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AMMONOLYSIS AND AMINOLYSIS REACTIONS OF DICHLORODIMETHYLSILANE

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The final composition of the products of ammonolysis of aminolysis of dichlorodimethylsilane depends on the reaction temperature, the concentration of the starting materials the nature of the solvent and of the organic groups bonded to silicon and to nitrogen. When dichlorodimethylsilane in excess reacts with methylamine, the condensation of the Si – Cl and Si – NH_2 groups to give the silazane bond is the basic reaction. The rate of the reaction is decreased by an increase of the length of the organic radicals on silicon or nitrogen. In the ammonolysis or aminolysis of organochlorosilanes with small organic groups the ratio of the rates of halogen displacement by amine and of condensation is the factor which determines whether aminosilanes or silazanes are formed. The yield of silazane falls as the difference in rates increases.

The conditions of the amination of organochlorosilanes have a considerable effect on the final reaction products. For example, ammonolysis of dichlorodiphenylsilane in ether at 0°-33° gave bis(diphenylamino)disilazane, whereas in boiling toluene or in carbon tetrachloride [1] it gave only hexaphenylcyclotrisilazane. The formation of decaethyldiaminotetrasilazane as an intermediate was observed during the ammonolysis of dichlorodiethylsilane in ether [2]. Ammonolysis of dichlorodimethylsilane gave a mixture of hexamethylcyclotri- and octamethylcyclotetra-silazane. The ratio of trimer to tetramer varied between 1:1 and 1.6:1 and depended on the reaction conditions, which is why different authors obtained different results [3-5]. Aminolysis of dichlorodimethylsilane with ethylamine gave either 1,3,5-hexamethyl-2,4,5-hexamethyl-2,4,6-triethylcyclotrisilazane or bis(ethylaminodimethylsilyl) ethylamine, depending on the ratio of the reactants [6]. No matter what the synthesis conditions the reaction between dichlorodimethylsilane and methylamine or ethylamine gave mainly the corresponding diaminodimethylsilane with a small amount of disilazanes and cyclosilazanes [7].

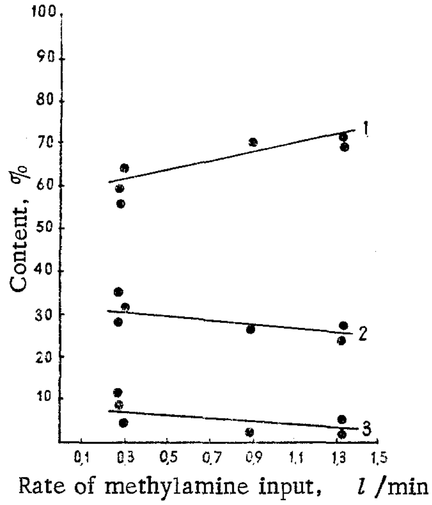

Fig. 1. Change in the composition of the products of the ammonolysis of dichlorodimethylsilane in ether with the rate of methylamine input; 1) Bis(methylamino)dimethylsilane; 2) bis(methylaminodimethylsilyl) methylamine; 3) polymer.

In the present work we have studied the effect of temperature, solvent, and concentration of reagents on the product composition, using the ammonolysis and aminolysis of dichlorodimethylsilane (I) as examples.

(I) was aminolyzed by passage of gaseous methylamine into ether or benzene solutions of (I) or with liquid methylamine taken in two-fold excess over equimolar amounts. When (I) was added as an ethereal solution to liquid methylamine at −10°, only bis (methylamino) dimethylsilane was obtained $-(CH_3)_2Si(NHCH_3)_2$ (II). When (I) was aminolyzed in solution with gaseous methylamine the products included bis(methylaminodimethylsilyl) methylamine $[CH_3NHSi(CH_3)_2]_2NCH_3$ (III) and 1,3,5-hexamethyl-2,4,6-trimethylcyclotrisilazane $[CH_3)_2SiNCH_3]_3$ (IV) in addition to II. The rate of passage of methylamine through the solution of I and the nature of the solvent used had an effect on the ratio of the products. IV was formed only when a very slow stream of methylamine (0.05 l/min) was passed into a solution of I in either ether or benzene. With a rate of amine input of 0.28 to 1.33 l/min only II and III were formed, but in ether solution II was formed preferentially and its content rose linearly with increased rate of amine input (Fig. 1). When the reaction was carried out in benzene the relative content of III was highest. The yield of III decreased linearly with increasing amine input (Fig. 2). The total yield of nitrogen-containing compounds was also lower in benzene (40-48%) than in ether (65-73%).

