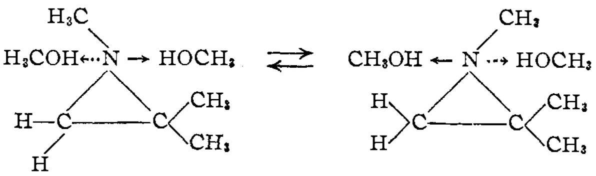
"width" of the ring methylene line at very fast exchange. The results are shown in Fig. 6. The activation energy obtained is $\Delta E = 6.4 \pm 0.6$ kcal. and $\nu_0 = 1 \times 10^9$ sec.$^{-1}$.

The measured activation energies for the two substituted 1-methylaziridines here investigated are very much smaller than most of the previous estimates and the experimental value obtained by Heeschen for 1-methylaziridine itself.[9] It is interesting that our activation energies are quite close to the calculated value of 6 kcal. given by Manning[10] for ammonia. The frequency factors, however, are much below the "normal" value of 10^{13}, indicating that the transmission coefficients are much smaller than unity. This, however, is not too surprising in view of the similar order of magnitude for ν_0 obtained for another "unimolecular" reaction of this type, namely, the rotation around the C–N bond in amides.[11,12]

The effect of solvents on the inversion of I is shown in Figs. 4 and 5. Both polar (methanol) and non-polar (carbon tetrachloride) solvents reduced the activation energy and frequency factor. It should be noted that the rate of inversion of I is considerably slower in methanolic solution than in the pure liquid or carbon tetrachloride. This has been attributed to the effect of hydrogen bonding between the hydroxyl group in methanol and the nitrogen atom in the aziridine ring.[4] However, it seems quite significant that the effect on such hydrogen bonding shows up in a greatly decreased frequency factor rather than in an increase in activation energy. This may be due to a bimolecular mechanism for inversion in methanol solution where one methanol molecule attacks the rear of the nitrogen in an imine–methanol, hydrogen-bonded complex.



It is clear that further experimental and theoretical investigation of these processes would be very fruitful.

Experimental

1-Methyl-2,2-dimethylaziridine (b.p. 67.8–68.2°) was prepared by alkaline treatment of the sulfonate ester salt of 2-N-methylamino-2-methyl-1-propanol. 1-Methyl-2-methyleneaziridine (b.p. 52.2–52.6°) was kindly supplied by Dr. A. T. Bottini.

All measurements were taken with the Varian model 4300B spectrometer. Frequency calibration was accomplished by the side-band technique. All measurements were performed at a proton frequency of 60 Mc., except those presented in Fig. 4, which were taken at 40 Mc. The measurements on pure I were taken at both 40 and 60 Mc.; the results were identical within the experimental accuracy.

Two types of inserts for heating and cooling were used: (1) the type described by Shoolery and Roberts[13] (supplied commercially by the Varian Associates) and (2) a modified type described by Fraenkel and Franconi.[12] The concentration of the solution of I in methanol and carbon tetrachloride was about 25% by volume. The methanol was made slightly basic by dissolving a small quantity of sodium in it. The purpose of the base was to inhibit reaction between the imine and methanol.[4]

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[9] The reason for the sizable differences between the measured values ΔE for our compounds and 1-methylaziridine[5] is not clear to us. It seems unlikely that the rather small change in structure could account for all of the discrepancy, which appears to be well outside experimental error.

[10] M. F. Manning, *J. Chem. Phys.*, **3**, 136 (1935).

[11] H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

[12] G. Fraenkel and C. Franconi, to be published.

[13] J. N. Shoolery and J. D. Roberts, *Rev. Sci. Instr.*, **28**, 61 (1957).

PASADENA, CALIF.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part V. The Addition to Allyl and Methallyl Chlorides

BY JOHN W. RYAN, GERALD K. MENZIE AND JOHN L. SPEIER

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The addition of trichlorosilane, methyldichlorosilane, dimethylchlorosilane and phenyldichlorosilane to allyl and methallyl chloride was studied. In the presence of chloroplatinic acid, each of these forms propylene from allyl chloride as well as 3-chloropropyl- and *n*-propylsilane derivatives. With methallyl chloride little or no isobutylene or isobutylsilane derivative forms under the same conditions and excellent yields of 3-chloro-2-methylpropylsilanes are obtained. The preparation and properties of twenty-nine 3-chloroalkylsilicon compounds are described.

