only one arrest, and melting is completed at the same temperature at which freezing occurs within the limits of experimental precision. The addition of either component to the other permits the realization of both forms. This fact has been demonstrated for compositions of approximately 99 mole per cent. of either of the nitriles. This behavior is identical with that observed by Smith[6,7] in his study of hydrocarbon systems, and is apparently a common phenomenon in systems of aliphatic compounds of high molecular weight.[14]

When the β-form melts it does not form an isotropic liquid immediately but goes through a series of mesomorphic states as represented by the transition curves T, U and V, finally becoming clear along curve W. Samples in this concentration range were examined by means of a polarizing microscope and gave no evidence of any crystalline structure at temperatures above the curves AM, MN, NB. Curve W was obtained readily on visual observation. There was evidence for curves T, U and V from thermal data, but the changes in direction of the curves were insufficient to establish definitely the location of these transitions. This was accomplished by determining the solubility in acetone and in cyclohexane of several samples at various concentrations of solute and extrapolating to the pure solute. Points obtained in this manner have been used in conjunction with the thermal data in the establishment of curves T, U and V. Solubility measurements of this sort on the pure nitriles indicated the existence of only one form since in both cases extrapolation of all solution temperatures gave only one melting point for each.

A mixture of stearonitrile and palmitonitrile of any composition whatsoever, if initially heated to a temperature above curve W, will remain entirely an isotropic liquid for an indefinite period on cooling so long as the temperature does not fall below the corresponding point on the α-liquidus (AC, CD, DB). Likewise, if a sample has been cooled and allowed to transform to the β-modification, it may be warmed but will not become an isotropic liquid below the corresponding temperature on curve W. Samples in the composition range 10–80 mole per cent. stearonitrile in sealed glass tubes have exhibited the above described behavior when held at the proper temperatures in a water-bath over a period of ten days.

Summary

1. The investigation of the system stearonitrile–palmitonitrile shows that mixtures of these compounds exhibit dimorphism, although no such behavior was observed in the case of the pure components.

2. The α-form shows the formation of a compound containing one mole of each component, with a meritectic or incongruent melting point.

3. The α-form can be obtained only by cooling a molten mixture of the nitriles.

4. The β-form, which can be obtained only by transition from the α-form, exhibits the same type of system as the α-form.

5. The α-form melts to form an isotropic liquid whereas the β-form passes through a series of mesomorphic states before producing an isotropic liquid.

CHICAGO, ILLINOIS RECEIVED DECEMBER 1, 1944

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[14] Unpublished observations in this Laboratory.

[CONTRIBUTION FROM GENERAL ELECTRIC RESEARCH LABORATORY]

The Vapor Phase Alkylation and Hydrogenation of Chlorosilanes

BY DALLAS T. HURD

In 1919 Stock and Somieski[1] reported the methylation of monochlorosilane and dichlorosilane to methylsilane and dimethylsilane, respectively, by the reaction of the chlorosilanes with zinc dimethyl at room temperature. Attempts in this Laboratory to apply this reaction to the methylation of silicon tetrachloride and dimethyldichlorosilane have been made using aluminum trimethyl and mercury dimethyl as well as zinc dimethyl. Although temperatures as high as 150° have been employed, such attempts have been without success. The mixtures have stood for over four months with no indication of any reaction.

It recently has been found possible to effect the alkylation of silicon tetrachloride and various organochlorosilanes by passing the vapors of a chlorosilane together with an alkyl halide over finely divided aluminum, zinc or other reactive metal at elevated temperatures, 300–500°. A reaction occurs under these conditions with replacement of part or all of the chlorine on the chlorosilane by alkyl groups.

In addition it has been found that the reaction of a chlorosilane with hydrogen gas or with hydrogen chloride under similar conditions results in the removal of chlorine and the formation of Si–H bonds. The halogen involved in these reactions is removed as a chloride of the particular metal used. Although aluminum and zinc have so far been found to be the most suitable reactive metals, others may possibly be of use.

