DEHYDROCONDENSATION OF TRIORGANOSILANES WITH PIPERAZINE AND SOME ALIPHATIC AMINES IN THE PRESENCE OF POTASSIUM METAL

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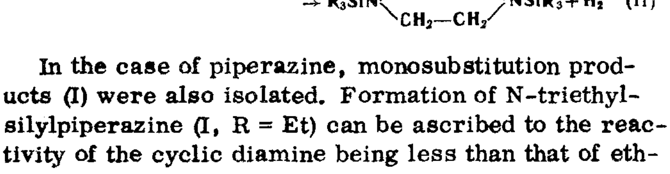
Reaction of $CH_3(C_6H_5)_2SiH$ with $C_4H_9NH_2$ in the presence of potassium metal gives, instead of the expected $CH_3(C_6H_5)_2SiNHC_4H_9$, benzene, diphenyl, and what is apparently a hitherto unknown substituted cyclodisolazane $CH_3(C_6H_5)\overline{SiN(C_4H_9)SiCH_3(C_6H_5)N}C_4H_9$. The Si—$C_6H_5$ bond is broken not only by alkali metals, but also by their amides. For the case of piperazine it is shown that heterocyclic diamines react considerably more readily with trialkylsilanes than do aliphatic secondary amines.

A few investigations have been concerned with dehydrocondensation of amines with hydrosilanes [1–3], and of these only one gives some concepts of the regularities exhibited by the reaction. The relevant paper gives data regarding reactivities of amines of various structures, and the authors establish that secondary aliphatic amines react with trialkylsilanes at 200°, while aliphatic amines with branched chains do not react even at 250°. The papers referred to used group I alkali metals as the dehydrocondensation catalysts.

The comparative reactivities of aliphatic and heterocyclic diamines towards hydrosilanes have not been investigated, and it appeared to us to be of interest to investigate the laws involved in reaction between hydrosilanes and amines of various kinds and structures, and to settle the question of the strength of the Si—C_6H_5 bond in hydrosilanes in the presence of alkali metals and amines. The following were selected for investigation: triethyl-, methyldiethyl, and methyldiphenylsilane, ethylene diamine, n-butylamine, and piperazine. The catalyst was potassium.

Dehydrocondensation of diamines with hydrosilanes having aliphatic substituents at the silicon atom proceeded in every case with formation of products of the presumed structure. Thus for example triethyl- and methyldiethylsilane gave with ethylene diamine and piperazine (2:1) the corresponding N,N'-disilylamines (II).

$$2R_3SiH + H_2NCH_2CH_2NH_2 \xrightarrow{K} R_3SiHNCH_2CH_2NHSiR_3 + H_2$$



(II)

In the case of piperazine, monosubstitution products (I) were also isolated. Formation of N-triethylsilylpiperazine (I, R = Et) can be ascribed to the reactivity of the cyclic diamine being less than that of ethylene diamine. It must also be noted that piperazine has a higher reactivity than secondary aliphatic amines, for it undergoes dehydrocondensation at 85–90°, while diethylamine [1] requires 200°.

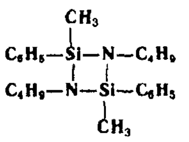
We previously showed that a phenyl group at the silicon atom raises the reactivity of the hydrosilane in dehydrocondensation with ethylenediamine [4]. Study of the reaction of methyldiphenylsilane with ethylenediamine showed it to be anomalous. The product was a thick viscous liquid, distillation of which gave only diphenyl. It proved impossible to identify an actual disilyl-substituted ethylenediamine.

In this connection a series of experiments were carried out to determine the direction of dehydrocondensation of hydrosilanes with amines in the presence of potassium. The amine used was n-butylamine (to facilitate identification of the compounds formed).