The addition of four hydrides of silicon to allyl and methallyl chlorides in the presence of chloroplatinic acid was studied. The four hydrides, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, and phenyldichlorosilane each formed only one adduct, either the 3-chloropropyl- or 3-chloro-2-methylpropylsilane derivatives with allyl or methallyl chloride. No isomeric adducts such as 2-chloro-1-methylethylsilane were detectable.

Some of the compounds described in this paper have been reported previously. Sommer, *et al.*,[1] separated 3-chloropropyltrichlorosilane from a mixture obtained by chlorination of propyltrichlorosilane. More recently, Wagner[2] reported the synthesis of this compound from trichlorosilane and allyl chloride in 51% yield in the presence of platinized carbon at 160–166° in an autoclave. Wagner found propyltrichlorosilane and tetrachlorosilane as by-products.

Petrov[3] apparently had difficulties with this system and reported that under essentially the

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[1] L. H. Sommer, E. Dorfman, G. H. Goldberg and F. C. Whitmore, THIS JOURNAL, **68**, 488 (1946).

[2] G. H. Wagner, U. S. Patent 2,637,738, May 5, 1953.

[3] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov and G. V. Odabashyan, *Izvestia Akad. Nauk. S.S.S.R.*, **10**, 1206 (1957).

same conditions trichlorosilane and allyl chloride formed only a small amount of gas. No adducts were detected. The same reagents heated with acetyl peroxide[4] or irradiated with γ-radiation[5] also formed 3-chloropropyltrichlorosilane.

3-Chloropropylmethyldichlorosilane has been made from allyl chloride and methyldichlorosilane in several investigations. γ-Radiation[5] gave only a 4% yield. Better results (30% yield) were obtained[6] by use of 1% platinized carbon at 160°. In this case large amounts of methylpropyldichlorosilane and methyltrichlorosilane were also formed. Petrov, *et al.*,[3] pursued this method further and concluded that although platinized carbon was an ineffective catalyst with trichlorosilane, it was effective with silanes such as RCl_2SiH and R_2ClSiH if R is methyl, ethyl, propyl or butyl. They advanced an hypothesis that propylsilanes form in consecutive reactions outlined in equations 1 and 2.

$$\equiv SiH + CH_2{=}CRCH_2Cl \longrightarrow \equiv SiCH_2CHRCH_2Cl \quad (1)$$

$$\equiv SiCH_2CHRCH_2Cl + \equiv SiH \longrightarrow \equiv SiCH_2CHRCH_3 + \equiv SiCl \quad (2)$$

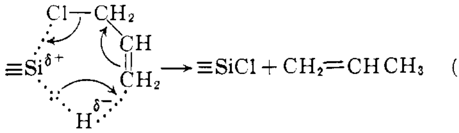
In this case R could be H or methyl.

We have found that use of chloroplatinic acid[7] brings about rapid addition reactions with either allyl or methallyl chloride. As nearly as the data permit judgment, temperature has no effect upon the distribution of products or yields between about 40 and 140°.

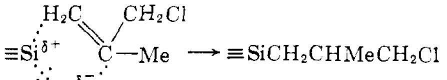
Our results indicate that the reaction of eq. 2 does not take place, at least with chloroplatinic acid as the catalyst. The heating of chloropropylsilanes with several silicon hydrides and chloroplatinic acid caused no reaction under the conditions of an addition reaction. During experiments with allyl chloride, however, propylene was observed. Propylene might form by a simple metathesis.

$$\equiv SiH + ClCH_2CH{=}CH_2 \longrightarrow \equiv SiCl + HCH_2CH{=}CH_2 \quad (3)$$

To test the likelihood of this, benzyl chloride, which is much like allyl chloride in reactivity but which does not form an adduct, was heated with methyldichlorosilane and chloroplatinic acid. No reaction occurred. Methallyl chloride formed adducts in excellent yield, but formed neither isobutylene nor isobutylsilanes in appreciable amounts. These facts suggest that possibly the propylene is liberated from a reaction complex formed during the addition reaction. A plausible complex might be represented according to eq. 4.


