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PREPARATION OF SOME α- AND β-HYDROXYALKYL SILICON COMPOUNDS

MAKOTO KUMADA, NAOSHI IMAKI AND KEIJI YAMAMOTO
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)
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INTRODUCTION

As part of a program of study concerned with carbon-functional organopolysilanes we wished to prepare α- and β-hydroxyalkyl disilanes, and we report here the preparation of some of these and related compounds.

Seyferth and his co-workers[1-3] have suggested that oxidation of silicon-containing organoboranes, which are prepared either by the Grignard reaction or hydroboration of vinyl- and allylsilanes, affords a useful method for preparation of α-, β- or γ-hydroxyalkyl silanes.

We have now prepared in a similar way five new hydroxyalkyl silicon compounds: (hydroxymethyl)pentamethyldisilane (I) (eqn. 1); (α-hydroxyethyl)- (II) and (β-hydroxyethyl)pentamethyldisilane (III) [eqn. 2, R = $(CH_3)_3Si$]; and (α-hydroxyethyl)- (IV) and (β-hydroxyethyl)-tert-butyldimethylsilane (V) [eqn. 2, R = $(CH_3)_3C$].

$$(CH_3)_3SiSi(CH_3)_2CH_2Cl \xrightarrow[2.\ BF_3\text{-}O(C_2H_5)_2]{1.\ Mg,\ ether} [(CH_3)_3SiSi(CH_3)_2CH_2]_3B \xrightarrow{[O]} (CH_3)_3SiSi(CH_3)_2CH_2OH\ (I) \qquad (1)$$

$$R(CH_3)_2SiCH{=}CH_2 \xrightarrow[2.\ [O]]{1.\ NaBH_4 + BF_3\text{-}O(C_2H_5)_2} R(CH_3)_2SiCH(OH)CH_3 + R(CH_3)_2SiCH_2CH_2OH \qquad (2)$$

(II) R = $(CH_3)_3Si$ (III) R = $(CH_3)_3Si$
(IV) R = $(CH_3)_3C$ (V) R = $(CH_3)_3C$

Compound (III) was also prepared through an alternative route shown by eqn. (3).

$$(CH_3)_3SiSi(CH_3)_2CH_2Cl \xrightarrow[2.\ ClCO_2C_2H_5]{1.\ Mg,\ ether} (CH_3)_3SiSi(CH_3)_2CH_2CO_2C_2H_5 \xrightarrow{LiAlH_4} (CH_3)_3SiSi(CH_3)_2CH_2CH_2OH\ (III) \qquad (3)$$

RESULTS AND DISCUSSION

Formulas and some physical properties for five new hydroxyalkyl silicon compounds are listed in Table 1.

The hydroboration technique in the present investigation followed that used by Brown and Subba Rao[4], who added boron trifluoride etherate to the solution of an olefin and sodium borohydride in diglyme, and subsequently treated the reaction

TABLE 1

SOME PHYSICAL CONSTANTS FOR α- AND β-HYDROXYALKYL SILICON COMPOUNDS

No.	*Formula*	*B.p. °C/mm*	n_D^{20}	d_4^{20}
(I)	$(CH_3)_3SiSi(CH_3)_2CH_2OH$	90/40	1.4563	0.8414
(II)	$(CH_3)_3SiSi(CH_3)_2CH(OH)CH_3$	80/23	1.4583	0.8413
(III)	$(CH_3)_3SiSi(CH_3)_2CH_2CH_2OH$	98/23	1.4607	0.8466
(IV)	$(CH_3)_3CSi(CH_3)_2CH(OH)CH_3$[a]	67/12		
(V)	$(CH_3)_3CSi(CH_3)_2CH_2CH_2OH$	84/12	1.4487	0.8599

[a] M.p. 43°.