The observed changes in the composition of the final product mixture with changes in conditions can evidently be explained by differences in the rates of the probable reactions: replacement of chlorine by an amino-group

$\geqslant SiCl + RNH_2 \xrightarrow{RNH_2} \geqslant SiNH_2 + HCl \cdot RNH_2$ (1),, condensation of the alkylchlorosilazane, formation of the alkylaminochlorosilazanes $\geqslant SiCl + RNHSi\leqslant \xrightarrow{RNH_2} \geqslant Si{-}NR{-}Si\leqslant + HClRNH_2$ (2), and both intermolecular and intramolelcular condensation of alkylaminosilanes $\geqslant SiNHR + RNHSi\leqslant \rightarrow \geqslant Si{-}NR{-}Si\leqslant + RNH_2$ (3). When amination was carried out in an excesss of methylamine (addition of I solution to liquid methylamine) the predominant reaction was (1) and reaction (3) was virtually absent, despite the presence of methylammonium chloride which is a catalyst for the condensation of amino groups. Reaction (2) was suppressed by the excess of amine and had virtually no effect. When the reaction was carried out with excess of I (passage of gaseous methylamine through solutions of I) reaction (2) predominated and gave III and IV. This was confirmed by treating bis (methylamino) dimethylsilane with an excess of I in the absence of a hydrogen chloride acceptor when an exothermal reaction occurred to give methylammonium chloride and a mixture of unidentified products. In the presence of methylamine a rapid formation of III and methylammonium chloride occurred, whereas I was completely stable even on heating and showed no tendency to condense even at its boiling point. The solvent used had a marked effect on the direction of the aminolysis reactions. Ether facilitated the formation of aminosilanes, whereas benzene favored the formation of silazanes. A comparison of the above results with those for the aminolysis of other alkylchlorosilanes with methylamine [8] shows that, apart from the synthesis conditions examined here, the size of the organic radicals attached to silicon affects the formation of the products by influencing the ratio of the rates of reactions (1) and (2). The yield of alkylaminosilanes and disilazanes increases and that of the alkylcyclosilazanes decreases with increasing length of the alkyl radical. The reaction of dichloromethylsilane with methylamine gave mostly alkylcyclosilazanes [8] while amination of dichloroethylsilane gave a 1:1 ratio of bis (ethylaminodiethylsilyl) methylamine and 1, 3, 5-triethyl-2, 4, 6-trimethylcyclotrisilazane [8]. Amination of I with methylamine under the same conditions gave predominantly bis (methylamino) dimethylsilane and bis (methylaminodimethylsilyl) methylamine, while aminolysis of dichlorodiethylsilane gave only bis (methylamino) diethylsilane [8]. If the rate of amination, which probably changes, is taken to be constant for comparison, then the rate of condensation of the Si – Cl and Si – NH_2 bond falls in the series shown according to the size of the radicals:

$$H{-}\overset{|}{\underset{|}{Si}}{-}CH_3 > H{-}\overset{|}{\underset{|}{Si}}{-}C_2H_5 > CH_3\overset{|}{\underset{|}{Si}}CH_3 > C_2H_5\overset{|}{\underset{|}{Si}}C_2H_5.$$

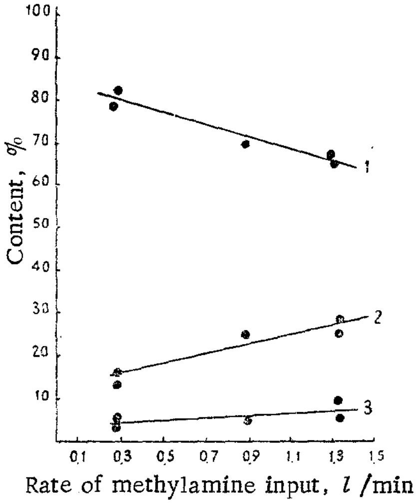

Fig. 2. Change in the composition of the products of ammonolysis of dichlorodimethylsilane in benzene with the rate of methylamine input; 1) Bis (methylamino) dimethylsilane; 2) bis (methylaminodimethylsilyl) methylamine; 3) polymer.

Similar effects were observed for the ammonolysis of I. When a solution of I in heptane was added to liquid ammonia the principal product was the cyclotrisilazane (86%) with a small amount of the cyclotetrasilazane (6%), while passage of gaseous ammonia through a solution of I at the same temperature (−33°) gave an increase in the tetramer content (35–40%), and an increase of the temperature to 70° raised the yield to 50% (Fig. 3). The effect of the ammonolysis conditions on the final product composition can again be attributed to the ratio of the rates of the reactions mentioned above. Reaction (2) is again predominant, but its rate is considerably greater than that of the corresponding amination reaction. In this connection, ammonolysis, liquid or gaseous, proceeds mainly with the formation of silizane bonds. The predominant formation of the trimer whether ammonia or I is in excess shows that the rate of intermolecular condensation, which leads to chain growth, is equal to or less than the rate of intramolecular condensation, which leads to ring formation. It is known that condensation of amino groups plays an important part in the formation of silazane groups during ammonolysis, e.g., [4, 5], the intermediate diaminopolysilazanes, isolated from the ammonolysis of diphenyl- and diethyl-dichlorosilanes, underwent spontaneous condensation to cyclosilazanes with evolution of ammonia. Because of their great tendency to self-condense, similar diamino compounds could not be isolated from the ammonolysis of I. Consequently, the rates of reactions (2) and (3) depend on the lengths of the organic chains on nitrogen and decrease with increase in length of the latter. However, it is possible that the changes in rates of these reactions are not the only reasons for the change in composition of the ammonolysis products. Rearrangement of the cyclosilazanes, a reaction which occurs easily in acid media [9] may also affect the final reaction products.

