The Synthesis of Some Organosilicon Alcohols. III

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Some of the reactions of 4-trimethylsilylbutylene-1,2-oxide were studied from a synthetic point of view. Water and ammonia were added under formation of 4-trimethylsilylbutylene-1,2-glycol and 4-trimethylsilyl-1-aminobutanol-2, respectively. The oxide reacted with ethylmagnesium bromide under formation of 1-trimethylsilyl-3-methylpentanol-3 and 1-trimethylsilylhexanol-3.

In a previous paper ¹ the synthesis of 4-trimethylsilylbutylene-1,2-oxide (I) from trimethylsilylmethylmagnesium bromide and epichlorohydrin *via* 4-trimethylsilyl-1-chlorobutanol-2 was reported. In this paper some of the reactions of (I) were studied from a synthetic point of view. The addition of water with perchloric acid as a catalyst yielded 4-trimethylsilylbutylene-1,2-glycol.

In analogy with the investigations carried out by Andersson ² (I) reacted with ammonia under formation of only one product, 4-trimethylsilyl-1-aminobutanol-2 (A), resulting from interaction of one mole of (I) with one mole of ammonia.

The constitution of (A) followed from the fact that its phthalimidoderivative, 4-trimethylsilyl-1-phthalimidobutanol-2 (B), on oxidation with chromic acid in boiling acetic acid yielded a ketone whose analyses agreed with those calculated for 4-trimethylsilyl-1-phthalimidobutanone-2. (B) was partly synthesized from (A) and phthalic anhydride and partly from (I) and phthalimide.

On interaction with ethylmagnesium bromide (I) reacted anomalously, inasmuch as it reacted both as a ketone and as an ethylene oxide. Theoretically four alcohols may be obtained; partly the oxide ring may be opened in two ways

and partly the oxide may react as if it had been rearranged to one or both of the isomeric oxo-compounds 4-trimethylsilylbutanone-2 and 4-trimethylsilylbutanal-1.

Out of the reaction mixture resulting from interaction of ethylmagnesium bromide with 4-trimethylsilylbutylene-1,2-oxide (I) two silicon-containing alcohols, (C) and (D), could be isolated. Those of their properties that were studied agreed with the corresponding properties of the alcohols (IV), 1-trimethylsilyl-3-methylpentanol-3 and (II), 1-trimethylsilylhexanol-3. (IV) was synthesized from 4-trimethylsilylbutanone-2, prepared according to Sommer and Marans³, and ethylmagnesium bromide, and (II) from 1-trimethylsilylhexanone-3 by reduction with lithium aluminium hydride. The 1-trimethylsilylhexanone-3 was synthesized from β -trimethylsilylpropionyl chloride, prepared according to Sommer, Goldberg and Stone⁴, and dipropylcadmium.

Besides it was shown that both (C) and (D) were non-identical with the alcohol (V), 1-trimethylsilylhexanol-4, which was obtained from 3-trimethylsilylpropylmagnesium bromide and propionaldehyde.

The 3-trimethylsilylpropyl bromide was synthesized according to Sommer, Van Strien and Whitmore⁵ from phosphorus tribromide and 3-trimethylsilylpropanol-1, which in its turn was prepared from trimethylsilylmethylmagnesium bromide and ethylene oxide.

It is often reported that ethylene oxides, especially the polysubstituted ones, rearrange into the isomeric ketones or aldehydes on reaction with Grignard reagents⁶. This isomerization is considered due to the presence of magnesium halide in the Grignard reagents according to the equation:

In accordance with this theory no rearrangements have been observed when ethylene oxides are allowed to react with dialkylmagnesium⁶. In agreement with this the only silicon-containing alcohol (E) that could be obtained from (I) and diethylmagnesium was 1-trimethylsilylhexanol-3 (II).

In Table 1 the data of the alcohols (II), (IV), (V), (C), (D) and (E) and their 3,5-dinitrobenzoates are collected.