TABLE 2

CHEMICAL SHIFTS OF α- AND β-HYDROXYETHYL SILICON COMPOUNDS

No.	*Compound*	*Chemical shift*[a]
(II)	$(CH_3)_3SiSi(CH_3)_2CH(OH)CH_3$ a a′ d c b	a 0.04 a′ 0.10 b 1.27 (doublet, J = 7.4 cps) c 2.71 d 3.58 (quartet, J = 7.4 cps)
(III)	$(CH_3)_3SiSi(CH_3)_2CH_2CH_2OH$ a a b d c	a 0.06 b 0.97 (triplet, J = 8.2 cps) c 2.68 d 3.14 (triplet, J = 8.2 cps)
(IV)	$(CH_3)_3CSi(CH_3)_2CH(OH)CH_3$ b a,a′ e d c	a −0.08 a′ −0.03 b 0.94 c 1.27 (doublet, J = 7.5 cps) d 2.45 e 3.52 (quartet, J = 7.5 cps)
(V)	$(CH_3)_3CSi(CH_3)_2CH_2CH_2OH$ b a c e d	a −0.03 b 0.91 c 0.94 (triplet, J = 8.3 cps) d 3.57 e 3.67 (triplet, J = 8.3 cps)

[a] Chemical shifts were given in ppm downfield from tetramethylsilane.

mixture with alkaline hydrogen peroxide. Two isomeric substituted ethanols produced from each of the vinylsilanes, $(CH_3)_3SiSi(CH_3)_2CH=CH_2$ and $(CH_3)_3CSi(CH_3)_2$-$CH=CH_2$, were separated successfully by fractional distillation in an efficient column. Assignment of α- or β-hydroxyethyl structure to the isolated ethanols was made on the basis of their NMR spectra (see Table 2).

It should be noteworthy that the silicon–silicon bond does not undergo oxidation at all by alkaline hydrogen peroxide, whereas it is quantitatively oxidized to the silicon–oxygen–silicon bond by perbenzoic acid by electrophilic mechanism[5]. Thus, the infrared spectra of compounds (I), (II) and (III) showed no absorptions characteristic of the siloxane bond.

As to hydroboration of alkenylsilanes, the direction of addition of the boron–hydrogen bond has been an interesting subject of discussion. In connection with this

problem we have determined by vapor phase chromatography the distribution of the two isomeric organosilicon-substituted ethanols produced by hydroboration of a given vinylsilane. Table 3 summarizes the results obtained for the two reactions indicated by eqn. (2), together with those for the hydroboration of vinyltrimethylsilane, which was first reported by Seyferth[1].

In accordance with the observation by Seyferth, it can be seen from Table 3 that organosilicon substituents, as compared with any alkyl group, have, in general, a marked tendency to direct a boron atom to the α-carbon of the vinyl group. The relatively high yield of (α-hydroxyethyl)-tert-butyldimethylsilane (IV) was unexpected in view of the larger steric influence and nearly the same electronic effect of the tert-butyldimethylsilyl as compared with the trimethylsilyl group. This unexpected distribution of isomeric alcohols from $(CH_3)_3CSi(CH_3)_2CH=CH_2$ can be ascribed to the difficulty with which the second molecule of the olefin becomes attached to a boron atom having already bound to the first one. In fact, two types of incompletely alkylated organoboron compounds, *i.e.*, $(CH_3)_3CSi(CH_3)_2C_2H_4B(OC_2H_5)_2$ and $\{(CH_3)_3CSi(CH_3)_2C_2H_4\}_2BOC_2H_5$, were isolated after hydrolysis of the hydroboration product of $(CH_3)_3CSi(CH_3)_2CH=CH_2$ followed by refluxing in ethanol. When these compounds were oxidized separately, there was obtained a mixture of the α- and β-hydroxyethyl silicon compounds in the molar ratio of 89:11 from $(CH_3)_3CSi(CH_3)_2C_2H_4B(OC_2H_5)_2$, while in 45:55 from $\{(CH_3)_3CSi(CH_3)_2C_2H_4\}_2BOC_2H_5$.

