The Synthesis of Some Organosilicon Alcohols. I

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In order to prepare some organosilicon compounds containing hydroxyl groups attached to carbon atoms the reaction between propylene oxide and trimethylsilylmethylmagnesium bromide was investigated. The only silicon-containing alcohol that could be isolated was 4-trimethylsilyl-butanol-2. The constitution of this compound was proved by comparing it with authentic samples of the two alcohols that theoretically could be obtained.

A widely applied method of synthesizing alcohols is to let ethylene oxides react with Grignard compounds. A review is published by Gaylord and Becker¹. Sommer, Van Strien and Whitmore² applied these reactions to silicon-containing materials. The Grignard reagents from chloromethyltrimethylsilane and 3-trimethylsilyl-1-bromopropane yielded on interaction with ethylene oxide 3-trimethylsilyl-propanol-1 and 5-trimethylsilyl-pentanol-1, respectively.

During attempts to repeat the former synthesis with trimethylsilylmethylmagnesium bromide instead of chloride, as in the paper², a low yield of the desired alcohol and a large amount of higher boiling materials were obtained. However, when the synthesis was made with the chloride, the stated yield was obtained.

In this work the reaction between propylene oxide and trimethylsilylmethylmagnesium bromide has been studied. Theoretically one or both of the two alcohols (I) and (II) may be formed, depending upon which way the oxide ring is opened.

(I)

(II)

The only silicon-containing alcohol (A) that could be isolated from the reaction mixture must have had the constitution (I). This was evident partly from the fact that it was non-identical with the alcohol (II) that was obtained from α -methyl- β -trimethylsilyl-propionic acid, prepared by Sommer *et al.*³ by reduction with lithium aluminium hydride; partly from the fact that those

of its properties that were studied were identical with the corresponding properties of the alcohol (I), obtained from 4-trimethylsilyl-butanone-2 by reduction with lithium aluminium hydride according to Perklev ⁴. The data of the alcohols (I), (II) and (A) and their 3,5-dinitrobenzoates are collected in Table 1.

Table 1.

Alcohol	Bp °C	n_D^{20}	d_4^{20}	Mp °C of 3,5-dinitrobenzoate
(A)	81–82°	1.4301	0.8279	65–66° *
(I)	82° **	1.4301 **	—	65.5–66°
(II)	88–89°	1.4357	0.8375	44.5–45.5°

* Mixed m. p. with (I) 65.5–66° C.

** Data recorded by Perklev ⁴.

EXPERIMENTAL

4-Trimethylsilyl-butan-2-ol from propylene oxide (A = I)

58.0 g (1.0 mole) of propylene oxide were dropped with stirring to the Grignard reagent prepared from 83.5 g (0.5 mole) of bromomethyltrimethylsilane, 12.0 g magnesium and 100 ml of absolute ether in a 1-litre flask equipped with a stirrer, a reflux condenser and a dropping funnel, and immersed in an ice-bath. When all the oxide had been added the ice-bath was removed, whereupon the temperature of the mixture generally rose enough to cause boiling. When this ceased the mixture was warmed on a water bath (45°–46°C) for 5–6 hours. The reaction mixture was decomposed with ice-water. Simultaneously the ether, tetramethylsilane and unreacted propylene oxide were distilled over. *Ca.* 8 g (0.1 mole) of tetramethylsilane could be recovered from the distillate by dropping it into concentrated sulphuric acid, cooled in an ice-and-salt bath.

The magnesium hydroxide precipitated by hydrolysis was dissolved by adding a sufficient quantity of dilute hydrochloric acid. The organic layer was separated and the water layer extracted with ether. The combined ether solutions were washed with a small quantity of water.

In an earlier experiment the resulting silicon-containing product was found to contain some bromine, probably due to the presence of propylene bromohydrin, formed upon hydrolysis of the reaction mixture. It was difficult to separate the bromohydrin from the formed silicon-containing alcohol through distillation and, therefore, the ether solution was shaken with small portions of dilute sodium hydroxide solution until a lasting red colour with phenolphthalein was obtained.