The diethylmagnesium was prepared from an ether solution of ethyl magnesiumbromide by precipitating magnesium bromide with dioxan and separating from the precipitate by centrifuging.

Table 1.

Alcohol	B. p.		n_D^{20}	d_4^{20}	3,5-dinitrobenzoate, M. p.
	13 mm Hg				
(CH ₃) ₃ SiCH ₂ CH ₂ CHOHCH ₂ CH ₂ CH ₃ (II)	91–92°		1.4370	0.830	82–83°
(D)	91–92°		1.4374	0.832	79–81°*
(E)	92–93°		1.4370	0.831	82–83°**
(CH ₃) ₃ SiCH ₂ CH ₂ COH(CH ₂)CH ₂ CH ₃ (IV)	80–81°		1.4380	0.837	89–90°
(C)	81–82°		1.4377	0.837	88–90°***
(CH ₃) ₃ SiCH ₂ CH ₂ CH ₂ CHOHCH ₂ CH ₃ (V)	91–92°		1.4372	0.837	26–27°

* Mixed m.p. with (II) 81–82°.

** Mixed m.p. with (II) 82–83°.

*** Mixed m.p. with (IV) 88–90°.

EXPERIMENTAL

4-Trimethylsilylbutylene-1,2-glycol

14 g (0.10 mole) of 4-trimethylsilylbutylene-1,2-oxide (I) were shaken for one week with 1 liter of water mixed with 2 ml of 70 % perchloric acid. The resulting aqueous solution was extracted with 300 ml of ether in an extraction apparatus. The obtained ether solution was dried with anhydrous sodium sulphate and the ether removed by distillation. Fractionation at 15 mm Hg yielded 2.0 g (0.0014 mole) of unreacted 4-trimethylsilylbutylene-1,2-oxide at 53–55° and 6.6 g (0.041 mole) of 4-trimethylsilylbutylene-1,2-glycol at 130–131°; $n_D^{20} = 1.4519$; $d_4^{20} = 0.928$. (Found: C 51.1; H 11.1; Si 17.0; M_{RD} 47.1. Calc. for C₇H₁₈O₂Si: C 51.8; H 11.2; Si 17.3; M_{RD} 47.3.)

4-Trimethylsilyl-1-aminobutanol-2 (A)

10 g (0.069 mole) of 4-trimethylsilylbutylene-1,2-oxide (I) dissolved in 50 ml of ethanol were dropped into a stirred ice-cooled mixture of 150 ml of conc. ammonia and 200 ml of ethanol. The reaction mixture was allowed to come slowly to room temperature. After 3 days most of the ethanol was distilled off at ordinary pressure and the resulting water solution was extracted with ether. The ether solution was dried with anhydrous sodium sulphate and fractionated. 7.5 g (0.046 mole) of 4-trimethylsilyl-1-aminobutanol-2 (A) were collected at 113–114°, 13 mm Hg; $n_D^{20} = 1.4589$; $d_4^{20} = 0.898$. After some days the aminoalcohol (A) solidified to crystals melting at 31–33°. (Found: C 52.1; H 12.0; Si 17.4; M_{RD} 49.1. Calc. for C₇H₁₉ONSi: C 52.1; H 11.9; Si 17.4; M_{RD} 49.2.)

The distillation residue yielded after crystallization four times from petroleum ether (b. p. 40–60°) 1.9 g of crystals melting at 89.5–92.5°, probably consisting of di-(4-trimethylsilyl-2-hydroxybutyl-1)amine, [(CH₃)₃SiCH₂CH₂CHOHCH₂]₂NH. (Found: C 53.9; H 11.4; Si 18.3. Calc. for C₁₄H₃₈O₂NSi: C 55.0; H 11.5; Si 18.4.)

