The oxidizing agent was potassium ferricyanide, used in aqueous buffer solutions for the pyridine runs; the concentrations were chosen so that from 3 to 5 cc. of oxidizing solution was added to the 50-cc. volume containing the oxidation–reduction system in the titration cell. In the dioxane runs the ferricyanide was dissolved freshly for each experiment in the same solvent mixture that was used as buffer in the titration cell; the volumes added were between 3 and 4 cc. for 50 cc. of buffer containing the oxidation–reduction system.

In most runs the potentials were established about as rapidly as the potentiometer could be adjusted, and the potentials registered by the two electrodes agreed with one another within ±0.1 mv. or better, except in the regions of 0 to 5% and 95 to 100% completion. The potentials were stable with time and in general showed no noticeable drift. At the lower alkalinities potentials were established more and more sluggishly and, particularly toward the end-point, long periods of waiting became necessary. In such cases it was advantageous to use the return of the blue color as a guide rather than to wait for the potential to fall to a constant value.

Finally the *p*H was measured again after addition of more palladium colloid, and the tables give the average of the initial and final *p*H value together with the deviation of these figures from the average. In all cases the higher *p*H is the initial one.

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Summary

1. Thiaxanthenol-5-dioxide and several of its derivatives have been prepared and characterized.

2. The existence of a mobile, two-step oxidation–reduction equilibrium between thiaxanthenol-5-dioxide and thiaxanthone-5-dioxide in alkaline solution has been established. By optical, chemical and electrochemical means it was shown that the colored entity in this equilibrium is a semiquinone.

3. The structure of the semiquinone is discussed with particular reference to potential *vs.* *p*H diagrams.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Relative Reactivities of Chloromethyltrimethylsilane and Chloromethylpentamethyldisiloxane

BY GEORGE F. ROEDEL

When chloromethyl siloxanes are treated with alkaline reagents, Si–C cleavage of the $-SiCH_2Cl$ group occurs to form methyl chloride.[1] It has been claimed that the cleavage is accompanied by a competitive hydrolysis of the C–Cl bond.[1] On the other hand no Si–C cleavage of the $-SiCH_2Cl$ group was reported when chloromethyltrimethylsilane was treated with basic reagents.[2] Since methyl chloride, the cleavage product, reacts with the alkaline reagents used in the previous work cited, it was not clearly established that hydrolysis of the C–Cl bond in chloromethyl siloxanes occurs to any significant degree nor that Si–C cleavage is absent with chloromethyltrimethylsilane. In an effort to establish these points and to further elaborate the effect of silicon-bonded oxygen on the behavior of the functional group attached to the silicon, the reactivities of $(CH_3)_3SiCH_2Cl$ (I) and $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ (II) have been compared in this paper.

The activating effect of oxygen bound to silicon has previously been shown by Sommer, Bailey, Strong and Whitmore.[3] They found markedly greater reactivity of the C–Cl bond in α-chloroethyldiethylsilanol as compared with α-chloroethylmethyldiethylsilane toward such reagents as sodium ethoxide in ethanol and potassium acetate in glacial acetic acid.

Whitmore and Sommer[2] found that chloromethyltrimethylsilane (I) with sodium iodide in dry acetone gave a good yield of the corresponding iodide. In this study chloromethylpentamethyldisiloxane (II) was found to behave similarly with this reagent to also give the iodide in good yield.

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + NaI \longrightarrow \underset{\text{III}}{(CH_3)_3SiOSi(CH_3)_2CH_2I} + NaCl$$

Neither α-chloroethyldiethylsilanol,[3] nor I, nor II reacts with aqueous or ethanolic silver nitrate. Iodomethyltrimethylsilane is also unreactive with silver nitrate reagents,[2] but iodomethylpentamethyldisiloxane (III) reacts readily with ethanolic silver nitrate to precipitate silver iodide.

Both chloro-(II) and iodomethylpentamethyldisiloxane (III) readily form Grignard reagents in a similar manner to chloro-(I) and iodomethyltrimethylsilane.[2]

The Si–C bond of the chloromethylsilyl group, $-SiCH_2Cl$, is not split by sulfuric acid at room temperature. This was shown by adding small amounts of I and II to methyl siloxane systems of known functionality and equilibrating with sulfuric acid.[4] The viscosities of the oils obtained

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[1] Krieble and Elliott, THIS JOURNAL, **68**, 2291 (1946).