The ether layer was separated and the water layer extracted with ether. The combined ether layers were washed with water and dried with anhydrous sodium sulphate. The ether was removed and the mixture distilled in a Claisen flask at 25 mm Hg. A viscous residue was obtained. The distillate was fractionated in an efficient column and the fraction boiling at 81–82° at 25 mm Hg, 29.0 g (0.20 mole), was collected as pure 4-trimethylsilyl-butan-2-ol. $n_D^{20} = 1.4301$, $d_4^{20} = 0.8279$. (Found: C 57.0; H 12.5; Si 19.2, MR_D 45.6. Calculated for $C_7H_{18}OSi$: C 57.5; H 12.4; Si 19.2, MR_D 45.8).

3,5-Dinitrobenzoate was prepared according to a method described by Vogel ⁵. 2.0 g of the 4-trimethylsilyl-butan-2-ol were heated with 4.0 g 3,5-dinitrobenzoyl chloride in an oil bath at 110°C until the evolution of hydrogen chloride ceased. The mixture was cooled, and 40 ml of saturated sodium bicarbonate solution was added. The resulting ester was stirred until crystallization occurred. The precipitate was filtered at the pump and washed with a little sodium bicarbonate solution followed by water. The crystals were recrystallized twice from ethanol and water. The yield of crystals melting at 65.0–66.0°C was 2.8 g (*ca.* 60 %). (Found: C 49.1; H 5.8; Si 8.1. Calculated for $C_{14}H_{21}N_2O_6Si$: C 49.4; H 5.9; Si 8.2).

4-Trimethylsilyl-butanol-2 (I) from 4-trimethylsilyl-butanone-2

A few drops of the alcohol (I) were kindly placed at my disposal by Perklev, who synthesized it from 4-trimethylsilyl-butanone-2 by reduction with lithium aluminium hydride ⁴.

The 3,5-dinitrobenzoate was synthesized in the same way as above for the alcohol (A). M.p. 65.5–66°.

2-Methyl-3-trimethylsilyl-propanol-1 from α -methyl- β -trimethylsilylpropionic acid

22.8 g (0.143 mole) of α -methyl- β -trimethylsilyl-propionic acid dissolved in 215 ml of absolute ether were dropped into 7.6 g (0.20 mole) of lithium aluminium hydride in 260 ml of absolute ether. When all had been added the mixture was refluxed for 3 hours. Hydrolysis with water and diluted hydrochloric acid and extraction and drying were carried out in the usual way. Fractionation of the ether solution yielded 14.2 g (0.097 mole) of the desired alcohol, b.p. 88–89°C at 25 mm Hg. (Found: C 57.2; H 12.6; Si 19.4, MR_D 45.6. Calculated for $C_7H_{18}OSi$: C 57.5; H 12.4; Si 19.2, MR_D 45.8).

3,5-Dinitrobenzoate. From 2.0 g of 2-methyl-3-trimethylsilylpropanol-1 2.3 g of the 3,5-dinitrobenzoate of m.p. 44.5–45.5° were obtained. (Yield 50 %.)

The author wishes to express his gratitude to Professor Erik Larsson for his kind interest in this work.

REFERENCES

1. Gaylord, N. G. and Becker, E. I. *Chem. Revs.* **49** (1951) 413.
2. Sommer, L. H., Van Strien, R. E. and Whitmore, F. C. *J. Am. Chem. Soc.* **71** (1949) 3056.
3. Sommer, L. H., Goldberg, G. M., Barnes, G. H. and Stone, L. S. *J. Am. Chem. Soc.* **76** (1954) 1609.
4. Perklev, T. *Svensk Kem. Tidskr.* **65** (1953) 253.
5. Vogel, A. I. *Text-Book of Practical Organic Chemistry*, 2:d ed. Longmans, Green and Co, London 1951.

Received May 9, 1956.