TABLE 3

DISTRIBUTION OF α- AND β-HYDROXYALKYL SILICON COMPOUNDS IN HYDROBORATION

Compound	*Overall yield (%)*	*Isomers (mole %)*	
		α-	β-
$(CH_3)_3SiCH=CH_2$[a]	70	50	50
$(CH_3)_3SiSi(CH_3)_2CH=CH_2$	65	25	75
$(CH_3)_3CSi(CH_3)_2CH=CH_2$	60	56	44

[a] Seyferth[2] obtained the α- and β-isomer in 51.5–53.5:47–48.5 from $(CH_3)_3SiCH=CH_2$ and $NaBH_4$ in 1:1.6 molar ratio in the presence of aluminum chloride in diglyme.

A rather favorable β-direction of addition of boron atom that was observed in the hydroboration of $(CH_3)_3SiSi(CH_3)_2CH=CH_2$ seems to be due to somewhat stronger electron-donating nature as well as larger steric requirement of $(CH_3)_3SiSi(CH_3)_2$- group relative to those of the $(CH_3)_3Si$-.

EXPERIMENTAL

All compounds reported here were fractionally distilled satisfactorily in a 1.0 × 30 cm column packed with glass helices and their purities were examined by vapor phase chromatography (VPC). Boiling and melting points were uncorrected. PMR spectra were obtained by Dr. K. TORI of Shionogi Research Laboratory in carbon tetrachloride solutions containing cyclohexane as an internal standard.

Vinyltrimethylsilane[6] and vinylpentamethyldisilane[7,8] were prepared by the method described in the literature.

Vinyl-tert-butyldimethylsilane

To a stirred tetrahydrofuran solution containing about 2 moles of vinylmagnesium chloride was added 90.5 g (0.68 mole) of tert-butyldimethylfluorosilane[9] diluted with 100 ml of tetrahydrofuran. The reaction mixture was refluxed for 40 h. After hydrolysis with dilute hydrochloric acid, fractional distillation of the organic layer gave 38.5 g (40% yield) of vinyl-tert-butyldimethylsilane, b.p. 127°, n_D^{20} 1.4281, d_4^{20} 0.7565, MR_D 48.40 (calcd. 48.31). (Found: C, 67.79; H, 12.74. $C_8H_{18}Si$ calcd.: C, 67.51; H, 12.75%.)

(Hydroxymethyl)pentamethyldisilane (I)

To a Grignard reagent prepared from 24 g (0.13 mole) of (chloromethyl)pentamethyldisilane[10] and 2.7 g (0.11 g-atom) of magnesium in 40 ml of ether was added 4.3 g (0.03 mole) of boron trifluoride etherate. The reaction mixture was heated to reflux for 10 h, hydrolyzed with a saturated solution of ammonium chloride and then distilled to give 10 g (70% yield) of tris[(pentamethyldisilanyl)methyl]borane, b.p. 156°/3.6 mm, n_D^{20} 1.4854, d_4^{20} 0.8341. (Found: C, 48.57; H, 11.44. $C_{18}H_{51}BSi_6$ calcd.: C, 48.37; H, 11.50%.) Its NMR spectrum showed three singlet peaks at 0.04 [$(CH_3)_3Si$–], 0.08 [–$Si(CH_3)_2$–] and 0.81 ppm (CH_2 bonded to boron). This borane is a colorless, viscous liquid with unpleasant odor and so air-sensitive as to ignite on a filter paper.

To a mixture of 4.4 g (0.01 mole) of this borane and 9 ml of about 0.5% sodium hydroxide solution in ethanol was added slowly at room temperature 4.3 g of 30% hydrogen peroxide. After 1 h stirring, the reaction mixture was treated with 7 ml of distilled water and extracted with ether. Fractional distillation of the ether extract gave 3.5 g (72% yield) of (hydroxymethyl)pentamethyldisilane (I) (Found: C, 44.39; H, 11.07. $C_6H_{18}OSi_2$ calcd.: C, 44.38; H, 11.17%.) The NMR spectrum showed three singlet peaks at 0.08 [$(CH_3)_3SiSi(CH_3)_2$–], 1.58 (OH) and 3.42 ppm (CH_2 bonded to silicon). The IR spectra indicated a broad band characteristic of bonded OH stretching at 3345 cm^{-1} (liquid film) and a sharp but medium band of free OH at 3614 cm^{-1} (carbon tetrachloride solution). No bands characteristic of the siloxane bond were observed.

