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THE REACTION OF METHYLCHLOROSILANES WITH MIXTURES OF PYRIDINE AND NITROMETHANE

J. MANZUR and W. ZAMUDIO

Department of Chemistry, Faculty of Physics and Mathematics, University of Chile, Santiago (Chile)

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SUMMARY

Trimethylchlorosilane reacts with anhydrous pyridine/nitromethane mixtures to give hexamethyldisiloxane in 75% yield. Dimethyldichlorosilane undergoes a more complex reaction, apparently to give the siloxanes $ClMe_2SiO(Me_2SiO)_n$-$SiHMe(CH_2Cl)$ with $n = 0,1$, and 2.

INTRODUCTION

In view of the unusual reactions which occur between nitromethane/pyridine mixtures and certain inorganic compounds, *e.g.* (*i*) $[Co(1,10\text{-Phenanthroline})_3]$-$(ClO_4)_3$, and (*ii*) $SiCl_4$[1], we decided to study the reaction of dimethyldichlorosilane and trimethylchlorosilane with such mixtures. These halides do not react with pyridine alone[2].

EXPERIMENTAL

General

IR spectra were determined with a Perkin Elmer M.421. Hydrolyzable chlorine was determined by treating a solution of the siloxane in carbon tetrachloride with deionized water. The aqueous layer was separated, and the hydrochloric acid titrated against standard alkali. The total chlorine content was obtained by combustion with sodium peroxide in a Parr bomb followed by potentiometric titration of the liberated chloride ion[3]. Silicon was determined by acid digestion, followed by ignition to constant weight.

Molecular weights were measured cryoscopically in benzene with a standard apparatus.

All reactions were carried out under dry nitrogen at 23°. Solvents were carefully dried by standard methods.

Reactions

To 0.5 moles of the alkylchlorosilane in 50 ml of nitromethane was added 0.5 moles of pyridine. After several hours a second liquid phase appeared, and increased in size as the reaction proceeded. Reaction was judged to be complete after about 70 h, and the new phase was separated off. Siloxanes were extracted from it with cyclohexane and finally purified by fractional distillation under vacuum. The lower phase consisted of a red-brown liquid mixed with solid pyridine hydrochloride.

RESULTS

The reaction between trimethylchlorosilane with pyridine gave 30 g (75%) of pure hexamethyldisiloxane, 100.5°/760 mmHg, m.p.[4] −58.7°. (Found: C, 44.32; H, 11.19; Si, 34.45; mol. wt., 161. $C_6H_{18}OSi_2$ calcd.: C, 44.39; H, 11.11; Si, 34.57%; mol. wt., 162.) The IR spectrum was identical with that described in the literature[5,6].

The reaction between dimethyldichlorosilane and pyridine gave three principal fractions: (*a*) 11 g (21.5%), b.p. 30–31° (6 mmHg). (Found: C, 23.85; H, 5.9; total Cl, 33.91; hydrolyzable Cl, 16.40; Si, 27.45; mol. wt., 205. $C_4H_{12}Cl_2OSi_2$ calcd.: C, 23.64; H, 5.9; total Cl, 34.98; hydrolyzable Cl, 17.49; Si, 27.58%; mol. wt., 203.) (*b*) 7 g (15%), b.p. 60–61° (6 mmHg). (Found: C, 25.98; H, 6.4; total Cl, 22.25; hydrolyzable Cl, 13.73; Si, 30.77; mol. wt., 280. $C_6H_{18}Cl_2O_2Si_3$ calcd.: C, 25.99; H, 6.5; total Cl, 25.63; hydrolyzable Cl, 12.82; Si, 30.32%; mol. wt., 277.) (*c*) 4 g (9%), b.p. 89° (6 mmHg). (Found: C, 28.06; H, 6.6; total Cl, 20.84; hydrolyzable Cl, 10.59; Si, 30.34; mol. wt., 351. $C_8H_{24}Cl_2O_3Si_4$ calcd.: C, 27.35; H, 6.8; total Cl, 20.22; hydrolyzable Cl, 10.11; Si, 31.91%; mol. wt., 351.)

All these products showed IR bands at 2280 s and 960 s cm^{-1}, characteristic of the Si–H bond, and at 1100–1030 cm^{-1} vs (br) assigned to Si–O stretching[5]. The presence of CH_2Cl groups was confirmed by examining the reaction between the siloxanes and thiourea in absolute alcohol[7].

The results indicate that the products (*a*), (*b*), and (*c*) are the siloxanes $ClMe_2SiO(Me_2SiO)_nSiHMe(CH_2Cl)$, with $n=0$, 1, 2 respectively.

From the lower liquid phases obtained in both experiments above, we obtained a solid by partial evaporation of the solvent. This solid was recrystallized from absolute alcohol to yield a slightly brown compound. (Found: C, 45.5; H, 4.5: Cl, 22.34 N, 17.3. $C_6H_7ClN_2O$: calcd.: C, 45.42; H, 4.41; Cl, 22.40; N, 17.67 %.)

The yellow-brown colour of the aqueous solution of this solid faded when it was passed through a cation exchange resin (Dowex 50W-X2).

A concentrated aqueous solution of the product was treated with $NaClO_4$ to give a compound having the same principal infrared bands as the organic chloride, revealing the cationic nature of the compound, $C_6H_7N_2OClO_4$. (Found: Cl, 16.4. $C_6H_7ClN_2O_5$ calcd.: Cl, 16.0%.)

DISCUSSION

Trimethylchlorosilane reacts with anhydrous C_5H_5N/CH_3NO_2 mixtures to give hexamethyldisiloxane in 75% yield. The reaction with dimethyldichlorosiloxane is more complex, and seems to give the series of siloxanes $ClMe_2SiO(Me_2SiO)_nSiHMe(CH_2Cl)$ with $n=0$, 1, 2. The presence of the Si–H linkage is indicated by the IR spectra, while the rather surprising production of CH_2Cl groups is indicated strongly by the difference between the amounts of hydrolysable and non-hydrolysable chlorine present, and by the positive behaviour of the siloxanes in a reaction with thiourea in alcohol which is characteristic of the $SiCH_2Cl$ grouping[7].

The silicon chlorides examined do not react with pyridine/acetonitrile mixtures. Acid–base interaction between the pyridine and the nitromethane, to give $C_5H_5NH^+\cdots CH_2NO_2^-$ species, may be an important step in the unusual reactions observed, and the Si–O–Si linkages are possibly produced by decomposition of intermediates of the type $Me_3Si–O_2NCH_2$.

Studies of the mechanism of formation of Si–H and $Si–CH_2Cl$ linkages are in progress, and the synthetic aspects of the reactions are being explored further.

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