Experimental

Apparatus.—The reactions were generally carried out in vertical Pyrex tubes 3" in diameter and 24" long, although

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[1] A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

a few runs were made in horizontal 1″ tubes of the same length. The tubes were heated by conventional electric furnaces. The usual charge consisted of about 500 g. of 20-mesh granular aluminum or zinc, although occasionally material as small as 80-mesh was employed. The reactants were charged into the tubes in the vapor phase, the alkyl halide or hydrogen being first bubbled through the chlorosilane in a gas washing bottle and the mixed vapors then passed into the bottom of the vertical reaction tube. The concentration of chlorosilane in the gas stream was adjusted by varying the temperature of the gas washing bottle. The outlet from the reaction tube was of 1″ diameter tubing or larger and led directly into a large trap held at 100° and designed to retain the aluminum chloride which is produced by the reaction of aluminum and which sublimes out of the reaction zone. The reaction products were then condensed by a water-cooled condenser, and if volatile products were expected the receiver was followed by a condenser held at −80°. Distillation analyses of the products generally were made in a 100-plate Stedman column although some fractionations could be carried out in 20-plate laboratory stills of conventional design.[2]

Alkylation

A. Silicon Tetrachloride.—Mixed vapors of silicon tetrachloride (83.5% Cl) and methyl chloride in 1:2 ratio by volume were passed over aluminum at 350–400°. A reaction ensued with the formation of aluminum chloride and a liquid product having a chlorine content of 78.9%. As the amount of product was too small for precise fractionation of the methyl chlorosilanes presumably present, the liquid was hydrolyzed in a mixture of ether and ice. Evaporation of the resulting ether solution left a resinous deposit which resembled the methyl silicone polymers reported by Rochow and Gilliam.[3]

B. Methyl Trichlorosilane.—Mixed vapors of pure methyltrichlorosilane[4] (liquid density 1.27) and methyl chloride in 1:1 ratio were passed over aluminum granules at 450° to produce aluminum chloride and a liquid product of density 1.13. A distillation analysis of the product revealed a composition of 21% trimethylchlorosilane[5] (b. p. 57°, 32.63% Cl), 11% of dimethyldichlorosilane[4] (b. p[6] 70°, 54.95% Cl), and traces of methyldichlorosilane. (b. p. 41°), the remainder being largely unreacted methyltrichlorosilane. A similar experiment at 350° gave a product containing 6.3% trimethylchlorosilane and 4.5% dimethyldichlorosilane, in addition to unreacted starting material. A small scale run at 400° with an excess of methyl chloride yielded a product containing silicon tetramethyl, b. p. 26°.

C. Dimethyldichlorosilane.—Mixed vapors of pure dimethyldichlorosilane[4] (liquid density 1.067) and methyl chloride in 1:1 ratio were passed over aluminum at 350° to produce aluminum chloride and a liquid product of density 0.983. A distillation analysis of the product revealed a composition of approximately 30% trimethylchlorosilane, a trace of silicon tetramethyl and 70% unreacted dimethyldichlorosilane. A small scale run with an excess of methyl chloride yielded a product in which the content of trimethylchlorosilane was estimated at over 50%.

In a similar experiment the mixed vapors of pure dimethyldichlorosilane (54.95% Cl) and methyl chloride in 1:1 ratio were passed over 80-mesh granular zinc at 375°. A reaction ensued, considerable amounts of zinc chloride were formed, and a liquid product (47.23% Cl) was condensed. The chlorine content of the product indicated the presence of *ca.* 30% trimethylchlorosilane. Although the total amount of sample was too small for a precise distillation analysis, fractionation showed that a substantial portion of the product was trimethylchlorosilane.

Similarly, the mixed vapors of dimethyldichlorosilane and ethyl chloride in 1:1 ratio were passed over aluminum at 350°. A reaction ensued with the production of aluminum chloride and a liquid product of density 1.05. Distillation of this product yielded a small amount of material boiling at 88–92° which, since it exhibited the chemical properties of a trialkylmonohalosilane, was believed to be dimethylethylchlorosilane.