(4)

Methallyl chloride is less likely to form isobutylene because the negative hydride hydrogen should be strongly oriented toward the tertiary carbon,


(5)

The relative extent of each of these two modes of orientation in allyl chloride is thought to control the ratio of 3-chloropropylsilanes/propylene which results.

The formation of β-chloroisopropylsilanes followed by immediate decomposition leads to the same result shown in eq. 4. Because of the relative stability of β-chloroisopropylsilanes,[8] it seems unlikely that they should decompose. Further experiments in the presence of platinum are required to decide if the two-step mechanism is a plausible one to explain the formation of propylene.

Propylsilanes observed in the products are readily explained as formed by a subsequent addition of silicon hydrides to propylene.

$$\equiv SiH + CH_3CH{=}CH_2 \longrightarrow \equiv SiCH_2CH_2CH_3 \quad (6)$$

Although the mechanism of catalysis in these reactions is not known, the catalyst does influence the amount of allyl chloride which is converted to propylene. An example of this influence was found by use of 0.5% palladium-on-alumina. In the presence of this catalyst allyl chloride and methyldichlorosilane in a flask at reflux formed propylene and methyltrichlorosilane nearly quantitatively with no indication of any adducts. Petrov[3] observed that ethyldichlorosilane and allyl chloride with a palladium catalyst in a bomb formed only ethyltrichlorosilane and ethylpropyldichlorosilane.

The ratio of allyl chloride to the silicon hydride is also important. In the presence of excess allyl chloride, the formation of propylsilanes is reduced. This presumably is due to the suppression of the addition of silicon hydrides to propylene in the presence of allyl chloride. It does not seem to be due to a reduction in the amount of propylene formed.

Both the 3-chloropropyl- and 3-chloro-2-methylpropylsilicon compounds are quite stable, and the formation of alkoxysilanes or of polysiloxanes (shown in Table I) from them presented no difficulties. Neither dilute acids nor bases attack the chloroalkyl groups.

However, the 1,3-bis-(3-chloro-2-methylpropyl)-tetramethyldisiloxane (XX) heated to about 260° slowly liberated isobutylene. Compound (XXV), 1-chloro-3-(3-chloro-2-methylpropyl)-tetramethyldisiloxane, was isolated as the other product. In the presence of a catalytic amount of aluminum chloride at 100°, isobutylene formed rapidly. Strong hot aqueous sodium hydroxide caused the liberation of methylcyclopropane. This is quite analogous to the formation of cyclopropane found by Sommer[1] by treatment of 3-chloropropylsilanes with strong alkali.

Experimental

Chlorosilanes.—Two methods, A and B, used to prepare the chloroalkylchlorosilanes are illustrated below.

3-Chloropropyltrichlorosilane (I). **Method A.**—Allyl chloride (0.5 mole), trichlorosilane (0.5 mole) and chloroplatinic acid (about 10^{-5} mole) were heated to reflux in a

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[4] E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **70**, 484 (1948).

[5] A. M. El-Abbady and L. C. Anderson, *ibid.*, **80**, 1737 (1958).

[6] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev and A. D. Petrov, *Doklady Akad. Nauk. S.S.S.R.*, **106**, 76 (1956).

[7] J. L. Speier, J. A. Webster and G. H. Barnes, THIS JOURNAL, **79** 974 (1957).

[8] L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1186 (1954)

