theoretical. At temperatures below 0° about 100 ml of *n*-hexane was added to prevent the benzene from freezing.[35]

The same procedure was followed for the alkylation of benzene with *trans*-6-dodecene. The olefin (0.15 mol) was mixed with 0.01 mol of 2-phenyldecane, and the alkylation reaction was completed as above. The mixture was worked up as usual and the analysis of the product appears in Table I. The yields were similar to those obtained with 1-dodecene.

Alkylation in the Presence of Aluminum Chloride–Nitromethane.—Benzene (2.5 mol) was added to the yellowish solution prepared by dissolving 0.037 mol of anhydrous aluminum chloride in 0.08 mol of nitromethane. The temperature was kept at 35–37°, and a mixture of 0.15 mol of 1-dodecene and 0.01 mol of 2-phenyldecane in 0.5 mol of benzene was added over a period of 15 min. The mixture was stirred for 45 more minutes and was quenched with water and washed with dilute HCl, 10% NaOH solution, and water. The product was analyzed by glpc and distilled as usual. The yield was 28.5 g or 78%. Infrared analysis of the residue (7.3 g) showed it to be mainly *p*- and *m*-dialkylbenzene in the ratio of 5:1 (12.1 and 12.65 μ, respectively).

The same procedure was followed for the alkylation reactions in nitromethane solution. A mixture of 0.15 mol of 1-dodecene, 0.01 mol of 2-phenyldecane, and 0.1 mol of benzene was added to a solution of 0.037 mol of anhydrous aluminum chloride in 4.0 mol of nitromethane and 0.4 mol of benzene maintained at 35–37°. Stirring was continued for 1 hr, and the reaction mixture was quenched with 10 g of ice and extracted three times with 200 ml of *n*-hexane. The combined hexane extracts were washed with dilute hydrochloric acid, water, 10% sodium hydroxide solution, and finally water. The solution was dried with anhydrous magnesium sulfate, and the solvent was removed on a water bath. The product was analyzed for isomer distribution and then distilled as above. The yield was 68% of theoretical.

Alkylation with Dichloroaluminum Sulfate.—This catalyst was prepared according to the directions of Topchiev, *et al.*[36] Ground $AlCl_2 \cdot HSO_4$ (0.074 mol) and anhydrous benzene (3.0 mol) were placed in the alkylation flask. The temperature was raised to 35°, and a mixture of 0.15 mol of 1-dodecene and 0.01 mol of 2-phenyldecane was added. Stirring was continued for 2 hr after which time an oily layer appeared at the bottom of the flask. The mixture was allowed to stand overnight before it was quenched with water and acidified with dilute HCl. The organic layer was washed successively with dilute HCl, water, dilute alkali, and finally water. The product was then analyzed by glpc and distilled as usual. The yield was 27.5 g or 75%.

Registry No.—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-17-9; aluminum chloride, 7446-70-0.

Acknowledgment.—Mr. Minor T. Jackson and Mr. Donald A. Wallace of the Central Research Department of the Monsanto Co. carried out the mass spectral analysis.

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(35) Special alkylations were carried out at 0 and 35° in which *n*-hexane, in contrast to hydrogen fluoride alkylations, was shown to have no effect on the isomer distribution of the product.

(36) A. V. Topchiev, S. V. Zavgorodnii, and V. G. Kryuchkova, "Alkylation with Olefins," Elsevier Publishing Co., Amsterdam, 1964, p 141.

The Synthesis and Properties of 1- and 2-(Dichloromethyl)heptamethyltrisilane and Related Compounds[1]

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The first carbon-functional organotrisilanes, 1- and 2-(dichloromethyl)heptamethyltrisilane, have been prepared from the corresponding chloroheptamethyltrisilanes with α-dichloromethyllithium. 1-(Chloromethyl)-heptamethyltrisilane as well as (chloromethyl)pentamethyldisilane were also prepared by *in situ* coupling of bromochloromethane with the corresponding chlorosilanes. Aluminum chloride catalyzed reactions of 1- and 2-(dichloromethyl)heptamethyltrisilane were examined. Both compounds undergo intramolecular rearrangement followed by a redistribution reaction. Nmr spectral data are reported for several chloromethyl- and dichloromethyl-substituted silanes.