We have examined the effects of substances with small straight chain alkyl radicals at silicon and nitrogen. Definite steric hindrance to the condensation reaction is caused by large changes in the size and structure of the organic radicals [10-12]. It is known that only aminosilanes are formed under these conditions.

Experimental

Ammonolysis of I with gaseous methylamine carried out as in [8].

a) After treatment of 264.86 g I in 1000 ml benzene with gaseous methylamine (flow rate 0.05 *l*/min) the products were 4.86 g [4.5% content in the mixture] of bis(methylamino)dimethylsilane (II), bp 104°-109° (759 mm), n_D^{20} 1.4140, 50.18 g (45.7%) bis(methylaminodimethylsilyl)methylamine (III), bp 57°-63° (3 mm) n_D^{20} 1.4440; 19.0% N, 23.67 g (21.5%) 1,3,5-hexamethyl-2,4,6-trimethylcyclotrisilazane (IV), bp 222°-226° (759 mm), mp 34°, 15.87% N, Mol. vol. 280, and 31.07 g (28.3%) of nondistillable residue.

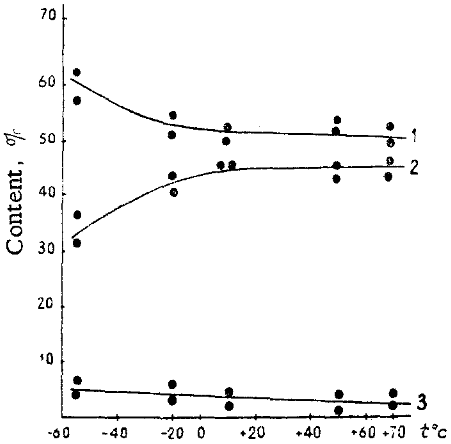

Fig. 3. Change in the composition of the products of ammonolysis of dichlorodimethylsilane with reaction temperature; 1) Hexamethylcyclotrisilazane; 2) octamethylcyclotetrasilazane; 3) polymer.

b) Under analogous conditions the products from 200 g I in 1000 ml ether were 34.01 g (28.8%) II with bp 107°-108° (759 mm) n_D^{20} 1.4140; 64.55 g (55%) III with bp 49°-52° (1.5 mm) n_D^{20} 1.4435, 8.23 g (7.0%) IV with bp 82° (1 mm), mp 33.7°-34.0°; 16.3% N, and 11.11 g (9.2%) of nondistillable residue.

c) Under similar conditions, but with the flow rate of amine varied from 0.28 to 1.33 *l*/min, 100 g I in 1000 ml ether (or benzene) gave II and III. The ratio of II to III in the products relative to the flow rate of the amine is shown in Fig. 1 and 2.

Ammonolysis of dichlorodimethylsilane with gaseous ammonia was carried out by an analogous method. 100 g of dichlorodimethylsilane in 500 ml heptane was placed in a flask and ammonia was passed in at a rate of 0.5 *l*/min. The reaction was carried out at -55° to +70°. The products were hexamethylcyclotrisilazane, octamethylcyclotetrasilazane and a pot residue with 7-8% and M = 700-800. The variation of the composition of the reaction products with the reaction temperature is shown in Fig. 3.

Aminolysis of dichlorodimethylsilane with liquid methylamine. 76 g of liquid methylamine was added at -10° to 200 ml ether in a fournecked flask fitted with a stirrer, reflux condenser cooled with dry ice, a thermometer, and a dropping funnel. To this solution 40 g dichlorodimethylsilane in 100 ml ether was added, the solid methylammonium chloride was filtered off, the solvent removed, and the residue fractionated to give 26.88 g (89.5%) bis(methylamino) dimethylsilane, bp 107°-110° (758 mm) n_D^{20} 1.4145 and 3.38 g (10.5%) nondistillable pot residue.

Ammonolysis of dichlorodimethylsilane with liquid ammonia was carried out in an analogous manner. 150 g of liquid ammonia was placed in the flask and a solution of dichlorodimethylsilane in heptane was added dropwise under the liquid ammonia. Fractionation of the filtrate gave 37.71 g (86.0%) hexamethylcyclotrisilazane, 2.06 g (5.6%) octamethylcyclotetrasilazane, and 3.13 g (8.4%) nondistillable pot residue.

Interaction of dichlorodimethylsilane with bis(methylamino) dimethylsilane. 15 g of bis(methylamino) dimethylsilane was placed in a fournecked flask fitted with a reflux condenser, a stirrer, a thermometer, and a dropping funnel. To this was added 16.4 g dichlorodimethylsilane dropwise over 30 min. The temperature in the flask rose to 80°. Gaseous methylamine was then passed into the flask to remove hydrogen chloride. The reaction products were dissolved in benzene and the methylammonium chloride was filtered off. Benzene was removed and the residue fractionated to give 18 g bis(methylaminodimethylsilyl) methylamine, bp 88°-90° (15 mm); n_D^{20} 1.4450, M 232, Si 28.16%, N 19.6%.

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