TABLE I

3-CHLOROALKYLSILICON COMPOUNDS

No.	Structure	Yield, %	B.p.		$n^{25}D$	d^{25}_4	R_D		Silicon, %		Analyses	
			° C.	Mm.			Found	Calcd.[a]	Found	Calcd.	Found	Calcd.
I	$Cl_3SiCH_2CH_2CH_2Cl$[b]	66[c]	181.5	750	1.4638	1.354	0.2041	0.2029				
II	$Cl_2MeSiCH_2CH_2CH_2Cl$[d]	60[e]	186	750	1.4597	1.199	.2278	.2268	14.7	15.0		
III	$ClMe_2SiCH_2CH_2CH_2Cl$	50[e]	179	750	1.4488	1.043	.2572	.2566	16.4	16.7	171[i]	171
IV	$Me_3SiCH_2CH_2CH_2Cl$[f]		151.5	752	1.4288	0.8718	.2956	.2941				
V	$Cl_3SiCH_2CHMeCH_2Cl$	92[c]	194	750	1.4662	1.310	.2112	.2109	12.4	12.5	75.3[i]	75.5
VI	$Cl_2MeSiCH_2CHMeCH_2Cl$[g]	100[e]	106	40	1.4620	1.168	.2352	.2339			102.8[i]	104
VII	$ClMe_2SiCH_2CHMeCH_2Cl$	87[e]	89	25	1.4522	1.030	.2619	.2621	15.1	15.2	185.2[i]	185.9
VIII	$Me_3SiCH_2CHMeCH_2Cl$		93	73	1.4345	0.8769	.2973	.2973	17.1	17.1		
IX	$C_6H_5Cl_2SiCH_2CH_2CH_2Cl$	62	141–2	10	1.5332	1.241	.2502	.2498	11.0	11.1	126.1	126.8
X	$(MeO)_3Si(CH_2)_3Cl$	97	195	750	1.4183	1.077	.2341	.2354	14.1	14.1		
XI	$(MeO)_2MeSi(CH_2)_3Cl$	78	185	750	1.4242	1.019	.2505	.2516	15.3	15.0		
XII	$(MeO)Me_2Si(CH_2)_3Cl$	75	169.5	751	1.4283	0.953	.2698	.2707	16.9	16.8		
XIII	$(EtO)_3Si(CH_2)_3Cl$	85	124	30	1.4175	1.002	.2512	.2522	11.6	11.8		
XIV	$(EtO)_2MeSi(CH_2)_3Cl$	76	109	30	1.4232	0.973	.2618	.2621	13.3	13.5		
XV	$(EtO)Me_2Si(CH_2)_3Cl$[h]	69	87	30	1.4270	0.932	.2755	.2755	15.5	15.5		
XVI	$(MeO)_3SiCH_2CHMeCH_2Cl$	90	202.5	747	1.4223	1.059	.2401	.2417	13.2	13.2		
XVII	$(MeO)_2MeSiCH_2CHMeCH_2Cl$	94	193.5	756	1.4289	1.009	.2555	.2573	14.2	14.2		
XVIII	$(MeO)Me_2SiCH_2CHMeCH_2Cl$	89	181	751	1.4331	0.948	.2741	.2755	15.5	14.8		
XIX	$O[SiMe_2(CH_2)_3Cl]_2$		128	7	1.4484	.9958	.2689	.2685	19.5	19.5		
XX	$O[SiMe_2CH_2CHMeCH_2Cl]_2$		Dec.		1.4528	.9886	.2733	.2741	18.2	17.8	45.8[j]	45.8
											9.1[k]	8.95
XXI	$[OMeSi(CH_2)_3Cl]_n$				1.4709	1.171	.2386	.2401	20.6	20.8	26.0[l]	25.6
XXII	$[OMeSiCH_2CHMeCH_2Cl]_n$				1.4700	1.127	.2475	.2487	18.6	18.6		
XXIII	$O[Si(OMe)_2(CH_2)_3Cl]_2$		188	24	1.4347	1.136	.2293	.2289	16.0	15.8		
XXIV	$C_3H_7SiMe_2OSiMe_2(CH_2)_3Cl$		104	12	1.4282	0.8997	.2861	.2860	22.2	22.5	13.9[l]	14.0
XXV	$ClMe_2SiOSiMe_2CH_2CHMeCH_2Cl$		105	17	1.4346	1.005	.2595	.2593	21.6	21.6	258.4[i]	259.3
XXVI	$Me_3SiOSiMe_2(CH_2)_3Cl$		98	39	1.4189	0.8991	.2808	.2803	25.1	24.2		
XXVII	$(Me_3SiO)_2SiMe(CH_2)_3Cl$		111	17	1.4147	.9131	.2741	.2733	28.2	28.2		
XXVIII	$[Me_3SiOSiMe(CH_2)_3Cl]_2O$		115	1	1.4320	.9851	.2633	.2629	25.8	25.8		
XXIX	$(Me_3SiO)_3Si(CH_2)_3Cl$		181	100	1.4108	.9223	.2691	.2691	30.1	30.1	9.5[l]	9.5

