Reactions of Chloromethylpolysiloxanes with Thiourea[1]

By Shunichi NOZAKURA

(Received January 31, 1955)

Concerning the reaction of halogenomethylsilicon compound with thiourea, the synthesis of thiuronium salts from bromomethyltrimethylsilane has been reported.[2] Recently, Noller and Post also carried out the reaction of chloromethyltrimethylsilane[3] with thiourea, and thereby synthesized trimethylsilylmethylmercaptan.

I have reported in a previous paper[4] that the silicon-containing thiuronium salts were obtained from the reaction of the various chloromethylsilicon compounds, $ClCH_2Si(CH_3)_2R$, ($R=CH_3—$, $CH_3(CH_2)_3—$, $CH_3(CH_2)_7—$, $C_6H_5—$ and $ClCH_2(CH_3)_2SiO—$) with thiourea and

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[1] Paper III in a series on the study of organosilicon compound.

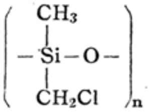
[2] D.C. Noller and H.W. Post, *J. Org. Chem.*, **17**, 1393 (1952).

[3] G.D. Cooper, *J. Am. Chem. Soc.*, **76**, 2500 (1954).

[4] S. Nozakura, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **75**, 958 (1954).

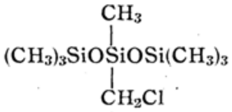
that no fission of silicon-carbon bonds took place. It was of great interest that the difunctional bischloromethyltetramethyldisiloxane gave only the corresponding dithiuronium salt even when an excess of disiloxane was used.

The present study has been undertaken in order to clarify the nature of the above reaction. Thus we have studied the reactions between the chloromethylpolysiloxanes (I, II, III and IV) and thiourea and the decomposition of thiuronium salts by an aqueous solution of alkali.



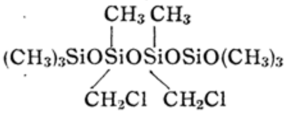
$\left(-\overset{CH_3}{\underset{CH_2Cl}{Si}}-O-\right)_n$

(I)



$(CH_3)_3SiO\overset{CH_3}{\underset{CH_2Cl}{Si}}OSi(CH_3)_3$

(II)

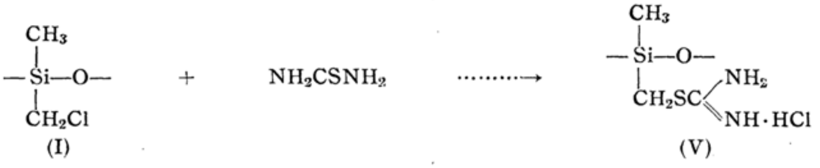


(III)

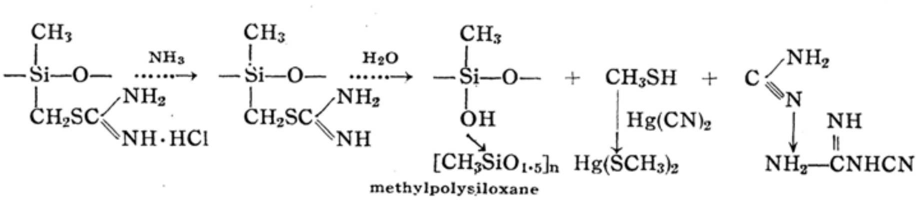
$[ClCH_2SiO_{1.5}]_n$

(IV)

Chloromethylmethylpolysiloxanes and Thiourea.—Because of the low solubility of the compound (I) in hot alcohol, the reaction apparently was found to be heterogeneous in the first stage and gradually became homogeneous as the reaction proceeded. The water-soluble polythiuronium chloride (V) was obtained quantitatively as a glassy solid after refluxing for several hours.



The addition of an excess of aqueous ammonia to an aqueous solution of the compound (V) gave a white amorphous precipitate, methylpolysiloxane, with an evolution of methylmercaptan. Probably the fission of silicon-carbon linkage would take place in the first place, followed by the usual fission of sulfur-carbon bond[5] and the immediate condensation of the newly formed silanol to give a new siloxane linkage, as shown below;



The chlorine content of the methylpolysiloxane was found to be very low (0.25%). This would suggest that the chlorine of chloromethylpolysiloxane (I) might be quite active in the reaction with thiourea.

