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Abstract

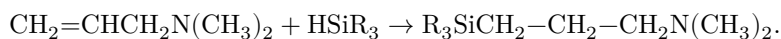
Full Text

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ADDITION OF HYDRIDOSILANES TO ALLYLAMINE

In recent years a considerable number of works have appeared on the addition of hydridosilanes to various unsaturated compounds containing functional groups.

Unsaturated aliphatic and heterocyclic amines, on interaction with silicon hydrides, give the corresponding organosilicon amines. Thus, organosilicon compounds with an amino group in the organic radical were obtained (¹) by the addition reaction of hydridosilanes to tertiary unsaturated amines, with initiation of the reaction by benzoyl peroxide or tert-butyl perbenzoate,



It seemed of interest to us to study the addition of hydridosilanes to allylamine, i.e., to an amine with a free amino group. Addition to allylamine was carried out with triethylsilane, tripropylsilane, tributylsilane, dimethylphenylsilane, diethylphenylsilane, methylphenylsilane, ethylphenylsilane, triphenylsilane, and triethoxysilane. The hydridosilanes, obtained by organomagnesium synthesis, corresponded in their properties to the literature data (^{2,3}).

Addition in the presence of chloroplatinic acid proceeded according to the scheme:

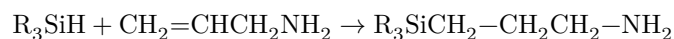


Table 1

No.	Compound	B.p., d/mm	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Yield, %
1	$(\text{C}_2\text{H}_5)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	83/4	1.4523	1.4523	56.16	56.54	62.6
2	$(\text{C}_3\text{H}_7)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	108/4	1.4560	1.4560	70.64	70.79	54.2
3	$(\text{C}_4\text{H}_9)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	174/6	1.4591	1.4591	84.72	84.68	86.6
4	$(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	99/2	1.5162	1.5162	62.40	62.85	27.0

Fig. 1. IR spectra of tripropyl- γ -propylaminosilane (a) and tributyl- γ -propylaminosilane (b)

Figure 1: Fig. 1. IR spectra of tripropyl- γ -propylaminosilane (a) and tributyl- γ -propylaminosilane (b)

No.	Compound	B.p., °/mm	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Yield, %
5	$(C_2H_5)_2CH_2SiCH_2CH_2CH_2NH_2$	122/2	0.8321	1.4225	71.82	71.85	50.1
6	$CH_3(C_6H_5)_2SiCH_2CH_2CH_2NH_2$	207/7	0.8321	1.4225	82.60	82.65	31.9
7	$C_2H_5(C_6H_5)_2SiCH_2CH_2CH_2NH_2$	12°					32.7
8	$(C_6H_5)_3SiCH_2CH_2CH_2NH_2$	99-101°					30.4
9	$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2$	104/2	0.8321	1.4225	59.43	59.18	10.0

The properties of the products obtained are given in Table 1, from which it is evident that, in the presence of chloroplatinic acid, hydridosilanes with alkyl radicals at silicon add to allylamine in higher yields. Thus, trialkylsilanes add to allylamine in yields of 60-70%, whereas diphenylethylsilane and triphenylsilane add to allylamine under the same conditions in yields of 30%.

For tributyl- γ -propylaminosilane and triethyl- γ -propylaminosilane, infrared spectra were recorded; these showed that the products obtained are primary amines. For tributyl- γ -propylaminosilane, potentiometric titration and Van Slyke analysis established that a primary amine had been obtained. Thus, the addition of hydridesilanes to allylamine proceeds at the double bond of the allyl group, without affecting the amino group.

Experimental Part

1. Triethyl- γ -propylaminosilane. From 31 g (0.26 mole) of triethylsilane and 15 g (0.26 mole) of allylamine, in the presence of 1 ml of a 10% solution of chloroplatinic acid in abs. isopropyl alcohol, there was obtained

Fig. 1. IR spectra of tripropyl- γ -propylaminosilane (a) and tributyl- γ -propylaminosilane (b)

28 g (yield 62%) of triethyl- γ -propylaminosilane. B.p. 81-83°/4 mm; n_D^{20} 1.4523; d_4^{20} 0.8321; MR_D found 56.15, calculated 56.54.

$C_9H_{23}SiN$. Found, %: C 62.31; 62.28; H 13.21; 13.25; NH_2 9.31; 9.30
 Calculated, %: C 62.42; H 13.29; NH_2 9.25

2. Tripropyl- γ -propylaminosilane. From 22.1 g of tripropylsilane and 8 g (0.14 mole) of allylamine, in the presence of 1 ml of a 10% solution of chloroplatinic acid in abs. isopropyl alcohol, there was obtained 9.02 g (yield 70%) of tripropyl- γ -propylaminosilane with b.p. 106–108°/4 mm; n_D^{20} 1.4560; d_4^{20} 0.8288; MR_D found 70.64, calculated 70.79.