[a] Calcd. by method of A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954). [b] A. C. Jenkins and G. F. Chambers, *Ind. Eng. Chem.*, 46, 2367 (1954), reported b.p. 182.3° at 760 mm. [c] See Experimental section for method A. [d] Ref. 3 reported b.p. 184.5° at 754 mm., $n^{20}D$ 1.4580, d^{20}_4 1.2045; ref. 5, reported $n^{25}D$ 1.4585. [e] See Experimental section for method B. [f] L. H. Sommer, F. P. Mackay, O. W. Steward, and P. G. Campbell, THIS JOURNAL, **79**, 2764 (1957), reported b.p. 148° at 733 mm., $n^{20}D$ 1.4310, d^{20}_4 0.8825. [g] Ref. 3 reported b.p. 195.5° at 745 mm., $n^{20}D$ 1.4629, d^{20}_4 1.1703. [h] This preparation was reported by J. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959). [i] Neut. equiv. [j] Carbon, %. [k] Hydrogen, %. [l] Chlorine, %.

flask equipped with a reflux condenser and a dropping funnel. During one hour the reflux temperature rose from 35 to 65° and a mixture containing allyl chloride and trichlorosilane in a molar ratio of 1.1/1 was added slowly from the dropping funnel at a rate to maintain the temperature in the flask at about 75–80°.

A cold trap connected to the top of the condenser collected a mixture of propylene and reactants. The mixture was warmed slowly to expel the propylene. The components in the mixture boiling above room temperature were returned to the dropping funnel. The propylene was identified as such by its infrared spectrum.

The products were distilled. A typical experiment used 829 g. (6.1 moles) of trichlorosilane and 421 g. (5.5 moles) of allyl chloride and yielded recovered trichlorosilane followed by tetrachlorosilane, b.p. 56°, 241 g., 1.4 moles; propyltrichlorosilane, b.p. 122–123°, 109 g., 0.7 mole[9]; and chloropropyltrichlorosilane (I), (see Table I), 768 g., 3.6 moles, 66% yield based on allyl chloride.

3-Chloropropylmethyldichlorosilane (II). **Method B.**—A 20-foot length of 0.5-inch stainless steel tubing was wound into a coil and immersed in an oil-bath. A mixture of reactants was pumped into this coil by a small reciprocating pump and left the coil through a spring loaded relief valve set to maintain a pressure of 500 p.s.i. within the tube.

A mixture of methyldichlorosilane (1150 g., 10 moles), allyl chloride (637 g., 8.33 moles) and chloroplatinic acid (1.1×10^{-6} mole) was pumped into the coil with the oil-bath maintained at 125–126°. After steady operating conditions had become established, 429 g., 24% of the total charge, was collected during 26 minutes as a sample of the product and analyzed by distillation, which indicated propylene, 21 g., 0.5 mole; methyldichlorosilane, 63 g., 0.54 mole; allyl chloride, 23 g., 0.3 mole; methyltrichlorosilane, 90 g., 0.61 mole; propylmethyldichlorosilane,[10] 54 g., 0.36 mole, b.p. 125–127° (755 mm.), $n^{25}D$ 1.4221; and 3-chloropropylmethyldichlorosilane (II) (see Table I), 178 g., 0.93 mole, 54% yield based on allyl chloride consumed or 51% yield based upon methyldichlorosilane consumed.

The yield of products by method B is dependent upon the molar ratio of reactants. In a similar experiment carried out with a methyldichlorosilane to allyl chloride ratio of 0.83/1, the yield of II rose to 60% based on the silane consumed or 63% based on allyl chloride.

The propylene was identified by its infrared spectrum.

Methallyl chloride under these conditions formed little or no isobutylene. Slight plateaus during analyses by distillation suggest the presence of isobutylsilanes among the products, but the amount was small in all cases and no isobutylsilanes were isolated as clearly recognizable compounds.

3-Chloropropyltrimethylsilane (IV).—Excess methylmagnesium bromide in ether with II gave IV in 85% yield.

3-Chloro-2-methylpropyltrimethylsilane (VIII).—Excess methylmagnesium bromide in ether with VI gave VIII in 71% yield. The nuclear magnetic spectrum of this com-

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(9) H. S. Booth and H. S. Halbedel, THIS JOURNAL, **68**, 2652 (1946), report b.p. 122.7 ± 1° at 760 mm.