When the compound (I) has been used in quantities double that calculated for thiourea, it was found that the ether-soluble part of the reaction product contained the compound (I), the unreacted substance. The decomposition of the water-soluble part by aqueous ammonia gave the precipitation of impure methylpolysiloxane, which contained a small amount of unreacted chloromethyl groups (Cl, 3.35%). These results indicate that nearly one half of the starting polysiloxane (I) reacted with thiourea and the other half remained unreacted. This may be interpreted to be due to the fission and recombination of siloxane bonds. Such an interpretation is confirmed experimentally by the reaction of trimethylsilyl-end-blocked simple chlormethylmethylpolysiloxanes (II) and (III) with thiourea as described below.

When a mixture of an alcoholic solution of the compound (II) and thiourea in equimolecular weight was heated under reflux for five hours, hexamethyldisiloxane was obtained as a volatile product. The ether-soluble part of the nonvolatile product contained thiuroniumchloride (VI) corresponding to the compound (II). The water-soluble part of the nonvolatile product gave methylpolysiloxane when treated with aqueous ammonia. Therefore, it is concluded that the reaction between 3-chloromethylheptamethyltrisiloxane (II) and thiourea gives the corresponding thiuronium chloride (VI) in the first stage and then the fission and recombination of siloxane bonds will take place, as shown below;

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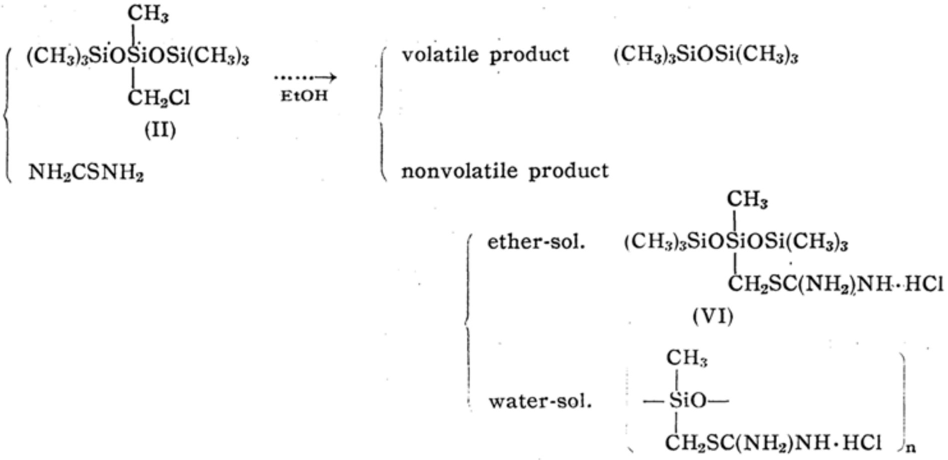
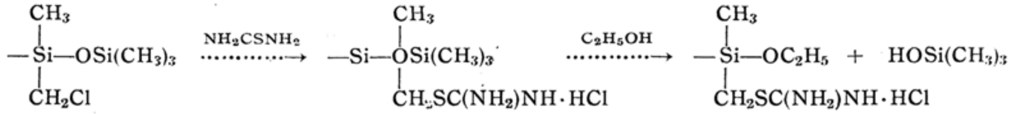
[5] F. Arndt, *Ber.*, 54, 2236 (1921).



$$\left\{\begin{array}{l}(CH_3)_3SiO\overset{CH_3}{\underset{CH_2Cl}{Si}}OSi(CH_3)_3 \\ \quad (II) \\ NH_2CSNH_2\end{array}\right. \xrightarrow[EtOH]{} \left\{\begin{array}{ll}\text{volatile product} & (CH_3)_3SiOSi(CH_3)_3 \\ \text{nonvolatile product} & \left\{\begin{array}{ll}\text{ether-sol.} & (CH_3)_3SiO\overset{CH_3}{\underset{CH_2SC(NH_2)NH\cdot HCl}{Si}}OSi(CH_3)_3 \quad (VI) \\ \text{water-sol.} & \left(-\overset{CH_3}{\underset{CH_2SC(NH_2)NH\cdot HCl}{Si}}O-\right)_n\end{array}\right.\end{array}\right.$$

The reaction of 3.5-di(chloromethyl)octamethyltetrasiloxane (III) with thiourea also showed the same type of fission of siloxane bonds and gave polythiuroniumchloride. However in this case no appreciable amount of corresponding thiuroniumchloride was detected.

