Chemistry

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Abstract

Full Text

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Synthesis of Trialkylbutadienylsilanes

The first representative of this series of silanes—triethylbutadienylsilane (1-triethylsilylbutadiene)—was obtained by Petrov and Sadykhzade ([1]) by incomplete hydrogenation over palladium oxide of the corresponding vinylethynylsilane:

$$\text{Si}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{Si}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$$

It had the following properties: b.p. 74-75° at 19 mm; d_4^{20} 0.7988; n_D^{20} 1.4585. With maleic anhydride it gave an adduct with m.p. 132°.

In the present investigation an attempt was made to carry out the synthesis of 2-trialkylsilylbutadienes by the interaction of chloroprene with a copper-silicon alloy under the conditions of the so-called direct synthesis. This attempt was unsuccessful because, before entering into the direct-synthesis reaction, chloroprene underwent cyclodimerization with the formation of two compounds:

[[structural formula: chlorinated cyclohexene bearing C(Cl)=CH$_2$ substituent]] and [[structural formula: di

which proved incapable of entering into direct synthesis. The synthesis of two trialkylsilylbutadienes was recently accomplished by Petrov and Shukovskaya ([2]) by dehydration of silicon analogs of substituted tertiary alcohols, synthesized according to the scheme:

$$\text{Si}-\text{H} + \text{CH}\equiv\text{C}-\text{C}(\text{OH})(\text{CH}_3)_2 \longrightarrow \text{Si}-\text{C}(=\text{CH}_2)-\text{C}(\text{OH})(\text{CH}_3)_2,$$

$$\text{Si}-\text{C}(=\text{CH}_2)-\text{C}(\text{OH})(\text{CH}_3)_2 \longrightarrow \text{H}_2\text{O} + \text{Si}-\text{C}(=\text{CH}_2)-\text{C}(\text{CH}_3)=\text{CH}_2$$

For the purpose of synthesizing trialkylbutadienylsilanes, it seemed of interest to investigate the behavior in the dehydration reaction of secondary unsaturated alcohols.

By the interaction of Grignard reagents of trialkyl α-chloromethylsilanes with acrylic and crotonic aldehydes, we obtained, in high yields, secondary alcohols whose physical properties are presented in Table 1.

Table 1

Compound	b.p., °C	P, mm Hg	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Yield, %	OH, %, found	OH, %, calc.	H, %, found	H, %, calc.	C, %, found	C, %, calc.	Si, %, found	Si, %, calc.
$(CH_3)_3Si–CH_2–CH(OH)–CH=CH_2$ Trimethylsilylbut-3-en-2-ol	70–70,5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11,10	[illegible]	57,45	[illegible]	19,15	[illegible]
$(CH_3)_2(C_2H_5)Si–CH_2–CH(OH)–CH=CH_2$ Dimethylethylsilylbut-3-en-2-ol	74–75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11,42	[illegible]	60,20	[illegible]	17,65	[illegible]
$(CH_3)(C_2H_5)_2Si–CH_2–CH(OH)–CH=CH_2$ Methyldiethylsilylbut-3-en-2-ol	79–80	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11,48	[illegible]	62,24	[illegible]	16,53	[illegible]
$(CH_3)_2(C_4H_9)Si–CH_2–CH(OH)–CH=CH_2$ Dimethylbutylsilylbut-3-en-2-ol	75–76	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	–	–	15,76	[illegible]
$(C_2H_5)_3Si–CH_2–CH(OH)–CH=CH_2$ Triethylsilylbut-3-en-2-ol	76–77	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–
$(CH_3)_2(C_2H_5)Si–CH_2–CH(OH)–CH=CH–CH_3$ Dimethylethylsilylpent-3-en-2-ol	70–71	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–

Compound	b.p., °C	P, mm Hg	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Yield, %	OH, %, found	OH, %, calc.	H, %, found	H, %, calc.	C, %, found	C, %, calc.	Si, %, found	Si, %, calc.
$(CH_3)_3Si-CH=CH-CH=CH_2$ Trimethylsilylbutadiene	113,5	759	1,4480	0,7534	48,41	48,23	35,0	—	—	11,34	11,89	65,54	66,54	22,38	22,19
$(CH_3)_2(C_2H_5)Si-CH=CH-CH=CH_2$ Dimethylethylsilylbutadiene	137,5–138,5	751	1,4490	0,7694	[illegible]	[illegible]	29,0	—	—	11,72	11,80	67,97	68,55	19,61	20,00
$(CH_3)(C_2H_5)_2Si-CH=CH-CH=CH_2$ Methyldiethylsilylbutadiene	162–162,5	752	1,4580	0,7875	[illegible]	[illegible]	17,3	—	—	12,00	11,99	69,25	70,03	17,78	18,03
$(C_2H_5)_3Si-CH=CH-CH=CH_2$ Triethylsilylbutadiene	184–185	756	1,4690	0,8076	[illegible]	[illegible]	21,0	—	—	12,50	11,98	71,30	71,90	16,10	16,63
$[(CH_3)_3Si-CH=CH]_2$	95	3,5	1,4790	0,8149	[illegible]	[illegible]	42,5	—	—	11,19	11,07	65,71	65,60	21,74	22,42
$[(CH_3)_2(C_2H_5)Si-CH=CH]_2$	117–118	2,5	1,4830	0,8635	[illegible]	72,40	10,0	—	—	11,41	11,49	67,67	67,51	19,67	20,03
$[(CH_3)(C_2H_5)_2Si-CH=CH]_2$	139–141	3	1,4930	0,8490	81,65	81,56	16,0	—	—	12,04	12,09	69,33	70,05	17,36	17,28
$(CH_3)_3Si$-substituted phthalic anhydride structure shown	124,5*	—	—	—	—	—	—	—	—	7,00	7,24	59,00	58,97	12,31	12,26

