V. E. ASTAKHIN, I. P. LOSEV, and Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV

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Abstract

Full Text

V. E. ASTAKHIN, I. P. LOSEV, and Corresponding Member of the Academy of Sciences of the USSR K. A. ANDRIANOV

ON THE REACTION OF ORGANOHYDROXYSILANES WITH ISOCYANATES

SYNTHESIS OF ORGANOSILICON URETHANES

From the literature it is known that the interaction of organic alcohols with isocyanates proceeds without the evolution of by-products. In this reaction, as Würtz first showed (1), the hydrogen atom of the hydroxyl group of the alcohol migrates to the nitrogen atom of the isocyanate group:

$$\mathrm{R-N=C=O+HOR\rightarrow RNHCOOR}$$

In the present work we set ourselves the task of studying the nature of the interaction of organohydroxysilanes with isocyanates. The following were taken as the starting products on which the reaction was studied: triethylhydroxysilane, diethylpropylhydroxysilane, diethylbutylhydroxysilane, and meta-tolylene diisocyanate.

Table 1

Name of substance	Formula	m.p., °C	b.p., °C at mm Hg	d_4^{20}	n_D^{20}	MR, found	MR, calculated
Diethylbutylchlorosilane	$(C_2H_5)_2C_4H_9SiCl$		181–182 (744)	0.8985	1.4410	52.46	53.06
Diethylbutylhydroxysilane	$(C_2H_5)_2C_4H_9SiOH$		190 (744)	0.8608	1.4390	48.89	49.37
Diethylpropylhydroxysilane	$(C_2H_5)_2C_3H_7SiOH$		171–172 (747)	0.8598	1.4365	44.46	44.71
Tolylene-2,4-biscarbamintriethylsilane	$CH_3C_6H_3(NHCOOSi(C_2H_5)_3)_2$	152–153					
Tolylene-2,4-biscarbamindiethylpropylsilane	$CH_3C_6H_3[NHCOOSi(C_2H_5)_2C_3H_7]_2$	140–141					

Name of substance	Formula	m.p., °C	b.p., °C at mm Hg	d_4^{20}	n_D^{20}	MR, found	MR, calculated
Tolylene-2,4-bis-carbamindiethylbutylsilane	$CH_3C_6H_3[NHCOOSi(C_2H_5)_2C_4H_9]_2$	104–106					

In the course of the investigations it was established for the first time that the interaction of isocyanates with trialkylhydroxysilanes proceeds analogously to the corresponding reaction with organic alcohols and may be represented in the following form:

$$\begin{array}{ccc} \text{NCO} & & \text{NHCOOSiR}_3 \\ \text{R} & + \ 2\text{HOSiR}_3 \rightarrow & \text{R} \\ \text{NCO} & & \text{NHCOOSiR}_3 \end{array}$$

According to this reaction scheme, the following organosilicon urethanes were obtained and characterized: toluylene-2,4-bis-carbaminotriethylsilane, toluylene-2,4-bis-carbamindiethylpropylsilane, and toluylene-2,4-bis-carbamindiethylbutylsilane. All the organosilicon urethanes obtained were white crystalline substances, soluble in benzene, toluene, and ether, and were very sensitive to hydrolysis. The properties of the organosilicon urethanes are given in Table 1, which also gives the properties of new organosilicon compounds not described in the literature.

Experimental Part

1. Synthesis of diethylbutylchlorosilane. In a three-necked 2.5-3-liter flask fitted with a reflux condenser, mechanical stirrer, dropping funnel, and thermometer were placed 48.6 g of magnesium turnings, 1000 ml of anhydrous sulfuric ether, and 0.6–1 ml of ethyl bromide. From the dropping funnel, 274 g of butyl bromide was added dropwise. After introduction of a small amount of butyl bromide, the reaction mixture was stirred at room temperature for 20–30 min. After the reaction had begun, further addition of butyl bromide was carried out at a temperature of the reaction mixture not higher than 30–35°. After its introduction, stirring at room temperature was continued for 1.0–1.5 h, after which the reaction mixture, freed from residues of magnesium (mechanically or by filtration through glass wool), was poured into the dropping funnel.

Into the emptied three-necked flask were introduced 314 g of diethyldichlorosilane (b.p. 128–130°; d_4^{20} = 1.1074) and 400 ml of anhydrous ether, and then, with constant stirring, magnesium bromobutyl was added. The reaction mixture was heated on a water bath for 8-10 h. After this, the reaction products were filtered with the aid of a vacuum filter, and the precipitate was washed with several portions of ether. After distillation of the ether from the ethereal extracts and the ethereal solution, and subsequent repeated fractionation of the reaction products, 215 g of a substance was isolated with the following constants: b.p. 181-182°/744 mm; $n_D^{20} = 1.4410$; $d_4^{20} = 0.8985$. Found MR 52.46; calculated for $C_8H_{19}SiCl$, MR 53.06.