[2] Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

[3] Sommer, Bailey, Strong and Whitmore, *ibid.*, **68**, 1881 (1946).

[4] Roedel, *Anal. Chem.*, **20**, 705 (1948).

showed that the change in functionality which would have accompanied cleavage of the Si–C bond did not occur.

The greater reactivity of the $-SiCH_2Cl$ group when oxygen is also bonded to the silicon is shown by the results tabulated in Table I. The reactivity of chloromethylpentamethyldisiloxane (II) was significantly greater than that of chloromethyltrimethylsilane (I) with sodium ethoxide in absolute ethanol and potassium acetate in glacial acetic acid. This behavior parallels closely the greater reactivity of α-chloroethyldiethylsilanol as compared to α-chloroethylmethyldiethylsilane with the same reagents.[3] With potassium hydroxide in *n*-butanol the difference in reactivity between I and II was slight.

TABLE I

RELATIVE REACTIVITIES OF CHLOROMETHYLTRIMETHYLSILANE AND CHLOROMETHYLPENTAMETHYLDISILOXANE

Reagent[a]	Reaction, % $(CH_3)_3SiCH_2Cl$ (I)	Reaction, % $(CH_3)_3$-SiOSi-$(CH_3)_2$-CH_2Cl (II)
2.0 M-C_2H_5ONa/abs. C_2H_5OH	36	91
($1^2/_3$ hours reflux)	(35-1-0)[b]	(59-29-3)
1.0 M-CH_3CO_2K/glacial CH_3CO_2H	2	76
($1^3/_4$ hours reflux)	(2-0-0)	(76-0-0)
1.0 M-KOH/moist C_4H_9OH	77	90
($1^3/_4$ hours reflux)	(67-10-trace)	(47-43)
1.0 M-KOH/moist C_4H_9OH	77	80
(1 hour reflux)	(71-6-0)	(62-17-1)

[a] Molar ratio of C_2H_5ONa, CH_3CO_2K and KOH to $(CH_3)_3SiCH_2Cl$ or $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$ was 2:1. [b] Figures in parentheses give % reaction determined for the reaction flask, trap 1 and trap 2, respectively.

Since it had previously been shown that alkaline reagents react with chloromethyl siloxanes to form methyl chloride,[1] provision was made for determining any methyl chloride which formed and escaped from the reaction mixtures. This was effected by using bubbler traps filled with sodium ethoxide in absolute ethanol. The reaction between methyl chloride and sodium ethoxide in absolute ethanol is rapid and complete when the reagent is warm. The decrease in concentration of the sodium ethoxide in the traps is a measure of that methyl chloride which formed and escaped from the reaction mixture.

Since methyl chloride does not react with 1.0 M potassium acetate in glacial acetic acid, the fact that all of the sodium ethoxide remained unreacted in the traps is good evidence that no –Si–C cleavage of the $-SiCH_2Cl$ group in I or II occurs with this reagent. This evidence indicates the reaction to be entirely bimolecular nucleophilic substitution on the methylene carbon as suggested by Whitmore and Sommer.[2]

With sodium ethoxide in absolute ethanol and potassium hydroxide in *n*-butanol, however, formation of methyl chloride shows that Si–C cleavage of the $-SiCH_2Cl$ group occurs with both I and II. The trap figures are minimum figures for the Si–C splitting, since methyl chloride can react with both reagents.

It is not shown in this work whether hydrolysis of the C–Cl bond accompanies cleavage of the Si–C bond in chloromethyl siloxanes. However, the inadequacy of a chloride ion determination in the reaction vessel as sole measure of a C–Cl hydrolysis reaction is established. The cleavage product methyl chloride reacts readily with alkaline reagents, and the amount which escapes from the reaction zone varies with the experimental conditions.[5] Actually determining the presence or absence of a hydrolytic reaction is not readily accomplished. Isolation of ethoxymethylpentamethyldisiloxane, the expected product of the hydrolytic reaction of II with sodium ethoxide in absolute ethanol, was attempted but was unsuccessful. Rearrangement of siloxane bonds during the reaction produces a series of methyl siloxanes[1] that make isolation by fractional distillation difficult. Even were it proved that no ethoxymethylpentamethyldisiloxane were present in the reaction product, the possibility would still exist that it formed but was in turn subjected to Si–C cleavage of the $Si-CH_2OC_2H_5$ group by the reagent. Such a cleavage would presumably produce methyl ethyl ether, but this is also the product of the methyl chloride–sodium ethoxide reaction.

