New Preparation of Diphenylsilanediol

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In separate papers[1,2] the author has described new methods of preparation of diphenylsilanediol (hereafter called diol), in which it has chiefly been aimed at for successful preparation to minimize the polymeric effect of hydrogen chloride produced thereby. In the present communication the author wishes to present some effective methods together with procedural details to prepare diol directly from diphenyldichlorosilane (DPDS). The first is the preparation from the reaction of DPDS with sodium or potassium hydrogen carbonate, the key feature of this method being the hydrolysis of DPDS with water produced by decomposition of the carbonates. The reaction can be represented summarily by the following equation for sodium hydrogen carbonate:

$$(C_6H_5)_2SiCl_2+2NaHCO_3$$
$$\rightarrow(C_6H_5)_2Si(OH)_2+2NaCl+2CO_2$$

The fairly stable character of this diol has also prompted the second method which is possibly the simplest among the related works[3] and involves the direct hydrolysis of DPDS with a theoretical amount of water dissolved in inert organic solvents followed by complete removal of hydrogen chloride by using some appropriate reagents, e.g., calcium carbonate, sodium carbonate anhydride, calcium hydroxide, aniline or pyridine.

Experimental

Fine powdered inorganic salts in reagent-grades were used after prolonged drying in a vacuum-desiccator. Aniline and pyridine were distilled under reduced pressure after drying over potassium hydroxide. Reagent-grade acetone, benzene, ethyl acetate and ether were used without further purification. Highest-purity DPDS was received from the Shin-etsu Chemical Industrial Company.

(A) From the Reaction with Sodium or Potassium Hydrogen Carbonate.—Each carbonate undergoes reaction entirely similar to that of DPDS; a typical procedure is shown below. 25 g. (0.3 mol.) of sodium hydrogen carbonate and 200 ml. of acetone-benzene were placed in a one liter flask which had been kept in a water bath maintained at 50°C. A 25 g. portion (0.1 mol.) of DPDS dissolved in 50 ml. of acetone was added portion-wise to the flask which was shaken gently during the addition. On adding the silane solution, carbon dioxide was evolved readily and sodium chloride precipitated as fine white crystalline powder. After the addition was complete, the mixture was refluxed gently for 20 min. and then filtered under suction after cooling. On evaporating the filtrate to dryness on a water bath, a white crystalline mass was obtained from

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[1] "Hydrolysis of Diphenyldichlorosilane in the Presence of Aniline", *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 601 (1959).

[2] "New Simple Preparation of Diphenylsilanediol", *J. Org. Chem.*, in the press.

[3] W. Dilthey and F. Eduardoff, *Ber.*, **37**, 1139 (1904); G. Martin, ibid., **45**, 403 (1912); F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912); C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945); J. F. Hyde and R. C. DeLong, ibid., **63**, 1194 (1941); S. Fukukawa, *Science & Industry, Japan* (*Kagaku to Kogyo*), **30**, 71 (1956).

which 20 g. (93%) of pure diol was obtained by recrystallization from ethyl acetate.

(B) Direct Hydrolysis Method.— In a one liter flask, were placed 400 ml. of acetone-benzene and 7 g. (0.4 mol.) of distilled water. After the addition of 51 g. (0.2 mol.) of DPDS to the flask, the mixture was shaken gently for a few minutes. Then, fine powdered calcium carbonate was added portion-wise to the flask which had been preheated at about 50°C, whereby the carbonate decomposed exothermally, evolving carbon dioxide. The addition was continued until the crystal violet indicator (1 drop of 1% ethanol solution) which had been added gradually should acquire a distinct purple color. After the reaction was over, the mixture was treated similarly to A, yielding 39 g. (90%) of white needles.

The use of sodium carbonate in place of calcium carbonate yielded 84% (mean) of diol, while the use of calcium hydroxide gave a considerable amount of uncrystallizable oily product caused by the presumable polymeryzing effect of the hydroxide.

Lastly, the use of aniline1) or pyridine as hydrogen chloride acceptor gave entirely similar results, whereby the hydrochloride of each base precipitated as fine crystalline powder, the yield of diol being 88～92%.

Some Properties of Diol.—The diol thus obtained has been identified by its infrared absorption data4) and the interplaner spacing data1) (by diffractometer). [Found: Si, 12.7; OH/molecule, 1.97 (Karl Fischer titration)5); mol. wt., 195～204 (glacial acetic acid)]. The density (measured in aqueous calcium chloride solution of the matched density) was 1.16. The melting point6) showed a variety of 132～133, 142～144, 147～148, 155 and 158～160°C in spite of all careful measurements. Melting was always accompanied by decomposition and successive fusion always lowered the melting point.

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4) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, **17**, 1555 (1952).

5) H. Cilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 2367 (1951).

6) Measured by using a clean Pyrex capillary tube and at the rate of heating 3～5°C per min., the bath being preheated at about 110°C.