Found, %: C 53.75; 53.54; H 10.46; 10.47; Si 14.97; 15.31; Cl 19.95; 19.85
$C_8H_{19}SiCl$. Calculated, %: C 53.78; H 10.64; Si 15.68; Cl 19.88

On the basis of the analytical data, the substance with b.p. 181-182°/744 mm is diethylbutylchlorosilane. The yield of diethylbutylchlorosilane was 60% of the theoretical amount, calculated on diethyldichlorosilane.

2. Synthesis of diethylbutylhydroxysilane. Into a three-necked flask were placed 100 g of diethylbutylchlorosilane (b.p. 181-182°/744 mm; d_4^{20} 0.8985; n_D^{20} 1.4410), 500 ml of anhydrous ether, and a few drops of phenolphthalein. The contents of the flask were cooled to $-5°$. From a dropping funnel, with vigorous stirring of the reaction mixture, 1 N aqueous sodium hydroxide solution was introduced until a stable pale-pink coloration appeared. The temperature of the reaction mixture did not exceed $+2°$. The contents of the flask were separated with the aid of a separatory funnel into two layers (ether and aqueous). The aqueous layer was washed with several portions of sulfuric ether of 70-100 ml each. The ether layer and the ethereal extracts were combined and dried over potash for 25-30 min. After distillation of the ether and subsequent fractionation in vacuum, 68 g of a substance was isolated with the following constants: b.p. 190°/744 mm; n_D^{20} 1.4390; d_4^{20} 0.8608. Found MR 48.89; calculated for $C_8H_{20}SiO$, MR 49.37.

Found, %: C 60.06; 60.20; H 12.6; 12.40; Si 17.45; 17.13
$C_8H_{20}SiO$. Calculated, %: C 60.00; H 12.50; Si 17.50

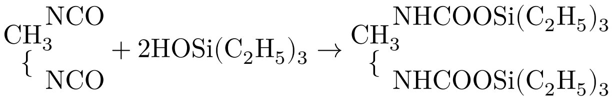
The compound obtained was diethylbutylhydroxysilane. Diethylbutylhydroxysilane is a colorless, low-viscosity liquid with a pleasant camphor odor. It is soluble in ether, acetone, and chlorinated hydrocarbons, and is almost insoluble in water.

3. Synthesis of diethylpropylhydroxysilane. Into a three-necked flask were placed 100 g of diethylpropylchlorosilane (b.p. 166°; d_4^{20} 0.8905; n_D^{20} 1.4352), 500 ml of anhydrous ether, and several drops of phenolphthalein. The contents of the flask were cooled to $-5°$. From a dropping funnel, with vigorous stirring of the reaction mixture, 1 N aqueous sodium hydroxide solution was introduced until a stable pale-pink coloration appeared. The temperature of the reaction mixture did not exceed +2°. The contents of the flask were separated with the aid of a separatory funnel into two layers (ether and aqueous). The aqueous layer was washed with several portions of sulfuric ether, 70-100 ml each. The ether layer and the ether extracts were combined and dried over potash for 25-30 min. After distillation of the ether and subsequent fractionation in vacuo, 66 g of a substance was isolated with the following constants: b.p. 171-172°/747 mm; n_D^{20} 1.4365; d_4^{20} 0.8598. Found MR 44.46; calculated for $C_7H_{18}SiO$, MR 44.71.

Found, %:	C 57.64; 57.40; H 12.29; 12.36; Si 18.72; 19.00
$C_7H_{18}SiO$. Calculated, %:	C 57.53; H 12.32; Si 19.17

The compound obtained was diethylpropylhydroxysilane. Diethylpropylhydroxysilane is a colorless, low-viscosity liquid with a pleasant camphor odor. It is soluble in ether, acetone, and chlorinated hydrocarbons, and is almost insoluble in water.

