

Claisen head from which the solid was removed with a glass spatula, yield 17 g. (80%). It was free of oxalic acid as shown by the absence of the color reaction with diphenylamine.¹⁵ The product was purified by sublimation *in vacuo* (at 70–80°/0.5–0.7 mm.) and obtained as a fine white crystalline powder. The m.p. of the product was 86° immediately after drying *in vacuo* over P₂O₅. The product is very hygroscopic.

Semicarbazone (recrystallized from 95% alcohol) turns brown at 198–200° and decomposes at 205°.

Anal. Calcd. for C₄H₆N₄F: C, 29.45; H, 3.7; N, 25.7. Found: C, 29.8; H, 3.43; N, 25.17%.

*Dinitrophenylhydrazones*¹⁶ (crystallized 4 times from alcohol) begins to melt at 163° and decomposes at 165°.

Anal. Calcd. for C₈H₇N₄O₆F: C, 37.77; H, 2.47; N, 19.58. Found: C, 37.8; H, 2.66; N, 19.8%.

Diethyl chlorooxaloacetate. This compound was prepared by the method of Wislicenus.⁸ Light yellow liquid, b.p. 114°/1.4 mm., yield, 53% (Wislicenus reported a yield of 28%, b.p. 150–152°/56 mm.).

Monochloropyruvic acid. A procedure similar to that described for the preparation of monofluoropyruvic acid was followed to obtain this compound. Diethyl chlorooxaloacetate (22.25 g., 0.1 mole) yielded 3 g. (25%) of chloropyruvic acid (distilled at 92°/3 mm. and solidified to a white solid in the condenser).

The product was purified by sublimation *in vacuo* (70°/0.1 mm.) and dried *in vacuo* over P₂O₅, m.p., 83–84° (Garino and Muzio,¹⁰ m.p., 45°; product + H₂O, m.p., 55°). Neutral equivalent, found: 122.9 (theory, 122.5). *Dinitrophenylhydrazones* (recrystallized from alcohol) melted at 167–168°.

Anal. Calcd. for C₉H₇N₄O₆Cl: C, 35.71; H, 2.33; N, 18.51; Cl, 11.72. Found: C, 35.94; H, 2.67; N, 18.55; Cl, 11.78%.

Diethyl oxaloacetate was obtained from the commercially available sodium salt of the ester, as in the case of the fluoro derivative, as a clear colorless liquid, b.p. 96–97°/2.5 mm., yield 64%.

Pyruvic acid. Diethyl oxaloacetate (18.8 g., 0.1 mole) was hydrolyzed under the same conditions as in the case of the fluoro derivative, 0.5–1 g. (5–9%) of pyruvic acid was obtained. The product distilled at 40°/2 mm.; a specimen of pure pyruvic acid distilled at 40°/3.5 mm. *Phenylhydrazones* (crystallized from alcohol), m.p. 193° (Fischer,¹⁷ m.p. 192°); mixed m.p. with an authentic specimen of the phenylhydrazones of pyruvic acid, 192–193°.

DEPARTMENT OF PHARMACOLOGY
UNIVERSITY OF ILLINOIS
COLLEGE OF MEDICINE
CHICAGO 12, ILL.

(15) F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Inc., New York, 1956.

(16) In comparing the melting points of the dinitrophenylhydrazones the *cis-trans* isomerism that is possible in these compounds must be taken into consideration.

(17) E. Fischer, *Ber.*, **17**, 578 (1884).

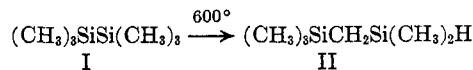
Thermal Rearrangement of Hexamethyldisilane to Trimethyl(dimethylsilylmethyl)silane

KYO SHIINA AND MAKOTO KUMADA

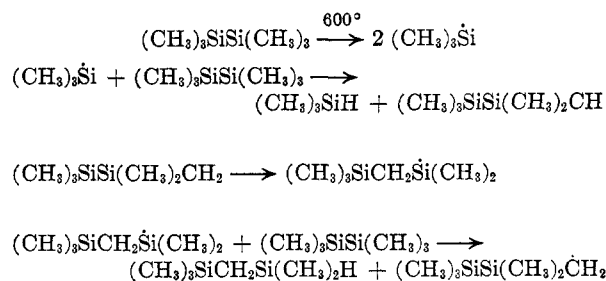
Received July 8, 1957

During the course of a recent investigation of the organo-substituted disilanes we have found that

hexamethyldisilane (I) readily undergoes rearrangement at 600° to give trimethyl(dimethylsilylmethyl)silane (II). At 400°, no thermal reaction of I occurred.



It has been found in this laboratory¹ that chloromethyldisilane derivatives such as ClCH₂(CH₃)₂SiSi(CH₃)₃ and ClCH₂(CH₃)₂SiSi(CH₃)₂Cl rearrange in the presence of aluminum chloride to the corresponding disilylmethane, *i.e.*, (CH₃)₃SiCH₂Si(CH₃)₂Cl and Cl(CH₃)₂SiCH₂Si(CH₃)₂Cl, respectively. The present reaction may be described tentatively in terms of the following scheme:



EXPERIMENTAL²

Hexamethyldisilane (40 g., 0.27 mole) was passed slowly through a 4.0 × 100 cm. quartz tube heated to 600°. Fractional distillation in 1.0 × 30 cm. Stedman column of the product gave 33 g. of a mixture of I and II, boiling over the range 112–120°, in addition to 2 g. of very volatile matter which was believed to be trimethylsilane.

A sample of the former distillate, b.p. 120°, *n*_D²⁰ 1.4122, *d*₄²⁰ 0.7462 (reported³ for compound II: b.p. 119–121°, *n*_D²⁰ 1.4158, *d*₄²⁰ 0.7454) was analyzed for silane hydrogen in the Zerewitinoff apparatus using sodium *n*-butoxide in *n*-butyl alcohol as alkaline reagent. Ninety-three per cent of the theoretical quantity of hydrogen was evolved. Under these conditions compound I is quite stable to cleavage.

Further proof of II was afforded by treatment of the distillate (30 g.) with ethanolic solution of sodium ethoxide at 60°. Fractionation of the reaction mixture was made after complete evolution of hydrogen to give 7.2 g. of unchanged hexamethyldisilane and 12 g. of trimethyl(dimethylethoxy-silylmethyl)silane, b.p. 159°, *n*_D²⁰ 1.4183 (reported³ b.p. 161–161.5°, *n*_D²⁰ 1.4169).

Anal. Calcd. for C₈H₂₂OSi₂: Si, 29.5. Found: Si, 29.5, 29.3.

INSTITUTE OF POLYTECHNICS
OSAKA CITY UNIVERSITY
OSAKA, JAPAN

(1) M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, in press.

(2) Boiling points are uncorrected.

(3) A. V. Topchier, N. S. Nametkin, and L. S. Povarov, *Doklady Akad. Nauk S.S.S.R.*, **97**, 99 (1954); *Chem. Abstr.*, **49**, 8792 (1955).