However, the reaction of sodium ethoxide in absolute ethanol with chloromethyltrimethylsilane (I) has been elaborated. The chief attack is at the methylene carbon (1). Of the total reaction, however, 5–10% is attack at the silicon

$$(CH_3)_3SiCH_2Cl + C_2H_5ONa \xrightarrow{C_2H_5OH} \underset{\text{IV}}{(CH_3)_3SiCH_2OC_2H_5} + NaCl \quad (1)$$

with resultant Si–C bond cleavage. This cleavage reaction is primarily reaction (2) but some Si–C cleavage of the $-SiCH_2OC_2H_5$ group of

$$(CH_3)_3SiCH_2Cl + C_2H_5OH \xrightarrow{C_2H_5ONa} (CH_3)_3SiOC_2H_5 + CH_3Cl \quad (2)$$

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(5) When 1.95 g. of chloromethylpentamethyldisiloxane and 9.9 cc. of 2.0 M sodium ethoxide in absolute ethanol were allowed to react in a 25-cc. test-tube, the methyl chloride detected in the trap system varied with the rate of reflux. Vigorous reflux for one hour and forty minutes gave a total reaction of 91%. The methyl chloride escaping to the trap system represented 32% of the reaction. Gentle reflux for a similar period produced 90% total reaction with methyl chloride caught in the traps representing but 21%. In these reactions a hot bath was raised around the reaction tube. In another experiment 150 g. of chloromethylpentamethyldisiloxane and 755 cc. of 2.0 M sodium ethoxide in absolute ethanol were allowed to react in a one liter round-bottomed flask, the mixture being heated to reflux by means of a heating mantle over a forty-five minute period and continued at reflux for four hours. Methyl chloride which escaped from the reaction mixture was not determined but an extent of reaction of 86% in the reaction flask indicates that under such conditions much less methyl chloride escapes. It is, however, possible that when the temperature is raised slowly the course of the reaction is changed and less Si–C cleavage occurs.

ethoxymethyltrimethylsilane (IV) may also occur. The evidence for these conclusions consists of (a) the isolation and characterization of ethoxymethyltrimethylsilane (IV), (b) the determination of the amount of monofunctional methyl siloxane, $(CH_3)_3SiO_{1/2}$, in the product, (c) the measurement of methyl chloride evolved, and (d) the identification of hexamethyldisiloxane and IV in the product by means of the mass spectrometer.

Experimental

Preparation of Chloromethylpentamethyldisiloxane (II) and Chloromethyltrimethylsilane (I).—The method described by Krieble and Elliott[6] was employed in preparing chloromethylpentamethyldisiloxane, $n^{20}D$ 1.4102, b.p. 151–152°.

Chloromethyltrimethylsilane[2] was made by treating a mixture of chloromethylmethyldichlorosilane[1] and chloromethyldimethylchlorosilane[1] with methylmagnesium bromide.[7] Dibutyl ether was used as the solvent. The chloromethyltrimethylsilane used for the comparative reactivity experiments had these properties: b.p. 98.2–98.7° (747 mm.), $n^{20}D$ 1.4169, Cl, 28.4, 28.5 (calcd. for $C_4H_{11}SiCl$, 28.9 Cl).

Iodomethylpentamethyldisiloxane (III).—The technique employed for the preparation of III followed in detail that used by Whitmore and Sommer in the preparation of iodomethyltrimethylsilane.[2] From the reaction of 65.5 g. (0.44 mole) of dry sodium iodide and 49.5 g. (0.25 mole) of chloromethylpentamethyldisiloxane (II) and 500 cc. of dry acetone was obtained upon fractionation 54.5 g. (0.19 mole) of iodomethylpentamethyldisiloxane, b.p. 77° (20 mm.), 187° (757 mm.), $n^{20}D$ 1.4575. The yield was 76%.

Anal. Calcd. for $C_6H_{17}Si_2OI$: I, 44.0. Found: I, 43.6, 43.6.

Reactions with Silver Nitrate.—One gram of chloromethylpentamethyldisiloxane was added to 25 cc. of 20% aqueous silver nitrate. No precipitate formed even after five minutes of boiling. The result was the same when a saturated ethanol solution of silver nitrate was used. Treating chloromethyltrimethylsilane with the same reagents likewise produced no reaction.