Recently considerable attention has been directed toward a study of the organopolysilanes.[2] However, no carbon-functional organotrisilane except vinylheptamethyltrisilanes[3] has been known to date. We now report the synthesis and aluminum chloride catalyzed rearrangement of the first examples of the carbon-functional organotrisilanes, 1- and 2-(dichloromethyl)-heptamethyltrisilane.

Many procedures for preparing carbon-functional silanes or disilanes[4] cannot be extended to higher polysilanes because of extensive silicon–silicon bond cleavage. These procedures involve halogenation or other substitution reactions on carbon. Alternatively, nucleophilic substitution reaction on a silicon atom would be a preferred route to the carbon-functional organopolysilanes. The (dichloromethyl)heptamethyltrisilanes were thus prepared by the reaction of the corresponding chloroheptamethyltrisilanes with α-dichloromethyllithium.

Recently the reaction of polychloromethane with *n*-butyllithium in tetrahydrofuran at low temperature has been shown to lead to the formation of a new class of organolithium reagents, the α-chloroalkyllithium compounds.[5] It was reported that the action of *n*-butyllithium on methylene chloride at $-65°$ afforded dichloromethyllithium in high yield and this reagent served as an intermediate in the preparation of some dichloromethyl-substituted compounds.[6]

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(1) (a) Aluminum Chloride-Catalyzed Reactions of Organosilicon Compounds. V. (b) For part IV, see H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).

(2) For pertinent reviews, see (a) H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, **4**, 1 (1966); (b) M. Kumada and K. Tamao, *ibid.*, in press; (c) H. Sakurai, *J. Soc. Org. Syn. Chem. Jap.*, **25**, 555, 642 (1967).

(3) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, **39**, 1279 (1966).

(4) C. Eaborn, "Organosilicon Chemistry," Butterworth and Co. Ltd., London, 1960, p 377.

(5) (a) H. Heaney, *Organometal. Chem. Rev.*, **1**, 27 (1966); (b) G. Köbrich, *et al.*, *Angew. Chem.*, **79**, 15 (1967); (c) D. F. Hoeg, D. L. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1967), and references cited therein.

(6) G. Köbrich, K. Flory, and W. Drischel, *Angew. Chem.*, **76**, 536 (1964).

TABLE I
PROPERTIES OF NEW COMPOUNDS

Compound	Bp, °C (mm)	n^{20}_D	d^{20}_4	MRD Calcd	MRD Found	Calcd, % C	Calcd, % H	Found, % C	Found, % H
$Cl_2CHSi(CH_3)_2Si(CH_3)_2Si(CH_3)_3$	78 (4)	1.4993	0.9858	81.8	81.0	35.14	8.12	35.24	8.25
$(CH_3)_3SiSi(CH_3)Si(CH_3)_3$ $\vert$ $CHCl_2$	104–105 (10)	1.5009	0.9946	81.8	80.9	35.14	8.12	34.99	7.92
$ClCH_2Si(CH_3)_2Si(CH_3)_2Si(CH_3)_3$	50 (4)	1.4842	0.8942	77.0	76.8	40.04	9.66	40.30	9.78

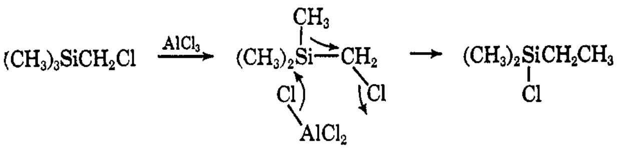
(Dichloromethyl)heptamethyltrisilanes together with the known (dichloromethyl)pentamethyldisilane[7] were prepared successfully by the following route.[8]

$$CH_2Cl_2 \xrightarrow[THF]{n\text{-BuLi}} Cl_2CHLi \xrightarrow{RR'(CH_3)SiCl} RR'(CH_3)SiCHCl_2$$