D. Dimethyldibromosilane.—The vapors of pure dimethyldibromosilane[7] and methyl bromide were mixed in 2:1 ratio and were passed over aluminum at 350°. A reaction occurred with the formation of aluminum bromide and a liquid product. Fractionation of this product yielded trimethylbromosilane boiling at 80–81° and having a bromine content of 53.25% (theoretical Br, 52.23%).[7]

Hydrogenation

A. Silicon Tetrachloride.—Silicon tetrachloride vapor was mixed with hydrogen gas in 1:1 ratio and was passed over aluminum at 400°. Aluminum chloride was formed and a liquid product was condensed, a portion of which, when hydrolyzed in water and then treated with aqueous sodium hydroxide, dissolved with vigorous evolution of hydrogen, indicating the presence of Si-H bonds. A distillation of the product revealed about 3–5% of dichlorosilane,[6] SiH_2Cl_2, b. p. 8°, and 25% of trichlorosilane, $SiHCl_3$, b. p. 31.8°, the remainder being largely unreacted silicon tetrachloride. No evidence for the formation of disilanes was observed.

Silicon tetrachloride vapor and hydrogen mixed in 1:2 ratio and passed over granular zinc at 350–400° reacted to produce zinc chloride and a liquid whose hydrolysis product dissolved in aqueous alkali with a vigorous evolution of hydrogen. Distillation revealed the presence of volatile compounds containing silicon-hydrogen bonds, although no quantitative separation was made. Similar experiments carried out with magnesium and iron yielded only traces of silanes; no conclusive data were obtained.

B. Methyltrichlorosilane.—The vapor of pure methyltrichlorosilane was mixed with hydrogen gas in 1:1 ratio and passed over aluminum at 450°. Aluminum chloride was produced and a liquid product (density 1.21) was condensed. A portion of this product was hydrolyzed and the resulting gel was found to react with dilute alkali with vigorous evolution of gas. Distillation of the product revealed the presence of approximately 5% of methyldichlorosilane,[6] $(CH_3)HSiCl_2$, b. p. 41°, plus smaller amounts of unidentified volatile material boiling below room temperature and also containing silicon-bonded hydrogen. Other small scale hydrogenations of methyltrichlorosilane yielded products containing from 4 to 10% of methyldichlorosilane.

A similar experiment with hydrogen chloride and methyltrichlorosilane vapor in 1:2 ratio over aluminum at 350° yielded aluminum chloride and a product of density 1.25. Distillation of this product revealed the presence of volatile compounds containing silicon-bonded hydrogen although no quantitative data were obtained.

C. Silicochloroform.—Silicochloroform ($SiHCl_3$) and hydrogen in *ca.* 1:2 ratio were passed over 20-mesh aluminum at 350°. Aluminum chloride was produced and a liquid product was collected in a trap at −80° followed by a trap at −190°. Distillation of the product was carried out by separation of the spontaneously inflammable monosilane (SiH_4), b. p. −112°, in a vacuum chain followed by fractionation of the remainder in a simple packed

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[2] Grateful acknowledgment is made to Mr. E. M. Hadsell for conducting the distillation analyses reported in this paper. Routine analytical distillations of chlorosilanes are made daily in this Laboratory and the physical constants of the methylchlorosilanes are known with a high degree of precision. Such analyses include determinations of the density and chlorine content of each fraction as a check on the identity of the component.

[3] E. G. Rochow and W. F. Gilliam, THIS JOURNAL, **63**, 798 (1941).

[4] W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *ibid.*, **63**, 801 (1941).

[5] W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

[6] A. Stock and C. Somieski, *Ber.*, **52B**, 695 (1919).