4-Trimethylsilyl-1-phthalimidobutanol-2 (B) from (A)

1.5 g (0.0093 mole) of (A) and 1.4 g (0.0093 mole) of phthalic anhydride were mixed with 5 ml of water. After removing of the water by warming on a water bath, the residue was distilled at 1.5 mm Hg. The main part distilled at about 205°. The distillate yielded after crystallization once from ligroin (b. p. 80–100°) 1.6 g (0.0059 mole) of 4-trimethylsilyl-1-phthalimidobutanol-2 (B). M. p. 85.5–87°. (Found: C 61.8; H 7.2; Si 9.6. Calc. for $C_{15}H_{21}O_3NSi$: C 61.8; H 7.2; Si 9.6.)

4-Trimethylsilyl-1-phthalimidobutanol-2 (B) from
4-trimethylsilylbutylene-1,2-oxide (I) and
phthalimide

10 g (0.07 mole) of 4-trimethylsilylbutylene-1,2-oxide (I) and 10 g (0.07 mole) of phthalimide were warmed for 18 h in a sealed tube at 190°. The resulting reaction product was crystallized twice from ligroin (b. p. 80–100°) and yielded 10 g (0.035 mole) of (B). M. p. 86.5–87.5°. Mixed m. p. with the product prepared from 4-trimethylsilyl-1-aminobutanol-2 (A) 86–87.5°.

4-Trimethylsilyl-1-phthalimidobutanone-2 from (B)

4.0 g (0.014 mole) of 4-trimethylsilyl-1-phthalimidobutanol-2 (B) were dissolved in 20 ml of acetic acid and warmed on a boiling water bath. A solution of 1.2 g (0.012 mole) of chromium trioxide in 5 ml of water was slowly dropped into the acetic acid solution. When all the chromic acid had been added and the solution had become brightly green, the reaction mixture was diluted with 100 ml of water. After cooling in ice the crystals were filtered off and recrystallized from ethanol. 2.8 g (0.0097 mole) of 4-trimethylsilyl-1-phthalimidobutanone-2 were obtained. M. p. 92–92.5°. (Found: C 62.3; H 6.6; Si 9.7. Calc. for $C_{15}H_{19}O_3NSi$: C 62.2; H 6.6; Si 9.7.)

2,4-Dinitrophenylhydrazone. 1.0 g (0.0035 mole) of 4-trimethylsilyl-1-phthalimidobutanone-2 was boiled for one minute with a solution of 0.7 g (0.0035 mole) of 2,4-dinitrophenylhydrazine in 15 ml of ethanol and 2 ml of conc. hydrochloric acid. After cooling the formed crystals were filtered off and crystallized twice from ethanol. 1.1 g (0.0021 mole) of the 2,4-dinitrophenylhydrazone of 4-trimethylsilyl-1-phthalimidobutanone-2 were obtained. M. p. 208.5–210°. (Found: C 53.3; H 4.9; Si 6.0. Calc. for $C_{21}H_{23}O_5N_3Si$: C 53.6; H 4.9; Si 6.0.)

Reaction of 4-trimethylsilylbutylene-1,2-oxide (I)
with ethylmagnesium bromide

10 g (0.07 mole) of 4-trimethylsilylbutylene-1,2-oxide in 50 ml of abs. ether were dropped into the stirred and ice-cooled Grignard reagent prepared from 21 g (0.2 mole) of ethyl bromide, 4.9 g (0.2 mole) of magnesium and 100 ml of abs. ether. When all had been added the ice-bath was removed, and when the solution had come to room temperature it was refluxed for 20 h. The reaction mixture was hydrolyzed with water and the basic salts were dissolved in dilute hydrochloric acid. The ether layer was separated and the water layer extracted with ether. The combined ether solutions were washed with some water and refluxed for 3 h with 8 g (0.2 mole) of pulverized sodium hydroxide in order to remove the formed chloro- and bromohydrines of 4-trimethylsilylbutylene-1,2-oxide. (In a previous experiment it proved difficult to separate these from the formed silicon-containing alcohols by distillation.) The excess of sodium hydroxide and the formed sodium halides were filtered off and washed with ether. After removal of the ether by distillation at ordinary pressure, fractionation at 13 mm Hg yielded 1.8 g (0.013 mole) of 4-trimethylsilylbutylene-1,2-oxide at 48–49°, 2.8 g (0.016 mole) of 1-trimethylsilyl-3-methylpentanol-3 (C) at 81–82° and 2.6 g (0.015 mole) of 1-trimethylsilylhexanol-3 (D) at 91–92°. Data for (C): $n_D^{20} = 1.4377$; $d_4^{20} = 0.837$. (Found: C 61.5; H 12.6; Si 16.1; M_{RD} 54.6.) Data for (D): $n_D^{20} = 1.4374$; $d_4^{20} = 0.832$. (Found: C 61.8; H 12.7; Si 15.9; M_{RD} 54.9.) (Calc. for $C_9H_{22}OSi$: C 62.0; H 12.7; Si 16.1; M_{RD} 54.9.)