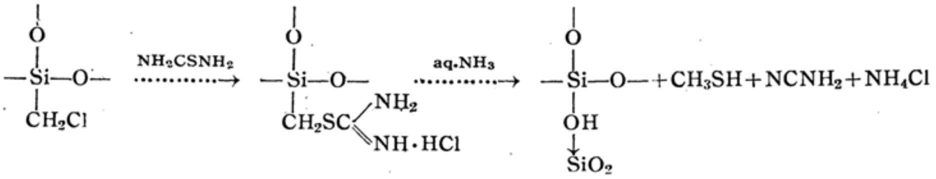
On the contrary the fission of siloxane bonds did not take place in the case of decamethyltetrasiloxane, which has no chloromethyl group, under the similar condition. Therefore the decrease in electron density on the silicon atom might facilitate the nucleophilic attack of the solvent molecule, as shown in following scheme;



$$-\overset{CH_3}{\underset{CH_2Cl}{Si}}-OSi(CH_3)_3 \xrightarrow{NH_2CSNH_2} -\overset{CH_3}{\underset{CH_2SC(NH_2)NH\cdot HCl}{Si}}-OSi(CH_3)_3 \xrightarrow{C_2H_5OH} -\overset{CH_3}{\underset{CH_2SC(NH_2)NH\cdot HCl}{Si}}-OC_2H_5 + HOSi(CH_3)_3$$

Consequently, the failure in obtaining the partially-reacted molecule in the case of bis(chloromethyl)tetramethyldisiloxane[4] and chloromethylmethylpolysiloxane (I) may be due to the fission of siloxane bonds.

Chloromethylpolysiloxane, which has the three dimensional structure, similarly gave the corresponding water-soluble thiuroniumchloride. Silicic acid was obtained by the treatment of the latter with aqueous ammonia. This is probably an additional evidence for the fission of siloxane bonds.



$$-\overset{\overset{|}{O}}{\underset{CH_2Cl}{Si}}-O- \xrightarrow{NH_2CSNH_2} -\overset{\overset{|}{O}}{\underset{CH_2SC(NH_2)=NH\cdot HCl}{Si}}-O- \xrightarrow{aq.NH_3} -\overset{\overset{|}{O}}{\underset{\underset{\downarrow}{OH}}{Si}}-O- + CH_3SH + NCNH_2 + NH_4Cl \quad SiO_2$$

The Effect of Various Alkalies on the Precipitation Phenomenon of Methylpolysiloxane from the Aqueous Polythiuroniumchloride (V).—The comparison of the reaction time required for the precipitation of methylpolysiloxane in the alkaline decomposition of polythiuronium salt (V) is shown in Table I. The rate of precipitation of methylpolysiloxane became slower in the order of ammonia, sodium carbonate, and sodium bicarbonate, and became faster as their concentration increased. However in the case of sodium hydroxide the higher the alkaline concentration in the region below the equivalent concentration, the faster the rate of

TABLE I

THE EFFECT OF VARIOUS ALKALIES ON THE PRECIPITATION OF METHYLPOLYSILOXANE FROM THE AQUEOUS POLYTHIURONIUM CHLORIDE (V) SOLUTION*

Conc.**	Alkali			
	NaOH	Na_2CO_3	$NaHCO_3$	NH_4OH
6 N	no ppt.	0.2 min.		0.5 min.
1 N	7.0 min.	0.7 ,,	8.5 min.	0.6 ,,
0.1 N	3.2 ,,	10.0 ,,	30.0 ,,	3.3 ,,
0.05 N	10.0 ,,	24.0 ,,		6.5 ,,

* 1 ml. of 10% aq. (V) was quickly mixed with 1 ml. of aq. alkali and the time required till ppt. or turbidity began to appear was measured.

