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Reactions of Trimethylsilyl Isocyanate with Alcohols and Phenols

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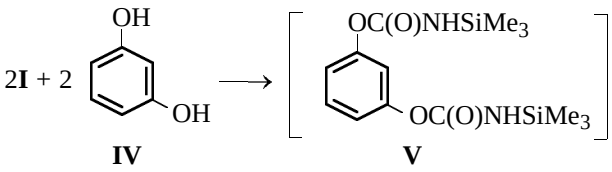
Abstract — Mono- and diphenols add to trimethyl isocyanate on heating to give the corresponding aryl urethanes. Ethanol reacts with trimethylsilyl isocyanate to give ethyl urethane and ethyl allophanate in a ratio determined by reaction conditions.

Reactions of phosphorylated isocyanates with protic nucleophiles have been studied in detail, and the results are summarized in [1]. These reactions are widely and successfully used for preparation of various organophosphorus derivatives. However, the organosilicon analog, trimethylsilyl isocyanate **I**, practically was not involved in such reactions. It is known only that amines add to trimethylsilyl isocyanate **I** to form silylated ureas [2, 3]. At the same time, reactions of tri- and tetraisocyanatosilanes with alcohols result in substitution of isocyanato groups by alkoxy groups, instead of addition [4]. Trimethylsilyl isocyanate can be relatively simply prepared from cheap reagents [5, 6], and it shows promise for organic synthesis.

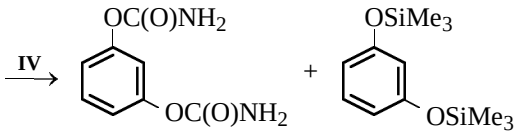
In this work we studied the reactions of isocyanate **I** with phenol, resorcinol, and ethanol. Reaction of **I** with phenol was performed both in a solvent and without a solvent. In both cases the final product is phenyl urethane **III**, but in the latter case its yield is higher.

$$\underset{\mathbf{I}}{Me_3SiNCO} + PhOH \longrightarrow \underset{\mathbf{II}}{[Me_3SiNHC(O)OPh]} \xrightarrow[-PhOSiMe_3]{PhOH} \underset{\mathbf{III}}{H_2NC(O)OPh}.$$

Apparently, the reaction initially yields the addition product, silylated urethane **II**, which under the action of phenol transforms into the final product **III**. The highest yield is attained at the ratio isocyanate : phenol = 1 : 2. The reaction of isocyanate **I** with resorcinol gives compound **VI** with two urethane fragments. In this case the reaction probably also involves intermediate formation of addition product **V** which is desilylated under the action of resorcinol.



IV **V**



VI **VII**

In contrast to phenols, alcohols add to isocyanate **I** to give two products, alkyl urethanes and alkyl allophanates, in the ratio depending on the reaction conditions. Isocyanate **I** reacts with ethanol in toluene on heating for several hours to give ethyl urethane **IX** and ethyl allophanate **XI** in yields of 54 and 27%, respectively. When the same reaction was performed without a solvent, the yield of **XI** increased to 44%, and that of **IX** decreased to 39%.

$$\underset{\mathbf{I}}{} + EtOH \longrightarrow \underset{\mathbf{VIII}}{[Me_3SiNHC(O)OEt]} \begin{cases} \xrightarrow[1]{EtOH} \underset{\mathbf{IX}}{H_2NC(O)OEt} \\ \xrightarrow[2]{\mathbf{I}} \underset{\mathbf{X}}{[Me_3SiNHC(O)N(SiMe_3)C(O)OEt]} \xrightarrow{2EtOH} \underset{\mathbf{XI}}{H_2NC(O)NHC(O)OEt}. \end{cases}$$

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The first reaction stage involves addition of alcohol to the isocyanato group of **I** to form silylated urethane **VIII**. The latter contains a labile Si–N bond which is readily cleaved under the action of excess alcohol to form urethane **IX** (pathway *1*). Concurrently, silyl urethane **VIII** reacts with the initial isocyanate I (pathway *2*) to give silicon-containing allophanate **X**. The latter under the action of ethanol readily transforms into allophanate **XI** by cleavage of the Si–N bond. These reactions can be considered as a new convenient method for generation of the urethane fragment from hydroxyl-containing compounds. Trimethylsilyl isocyanate does not react with acetic acid on heating for several hours.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer, internal reference TMS.

Phenyl urethane III. *a*. A mixture of 2.12 g of phenol and 3.52 g of isocyanate **I** was heated for 5 h at 100°C. The resulting crystals were separated, washed with benzene, and recrystallized from ethanol–benzene. Yield of **III** 1.8 g (71%), mp 149°C [7]. IR spectrum (KBr), ν, cm^{-1}: 1700 (C=O); 3180, 3270, 3330, 3410 (NH_2). Found, %: C 61.47; H 5.16; N 10.48. $C_7H_7NO_2$. Calculated, %: C 61.20; H 5.10; N 10.20.

b. A solution of 3.36 g of phenol and 2.74 g of isocyanate **I** in 20 ml of toluene was refluxed for 7 h. The crystals were filtered off and washed with benzene. Yield of **III** 1.38 g (56%), mp 149°C.

***m*-Phenylene diurethane VI.** A mixture of 2.2 g of resorcinol and 2.3 g of trimethylsilyl isocyanate was heated for 8 h at 110°C. The crystals that formed on cooling were washed with ether and alcohol. Yield of **VI** 0.62 g (31%), mp 188–190°C [8]. IR spectrum (KBr), ν, cm^{-1}: 1690–1720 (C=O), 3180–3410 (NH_2). Found, %: C 48.57; H 4.08; N 14.47. $C_8H_8N_2O_4$. Calculated, %: C 49.02; H 4.08; N 14.28. Vacuum fractionation of the mother liquor gave 0.72 g of a mixture consisting of 1,2-bis(trimethylsiloxy)benzene **VII** and an impurity of resorcinol, bp 124–127°C (10 mm), n_D^{20} 1.4767 [9]. ^{1}H NMR spectrum ($CHCl_3$), δ, ppm: 0.15 s (18H, $SiMe_3$); 6.95–7.33 m (4H, C_6H_4).

Reaction of trimethylsilyl isocyanate with ethanol. *a*. A mixture of 2.12 g of anhydrous ethanol and 3.52 g of trimethylsilyl isocyanate was heated for 5 h at 100°C. The resulting crystals of **XI** were filtered off and washed with benzene. Yield of **XI** 0.9 g (44%), mp 189–191°C [10]. IR spectrum (KBr), ν, cm^{-1}: 1695, 1740 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.38 s (2H, NH_2); 9.95 s (1H, NH). From the mother liquor, after removal of volatiles, 0.61 g (39%) of ethyl urethane **IX** was isolated, mp 48–50°C [11].

b. A solution of 2.33 g of ethanol and 3.89 g of **I** in 15 ml of toluene was heated for 7 h. The resulting crystals of **XI** were filtered off and washed with benzene. Yield of **XI** 0.61 g (27%), mp 188–190°C. From the mother liquor, after removal of volatiles, 1.23 g (54%) of ethyl urethane was isolated, mp 48–50°C.

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