1a, R = $(CH_3)_3SiSi(CH_3)_2$; R′ = CH_3
b, R = R′ = $(CH_3)_3Si$
c, R = $(CH_3)_3Si$; R′ = CH_3

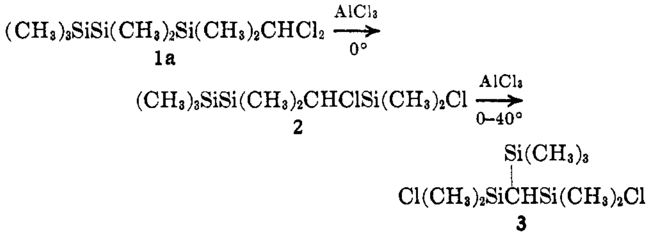
Physical properties of these compounds are listed in Table I.

It has been described in the literature[9] that the chloromethyl-substituted methylsilanes undergo Lewis acid catalyzed rearrangement resulting in migration of a methyl group from silicon to adjacent carbon.



An interesting example involving two successive and discrete intramolecular rearrangements of **1c** with anhydrous aluminum chloride has been reported previously from this laboratory.[7]

In the present study, we have also examined an aluminum chloride catalyzed rearrangement of **1a**. It was expected to obtain a rearranged compound like **3** by the following reactions.



$$\underset{\mathbf{1a}}{(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2CHCl_2} \xrightarrow[0°]{AlCl_3} \underset{\mathbf{2}}{(CH_3)_3SiSi(CH_3)_2CHClSi(CH_3)_2Cl} \xrightarrow[0\text{–}40°]{AlCl_3} \underset{\mathbf{3}}{Cl(CH_3)_2Si\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{C}HSi(CH_3)_2Cl}$$

When a catalytic amount of anhydrous aluminum chloride was added to **4a** at about 0°, a vigorous exothermic reaction took place. By raising the reaction temperature to about 40° and employing a larger amount of the catalyst, the second exothermic reaction occurred. The reaction products were isolated by simple distillation from the mixture. However, contrary to our expectation, the reaction product (83.0% yield) was found to be a mixture consisting of four components, two of which were identified as tris(trimethysilyl)methane[10] (**4**) and tris(dimethylclorosilyl)-methane[11] (**5**) by comparing retention times of glpc with those of the corresponding authentic samples. This mixture gave **4** as a single product by methylation with methylmagnesium bromide in good yield (86.4%). Determination of the chlorine content of the mixture by alkaline titration indicated that the mixture had two hydrolyzable chlorine atoms in a molecule on an average. These facts suggest that other unidentified components must be bis(trimethylsilyl)dimethylchlorosilylmethane (**6**) and bis(dimethylchlorosilyl)trimethylsilylmethane (**7**).

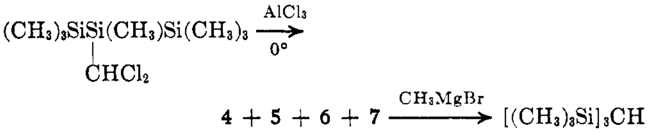
$$\mathbf{3} \xrightarrow{AlCl_3} \underset{\mathbf{4}}{[(CH_3)_3Si]_3CH} + \underset{\mathbf{5}}{[Cl(CH_3)_2Si]_3CH} + \underset{\mathbf{6}}{[(CH_3)_3Si]_2CHSi(CH_3)_2Cl} + \underset{\mathbf{7}}{[Cl(CH_3)_2Si]_2CHSi(CH_3)_3}$$

$$\text{mixture} \xrightarrow{CH_3MgBr} [(CH_3)_3Si]_3CH$$

Accordingly, the rearranged product must undergo aluminum chloride catalyzed redistributions rather readily under the present reaction condition. This unexpected facile redistribution has been confirmed further by an experiment on the aluminum chloride catalyzed redistribution starting from an equimolar mixture of **4** and **5** at 70°. After 9 hr it was disclosed that the mixture was also composed of **4**, **5**, **6**, and **7**.