** The equivalent quantity of alkali is about 1 ml. of about 0.5 N.

precipitation; on the contrary the higher the concentration in the region above the equivalent concentration, the slower the rate. Finally no precipitate was obtained. This means that sodium methylsilanolate would be produced in high alkaline concentration. In fact, the clear alkaline solution gave precipitation of methylpolysiloxane when neutralized with a dilute aqueous solution of hydrochloric acid.

The Fission of Silicon-Carbon Bonds in Various Silicon-containing Thiuronium Chloride.—The alkaline fission of silicon-carbon bonds in silicon-containing thiuronium chloride seemed to be a type of reaction analogous to the one which was found by Krieble and Elliott[6] in the reaction of chloromethylpolysiloxanes with an aqueous solution of alkali. They observed there the evolution of methylchloride. The effect of various substituents of the silicon atom on the fission of silicon-carbon bonds was compared qualitatively by titrating immediately the amount of methylmercaptan evolved on the decomposition of silicoalkylisothiourea at 100°C, as shown in Fig. 1. The polythiuronium salts of disiloxane and polysiloxane, in which the electron attracting oxygen atom is attached to the silicon atom, was decomposed much faster than the silicoalkylthiuronium salts in which the electron releasing *n*-butyl or *n*-octyl group is attached to the silicon atom. Phenyldimethylsilylmethylthiuronium chloride is situated between these two groups.

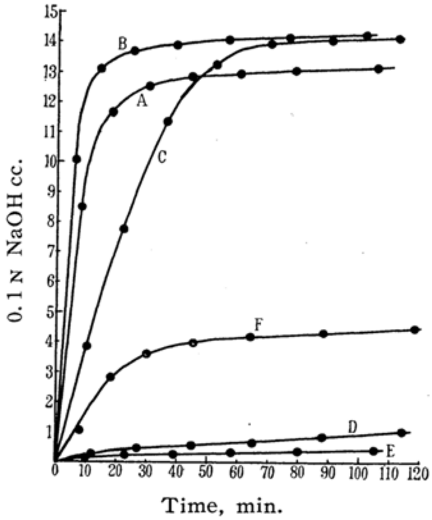
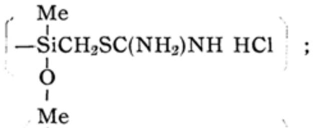
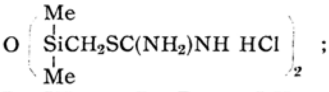


Fig. 1. Rate of alkaline decomposition of silicon-containing thiuronium chlorides.

A,

$\left[-\overset{\text{Me}}{\underset{\text{O}}{\text{Si}}}\text{CH}_2\text{SC(NH}_2\text{)NH HCl}\right]$;

B,

$\text{O}\left[\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{CH}_2\text{SC(NH}_2\text{)NH HCl}\right]_2$;

C, $R=CH_3$; D, $R=n-C_4H_9$;
E, $R=n-C_8H_{17}$; F, $R=C_6H_5$ in $RSi(Me)_2CH_2SC(NH_2)NH\cdot HCl$
The theoretical value of 0.1 N NaOH is 15.08 ml.

Trimethylsilylmethylthiuronium chloride showed an abnormal curve (C) as compared to those of other homologues. However unusual behaviour of this compound was observed by titrating amounts of volatile trimethylsilylmethylmercaptan which distilled over prior to the decomposition to methylmercaptan. Trimethylsilylmethylmercaptan is considered to be rather stable under this condition, because the methyl group has an electron releasing effect.

Experimental

Methylchloromethylpolysiloxane (I). — One hundred and sixty-three grams of dimethyldichlorosilane was chlorinated by the usual vapor phase method,[7] until the temperature of the boiling mixture reached 114°C. The fractional distillation of the reaction mixture gave 161 g. (78%) of chlormethylmethyldichlorosilane, b.p. 120–2°C.