The main product of reaction of excess n-butylamine with methyldiphenylsilane in the presence of potassium was methyltri-n-butylaminosilane:

$$CH_3(C_6H_5)_2SiH + 3H_2NC_4H_9 \xrightarrow{K} CH_3Si(HNC_4H_9)_3 + 2C_6H_6 + H_2 \ .$$

Using a methyldiphenylsilane:n-butylamine ratio of 1:1, the products were methyldiphenylbutylaminosilane, benzene, diphenyl and a substance to which structure III can be assigned, judging from its elementary analytical data and molecular weight:



III

A number of facts are evidence in support of formation of type III heterocyclic compounds, and first and foremost is the possibility of breaking the Si—C_6H_5 bond by means of potassium or potassamides. In particular, splitting of the Si—C_6H_5 bond by potassium butylamide is indicated by the reaction of methyldiphenylsilane with excess butylamide in the presence of catalytic quantities of potassium metal. Using stoichiometric quantities of methyldiphenylsilane and butylamine, reaction can proceed in the direction of formation of polymers or heterocyclic silazanes. The benzene and diphenyl isolated in such cases are evidence in favor of the assumed reaction mechanism:

$$CH_3(C_6H_5)_2SiH + H_2NC_4H_9 \xrightarrow{K} CH_3(C_6H_5)_2SiNC_4H_9 + H_2$$

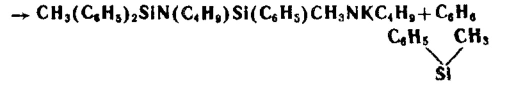
$$CH_3(C_6H_5)_2SiNHC_4H_9 + K \rightarrow CH_3(C_6H_5)Si(NHC_4H_9)K + C_6H_5K$$

$$CH_3(C_6H_5)_2SiNHC_4H_9 + C_6H_5K \rightarrow CH_3(C_4H_5)_2SiNKC_4H_9 + C_6H_6$$

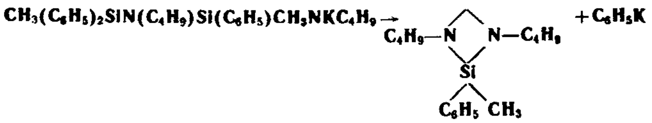
$$CH_3(C_6H_5)_2SiNKC_4H_9 + CH_3(C_6H_5)_2SiNHC_4H_9 \rightarrow$$

$$\rightarrow CH_3(C_6H_5)_2SiN(C_4H_9)Si(C_6H_5)CH_3NHC_4H_9 + C_6H_5K$$

$$CH_3(C_6H_5)_2SiN(C_4H_9)Si(C_6H_5)CH_3NHC_4H_9 + C_6H_5K \rightarrow$$



$$\rightarrow CH_3(C_6H_5)_2SiN(C_4H_9)Si(C_6H_5)CH_3NKC_4H_9 + C_6H_6$$



$$CH_3(C_6H_5)_2SiN(C_4H_9)SiCH_3(C_6H_5)NC_4H_9K + CH_3(C_6H_5)_2SiNH(C_4H_9) \rightarrow$$
$$\rightarrow CH_3(C_6H_5)_2Si[N(C_4H_9)SiCH_3(C_6H_5)]_n NHC_4H_9 + C_6H_5K$$

etc., with formation of further cyclic, crosslinked, or linear polymers. The time for which the reactants are heated together substantially affects the yield of methyldiphenylbutylaminesilane, increased heating time reducing the yields of monosilyl derivative and benzene. This also confirms the correctness of the assumed reaction mechanism.

EXPERIMENT

The starting trimethyl-, methyldiethyl-, and methyldiphenylsilane were prepared using Grignard reagents. Their physical constants agreed with those given in the literature. Amines were carefully dried before use.

N, N'-Bis(triethylsilyl)piperazine (II, R = Et), and N-triethylsilylpiperazine (I, R = Et). 0.1 g K was added to a mixture of 20 g (0.172 mole triethylsilane and 10 g (0.116 mole) piperazine which had been heated to 80°. Evolution of hydrogen ceased comparatively quickly. The mixture was heated for 5 hr, the K metal filtered off, and the filtrate fractionally distilled to give two substances.

I. Bp 120—123° (4mm), n_D^{20} 1.4734, d_4^{20} 0.8974. Found C 59.86; H 11.89; Si 13.80; N 13.95%, *M* 214; MR_D 62.58. Calculated for $C_{10}H_{24}N_2Si$. C 60.00; H 12.00; Si 14.00; N 14.00%; *M* 200; MR_D 62.23.

II. Bp 146—148° (4mm), n_D^{20} 1.4770, d_4^{20} 0.8915. Found C 61.70; H 12.17; Si 17.50; N 8.36%; *M* 318.2; MR_D 98.51. Calculated for $C_{16}H_{38}N_2Si$ C 61.15; H 12.10; Si 17.83; N 8.92%; *M* 314.1; MR_D 98.66.