* Melting point in °C.

$$R_3Si{-}CH_2MgCl + CH_2{=}CH{-}C({=}O)H \longrightarrow R_3Si{-}CH_2{-}CHOH{-}CH{=}CH_2 \quad (I)$$

$$R_3SiCH_2MgCl + CH_3{-}CH{=}CH{-}C({=}O)H \longrightarrow R_3SiCH_2{-}CHOH{-}CH{=}CH{-}CH_3 \quad (II)$$

These alcohols, with the hydroxyl group in the β-position relative to silicon, unlike the saturated alcohol studied by Whitmore [3],

$$>Si{-}CH_2{-}CHOH{-}CH_3,$$

did not undergo β-cleavage even during distillation at atmospheric pressure, apparently because of polarization of the Si—C bond caused by the structure of these alcohols.

It is interesting to note that the alcohols of group I dehydrated with little β-cleavage, whereas the alcohols of group II did so with almost quantitative β-cleavage. This difference is explained by the different direction of electron displacement caused by the methyl group, leading to an increase in polarization and, consequently, to a weakening of the Si—C bond. Dehydration of the alcohols of group I, with a high yield of butadienylsilanes, gives us a new method for synthesizing 1-trialkylsilylbutadienes. The characteristics of the 1-trialkylsilylbutadienes obtained by this method are presented in Table 1. In particular, 1-triethylsilylbutadiene was also obtained; its properties proved to be very close to those of this silicon hydrocarbon obtained by us, as mentioned above, earlier by another reaction. Along with monomeric trialkylbutadienylsilanes, their dimers were also isolated; their properties are given in Table 1. The structure of these dimers was not studied. It is possible that they are cyclodimers of the type:

cyclohexadiene ring bearing CH=CH—Si < and —Si < or cyclooctadiene ring bearing two —Si < su

The nature of the dehydrating reagent also influenced the extent of the β-cleavage reaction. It was greatest in the case of sulfuric acid. The optimal dehydrating reagent proved to be $KHSO_4$. However, dehydration of alcohols of the type

$$R_3SiCH_2—CHOH—CH=CH—CH_3$$

even with the minimum amount of $KHSO_4$ proceeded with 100% β-cleavage and formation of the corresponding siloxanes and piperylene.

Experimental Part

1. Direct synthesis from chloroprene. 2.5 kg of chloroprene was passed in a stream of nitrogen over a silicon–copper alloy at 420–450°. Fractionation of the condensate showed that 36% of it consisted of compounds

chlorovinylcyclohexadiene derivative chlorostyrene-type derivative dichlorocyclooctadiene derivative

which are readily identified from the properties of these compounds given in the literature [4].

2. 1-Trimethylsilylbuten-3-ol-2. To 26.4 g of Mg (1.1 mole) in 350 ml of ether, with cooling and stirring, was added dropwise

135 g (1.1 mol) of trimethylchloromethylsilane. Then 61.6 g (1.1 mol) of freshly distilled acrolein, b.p. 51-52°, was added dropwise to the resulting Grignard reagent. The reaction proceeded vigorously, with evolution of heat. After it was complete, the contents of the flask were heated for another 3 hours on a water bath and then poured onto ice. After neutralization with 3% HCl, the ether layer was separated and washed with 3% soda solution and with water. After drying over Na_2SO_4 and distilling off the ether, the reaction product was distilled under vacuum (at 24 mm): fraction I, b.p. up to 70°—10 g; fraction II, 70-70.5°—80 g. The residue, which decomposed during distillation, amounted to 25 g.

Under conditions analogous to those used with acrolein, other secondary alcohols were also obtained from crotonaldehyde; their properties are given in Table 1.

3. **Trimethylsilylbutadiene.** Into a flask equipped with a reflux condenser were placed 72 g of 1-trimethylsilylbuten-3-ol-2 and ~0.2 g of $KHSO_4$. The mixture was heated for one hour to 90-100°. The entire mass was then distilled at 100-115°. After separation of the water that had been liberated, the dehydration product was dried over Na_2SO_4. It was then distilled on a column at atmospheric pressure: fraction I, b.p. up to 98.5°—1 g; fraction II, 98.5-99°—14 g; fraction III, 99-113.5°—2 g; fraction IV, 113.5°—22 g. Residue—8 g. In fraction II, the β-cleavage product, $(CH_3)_3Si—O—Si(CH_3)_3$, was identified. Fraction IV was the dehydration product—trimethylbutadienylsilane. The residue was subjected to distillation under vacuum at 3.5 mm. A fraction with b.p. 95° was isolated—the dimer of trimethylbutadienylsilane (see Table 1); the residue was a solid, soluble and fusible polymer.

4. **Adduct.** 2 g of maleic anhydride and 1.5 g of trimethylbutadienylsilane were heated for 30 min to 100-115°. After cooling, the mixture was poured into a beaker with distilled water, which was then stirred for 10-15 min. The crystals that floated up were washed with water and recrystallized from acetone and petroleum ether (see Table 1).

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