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Short Communications

On the Preparation of bis-[Trimethylsilylmethyl]-acetic acid

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In a newly published paper [1] Sommer and co-workers reported that they were unable to prepare diethyl bis-[trimethylsilylmethyl]-malonate from diethyl trimethylsilylmethylmalonate and chloromethyltrimethylsilane. I consider that this was due to the unreactivity of the chlorine atom in chloromethyltrimethylsilane and that better results might be expected if the corresponding bromide was used instead.

In connection with other work [2] on aliphatic organosilicon acids the synthesis of diethyl bis-[trimethylsilylmethyl]-malonate from diethyl trimethylsilylmethylmalonate and bromomethyltrimethylsilane has been carried out successfully, the yield being 73 % (based on unrecovered material). The malonic ester was readily hydrolysed and decarboxylated to give bis-[trimethylsilylmethyl]-acetic acid in 93 % yield.

When treated with concentrated sulphuric acid at room temperature the acid liberated methane amounting to 80 % of the theoretically calculated volume (two moles of methane per mole of acid). Heating to 100° caused discolouration of the reaction mixture and carbon dioxide and sulphur dioxide were evolved.

Experimental. Diethyl bis-[trimethylsilylmethyl]-malonate. In a 250 ml flask equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer reaching into the flask 4.6 g (0.200 g at.) of sodium was dissolved in 70 ml of absolute ethanol. 49.2 g (0.200 mole) of diethyl trimethylsilylmethylmalonate was added in one portion, followed by the addition of 33.4 g (0.200 mole) of bromomethyltrimethylsilane during two hours. The temperature of the reaction mixture was maintained at 70—80°. The reaction mixture was then heated under reflux for twenty-four hours. After cooling it was neutralized with glacial acetic acid, the alcohol was distilled off, and 150 ml of water was added. The oil was taken up in ether, the ether solution washed with water and finally dried with anhydrous calcium chloride. After distilling off the ether the residue was fractionated through a glass-helix-packed column of about ten theoretical plates. There was obtained 25.6 (0.077 mole) of diethyl bis-[trimethylsilylmethyl]-malonate, b. p. 108—109°/1.5 mm, n_D^{20} 1.4483, d_4^{20} 0.9508. 23.2 g of diethyl trimethylsilylmethylmalonate was recovered. The yield, based on unrecovered material was 73 %. (Found: C 54.0; H 9.6; Si 16.7; r_D 0.2823. Calc. for $C_{15}H_{32}O_4Si_2$: C 54.2; H 9.7; Si 16.9; r_D 0.2817).

Bis-[trimethylsilylmethyl]-malonic acid. Diethyl bis-[trimethylsilylmethyl]-malonate was hydrolysed by boiling with excess alcoholic potassium hydroxide for twenty-four hours to give a quantitative yield of the corresponding acid. A small amount was recrystallized from acetone, m. p. 165—166° (decomp.). (Found: C 47.9; H 8.8; Si 20.5. Calc. for $C_{11}H_{24}O_4Si_2$: C 47.8; H 8.8; Si 20.3.)

Bis-[trimethylsilylmethyl]-acetic acid. The crude bis-[trimethylsilylmethyl]-malonic acid was decarboxylated by heating to 170—180° for twenty minutes. After cooling, the oil was dissolved in ether, the ether solution was filtered, and the ether was distilled off. The remaining oil was distilled *in vacuo* and there was obtained a 93 % yield of bis-[trimethylsilylmethyl]-acetic acid, b. p. 123—124°/1 mm. The compound solidified after standing overnight, m. p. 41—42°. One recrystallization from petroleum ether did not raise the melting point. (Found: C 51.7; H 10.5; Si 24.1; Eq.wt. 232.3. Calc. for $C_{10}H_{24}O_2Si_2$: C 51.7; H 10.4; Si 24.2; Eq. wt. 232.5.)

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1. Sommer, L. H., Goldberg, G. M., Barnes, G. H. and Stone, L. S. Jr. *J. Am. Chem. Soc.* **76** (1954) 1609.
2. Eberson, L. *Acta Chem. Scand.* **8** (1954) *In press.*

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