One gram of iodomethylpentamethyldisiloxane with 25 cc. of 20% aqueous silver nitrate showed only faint opalescence after five minutes of boiling. In ethanolic silver nitrate at room temperature a faint turbidity developed in a few seconds and after five minutes a curdy precipitate of silver iodide had settled.

Grignard Reagents from Chloro- and Iodomethylpentamethyldisiloxane: $(CH_3)_3SiOSi(CH_3)_2CH_2MgCl$ and $(CH_3)_3SiOSi(CH_3)_2CH_2MgI$.—A mixture of 3.9 g. (0.02 mole) of chloromethylpentamethyldisiloxane, 0.5 g. (0.02 mole) of magnesium turnings and 10 cc. of dry ethyl ether was placed in a 125-cc. flask topped by a reflux condenser and a Drierite–Ascarite tube. Reaction began upon adding a crystal of iodine and heating at gentle reflux for fifteen minutes. After twenty hours the customary titration indicated an 80% yield of $(CH_3)_3SiOSi(CH_3)_2CH_2MgCl$.

A mixture of 2.9 g. (0.01 mole) of iodomethylpentamethyldisiloxane, 0.24 g. (0.01 mole) of magnesium turnings and 5 cc. of dry ethyl ether was allowed to react as above. The reaction began readily without the application of heat. After twenty hours, titration showed a 93% yield of $(CH_3)_3SiOSi(CH_3)_2CH_2MgI$.

Chloromethyltrimethylsilane and Chloromethylpentamethyldisiloxane with Sulfuric Acid.—The general technique of equilibrating methyl silicone oils with sulfuric acid has been described by Patnode and Wilcock.[8] It has also been shown that the relationship existing between the viscosity of equilibrated methyl silicone oils and their functionality can be used as a sensitive analytical tool for the determination of mono- and trifunctional methyl siloxane units in an otherwise difunctional methyl siloxane system.[4]

To 18.0 g. of an equilibrated methyl silicone oil (A) composed of mono- and difunctional units was added 0.042 g. of chloromethyltrimethylsilane. The mixture was then equilibrated as has been described[4] by shaking for forty-eight hours with 0.7 cc. of concentrated sulfuric acid to yield oil B. Oil C was prepared by merely dissolving 0.030 g. of chloromethyltrimethylsilane in 12.0 g. of A. The viscosities obtained lie within the experimental range of accuracy. Had the $-CH_2Cl$ groups been completely split from the Si, the mono-functional groups, $(CH_3)_3SiO^1/_2$, resulting would have lowered the viscosity of oil B to 200 centistokes.[9] It was also found that chloromethyltrimethylsilane could be purified of –SiOSi– containing compounds by shaking with concentrated sulfuric acid. Compounds containing the siloxane linkage dissolved in the acid; the chloromethyltrimethylsilane separated as a second phase. No pressure buildup was noted during such operations to indicate volatile decomposition products.

Oil	Viscosity, centistokes-100°F.
A	242
B	239
C	241

A similar technique was used to check chloromethylpentamethyldisiloxane. Hexamethyldisiloxane and chloromethylpentamethyldisiloxane were equilibrated with octamethylcyclotetrasiloxane, contact with 1.2 cc. of concentrated sulfuric acid being effected for forty-eight hours. The amount of each disiloxane added was equivalent to 1.10 mole per cent monofunctional units. The greater viscosity of the oils prepared with chloromethylpentamethyldisiloxane is believed due to the greater polarity of the C—Cl bond. If no viscosity increase is attributed to the presence of C—Cl bonds, the cleavage of the Si—C bond of the —Si—CH_2Cl group in chloromethylpentamethyldisiloxane was at most 2%. This derives from the fact that a methyl silicone oil composed of mono- and difunctional units has a viscosity of 258 centistokes at 100°F. when the monofunctional unit content is 1.08 mole per cent.[9] The drop in monofunctionality of from 1.10 to 1.08 mole per cent would require but 2% cleavage to a difunctional unit.