3,5-Dinitrobenzoate. 3,5-Dinitrobenzoate was prepared according to a method described by Cameron and coworkers⁷. 1 g of the alcohol in question was mixed with 4 ml of pyridine (dried with potassium hydroxide), whereupon 2 g of 3,5-dinitrobenzoyl chloride were added. After heating for 3 h to 100° the cooled reaction mixture was diluted with 25 ml of ether. The ether solution was washed once with 15 ml of dilute hydrochloric acid and twice with 25 ml of a 5 % sodium hydroxide solution. The ether was evaporated from the obtained ethereal solution of the 3,5-dinitrobenzoate, and the resulting crystals were washed with some dilute hydrochloric acid followed by water and crystallized two times from ethanol.

1.0 g (0.0058 mole) of (C) yielded 1.5 g (0.0039 mole) of the 3,5-dinitrobenzoate. M. p. 88–90°. (Found: C 52.0; H 6.5; Si 7.5.)

1.0 g (0.0058 mole) of (D) yielded 1.2 g (0.0031 mole) of the 3,5-dinitrobenzoate. M. p. 79–81°. (Found: C 52.0; H 6.5; Si 7.5.) (Calc. for $C_{11}H_{24}O_6N_2Si$: C 52.2; H 6.6; Si 7.6.)

Reaction of 4-trimethylsilylbutylene-1,2-oxide (I) with diethylmagnesium

200 g of dioxan in 200 ml of abs. ether were dropped into the well stirred boiling Grignard reagent prepared from 109 g (1.0 mole) of ethyl bromide, 24.3 g (1.0 mole) of magnesium and 300 ml of abs. ether. The formed precipitate was removed by centrifuging. The resulting ether solution contained 0.2 mole of diethylmagnesium. 14.4 g (0.10 mole) of 4-trimethylsilylbutylene-1,2-oxide in 50 ml of abs. ether were dropped into the stirred and ice-cooled solution of diethylmagnesium mentioned above. After all had been added the mixture was allowed to come to room temperature and was then refluxed for 20 h. After decomposition with water and dilute hydrochloric acid the ether layer was separated and the water layer carefully extracted with ether. After drying of the resulting ether solution with anhydrous sodium sulphate, the ether and dioxan were removed by distillation at ordinary pressure. Fractionation at 13 mm Hg yielded 13.7 g (0.079 mole) of 1-trimethylsilylhexanol-3 (E) at 92–93°; $n_D^{20} = 1.4370$; $d_4^{20} 0.831$. (Found: C 61.4; H 12.4; Si 16.1; $M_{RD} 54.9$. Calc. for $C_8H_{22}OSi$: C 62.0; H 12.7; Si 16.1; $M_{RD} 54.9$.)

3,5-Dinitrobenzoate. 1.0 g (0.0058 mole) of (E) yielded 1.7 g (0.0044 mole) of 3,5-dinitrobenzoate. M. p. 82.5–83°. (Found: C 51.8; H 6.5; Si 7.5. Calc. for $C_{11}H_{24}O_6N_2Si$: C 52.2; H 6.6; Si 7.6.)