One hundred and seventy grams of chloromethylmethyldichlorosilane in 200 ml. of ether was added to 400 ml. of water cooled in an ice-bath under vigorous stirring at a temperature below 10°C during a period of one and a half hours. The ethereal layer was separated, washed with water, and dried over calcium chloride. When the solvent was removed in vacuo, 110 g. of (I) was obtained as a fairly viscous oil. Molecular weight, determined cryoscopically in benzene, was found to be 1810. Found: Cl, 32.1. Calculated for C_2H_5OSiCl: Cl, 32.6

3-Chloromethylheptamethyltrisiloxane (II) and 3,5-Di(chloromethyl)octamethyltetrasiloxane (III).—A mixture of 39.8 g. (0.367 mol.) of trimethylchlorosilane and 30.0 g. (0.184 mol.) of chloromethylmethyldichlorosilane in 30 ml. of dry ether was added gradually to 100 ml. of water cooled in an ice bath under vigorous stirring below 5°C, and then the ethereal layer was separated, washed with water and dried over calcium chloride. The ether solution was filtered, and after shaking with 4 ml. of concentrated sulfuric acid for one half hour, washed again with water, and dried over calcium chloride. Fractional distillation was carried out through a Stedman type column (about 30 theoretical plates) and the yields of various fractions were as follows; 100°/760 mm., 5.0 g. of hexamethyldisiloxane; 94–95°/30 mm. 10.1 g. of (II), d_4^{25} 0.9183, n_D^{25} 1.4042; 95°/30 mm.−126.5°/10 mm. 0.7 g.; 126.5−128°/10 mm., 7.0 g. of (III), d_4^{25} 1.0053, n_D^{25} 1.4199.

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[6] R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, 68, 2291 (1946).

[7] S. Nozakura, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 427 (1954).

(II). *Anal.* Found: Si, 30.7; Cl, 12.5; Mol. wt. (in benzene), 279; MR_D, 72.06. Calculated for $C_8H_{23}O_2Si_3Cl$: Si, 31.0; Cl, 13.1; Mol. wt., 271; MR_D, 72.40.

(III). *Anal.* Found: Si, 29.6; Cl, 18.4; Mol. wt. (in benzene), 387; MR_D, 95.38. Calculated for $C_{10}H_{28}O_3Si_4Cl$: Si, 29.5; Cl, 18.7; Mol.wt., 379; MR_D, 95.88.

Chloromethylmethylpolysiloxane (I) with Thiourea (1:1 mol.).—A mixture of 10.88 g. (0.100 eq.) of (I), 7.62 g. (0.100 mol.) of thiourea, and 25 ml. of absolute alcohol was refluxed on a water bath for seven hours with a reflux condenser equipped with a calcium chloride tube. At the beginning of the refluxing (I) did not dissolve but settled down to the bottom of the flask; however, it gradually came into a homogeneous solution. Removal of the solvent in vacuo gave 22.4 g. of glass-like crude polythiuronium chloride. On dissolving this product in 50 ml. of water a slightly turbid solution was obtained, due to the presence of a minor amount of unreacted (I), and so this aqueous solution was extracted with a small amount of ether and again concentrated to dryness in vacuo to yield 18.27 g. of polythiuronium chloride (V) which contained a small amount of thiourea.

When 3 ml. of 6 N aqueous ammonia was added to a solution of 0.88 g. of (V) in 5 ml. of water a white amorphous precipitate was formed and mercaptan was evolved. The precipitate was centrifuged, washed thoroughly with water, and dried at 100° to give 0.32 g. of crude methylpolysiloxane.

Anal. Found: Si, 39.4; C, 17.8; H, 4.21; Cl, 0.25. Calculated for CH_3OSi: Si, 41.7; C, 17.8; H, 4.48; Cl, 0.0.

