due to the action of the ·SH radical, as in the reaction of silicon with hydrogen sulphide.

EXPERIMENTAL

Materials.—Silicon powder and the organic starting materials were of reagent-grade purity. The silicon–copper catalyst was prepared by heating silicon with finely divided copper (10% by wt.) in a slowly rotated silica tube in a stream of dry hydrogen. Temperatures near the m. p. of copper (1050°) were maintained for at least 10 hr.

Analyses.—Carbon and hydrogen were determined by the Microanalytical Department of this Laboratory. Analysis for silicon was carried out by oxidising the samples with fuming nitric and sulphuric acids in platinum crucibles, then evaporating them off, and fuming the weighed residue with hydrofluoric acid. Infrared spectra were measured by using a Perkin–Elmer model 21 recording spectrophotometer equipped with a scale-expansion unit and rock-salt optics. Molecular weights were determined by the Rast method. *X*-Ray photographs were obtained with a 19 cm. camera and Cu-K_α radiation. Samples were contained in thin-walled Pyrex tubes sealed with picein wax.

Reaction Systems.—Standard stainless-steel autoclave bombs of 1·2, 0·1, and 0·025 l. were used. The flow system used for the reaction of methanethiol and thiophenol consisted of a

· [10] Schafer and Klemm, *J. prakt. Chem.*, 1958, **5**, 233; but see Barrow and Deutsch, *Proc. Chem. Soc.*, 1960, 122.

[11] von Bonin, Thesis, Munich University, 1959.

[12] Becker and Fan, *Phys. Rev.*, 1949, **76**, 1531; Burstein, Bell, Davisson, and Lax, *J. Phys. Chem.*, 1953, **57**, 849.

[13] Bellamy, " Infrared Spectra of Complex Molecules," Methuen, London, 1958.

[14] Peake and Nebergall, *J. Amer. Chem. Soc.*, 1952, **74**, 1526; Dolgov, Khudobin, and Kharitonov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1238.

[15] Sternbach and MacDiarmid, *J. Amer. Chem. Soc.*, 1959, **81**, 5109; *idem., ibid.*, 1961, **83**, 3384.

glass tube (2·5 cm. diam. and 50 cm. long) drawn at one end to fit a water condenser and trap maintained at −80°. The other end was connected through a standard taper joint to a head with an inlet for carrier gas and an aperture (sealed with a rubber plug) for admitting the thiol. Thiophenol was injected directly into the reaction tube by a 20 ml. hypodermic syringe clamped in position. With methanethiol a dropping funnel fitted with a cold finger reaching to the bottom was used with a curved adapter to the head of the reaction tube. The rate of thiol addition was 0·1—0·2 mole/hr. The reaction tube was heated in a tube furnace equipped with built-in thermocouple and controller.

Catechol.—Catechol (1 mole) was heated in a 1·2-l. autoclave in hydrogen at 106 atm. for 6·5 hr. with freshly sintered silicon–copper (3·2 g.-atom of Cu) at 265°. The product was a hard, brittle, brown resin which consisted of an excess of silicon–copper powder distributed in a matrix of solid ester. A drill-press was used to remove the material from the bomb. White needles of catechol were formed on the surface of the material overnight in air.

The product was distilled at 3 mm., giving a trace of starting material and a large fraction of water-white liquid which solidified immediately on reaching the cooler parts of the apparatus. This fraction distilled at 200—250°/3 mm. and gave *di-(o-phenylenedioxy)silane* as a white transparent glass on sublimation *in vacuo* at 237° (Found: C, 57·7; H, 3·85; Si, 11·6%; *M*, 227, 257. $C_{12}H_8O_4Si$ requires C, 59·0; H, 3·3; Si, 11·5%; *M*, 248). This compound was handled in a dry box. Hydrolysis regenerated catechol.

2,2′-Dihydroxybiphenyl.—2,2′-Dihydroxybiphenyl (0·2 mole) was heated for 45 hr. at 130° in hydrogen at 75 atm. with freshly sintered silicon–copper (1·6 g.-atom). The starting material was recovered by distillation at reduced pressure. Sublimation *in vacuo* of the residue of distillation gave a very small amount of di-(2,2′-biphenylenedioxy)silane (Found: C, 71·4; H, 4·1; Si, 7·0. Calc. for $C_{24}H_{16}O_4Si$: C, 72·8; H, 4·0; Si, 7·1%).

In another experiment, 2,2′-dihydroxybiphenyl (0·3 mole) was heated in hydrogen under at 230°/154 atm. for 6 hr. with freshly sintered silicon–copper. The resulting brittle, brown resin (excess of silicon–copper powder distributed in a matrix of the solid ester) gave the spiran in good yield with m. p. 314—315°. Hydrolysis required *ca.* 30 min. in aqueous base of pH 10; 2,2-dihydroxybiphenyl was regenerated.

Other Aromatic and Aliphatic Diols.—3-Methylquinol, 2,3-dihydroxynaphthalene, 2,2′-dihydroxy-1,1′-binaphthyl, 2,3-dihydroxyquinoxaline, alizarin, ethylene glycol, and diethylene glycol were treated in hydrogen at 98—265 atm. at temperatures of 198—300° for 4·5—12 hr. Distillation at reduced pressure and sublimation in a vacuum did not yield silicon-containing material.

Reactions of Thiols.—Thiophenol and silicon–copper reacted in a flow system at 20—800° in nitrogen and hydrogen as diluent gases. Copper was transported in the tube, and a grey-white powder (probably silicon sulphide as it liberated hydrogen sulphide on hydrolysis) was found in the contact mass. Dry benzene extracted a pungent yellow oil which contained organic sulphides and a non-sublimable silicon-containing residue (*ca.* 4·5% of silicon).

Methanethiol treated in an analogous manner gave similar products. The silicon content of the residue was *ca.* 7%.

3-Methylbenzene-1,2-dithiol, heated in hydrogen with silicon–copper at 122° for 6·5 hr. at 100 atm., failed to give a silicon-containing product.