$C_{12}H_{29}SiN$. Found, %: C 66.94; 66.92; H 13.74; 13.63; NH_2 8.03
 Calculated, %: C 69.99; H 13.49; NH_2 7.44

3. Tributyl- γ -propylaminosilane. From 54 g (0.27 g) of tributylsilane and 18 g (0.27 mole) of allylamine, in the presence of 1 ml of a 10% solution of chloroplatinic acid, there was obtained 60 g (yield 86%) of tributyl- γ -propylaminosilane with b.p. 170–174°/6 mm; n_D^{20} 1.4591; d_4^{20} 0.8291; MR_D found 84.72, calculated 84.68.

$C_{15}H_{33}SiN$. Found, %: C 69.51; 69.68; H 13.57; 13.58; NH_2 6.33; 5.99
 Calculated, %: C 70.00; H 13.61; NH_2 6.23

Percentage of primary nitrogen: 5.99; 6.05 (by Van Slyke); 5.25; 5.19 (potentiometric titration), calculated 6.22.

4. Dimethylphenyl- γ -propylaminosilane. From 23.8 g (0.17 mole) of dimethylphenylsilane and 10 g (0.17 mole) of allylamine, in the presence of 1 ml of a 10% solution of chloroplatinic acid in abs. isopropyl alcohol, there was obtained 27 g (yield 70.1%) of dimethylphenyl- γ -propyl-

aminosilane with b.p. 97–99°/2 mm; n_D^{20} 1.5162; d_4^{20} 0.9362; MR_D found 62.40, calculated 62.85.

$C_{11}H_{19}SiN$. Found, %: C 68.40; 67.98; H 9.90; 9.85; NH_2 8.43; 7.26
 Calculated, %: C 68.39; H 9.84; NH_2 8.29

5. Methylidiphenyl- γ -propylaminosilane. From 26 g (0.13 mole) of methylidiphenylsilane and 8 g (0.14 mole) of allylamine in the presence of 1 ml of a 10% solution of chloroplatinic acid in absolute isopropyl alcohol, 10.7 g (yield 31.9%) of methylidiphenylpropylaminosilane was obtained, with b.p. 206–207°/7 mm; n_D^{20} 1.5721; d_4^{20} 1.0159; MR_D found 82.60, calculated 82.65.

$C_{16}H_{21}SiN$. Found, %: C 75.18; 75.21; H 8.23; 8.17; NH_2 5.3; 6.4
 Calculated, %: C 75.29; H 8.23; NH_2 6.27

6. Diethylphenyl- γ -propylaminosilane. From 82 g (0.5 mole) of diethylphenylsilane and 28.5 g (0.5 mole) of allylamine in the presence of 1 ml of a 10% solution of chloroplatinic acid in absolute isopropyl alcohol, 55.25 g (yield 50%) of diethylphenylpropylaminosilane was obtained, with b.p. 120–122°/2 mm; n_D^{20} 1.5189; d_4^{20} 0.9352; MR_D found 71.82, calculated 71.85.

$C_{13}H_{23}SiN$. Found, %: C 70.65; 70.65; H 10.61; 10.60; NH_2 7.76; 7.58
 Calculated, %: C 70.58; H 10.40; NH_2 7.23

7. **Ethyldiphenyl- γ -propylaminosilane.** From 37.2 g (0.17 mole) of ethyldiphenylsilane and 10 g (1.17 mole) of allylamine in the presence of 1 ml of a 10% solution of chloroplatinic acid in absolute isopropyl alcohol, 15.5 g (yield 32.7%) of ethyldiphenyl- γ -propylaminosilane was obtained, with glass transition temperature 12°.

$C_{17}H_{23}SiN$. Found, %: C 75.77; 75.81; H 8.54; 8.78; NH_2 6.04; 6.12
 Calculated, %: C 75.83; H 8.55; NH_2 5.9

8. **Triphenyl- γ -propylaminosilane.** From 32 g (0.12 mole) of triphenylsilane and 14 g (0.24 mole) of allylamine in the presence of 1 ml of a 10% solution of chloroplatinic acid in absolute propyl alcohol, 12 g (yield 30.4%) of triphenyl- γ -propylaminosilane was obtained, with m.p. 99–100°.

$C_{21}H_{23}SiN$. Found, %: C 79.15; 79.16; H 7.24; 7.23; NH_2 5.21; 4.92
 Calculated, %: C 79.51; H 7.25; NH_2 5.04

9. **Triethoxy- γ -propylaminosilane.** From 23 g (0.14 mole) of triethoxysilane and 8 g (0.14 mole) of allylamine in the presence of 1 ml of a 10% solution of chloroplatinic acid in absolute isopropyl alcohol, 3 g (yield 10%) of triethoxypropylaminosilane was obtained, with b.p. 103–104°/2 mm; n_D^{20} 1.4225; d_4^{20} 0.9474; MR_D found 59.43, calculated 59.18.

$C_9H_{23}O_3SiN$. Found, %: C 48.83; 48.73; H 10.34; 10.33; NH_2 7.15; 7.06
 Calculated, %: C 48.86; H 10.40; NH_2 7.21

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