In order to identify the methylmercaptan evolved 2.7 ml. of 6 N aqueous sodium hydroxide was added to 0.4 g. of (V) in 10 ml. of water and the mixture was heated on the water bath, and the evolved gas was introduced into a solution of 1.0 g. of mercuric cyanide in 15 ml. of water. The resulted mercaptide (0.4 g.) was recrystallised from alcohol, m.p. 171. The mixed melting point with the known sample did not show any depression. The reaction mixture was filtered to remove the precipitated methylpolysiloxane and the filtrate was evaporated to a few mililiters on a water bath. After cooling 0.4 g. of crude dicyandiamide was obtained in colorless needles and showed the m.p. of 207.5–8° after a recrystallization from water. (207° in literature5))).

Chloromethylmethylpolysiloxane (I) and Thiourea (2:1 mol.).—A mixture of 10.7 g. (0.098 eq.) of (I), 3.8 g. (0.050 mol.) of thiourea, and 25 ml. of absolute alcohol was refluxed for four and a half hours. At the end of the reaction the unreacted (I) remained insoluble. After removing the solvent in vacuo, the residual semisolid was dissolved in 50 ml. of water and the aqueous solutions was extracted with ether. Four and a half grams of the unreacted (I) was recovered as an oil (qualitative test for N and S was negative.) from the ethereal layer and 10.1 g. of crude (V) was obtained as a glass-like solid from the water layer. This product gave an impure methylpolysiloxane on the decomposition with ammonia, the analysis of which was as follows: Qualitative test for N and S was negative; Si, 37.0; Cl, 3.35.

3-Chloromethylheptamethyltrisiloxane (II) with Thiourea.—A mixture of 6.0 g. (0.022 mol.) of (II), 1.68 g. (0.022 mol.) of thiourea, and 10 ml. of absolute alcohol was refluxed for six hours. When the reaction mixture was distilled under reduced pressure, the distilate was caught in a trap cooled in an ice-salt bath and was added into 25 ml. of water to separate 0.8 g. of an insoluble oil, which boiled mostly at 98–101° and had the camphor-like odor, characteristic of hexamethyldisiloxane. The residue which remained was dissolved in 25 ml. of water and extracted with 20 ml. of ether. After drying the ether solution over calcium chloride and evaporating the solvent on a water bath, a crystalline mass of thiuronium chloride (VI) corresponding to (II) was obtained. After repeated washing with petroleum ether it gave colorless needles which amounted to 2.12 g., m.p. 111–2°. Found: Si, 23.8. Calculated for $C_9H_{27}N_2O_2SSi_3Cl$: Si, 24.2.

Its picrate decomposed at 180–1°. Found: Si, 15.5; N, 12.8. Calculated for $C_{15}H_{29}O_9N_5SSi_3$: Si, 15.5; N, 12.9.

One fifth of the water-soluble part of the product was decomposed with 5 ml. of 6 N aqueous ammonia and on standing over night 0.11 g. of methylpolysiloxane was obtained as a precipitate. Found: Si, 41.4; C, 18.3; H, 4.47. Calculated for $CH_3O_{1.5}Si$: Si, 41.4; C, 17.8; H, 4.48.

Another one-fifth gave 0.31 g. of picrate. Found: Si, 6.75; N, 17.58; N/Si atomic ratio = 5.21.

3,5-Di(chlormethyl)octamethyltetrasiloxane (III) and Thiourea.—A mixture of 1.75 g. (0.0046 mol.) of (III), 0.36 g. (0.0048 mol.) of thiourea, and 6 ml. of absolute alcohol was refluxed for five hours. Removing the solvent in vacuo there remained a semisolid and an oil. This was dissolved in 15 ml. of water and extracted with 20 ml. of ether. The ethereal layer gave 0.66 g. of oil. Four-fifths of the water layer, when treated with 6 ml. of 6 N aqueous ammonia, gave 0.133 g. of crude methylpolysiloxane. Found: Si, 40.4; C, 17.9; H, 3.91. Calculated for $CH_3O_{1.5}Si$, 41.7; C, 17.8; H, 4.48.

The residual one-fifth of the water layer gave 0.29 g. of picrate. Found: Si, 7.31; N, 17.74; N/Si atomic ratio = 4.84.

