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Chemistry

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Abstract

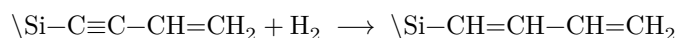
Full Text

Chemistry

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Petrov

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 vinyllethynylsilane:

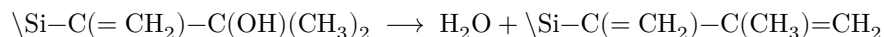
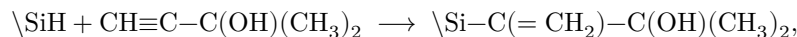


It had the following properties: b.p. 74-75° at 19 mm; d_4^{20} 0.7988; n_D^{20} 1.4585. With maleic anhydride it gave an adduct with m.p. 132°.

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)=CH₂ substituent]] and [[structural formula: d

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:



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

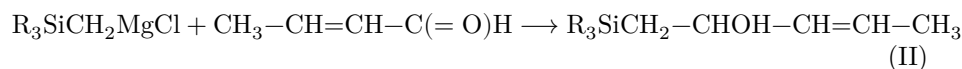
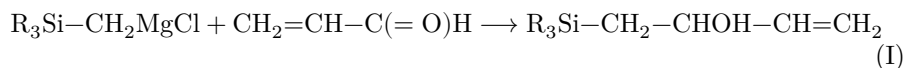
By the interaction of Grignard reagents of trialkyl α -chloromethylsilanes with acrylic and crotonic aldehydes, we obtained, in high yields, secondary alcohols whose physical properties are presented in Table 1.

Table 1

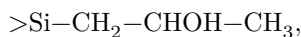
Compd	Formula	n_D^{20}	d_4^{20}	MR, MR_{calc}	Yield, %	OH, %	H, %	H, %	C, %	C, %	Si, %	Si, %
3-	(CH ₃) ₃ Si-2CH ₂ -CH(OH)-CH ₂ -CH ₃	1,477	0,8125	106,5	100,5	1,10	8,70	11,10	11,05	57,45	5,75	19,15
en-	Trimethylsilylbut-											
2-	3-	70,5										
ol	(CH ₃) ₂ (C ₂ H ₅)Si-2CH ₂ -CH(OH)-CH ₂ -CH ₃	1,491	0,8528	109,8	100,5	1,10	8,70	11,42	11,46	60,20	6,00	17,65
en-	Dimethylethylsilylbut-											
2-	3-	75										
ol	(CH ₃) ₂ (C ₂ H ₅)Si-CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₃	1,461	0,8631	107,4	100,5	1,10	8,70	11,60	11,62	62,24	6,20	16,53
en-	Methyldiethylsilylbut-											
2-	3-	80										
ol	(CH ₃) ₂ (C ₂ H ₅)Si-2CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₃	1,454	0,8509	105,9	100,5	1,10	8,70	11,51	11,50	—	—	15,76
en-	Dimethylbutylsilylbut-											
2-	3-	76										
ol	(C ₂ H ₅) ₃ Si-2CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₃	1,428	0,8168	105,6	100,5	1,10	8,70	—	—	—	—	—
en-	Triethylsilylbut-											
2-	3-	77										
ol	(CH ₃) ₂ (C ₂ H ₅)Si-2CH ₂ -CH(OH)-CH ₂ -CH ₂ -CH ₂ -CH ₃	1,458	0,8566	106,4	100,5	1,10	8,70	—	—	—	—	—
en-	Dimethylethylsilylpent-											
2-	3-	71										
ol												

Comp.	Formula	n_D^{20}	d_4^{20}	$MR, MR,$ foundcalc.	Yield %	OH, foundcalc.	OH, foundcalc.	H, foundcalc.	H, foundcalc.	C, foundcalc.	C, foundcalc.	Si, foundcalc.	Si, foundcalc.
	$P,$ b.p., mm												
(CH ₃) ₃ SiCH=CH-CH=CH ₂	(C ₁₀ H ₁₈ Si)	1,3575	0,7534	143,2335,0	—	—	—	—	—	11,3411,8965,5466,4122,3822,19			
Trimethylsilylbutadiene													
(CH ₃) ₂ Si(CH ₂ CH=CH-CH=CH ₂)	(C ₁₁ H ₂₀ Si)	1,4017	0,8018	147,8629,0	—	—	—	—	—	11,7211,8067,9768,5519,6120,08			
Dimethylethylsilylbutadiene													
138,5													
(CH ₃) ₂ Si(CH ₂ CH=CH-CH=CH ₂)	(C ₁₁ H ₂₀ Si)	1,5817	0,7615	151,4017,31	—	—	—	—	—	12,0011,0069,2560,0317,7818,08			
Methyldiethylsilylbutadiene													
162,5													
(C ₂ H ₅) ₂ SiCH=CH-CH=CH ₂	(C ₁₂ H ₂₂ Si)	1,5756	0,8078	155,7121,15	—	—	—	—	—	12,5012,4871,3071,0016,1016,08			
—													
185													
[(CH ₃) ₃ Si ₃ CH=CH-CH=CH ₂] ₂	(C ₁₉ H ₃₆ Si ₃)	1,7908	0,8192	188,142,5	—	—	—	—	—	11,1911,0765,7166,6021,7422,20			
[(CH ₃) ₂ Si(CH ₂ CH=CH-CH=CH ₂) ₂]	(C ₁₇ H ₃₀ Si ₂)	1,4830	0,8631	172,0917,4010,02	—	—	—	—	—	11,4111,4967,6768,5719,6720,08			
—													
118													
[(CH ₃) ₃ Si(CH ₂ CH=CH-CH=CH ₂) ₂]	(C ₁₉ H ₃₆ Si ₂)	1,4930	0,8800	171,6101,616,02	—	—	—	—	—	12,0412,0969,3370,0917,3618,28			
—													
141													
(CH ₃) ₃ Si*substituted					—	—	—	—	—	7,0077,214	59,0058,9312,3112,30		
ph- thalic an- hy- dride struc- ture shown													

* Melting point in °C.



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

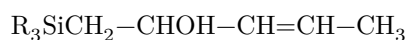


did not undergo β -cleavage even during distillation at atmospheric pressure, apparently because of polarization of the Si–C bond caused by the structure of these alcohols.

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 butadienyilsilanes, 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 trialkylbutadienyilsilanes, 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:



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



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



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 Na₂SO₄ 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 KHSO₄. 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 Na₂SO₄. 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, (CH₃)₃Si—O—Si(CH₃)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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