Wt. $[(CH_3)_2SiO]_4$, g.	Wt. chain stopper, g.	Viscosity (centistokes-100°F.)
30.0	0.363 $(CH_3)_3SiOSi(CH_3)_3$	242
30.0	.443 $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	257
30.0	.441 $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	259

Measurement of Evolved Methyl Chloride.—Isolation and identification of methyl chloride as the volatile cleavage product of chloromethyl siloxanes has been reported by Elliott and Krieble.[1,6] A readily effected quantitative method of determining methyl chloride evolved is bubbling the gases through sodium ethoxide in absolute ethanol. To the 25-cc. erlenmeyer flask in which the reactions of Table I were run was attached a 45-cm., water-cooled, Liebig reflux condenser. The condenser outlet was in turn connected to a pair of traps (25 cm., 1 cm. diameter) arranged in series with an Ascarite–Drierite tube at the trap outlet. All connections were glass tubing and ground glass joints since rubber absorbs methyl chloride. Into each trap was pipeted 9.9 cc. of 2.0 *M* sodium ethoxide in absolute ethanol. The first trap was heated by the vapors of refluxing acetone to increase the speed of reaction. The final trap was allowed to stand overnight before titration.

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[6] Krieble and Elliott, THIS JOURNAL, **67**, 1810 (1945).

[7] Whitmore, Sommer and Gold, *ibid.*, **69**, 1976 (1947).

[8] Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

[9] D. F. Wilcock, private communication.

When 54.9 cc. (0°, 760 mm.) of methyl chloride was bubbled into the trap system from a gas buret over a one and a half hour period, 94% of the methyl chloride reacted in trap 1. A negligible amount of methyl chloride was indicated in trap 2. In this experiment trap 2 was not allowed to stand before titration. The extent of reaction ($CH_3Cl + NaOC_2H_5 \rightarrow CH_3OC_2H_5 + NaCl$) was determined by diluting with water and titrating with standard sulfuric acid using phenol red as an indicator. Turbidity due to sodium chloride separation was marked after only 5 cc. of methyl chloride had been added.

Reaction of Chloromethyltrimethylsilane and Chloromethylpentamethyldisiloxane with Reagents of Table I.—The experimental setup was that described above. The reagent (9.9 cc.) and I or II were charged to the 25 cc. erlenmeyer flask, the molar ratio of sodium ethoxide, potassium hydroxide or potassium acetate to I or II being two. Heat was supplied by raising a hot silicone oil-bath around the reaction flask. The temperature of each reaction was the reflux temperature of the reaction mixture. At the conclusion of reaction the system was swept with a slow stream of nitrogen. For sodium ethoxide in absolute ethanol and potassium hydroxide in moist butanol the extent of reaction in the erlenmeyer flask and the methyl chloride evolved were then determined by dilution with water and titration with 0.990 *N* sulfuric acid employing a phenol red indicator. Twenty-five per cent. of the titrations were checked against Volhard chloride determinations with excellent agreement. For potassium acetate in glacial acetic acid the extent of reaction was determined by Volhard chloride analysis; no methyl chloride entered the traps. Blanks were titrated for the volume of alkaline reagents pipeted into the reaction flask and traps.

To check on the efficiency of the water condenser, 1.2 g. of chloromethyltrimethylsilane (I) was refluxed in the system with 10 cc. of moist butanol for one hour. Nitrogen was then swept through the system for one hour as the mixture cooled (nitrogen inlet just above neck of erlenmeyer flask). Only a very faint opalescence developed when the diluted trap I contents were tested with silver nitrate.

Reaction of Chloromethyltrimethylsilane (I) with Sodium Ethoxide in Absolute Ethanol.—To a 250-cc. round-bottomed flask were charged 210 cc. of 1.91 *M* sodium ethoxide (0.40 mole) in absolute ethanol and 24.5 g. (0.20 mole) of I (n^{20}_{D} 1.4179, Cl, 29.0%).[10] The condenser and trap system described above were attached. The reaction was continued for four hours at reflux. Titration showed 0.10 mole sodium ethoxide had reacted in the flask, an extent of reaction of 50%. The amount of sodium ethoxide reacted with in traps 1 and 2 was 0.0041 and 0.0004 mole, respectively. This increases the extent of reaction 2% and shows that a minimum of 4% of the total reaction was the cleavage reaction forming methyl chloride. Upon dilution of the reaction product with 1 l. of water, 18.5 g. of a water immiscible phase was separated. This reaction product contained 2.4% by weight of monofunctional methyl siloxane units [0.0054 mole $(CH_3)_3SiO_{1/2}$]. Thus 5% of the chloromethyltrimethylsilane which reacted was subjected to Si—C bond cleavage. Analysis of the reaction product in the mass spectrometer showed the typical main peak for hexamethyldisiloxane (mass number 147). Also the presence of ethoxymethyltrimethylsilane was indicated by significant peaks at mass numbers 103 and 117, corresponding to the fragments $(CH_3)_3SiCH_2O$ and $(CH_3)_2SiCH_2OC_2H_5$, respectively.