[7] These compounds previously have been prepared and characterized by Drs. W. F. Gilliam and R. N. Meals of this Laboratory and will be reported later (*cf.* E. G. Rochow, THIS JOURNAL, **67**, 963 (1945)).

column operating at low temperatures. The composition of the crude product was found to be: 1-2% of monosilane (SiH_4), 1-2% of monochlorosilane[6] (SiH_3Cl, b. p. −31°) and *ca.* 15% of dichlorosilane[6] (SiH_2Cl_2, b. p. +8°), the remainder being largely unreacted silicochloroform.

D. Dimethyldichlorosilane.—Attempts to hydrogenate this material generally were without success. In no case, except one with zinc as the reactive metal, did the hydrolyzed product show any gas evolution upon treatment with alkali, and even in the exceptional case the evolution of hydrogen was so slight as to be considered inconclusive.

"Automethylation" Reactions

In attempting to hydrogenate dimethyldichlorosilane with hydrogen over aluminum, several experiments were made at rather high temperatures (450–500°). In these runs some aluminum chloride was formed, and in one case the product had a chlorine content of only 34.88% (theoretical for $(CH_3)_2SiCl_2$, 54.95). Distillation of this product revealed the presence of a large proportion of trimethylchlorosilane. A similar experiment with methyltrichlorosilane and hydrogen over aluminum at 500° yielded a product containing nearly 17% of dimethyldichlorosilane as well as the methyldichlorosilane previously mentioned. In both of these cases a considerable darkening of the aluminum took place, presumably by the deposition of free silicon as this darkening did not occur when methyl chloride was present.

Discussion

It appears that the mechanism of the alkylation reaction with aluminum involves first the reaction of an alkyl halide with aluminum metal to form alkyl aluminum halides, and then the reaction of the alkyl aluminum halide with the chlorosilane to form an alkyl–silicon bond and aluminum chloride.

$$2Al + 3CH_3Cl \longrightarrow CH_3AlCl_2 + (CH_3)_2AlCl \quad (1)$$

$$CH_3AlCl_2 + (CH_3)_2SiCl_2 \longrightarrow (CH_3)_3SiCl + AlCl_3 \quad (2)$$

Moreover, the reaction of the methylchlorosilanes themselves with aluminum metal at higher temperatures seems to be additional evidence in favor of the proposed mechanism, for by Gilman's[8] rules governing the reactivities of metal alkyls, if the reaction

$$(Si\text{-}Cl) + (Al\text{-}R) \longrightarrow (Si\text{-}R) + (Al\text{-}Cl)$$

takes place one would expect that the reaction

$$(Si\text{-}R) + Al \longrightarrow Si + (Al\text{-}R)$$

also would occur. It is believed that the high temperature "automethylation" of a methyl chlorosilane with aluminum involves the following steps: first, the reaction of the methylchlorosilane with aluminum metal to form methyl aluminum chlorides and free silicon

$$(CH_3)_nSiCl_{4-n} + Al \longrightarrow (CH_3)_xAlCl_{3-x} + Si$$

then the reaction of the methylaluminum chlorides with more methylchlorosilane according to the before mentioned alkylation reaction. The net result of the process is the methylation of some molecules of methylchlorosilane at the expense of others which are reduced to free silicon. The chlorine which was attached to silicon appears as aluminum chloride.

A similar set of reactions can be proposed to explain alkylation of chlorosilanes using zinc or other metal in place of the aluminum, provided that it meets Gilman's rules by being more reactive than silicon.

The alkylation reaction seems to be quite general and presumably should be applicable to the alkylation of any halosilane. Actually the readiness with which different halosilanes can be alkylated varies considerably. Furthermore, the stability of the metal alkyl compounds involved as intermediates may have a great effect upon the yield of product obtained, for ethylation of dimethyldichlorosilane is much less efficient than methylation, presumably because of the lesser stability of the ethylaluminum compounds.

On the basis of this discussion, the criteria for the reactive metal appear to be:

1. It must be more electropositive than silicon, *i.e.*, capable of reducing the silicon–halogen bond.
2. It should form metal alkyl compounds by reaction with the alkyl halide at elevated temperatures.