(α-Hydroxyethyl)- (II) and (β-hydroxyethyl)pentamethyldisilane (III) via hydroboration

To a mixture of 37 g (0.23 mole) of vinylpentamethyldisilane and 4.4 g (0.12 mole) of sodium borohydride in 30 ml of diglyme was added with stirring and cooling 22.2 g (0.156 mole) of boron trifluoride etherate diluted with 20 ml of diglyme. The reaction mixture was stirred at room temperature for 5 h, and then allowed to stand overnight. After treatment with 25 ml of distilled water for the purpose of decomposing the unchanged hydride, the reaction mixture was oxidized by the addition of 34.4 g of 30% hydrogen peroxide and then 38 ml of 3 M sodium hydroxide solution. The contents of the reaction vessel were poured into water and the alcohols formed were extracted with ether. After evaporation of ether from the ether extract, the residual liquid was first analyzed by VPC for determination of its composition and then distilled under reduced pressure to give 26.5 g (65% yield) of a mixture of the isomeric alcohols, b.p. 80–110°/30 mm. Finally, it was fractionally distilled to give (α-hydroxymethyl)pentamethyldisilane (II) (Found: C, 47.80; H, 11.11. $C_7H_{20}OSi_2$ calcd.: C, 47.66; H, 11.42%.) and (β-hydroxymethyl)pentamethyldisilane (III). (Found: C, 47.80; H, 11.28. $C_7H_{20}OSi_2$ calcd.: C, 47.66; H, 11.42%.) The IR spectra of (II) and

(III) showed a broad band at 3427 and 3335 cm^{-1}, respectively, characteristic of associated OH stretching, and a weak absorption band at 3665 and 3615 cm^{-1}, respectively, due to free OH stretching. No bands characteristic of the siloxane bond were observed.

(β-Hydroxyethyl)pentamethyldisilane (III) via alternative route

To a Grignard solution prepared from 27.5 g (0.15 mole) of (chloromethyl)-pentamethyldisilane[10] and 3.6 g (0.15 g-atom) of magnesium turnings in 200 ml of ether was added 12 g (0.12 mole) of ethyl chloroformate with external cooling. After being allowed to stand overnight, the reaction mixture was hydrolyzed with 300 ml of saturated solution of ammonium chloride. Fractional distillation of the resulting organic layer gave 23 g (87 % yield) of (carbethoxymethyl)pentamethyldisilane, b.p. 108–110°/36 mm, n_D^{20} 1.4483, d_4^{20} 0.8662. (Found: C, 48.88; H, 9.76. $C_9H_{22}O_2Si_2$ calcd.: C, 49.49; H, 10.15 %.) To a cooled solution of 4.6 g (0.12 mole) of lithium aluminum hydride in 100 ml of dry ether was added 21 g (0.10 mole) of the ester over a 2-h period. The reaction mixture was refluxed for 12 h, and then hydrolyzed with 10 % sulfuric acid. The aqueous phase was extracted with ether. Fractional distillation of the combined ether extract gave 9.0 g (51 % yield) of the alcohol (III), slightly contaminated with the unchanged ester.