A similar experiment was performed on a larger scale. To a 1-liter round bottomed flask were charged 750 cc. of 2.01 *M* sodium ethoxide (1.51 moles) in absolute ethanol and 94.3 g. of I (n^{20}_{D} 1.4176, Cl, 28.2 %). After four hours at reflux, 0.50 mole of sodium ethoxide had reacted in the reaction flask, an extent of reaction of 67%. The amount of reaction in traps 1 and 2 was 0.0042 and 0.0010 mole of sodium ethoxide, respectively. The cleavage reaction resulting in methyl chloride formation is at least 1% of the total reaction. The reaction product was diluted with 2 l. of water and 85 g. of a water immiscible phase (A) separated. Upon washing free of alkali and drying with anhydrous sodium sulfate, A was analyzed by the gel test method[4] and found to have a monofunctional methyl siloxane unit concentration of 3–5% by weight. This represents 0.042 mole $(CH_3)_3SiO_{1/2}$ and shows that Si–C cleavage constituted 8% of the total reaction. Seventy-two grams of the water immiscible phase (A) was then shaken with concentrated sulfuric acid for one-half hour and 25 g. of a sulfuric acid insoluble layer (B) separated. B upon washing and drying was found to have a n^{20}_{D} of 1.4174 and represented unreacted chloromethyltrimethylsilane. The sulfuric acid solution was run slowly into 2 l. of water with cooling and 30 g. of an immiscible phase (C) separated. After drying with anhydrous sodium sulfate, a gel test analysis[4] showed the presence of 21% by weight of monofunctional methyl siloxane units. Degradation of some ethoxymethyltrimethylsilane to $(CH_3)_3SiO_{1/2}$ apparently occurred during solution in sulfuric acid. To rid C of most of these methyl siloxane units (presumably present as hexamethyldisiloxane boiling at 100°) a methyl silicone oil incorporating the $(CH_3)_3SiO_{1/2}$ units in a polymeric system was prepared.[11] Twenty-five grams of C was added to 475 g. of octamethylcyclotetrasiloxane and the solution equilibrated.[3,6] Before fractional distillation 75 cc. of xylene was added to reduce the viscosity. Three fractions boiling from 102.3–102.9° had the same refractive index (n^{20}_{D} 1.3940) and were combined (5.4 g.). Analysis showed this material to be ethoxymethyltrimethylsilane (IV).

Anal. Calcd. for $C_6H_{16}OSi$: C, 54.5; H, 12.2; mol. wt., 132.2. Found: C, 54.5; H, 12.0; mol. wt., 130 and 134.

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Summary

The reactivities of chloromethyltrimethylsilane and chloromethylpentamethyldisiloxane have been compared.

The replacement of an alkyl group attached to the Si holding the chloromethyl group by a trimethylsiloxy group greatly enhances the reactivity to such reagents as potassium acetate in glacial acetic acid and sodium ethoxide in absolute ethanol.

The reaction of sodium ethoxide with chloromethyltrimethylsilane results primarily in attack on the chloromethyl carbon and formation of ethoxymethyltrimethylsilane, a silicon containing ether. A small amount of Si–C cleavage of the $-SiCH_2Cl$ group also occurs. With chloromethylpentamethyldisiloxane the same reagent causes considerable attack at the Si resulting in Si–C cleavage of $-SiCH_2Cl$ group to form methyl chloride. This may be the sole reaction in this system.

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[10] The chloromethyltrimethylsilane was in addition checked both in the General Electric Nier Type (60 degree) mass spectrometer and by the gel test method.[4] In the mass spectrometer the main peak for hexamethyldisiloxane is the fragment of mass number 147, correspondng to $(CH_3)_2SiOSi(CH_3)_3$. No 147 hump appeared when I was run. Also the gel test showed no monofunctional, $(CH_3)_3SiO_{1/2}$ units, present.

[11] Scott, THIS JOURNAL, **68**, 2294 (1946).