Decamethyltetrasiloxane (VII) and Thiourea.—A mixture of 7.0 g. of (VII), 5.1 g. of thiourea, and 20 ml. of absolute alcohol was refluxed for eight and a half hours. An oil separated on pouring the reaction mixture onto 50 ml. of water. This was washed with a small quantity of water and distilled. Only 5.6 g. of the unreacted starting material was recovered, b.p. 188–193°.

Chlormethylpolysiloxane (IV) and Thiourea.—A mixture of 2.0 g. (0.020 eq.) of (IV), 1.6 g. (0.021 mol.) of thiourea, and 20 ml. of absolute alcohol was refluxed for four hours. The white powder of (IV) gradually became a transparent semisolid and stuck to the bottom of the flask.

After cooling, the upper alcoholic layer was decanted and the residual semisolid was washed several times with alcohol by decantation and dried in vacuo, yielding 2.8 g. of a glassy solid. Found: Si, 17.2; N, 12.8; N/Si atomic ratio = 1.5.

Five-tenths of a gram of this product was treated with 10 ml. of water. The insoluble part (about 0.06 g.) was filtered off and the filtrate gave 0.1 g. of an impure amorphous silica on decomposition with 5 ml. of 6 N aqueous ammonia, Found: Si, 44.7; Cl, 0.22. Calculated for SiO_2: Si, 46.6; Cl, 0.0.

The Fission of Silicon-Carbon Bonds in Various Silicon Containing Thiuronium Salts. —The method of the preparation of chlormethyldimethylalkylsilanes where alkyls are methyl. *n*-butyl, *n*-octyl, and chloromethyldimethylsiloxy group and of their corresponding thiuronium chloride has been described in the previous paper.[4]

The general procedure is as follows: A three necked flask of 30 ml. capacity was equipped through ground joints with a side flask of about 5 ml. capacity, a vertical air condenser 30 cm. long, and a nitrogen gas inlet tube, the tip of which reached to the bottom of the main flask. Four mililiters of 0.377 N aqueous sodium hydroxide was placed in the main flask and was heated on a water bath, and a stream of nitrogen gas with a constant flow (23–4 ml./min.) was introduced into it, and then the solution of the sample in the side flask was quickly poured into the main flask. The samples used were in a slight excess over an equivalent amount of sodium hydroxide (0.001508 eq.) and dissolved in 3–5 ml. of water. The evolved methylmercaptan was removed along with the stream of nitrogen gas and led into a two percent aqueous solution of mercuric chloride through the air condencer. The liberated hydrochloric acid was titrated with 0.1 N aqueous sodium hydroxide using methyl orange as the indicator under vigorous shaking. The results are given in Fig. 1. After the reaction, in the case of A a white precipitate was obtained. In B, the reaction mixture was trans-parent and gave an oil, on addition of aqueous dilute hydrochloric acid. In C, the reaction mixture was transparent. No silicon-containing fragment was found in it nor in the flask of the mercuric solution, except for the precipitate of mercaptide which was not analysed quantitatively but showed distinctly the existence of silicon on ignition with sulfuric acid.

In the cases of D, E, and F there remained oils which were insoluble in dilute aqueous hydrochloric acid.

Summary

Chloromethylmethylpolysiloxane (I), 3-chloromethylheptamethyltrisiloxane (II) 3,5-di(chloromethyl)octamethyltetrasiloxane (III), and chloromethylpolysiloxane (IV) were reacted with thiourea in absolute alcohol to give silicon-containing thiuronium chlorides.

Although in the case of (II) the corresponding thiuronium chloride was isolated, an extensive fission and recombination of siloxane bonds took place in every case.

Silicon-carbon bond in the thiuronium chloride derived from (I) was easily cleft by the treatment with an aqueous alkali to give three-dimensional methylpolysiloxane. In a similar manner the thiuronium chloride derived from (IV) gave silicic acid with aqueous alkali.

The fission of silicon-carbon bonds in the silicon-containing thiuronium salts was facilitated by the electron-attracting substituents on the silicon atom.

The author is much indebted to Shinetsu Chem. Ind. Co. for generous supplies of the materials used, to Profs. S. Murahashi and H. Tani for their many helpful suggestions, and to Mr. Konotsune for his help in some of the experiments.

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