(α-Hydroxyethyl)- and (β-hydroxyethyl)trimethylsilane

Hydroboration, followed by oxidation, of vinyltrimethylsilane in essentially the same manner as described above gave a mixture of these isomeric ethanols in 70 % yield. Fractional distillation gave a pure sample of each. (α-Hydroxyethyl)trimethylsilane had b.p. 126°, n_D^{20} 1.4242, d_4^{20} 0.8335 (lit.[11] b.p. 127.3°, n_D^{20} 1.4241, d_4^{20} 0.8303). (Found: C, 51.02; H, 11.86. $C_5H_{14}OSi$ calcd.: C, 50.78; H, 11.93 %.) The NMR spectrum showed a singlet at −0.02 [$(CH_3)_3Si$], a doublet at 1.21 (J = 7.6 cps) (terminal CH_3 split by the adjacent CH), a singlet at 2.40 (OH) and a quartet signal at 3.41 ppm (J = 7.6 cps) (CH bearing OH, split by the adjacent CH_3). (β-Hydroxyethyl)trimethylsilane had b.p. 146°, n_D^{20} 1.4231, d_4^{20} 0.8358. (lit.[12] b.p. 95°/100 mm, n_D^{25} 1.4220, d_4^{25} 0.8254). (Found: C, 50.89; H, 11.81. $C_5H_{14}OSi$ calcd.: C, 50.78; H, 11.93 %.) The NMR spectrum showed a singlet at 0.01 [$(CH_3)_3Si$], a triplet at 0.90 (J = 8.2 cps) (CH_2 linked to silicon, split by the adjacent, CH_2), a singlet at 3.12 (OH) and a triplet signal at 3.65 ppm (J = 8.2 cps) (CH_2 bearing OH, split by the adjacent CH_2).

(α-Hydroxyethyl)- (IV) and (β-hydroxyethyl)-tert-butyldimethylsilane (V)

By using substantially the same techniques as above, 13 g (60 % yield) of a mixture of the isomeric ethanols was obtained from 21.3 g (0.15 mole) of vinyl-tert-butyldimethylsilane. Fractional distillation gave pure samples of (α-hydroxyethyl)-tert-butyldimethylsilane (IV). (Found: C, 59.84; H, 12.76. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57 %.) and (β-hydroxyethyl)-tert-butyldimethylsilane (V). (Found: C, 60.15; H, 12.85. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57 %.)

In a second run, 10 g (0.07 mole) of vinyl-tert-butyldimethylsilane was subjected to hydroboration with 1.4 g (0.035 mole) of sodium borohydride and 5.6 g (0.047 mole) of boron trifluoride etherate in 65 ml of diglyme. The reaction mixture was hydrolyzed with distilled water. The organic layer and ether extracts from the aqueous phase were combined. After evaporation of ether, the residue was admixed with 100 ml of absolute

ethanol and refluxed for 12 h. Distillation of the reaction mixture gave 1.5 g of diethyl [(tert-butyldimethylsilyl)ethyl]boronate, b.p. 120–140°/2.8 mm (Found: C, 59.17; H, 11.69. $C_{12}H_{29}BO_2Si$ calcd.: C, 59.00; H, 11.97 %.) and 3 g of bis[(tert-butyldimethylsilyl)ethyl]borinic anhydride, b.p. 165–168°/2.8 mm, m.p. 52–56°. (Found: C, 62.82; H, 12.61. $C_{32}H_{76}B_2OSi_4$ calcd.: C, 62.91; H, 12.54 %.) VPC analysis of the oxidation products from the both compounds indicated that the α- (IV) and β-ethanol (V) were formed in the molar ratio 89:11 from the boronate, while in 45:55 from the borinic anhydride.

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SUMMARY

The preparation and characterization of five new hydroxyalkyl silicon compounds, (hydroxymethyl)pentamethyldisilane, (α-hydroxyethyl)- and (β-hydroxyethyl)pentamethyldisilane and (α-hydroxyethyl)- and (β-hydroxyethyl)-tert-butyldimethylsilane are described. In hydroboration of vinylsilanes used here, all the organosilicon substituents attached to the vinyl group, *i.e.*, $(CH_3)_3Si$, $(CH_3)_3SiSi(CH_3)_2$ and $(CH_3)_3CSi(CH_3)_2$, showed a marked tendency, as compared with any alkyl substituent, to direct a boron atom to become bonded to the α-carbon of the vinyl.

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