The mechanism whereby hydrogenation of a chlorosilane is effected is as yet obscure. It might be postulated that transient hydrides of the reactive metal involved may react like the metal alkyls in a reaction such as:

$$M + H_2 \longrightarrow (MH)$$

$$(M\text{-}H) + (Si\text{-}Cl) \longrightarrow (Si\text{-}H) + (M\text{-}Cl)$$

In view of the general absence of disilane formation in the runs made so far, it seems less probable that any mechanism involving a simple reduction of the chlorosilane followed by a reaction with hydrogen can account for the observed results. The only criterion found so far for the reactive metal is that it be more electropositive than silicon.

As yet unexplainable is the variation in the reactivity of the chlorosilanes in the alkylation and hydrogenation reactions. Silicon tetrachloride is methylated only with difficulty, methyltrichlorosilane more readily, while the methylation of dimethyldichlorosilane proceeds quite easily. Although no direct methylation of trimethylchlorosilane has been attempted, the very small yields of silicon tetramethyl and the proportionately large yields of trimethylchlorosilane in the methylation products of the other methylchlorosilanes lead to the conclusion that it is relatively difficult to methylate this material.

In the hydrogenation reaction the situation seems to be reversed, *i.e.*, silicon tetrachloride is hydrogenated with relative ease, as is silicochloroform, methyltrichlorosilane less readily, while attempts to hydrogenate dimethyldichlorosilane have been unsuccessful. No hydrogenation of trimethylchlorosilane has as yet been attempted.

Progress is being made in the extension of the above reactions to the alkylation and hydrogenation of volatile halides of other elements.

Summary

1. A vapor phase reaction has been found whereby chlorosilanes may be alkylated by reac-

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[8] Henry Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 520–524.

tion with alkyl halides in the presence of a suitable metal at elevated temperatures.

2. A similar reaction whereby chlorosilanes may be hydrogenated with hydrogen gas or hydrogen chloride to form silicon–hydrogen compounds also has been found. It has been possible, in effect, to produce SiH_4 from $SiCl_4$.

3. The mechanism of the alkylation and hydrogenation reactions has been discussed.

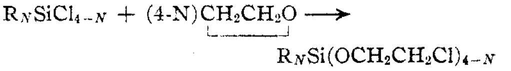
SCHENECTADY 5, N. Y. RECEIVED JUNE 11, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. II. 2-Chloroethoxysilanes

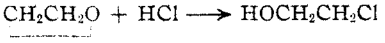
BY ROBERT O. SAUER AND WINTON PATNODE

The usual method of converting halogenosilanes to their alkoxy derivatives, namely, alcoholysis, possesses several obvious disadvantages, most of which attend the concomitant and vigorous evolution of hydrogen halide. In the hope of eliminating this corrosive, volatile by-product we have undertaken a study of the etherification of halogenosilanes by various epoxides. In the present paper the reaction products of several chlorosilanes with ethylene oxide[1] are described (eq. 1: R = H—, CH_3—, C_6H_5—).



$$R_NSiCl_{4-N} + (4\text{-}N)\underline{CH_2CH_2O} \longrightarrow R_NSi(OCH_2CH_2Cl)_{4-N} \quad (1)$$

Etherification with this reagent presumably occurs in two steps, the first and perhaps rate-determining one being the addition of hydrogen chloride (generally present in chlorosilanes in at least traces) to the ethylene oxide (eq. 2).

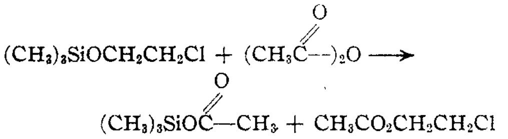


$$\underline{CH_2CH_2O} + HCl \longrightarrow HOCH_2CH_2Cl \quad (2)$$

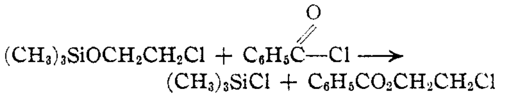
The second step is then the normal alcoholysis reaction accompanied by the regeneration of the hydrogen chloride.