N, N'-Bis(methyldiethylsilyl)piperazine. Prepared under similar conditions using a large excess of methyldiethylsilane. Bp 140—142° (4mm); n_D^{20} 1.4678; d_4^{20} 0.8915. Found C 58.73; H 11.94; Si 20.00; N 10.64%; MR_D 89.28. Calculated for $C_{14}H_{34}N_2Si_2$. C 58.73; H 11.89; Si 19.58; N 9.79%; MR_D 89.64.

N, N'-Bis(triethylsilyl)ethylenediamine. 3 g (0.05 mole) ethylenediamine was added dropwise to a stirred mixture of 23.5 g (0.2 mole) triethylsilane and 0.2 g K. When hydrogen evolution had ceased, the mixture was heated for 4 hr at 80–90°. Vacuum-fractionation gave 11.2 g material bp 136—138° (1mm); n_D^{20} 1.4575; d_4^{20} 0.8602. Found: C 58.51; H 12.77; Si 20.15; N 9.35%; *M* 282.2; MR_D 91.45. Calculated for $C_{14}H_{36}N_2Si_2$. C 58.33; H 12.50; Si 19.45; N 9.72%; *M*, 288.6; MR_D 91.19.

N, N'-Bis(methyldiethylsilyl)ethylenediamine. 6 g (0.1 mole) ethylenediamine was added to a stirred mixture of 22 g (0.2 mole) methyldiethylsilane and 0.1 g K. The mixture was left overnight, and after removing the K, distilled, to give a compound 125° (1mm): n_D^{20} 1.4490; d_4^{20} 0.8509. Found: C 55.67; H 12.40; Si 21.12; N 11.18%; *M* 259; MR_D 82.15. Calculated for $C_{12}H_{32}N_2Si_2$. C 55.38; H 12.30; Si 21.54; N 10.76%; *M* 260.5; MR_D 82.17.

Methyltri-n-butylaminosilane. 30 g (0.4 mole) n-$BuNH_2$ was added to a stirred mixture of 19.8 g (0.1 mole) methyldiphenylsilane and 0.1 g K. When evolution of hydrogen had ceased, the mixture was stirred for 8 hr at 50°. Distillation gave a mixture of benzene and butylamine bp 70—90° (760mm) and a compound bp 98—100° (3mm); n_D^{20} 1.4440; d_4^{20} 0.8586. Found: C 60.5; H 12.49; Si 11.06%; MR_D 80.2. Calculated for $C_{13}H_{33}N_3Si$. C 60.21; H 12.75; Si 10.80%; MR_D 80.5.

Methyldiphenyl-n-butylaminosilane and 1, 3-dimethyl-1, 3-diphenyl-2, 4-di-n-butylcyclodisilazane (III). 7.5 g (0.105 mole) n-$BuNH_2$ was added to a stirred mixture of 20 g (0.11 mole) methyldiphenylsilane and 0.1 g K. A vigorous reaction ensued. When evolution of hydrogen had ceased, the mixture was stirred for an hour at room temperature, unreacted K removed, and the products fractionally distilled, first at atmospheric pressure, then under vacuum. 4 cuts were obtained. The first (80–83°), after washing with water and drying and distilling had bp 80—81°; n_D^{20} 1.5012, and corresponded to benzene. The second (80–90° at 2 mm) was a crystalline substance mp 69.5–70°, and its elementary analysis and molecular weight corresponded to those of diphenyl. The 3rd cut (bp 156–158° at 2 mm) was methyldiphenyl-n-butylaminosilane n_D^{20} 1.5440; d_4^{20} 0.9821. Found: C 75.69; H 8.57; N 5.29; Si 10.57%; MR_D 86.35. Calculated for C 75.82; H 8.55; N 5.20; Si 10.40%; MR_D 86.66. The 4th cut (180–220° at 2 mm) gave, on repeated distillation, a cut bp 220—225° (2mm) n_D^{20} 1.5460; d_4^{20} 1.0280. Found: C 68.79; H 8.34; Si 14.96; N 7.00%; *M* 409; MR_D 118. Calculated for $C_{22}H_{34}N_2Si_2$. C 69.02; H 8.95; Si 14.68; N 7.32%; *M* 382; MR_D 118.9. This data enables structure II to be assigned to the latter compound.

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