$$[(CH_3)_3Si]_3CH + [Cl(CH_3)_2Si]_3CH \xrightarrow{AlCl_3} \mathbf{4} + \mathbf{5} + \mathbf{6} + \mathbf{7}$$

Essentially the same results were obtained from the aluminum chloride catalyzed reactions of **1b**; **4** was produced as the final product by methylation.



$$\underset{\underset{\displaystyle CHCl_2}{|}}{(CH_3)_3SiSi}(CH_3)Si(CH_3)_3 \xrightarrow[0°]{AlCl_3} \mathbf{4} + \mathbf{5} + \mathbf{6} + \mathbf{7} \xrightarrow{CH_3MgBr} [(CH_3)_3Si]_3CH$$

Attempts to isolate an intermediate like **2** has failed because of high reactivity of the intermediate itself toward aluminum chloride (see Experimental Section).

It seems noteworthy that **5** as well as the rearrangement mixtures from **1a** and **1b** are rather inert toward methylmagnesium bromide. Reflux for 20 hr was not sufficient for completing the methylation; additional refluxing (20–30 hr) was required. It seems reasonable that the low reactivity of these compounds might be due to steric crowding of atoms.[12]

Synthetic routes have been also examined which provide a general way to the chloromethyl-substituted polysilanes. (Chloromethyl)pentamethyldisilane was successfully prepared by photochlorination of methyl-

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[7] M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 411 (1964).

[8] After this manuscript had been completed, we received a paper of W. R. Bamford and B. C. Pant, *J. Chem. Soc.*, *Sect. C*, 1470 (1967), in which (dichloromethyl)trimethylsilane, (trichloromethyl)trimethylsilane, and related compounds have been prepared by the addition of *n*-butyllithium to a mixture of chlorotrimethylsilane and certain chloroalkanes in tetrahydrofuran at −120°.

[9] (a) See ref 4, p 434; (b) R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometal. Chem.*, **3**, 455 (1965).

[10] R. L. Merker and M. J. Scott, *J. Amer. Chem. Soc.*, **85**, 2243 (1963), *J. Organometal. Chem.*, **4**, 97 (1965).

[11] See ref 1b.

[12] H. Sakurai, T. Watanabe, and M. Kumada, *J. Organometal. Chem.*, **9**, 11 (1967).

$$(CH_3)_nSi_2Cl_{6-n} \xrightarrow{Cl_2,\ h\nu} (ClCH_2)(CH_3)_{n-1}Si_2Cl_{6-n} \xrightarrow{CH_3MgBr} ClCH_2Si_2(CH_3)_5$$

$$n = 3, 4$$

chlorodisilanes[13] followed by methylation. However, obviously this method cannot be applied to higher polysilanes.

Methoxymethyl-[14] and thiomethoxymethyl-substituted[15] silanes were prepared by the *in situ* Grignard method from chloromethyl methyl ether and chloromethyl methyl sulfide, respectively. Accordingly, *in situ* Grignard reaction of bromochloromethane with

$$CH_3YCH_2Cl + ClSiR_3 + Mg \longrightarrow CH_3YCH_2SiR_3$$
$$Y = O, S$$

chloropentamethyldisilane was examined but none of the expected compound was formed. Only partial success (16–18% yield) was achieved by the coupling reaction of bromochloromethane and chloropentamethyldisilane with lithium metal. A new carbon-functional organotrisilane, (chloromethyl)heptamethyl-

$$BrCH_2Cl + ClSi_2(CH_3)_5 + Li \longrightarrow ClCH_2Si_2(CH_3)_5$$

trisilane, was prepared in low yield by this method (Table I).

Nmr spectral data for these new compounds together with previously known chloromethyl- or dichloromethyl-substituted methylsilanes are recorded in Table II.