4. Synthesis of tolylene-2,4-bis-carbamatotriethylsilane.

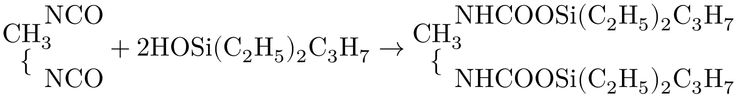


$$CH_3\left\{\begin{matrix}NCO\\NCO\end{matrix}\right. + 2HOSi(C_2H_5)_3 \rightarrow CH_3\left\{\begin{matrix}NHCOOSi(C_2H_5)_3\\NHCOOSi(C_2H_5)_3\end{matrix}\right.$$

A mixture of 43.5 g (0.25 mole) of metatolylene diisocyanate with m.p. 21°; d_4^{20} 1.2385; n_D^{20} 1.5663 and 132 g (1.0 mole) of triethylsilanol with b.p. 80° (30 mm); n_D^{20} 1.4320; with an OH-group content of 12.8%, was placed in a round-bottomed flask equipped with a condenser bearing a calcium chloride tube at the end. The contents of the flask were heated on a paraffin bath for one hour at a temperature of 80-85°, after which the flask with the reaction mixture was left overnight. On the next day the reaction mixture was transferred to a filter and washed repeatedly with benzene, and then, after drying in air, was recrystallized from hot toluene. A white powder was obtained with m.p. 152-153°. Found molecular weight 458.4; calculated 438.

Found, %:	C 57.61; 57.46; H 8.58; 8.44; Si 12.70; 12.38; N 6.35; 6.48
$C_{21}H_{38}N_2Si_2O_4$. Calculated, %:	C 57.53; H 8.67; Si 12.78; N 6.39

5. Synthesis of tolylene-2,4-bis-carbamatodiethylpropylsilane.



$$CH_3\left\{\begin{matrix}NCO\\NCO\end{matrix}\right. + 2HOSi(C_2H_5)_2C_3H_7 \rightarrow CH_3\left\{\begin{matrix}NHCOOSi(C_2H_5)_2C_3H_7\\NHCOOSi(C_2H_5)_2C_3H_7\end{matrix}\right.$$

A mixture of 43.5 g (0.25 mole) of metatolylene diisocyanate with m.p. 21°; d_4^{20} 1.2385; n_D^{20} 1.5663 and 73 g (0.5 mole) of diethylpropylhydroxysilane with b.p. 171-172°/747 mm; n_D^{20} 1.4365; d_4^{20} 0.8598, with an OH-group content of 11.7%

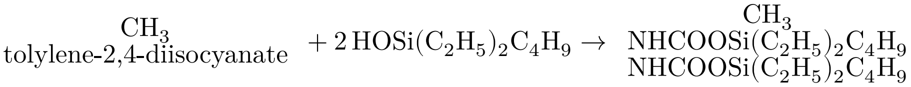
was placed in a round-bottom flask fitted with a condenser with a calcium chloride tube at the end.

The contents of the flask were heated on a paraffin bath for one hour at a temperature of 80-85°, after which the flask with the reaction mixture was left overnight. The next day the reaction mixture was transferred to a filter and washed repeatedly with benzine (at first with small portions of benzine), and then, after drying in air, was recrystallized from hot toluene. A white powder with m.p. 140-141° was obtained. Molecular weight found: 449.8; calculated: 466.

Found, %: C 58.97; 58.95; H 9.08; 9.12; N 6.2; 6.3; Si 12.02; 11.70

$C_{23}H_{42}N_2Si_2O_4$. Calculated, %: C 59.22; H 9.01; N 6.00; Si 12.01

6. Synthesis of tolylene-2,4-bis-carbamindiethylbutylsilane.



$$\underset{\text{tolylene-2,4-diisocyanate}}{CH_3} + 2\,HOSi(C_2H_5)_2C_4H_9 \rightarrow \begin{array}{c} CH_3 \\ NHCOOSi(C_2H_5)_2C_4H_9 \\ NHCOOSi(C_2H_5)_2C_4H_9 \end{array}$$

A mixture of 43.5 g (0.25 mole) of metatoluylenediisocyanate with m.p. 21°; d_4^{20} 1.2385; n_D^{20} 1.5663 and 80 g (0.5 mole) of diethylbutylhydroxysilane with b.p. 190°/744 mm; n_D^{20} 1.4390; d_4^{20} 0.8608, with an OH-group content of 10.6%, was placed in a round-bottom flask fitted with a condenser bearing a calcium chloride tube at the end.

The contents of the flask were heated on a paraffin bath for one hour at a temperature of 80-85°, after which the flask with the reaction mixture was left overnight. The next day the reaction mixture was transferred to a filter and washed repeatedly with benzine (at first with small portions of it), and then, after drying in air, was recrystallized from hot toluene. A white powder with m.p. 104-106° was obtained. Molecular weight found: 479; calculated: 494.

Found, %: C 60.66; 60.52; H 9.42; 9.47; N 6.05; 6.13; Si 11.3

$C_{25}H_{46}N_2Si_2O_4$. Calculated, %: C 60.72; H 9.31; N 5.66; Si 11.33

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CITED LITERATURE

1. A. Wurtz, *Lieb. Ann.*, **71**, 326 (1849).

Note: Figure translations are in progress. See original paper for figures.