1-Trimethylsilylhexanone-3

25.6 g (0.14 mole) of cadmium chloride (dried 10 h at 110°) were added to the stirred ice-cooled Grignard solution prepared from 34 g (0.28 mole) of *n*-propyl bromide, 6.5 g (0.27 mole) of magnesium and 300 ml of abs. ether. The main part of the ether was distilled off and 300 ml of anhydrous benzene added. The rest of the ether was now distilled off, whereupon 20 g (0.12 mole) of β -trimethylsilylpropionyl chloride were quickly dropped into the stirred boiling benzene solution. The mixture was refluxed for an hour and then hydrolyzed with water followed by dilute hydrochloric acid. The organic layer was separated and the water layer extracted twice with 25 ml of benzene. After drying with anhydrous sodium sulphate the benzene was distilled off at ordinary pressure. Fractionation of the rest at 20 mm Hg yielded 14 g (0.083 mole) of 1-trimethylsilylhexanone-3 at 99–100°; $n_D^{20} = 1.4303$. The semicarbazone melted at 73–74°. (Sommer, Bailey, Goldberg, Buck, Bye, Evans and Whitmore⁸ report $n_D^{20} = 1.4294$ and m. p. of the semicarbazone 72–73°.) (Found: C 62.1; H 11.7; Si 16.3. Calc. for $C_8H_{20}OSi$: C 62.7; H 11.7; Si 16.3.)

2,4-Dinitrophenylhydrazone. 1.0 g (0.0058 mole) of 1-trimethylsilylhexanone-3 was boiled for one minute with a solution of 1.1 g (0.0056 mole) of 2,4-dinitrophenyl hydrazine in 20 ml of ethanol and 2 ml of conc. hydrochloric acid. After the mixture had come to room temperature, it was cooled in ice and the obtained crystals were filtered off. Two crystallizations from ligroin (b. p. 80–100°) yielded 1.6 g (0.0045 mole) of the 2,4-dinitrophenylhydrazone of 1-trimethylsilylhexanone-3. Orange-coloured crystals melting at 96–98°. (Found: C 51.0; H 6.8; Si 7.9. Calc. for $C_{11}H_{24}O_6N_4Si$: C 51.1; H 6.9; Si 8.0.)

1-Trimethylsilylhexanol-3 (II)

8.5 g (0.049 mole) of 1-trimethylsilylhexanone-3 in 25 ml of abs. ether were dropped into the stirred mixture of 3.5 g (0.10 mole) of lithium aluminium hydride and 50 ml of abs. ether. After refluxing for two hours the reaction mixture was decomposed with water and dilute hydrochloric acid. The organic layer was separated and the water layer extracted with ether. After drying with anhydrous sodium sulphate fractionation at 13 mm Hg yielded 5.8 g (0.034 mole) of 1-trimethylsilylhexanol-3 (II) at 91–92°; $n_D^{20} = 1.4370$; $d_4^{20} = 0.830$. The alcohol gave a negative result on testing for ketone with 2,4-dinitrophenyl hydrazine according to the description above. (Found: C 61.9; H 12.6; Si 15.9; M_{RD} 54.9. Calc. for $C_9H_{22}OSi$: C 62.0; H 12.7; Si 16.1; M_{RD} 54.9.)

3,5-Dinitrobenzoate. 1.0 g (0.0058 mole) of 1-trimethylsilylhexanol-3 yielded 1.6 g (0.0042 mole) of the 3,5-dinitrobenzoate; M. p. 82–83°. (Found: C 51.9; H 6.5; Si 7.6. Calc. for $C_{16}H_{24}O_5N_2Si$: C 52.2; H 6.6; Si 7.6.)