In support of this hypothesis we have noted an unmistakable increase in the reaction rate when hydrogen chloride is added. We are presently unable to state, however, whether or not a chlorosilane will react at all with anhydrous ethylene oxide. This point is of interest in view of the statement[2] that silicon tetrachloride is without effect on ethylene oxide at room temperature.

To demonstrate unequivocally the structure of the ethers obtained in the reactions of equation 1 we have shown that the products from silicon tetrachloride and either ethylene chlorohydrin or ethylene oxide are identical. The chlorine atoms in the latter product have been replaced by piperidino groups yielding, after treatment with hydrogen chloride, the known 2-piperidinoethanol hydrochloride. Acetic anhydride and benzoyl chloride reacted with the chloroethoxy ether from trimethylchlorosilane according to equations 3 and 4, respectively



$$(CH_3)_3SiOCH_2CH_2Cl + (CH_3\overset{O}{\overset{\|}{C}}-)_2O \longrightarrow (CH_3)_3SiO\overset{O}{\overset{\|}{C}}-CH_3 + CH_3CO_2CH_2CH_2Cl \quad (3)$$



$$(CH_3)_3SiOCH_2CH_2Cl + C_6H_5\overset{O}{\overset{\|}{C}}-Cl \longrightarrow (CH_3)_3SiCl + C_6H_5CO_2CH_2CH_2Cl \quad (4)$$

indicating again that the chlorine atom is in the 2-position and further that no rearrangement of the methyl groups attached to silicon has occurred during etherification.

Experimental

Preparations.—Two general methods were used in this work. In the first (A) ethylene oxide gas was bubbled slowly through the boiling or heated chlorosilane at pressures a few millimeters above atmospheric, relying on a water-cooled reflux condenser to return the vaporized reaction mixture to the heating flask. As the reactions were generally exothermic little heating was required. In the second method (B) the ethylene oxide under pressure (maximum, 12–14 lb. gage) was brought into contact with the chlorosilane in a pressure bottle. In a few cases the rate of addition of ethylene oxide had to be controlled to prevent too great a rise in temperature; in general, the latter was kept at or below 60°. The products were purified by fractional distillation, usually at reduced pressure. The yields were generally 80–95% of the theoretical based on the chlorosilanes.

Table I lists the compounds prepared, their physical properties, the method of synthesis and the yields obtained.

Analyses.—The chlorine analyses recorded in Table I were made by three different methods. In Methods I and II the samples were digested in Pyrex test-tubes with concentrated aqueous (I) or ethanolic (II) potassium hydroxide solution for one and one-half to three hours. The chloride ion was then determined volumetrically by a Volhard titration. In weighing out the samples a variety of techniques were used depending upon the volatility of the sample. Method III utilized the regular semi-micro Parr bomb technique (combustion with sodium peroxide and sugar) followed by a Volhard titration. Blanks in all these procedures were found to be negligible.

Because instability of the ethers containing silicon-hydrogen bonds was anticipated, these substances were also analyzed for carbon, hydrogen and silicon (see footnotes to Table I).

Proof of Structure.—Tetrakis-2-chloroethyl silicate was prepared by treating silicon tetrachloride with four moles of ethylene chlorohydrin.[3] The product (n^{20}D 1.4640;

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[1] Compare the analogous reaction with the phosphorus halides [I. G. Farbenind. A.-G., British Patent 338,981, Aug. 31, 1929; *C. A.*, **25**, 2437 (1931)].

[2] Staudinger and Schweitzer, *Ber.*, **62**, 2011 (1929).

[3] Dearing and Reed [THIS JOURNAL, **50**, 3058 (1928)] report this reaction, but state that they could not distill the product without decomposition, even at reduced pressures. Taurke [*Ber.*, **38**, 1661 (1905); *Ann.*, **143**, 217 (1905)] first prepared tetrakis-2-chloroethyl silicate from silicon tetrachloride and ethylene glycol.