(10) A. J. Barry, L. DePree, J. W. Gilkey and D. Hook, *ibid.*, **69**, 2916 (1947), report for propylmethyldichlorosilane, b.p. 123–124° at 747 mm.; ref. 6 reports b.p. 124.4° at 750 mm., $n^{20}D$ 1.4250, d^{20}_4 1.0383.

pound[11] clearly showed the presence of the CH_2Cl, C–H, $C–CH_3$, $–SiCH_2$ and $SiMe_3$ groups.

3-Chloropropylphenyldichlorosilane (IX).—A mixture of phenyldichlorosilane (354 g., 2.0 moles) and allyl chloride (200 g., 2.6 moles) was added slowly to a flask containing 10^{-5} mole of chloroplatinic acid. A vigorous exothermic reaction took place with the evolution of a condensable gas, presumably propylene. After standing overnight, the mixture was distilled. There was recovered phenyltrichlorosilane (144 g., b.p. 105° at 40 mm.) and then propylphenyldichlorosilane, 31.4 g., b.p. 105° at 10 mm., n^{25}D 1.5137, d^{25}_4 1.125.

Anal. Calcd. for $C_9H_{12}Cl_2Si$: Si, 12.82; neut. equiv., 109.6; *R*D, 0.2669. Found: Si, 12.96; neut. equiv., 109.9; *R*D, 0.2675.

On continued fractionation there was recovered 3-chloropropylphenyldichlorosilane (IX), 313 g. (62% yield).

Preparation of Alkoxysilanes X to XVIII.—The experiment described below is typical for the synthesis of all the alkoxysilanes shown in Table I.

(3-Chloropropyl)-methyldimethoxysilane (XI).—3-Chloropropylmethyldichlorosilane (1535 g., 8.0 moles) was heated to 65° in a stirred flask fitted with a good reflux condenser. The top of the condenser was connected to an HCl scrubber. Methanol (550 g., 17.2 moles) was added through a glass tube to the bottom of the flask. The reaction was very rapid. The system was devolatilized by use of an aspirator at a vacuum of 150–200 mm. The product was distilled through a Vigreux column at atmospheric pressure. There was collected 1130 g. (78% yield) of XI. This product still contained some hydrolyzable chlorine. One hundred ml. of methanol was added and the product saturated with ammonia. The solid ammonium chloride which formed was removed by filtration and the product was again distilled to give pure XI, whose properties are given in Table I.

Preparation of Siloxanes XIX to XXVIII; 1,3-Bis-3-chloropropyltetramethyldisiloxane (XIX).—Hydrolysis of III (600 g., 3.5 moles) was carried out with a mixture of ice and water. The organic layer was separated. The aqueous layer was extracted once with ether. The ether extract was added to the bulk of the product, dried over calcium chloride, filtered and devolatilized to produce XIX, 539 g., 100% yield.

1,3-Bis-(3-chloro-2-methylpropyl)-tetramethyldisiloxane (XX).—3-Chloro-2-methylpropyldimethylchlorosilane (VII, 657 g., 3.5 moles) was hydrolyzed as above. The yield of XX was quantitative.

Poly-(3-chloropropylmethylsiloxane) (XXI).—3-Chloropropylmethyldichlorosilane (II) (629 g., 3.28 moles) was hydrolyzed in ice-water and followed by extraction of the polymer with benzene and azeotropically drying the benzene solution. Evaporation of the benzene gave XXI, 407 g., 91% yield, viscosity 190 cs. at 25°.

Poly-(3-chloro-2-methylpropylmethylsiloxane) (XXII).—Hydrolysis of 3-chloro-2-methylpropylmethyldichlorosilane (VI) as above gave the polysiloxane XXII.

1,3-Bis-(3-chloropropyl)-tetramethoxydisiloxane (XXIII).—Distillation of the residue from a large scale preparation of 3-chloropropyltrimethoxysilane (X) led to the isolation of XXIII. The yield was about 5% based on the original chlorosilane in this experiment and the yield of X was 85% instead of the 97% shown in Table I.

1-(3-Chloropropyl)-3-propyltetramethyldisiloxane (XXIV).—Hydrolysis of crude 3-chloropropyldimethylchlorosilane contaminated with some propyldimethylchlorosilane resulted in the isolation of 1-(3-chloropropyl)-3-propyltetramethyldisiloxane (XXIV).

