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 P_2O_5. The product is very hygroscopic.

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

Anal. Calcd. for $C_4H_6N_3N_3F$: C, 29.45; H, 3.7; N, 25.7. Found: C, 29.8; H, 3.43; N, 25.17%.

Dinitrophenylhydrazone[16] (crystallized 4 times from alcohol) begins to melt at 163° and decomposes at 165°.

Anal. Calcd. for $C_9H_7N_4O_6F$: 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 P_2O_5, m.p., 83–84° (Garino and Muzio,[10] m.p., 45°; product + H_2O, m.p., 55°). Neutral equivalent, found: 122.9 (theory, 122.5). *Dinitrophenylhydrazone* (recrystallized from alcohol) melted at 167–168°.

Anal. Calcd. for $C_9H_7N_4O_6Cl$: 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. *Phenylhydrazone* (crystallized from alcohol), m.p. 193° (Fischer,[17] m.p. 192°); mixed m.p. with an authentic specimen of the phenylhydrazone 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.

$$\underset{\text{I}}{(CH_3)_3SiSi(CH_3)_3} \xrightarrow{600^\circ} \underset{\text{II}}{(CH_3)_3SiCH_2Si(CH_3)_2H}$$

It has been found in this laboratory[1] that chloromethyldisilane derivatives such as $ClCH_2(CH_3)_2SiSi(CH_3)_3$ and $ClCH_2(CH_3)_2SiSi(CH_3)_2Cl$ rearrange in the presence of aluminum chloride to the corresponding disilylmethane, *i.e.*, $(CH_3)_3SiCH_2Si(CH_3)_2Cl$ and $Cl(CH_3)_2SiCH_2Si(CH_3)_2Cl$, respectively. The present reaction may be described tentatively in terms of the following scheme:

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{600^\circ} 2\,(CH_3)_3\dot{Si}$$

$$(CH_3)_3\dot{Si} + (CH_3)_3SiSi(CH_3)_3 \longrightarrow (CH_3)_3SiH + (CH_3)_3SiSi(CH_3)_2CH$$

$$(CH_3)_3SiSi(CH_3)_2CH_2 \longrightarrow (CH_3)_3SiCH_2\dot{Si}(CH_3)_2$$

$$(CH_3)_3SiCH_2\dot{Si}(CH_3)_2 + (CH_3)_3SiSi(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_2H + (CH_3)_3SiSi(CH_3)_2\dot{C}H_2$$

EXPERIMENTAL[2]

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_D^{20} 1.4122, d_4^{20} 0.7462 (reported[3] for compound II: b.p. 119–121°, n_D^{20} 1.4158, d_4^{20} 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(dimethylethoxysilylmethyl)silane, b.p. 159°, n_D^{20} 1.4183 (reported[3] b.p. 161–161.5°, n_D^{20} 1.4169).

Anal. Calcd. for $C_8H_{22}OSi_2$: 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).