1-Trimethylsilyl-3-methylpentanol-3 (III)

2.9 g (0.002 mole) of 4-trimethylsilylbutanone-2 in 5 ml of abs. ether were dropped into the stirred Grignard reagent prepared from 3.3 g (0.03 mole) of ethyl bromide, 0.7 g (0.03 mole) of magnesium and 10 ml of abs. ether. After having been refluxed for two hours the reaction mixture was decomposed and worked up in the usual way. Fractionation yielded 2.0 g (0.012 mole) of 1-trimethylsilyl-3-methylpentanol-3 (III); B. p. 80–81° (13 mm Hg); $n_D^{20} = 1.4380$; $d_4^{20} = 0.837$. (Found: C 61.5; H 12.6; Si 16.0; M_{RD} 54.9. Calc. for $C_9H_{22}OSi$: C 62.0; H 12.6; Si 16.1; M_{RD} 54.9.)

3,5-Dinitrobenzoate. 0.8 g (0.0046 mole) of 1-trimethylsilyl-3-methylpentanol-3 (III) yielded 1.3 g (0.0034 mole) of the 3,5-dinitrobenzoate; M. p. 89–90°. (Found: C 51.8; H 6.5; Si 7.5. Calc. for $C_{16}H_{24}O_5N_2Si$: C 52.2; H 6.6; Si 7.6.)

3-Trimethylsilylpropanol-1

88 g (2.0 moles) of ethylene oxide in 175 ml of abs. ether were dropped into the stirred and ice-cooled Grignard reagent prepared from 167 g (1.0 mole) of bromomethyltrimethylsilane, 24 g (1.0 mole) of magnesium and 300 ml of abs. ether. When all had been added the ice-cooling was removed, whereupon the reaction mixture boiled spontaneously. After the boiling had stopped the stirred mixture was refluxed for four hours and was then allowed to stand over night. The next day the reaction mixture had solidified to a gel. After decomposition with water and dilute hydrochloric acid, the ether layer was separated and the water layer extracted with ether. The combined ether solutions were washed with some water and boiled for 3 h with 40 g (1.0 mole) of finely powdered sodium hydroxide in order to remove the formed ethylene chloro- and bromohydrines. (In a previous experiment it proved difficult to separate the ethylene bromohydrine from the formed siliconcontaining alcohol by distillation.) The excess of sodium hydroxide and the formed sodium halides were filtered off and washed with ether. After removal of the ether by distillation at ordinary pressure fractionation at 27 mm Hg yielded 82 g (0.62 mole) of 3-trimethylsilylpropanol-1; B. p. 83–85°; $n_D^{20} = 1.4294$ (Sommer, Van Strien and Whitmore⁶ report b. p. 83° (27 mm Hg) and $n_D^{20} = 1.4290$). (Found: Si 21.0. Calculated for $C_6H_{16}OSi$: Si 21.2.)

1-Trimethylsilylhexanol-4 (IV)

1.2 g (0.002 mole) of propionaldehyde in 5 ml of abs. ether were dropped into the stirred Grignard reagent prepared from 3.8 g (0.002 mole) of 3-trimethylsilyl-1-bromopropane, 0.5 g (0.002 mole) of magnesium and 10 ml of abs. ether. After 2 h of refluxing the reaction mixture was worked up in the usual way and yielded 1.6 g (0.0092 mole) of 1-trimethylsilylhexanol-4 (IV); B. p. 91–92° (13 mm Hg); $n_D^{20} = 1.4372$; $d_4^{20} = 0.827$. (Found: C 61.8; H 12.6; Si 16.2; M_{RD} 55.1. Calc. for $C_9H_{22}OSi$: C 62.0; H 12.6; Si 16.1; M_{RD} 54.9.)

3,5-Dinitrobenzoate. 1.0 g (0.0058 mole) of 1-trimethylsilylhexanol-4 yielded 1.0 g (0.0026 mole) of the 3,5-dinitrobenzoate; M. p. 26–27°. (Found: C 51.5; H 6.5; Si 7.5. Calc. for $C_{18}H_{24}O_5N_2Si$: C 52.2; H 6.6; Si 7.6.)

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