1-(3-Chloro-2-methylpropyl)-3-chlorotetramethyldisiloxane (XXV).—Distillation of XX was attempted through a fractionating column at 13 to 17 mm. It was observed that the boiling point and refractive index of the distillate varied widely and both values decreased with slower takeoff rates. These values approached a minimum after two hours of total refluxing. A sample of the distillate after such a period proved to be XXV. Even at rapid takeoff, pure XX could not be isolated.

1-(3-Chloropropyl)-pentamethyldisiloxane (XXVI).—A mixture of hexamethyldisiloxane (457 g., 2.8 moles) and 3-chloropropyldimethylchlorosilane (100 g., 0.58 mole) was heated to reflux and water (5 ml., 0.28 mole) was added dropwise. The mixture was cooled and washed to neutrality with dilute sodium bicarbonate solution and water. Distillation of the mixture resulted in the recovery of the excess hexamethyldisiloxane, followed by XXVI (30 g., 23% yield). The remainder of the material was 1,3-bis-(3-chloropropyl)-tetramethyldisiloxane (XIX).

3-(3-Chloropropyl)-heptamethyltrisiloxane (XXVII) and 3,5-Bis-(3-chloropropyl)-octamethyltetrasiloxane (XXVIII).—A mixture of hexamethyldisiloxane (360 g., 2.22 moles), poly-(3-chloropropylmethylsiloxane) (200 g., 1.47 moles) and sulfuric acid (10 ml.) was refluxed overnight. The mixture then was cooled and washed with dilute ammonium hydroxide solution. The mixture was dried and distilled to give 3-(3-chloropropyl)-heptamethyltrisiloxane, (XXVII, 50.6 g., 11% yield) and 3,5-bis-(3-chloropropyl)-octamethyltetrasiloxane (XXVIII, 22 g., 7% yield). There remained 165 g. of material which could not be fractionated.

3-Chloropropyl-tris-(trimethylsiloxy)-silane (XXIX).—The method used is that of Haluska.[12] To a stirred mixture of trimethylchlorosilane (651 g., 6.0 moles) and 3-chloropropyltrichlorosilane (212 g., 1.0 mole) was added isopropyl alcohol (540 g., 9.0 moles) and then water (162 g., 9.0 moles). The organic layer was separated and washed with water until neutral. On distillation there was recovered XXIX 350 g., 94% yield.

Cleavage of 1,3-Bis-(3-chloro-2-methylpropyl)-tetramethyldisiloxane (XX).—A sample of XX (295 g.) was heated in a flask equipped with a reflux condenser and a cold trap to collect the volatile product. The evolution of a gas was observed at 190° and at 265° it was more rapid. A 10 g. sample of material was collected in the cold trap after 32 hours of heating at 260–270°. The sample was distilled twice and placed in a tensimeter. The vapor pressure of the sample was measured over the range of −46 to −19°. The observed vapor pressure was in excellent agreement with the recorded values for isobutylene.[13] An infrared spectrum of this material was identical with that of isobutylene.

Another sample of XX (110 g.) containing 0.1 g. of $AlCl_3$ was heated to 100°, where the evolution of isobutylene was very rapid. After 30 minutes at 100–135° the yield of isobutylene was almost quantitative. A plot of vapor pressure *versus* temperature made as above again confirmed the identity of the product.

A mixture of XX (141 g., 0.45 mole), sodium hydroxide (40 g., 1.0 mole), water (200 ml.) and ethanol (200 ml.) was heated to reflux for 4 hours. Methylcyclopropane (50 g., 99% yield) was collected in a cold trap connected to the system. A vapor pressure–temperature curve obtained as before showed good agreement with that given in the literature[14] for methylcyclopropane. The infrared spectrum confirmed the absence of a double bond in this product.

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[11] The nuclear magnetic spectra and their interpretation were carried out by John J. Burke, Mellon Institute, Pittsburgh, Penna.

[12] L. A. Haluska, unpublished work, Dow Corning Corp., Midland, Mich.

[13] A. B. Lamb and E. E. Roper, THIS JOURNAL, **62**, 806 (1940).

[14] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).