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA OF CHLOROMETHYL- AND DICHLOROMETHYL-SUBSTITUTED SILANES[a]

Silane (no.)	τ values
$(\overset{1}{C}H_3)_3Si\overset{2}{C}H_2Cl$ (1)	9.86 (H^1), 7.30 (H^2)
$(\overset{1}{C}H_3)_3SiSi(\overset{2}{C}H_3)_2\overset{3}{C}H_2Cl$ (2)	9.87 (H^1), 9.84 (H^2), 7.19 (H^3)
$(\overset{1}{C}H_3)_3SiSi(\overset{2}{C}H_3)_2Si(\overset{3}{C}H_3)_2\overset{4}{C}H_2Cl^b$ (3)	9.88 (H^1), 9.86 (H^2), 9.80 (H^3), 7.17 (H^4)
$(\overset{1}{C}H_3)_3Si\overset{2}{C}HCl_2$ (4)	9.73 (H^1), 4.86 (H^2)
$(\overset{1}{C}H_3)_3SiSi(\overset{2}{C}H_3)_2\overset{3}{C}HCl_2$ (5)	9.75 (H^1), 9.67 (H^2), 4.74 (H^3)
$(\overset{1}{C}H_3)_3SiSi(\overset{2}{C}H_3)_2Si(\overset{3}{C}H_3)_2\overset{4}{C}HCl_2{}^b$ (6)	9.86 (H^1), 9.80 (H^2), 9.71 (H^3), 4.64 (H^4)
$[(\overset{1}{C}H_3)_3Si]_2Si(\overset{2}{C}H_3)\overset{3}{C}HCl_2{}^c$ (7)	9.78 (H^1), 9.78 (H^2), 4.57 (H^3)

[a] These spectra were determined in carbon tetrachloride solution with cyclohexane as an internal standard. Chemical shifts are converted to τ values taking 1.43 ppm as the signal differences between cyclohexane and tetramethylsilane. A Jeol JNM-C-60 H nmr spectrometer was employed. [b] Assignments of H^2 and H^3 are tentative. [c] Only two kinds of proton peaks were observed; see ref 3.

Experimental Section

Materials.—Chloropentamethyldisilane and 1-chloroheptamethyltrisilane were prepared from hexamethyldisilane and octamethyltrisilane, respectively, by the procedure described before.[11] 2-Chloroheptamethyltrisilane was prepared from 2-phenylheptamethyltrisilane.[16] Tris(trimethylsilyl)methane[10] and tris(dimethylchlorosilyl)methane[11] were prepared by Watanabe in this laboratory. Trimethylchlorosilane was generously supplied by the Tokyo Shibaura Electric Co. Ltd. Methylene chloride and bromochloromethane were purchased and used after distillation.

Preparation of (Dichloromethyl)pentamethyldisilane.—A mixture of 400 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride), 100 ml of dry ether, and 9.0 g (0.1 mol) of dichloromethane was cooled to −78° and 0.065 mol of *n*-butyllithium in 100 ml of ether was added slowly. After the addition, the mixture was stirred 40 min and 16 g (0.1 mol) of chloropentamethyldisilane was added in one portion. The mixture was kept at −78° for 2 hr with stirring and then allowed to warm up gradually to room temperature. The reaction mixture was distilled under reduced pressure. After fractional distillation through a column packed with glass helicoils, 8 g (0.037 mol, 57% yield) of (dichloromethyl)pentamethyldisilane was obtained as a pure colorless liquid (homogeneous on glpc), bp 75–78° (17 mm). This compound exhibits an identical ir spectrum and the same retention times on glpc as a sample prepared by a different route.[7]

Preparation of 1-(Dichloromethyl)heptamethyltrisilane (1a).—A mixture of 400 ml of dry tetrahydrofuran and 29.5 g of dichloromethane (0.35 mol) was cooled to −78° and 0.08 mol of *n*-butyllithium was added slowly over 60 min. After a total of 100 min elapsed, 14.5 g of 1-chloroheptamethyltrisilane (0.06 mole) dissolved in 10 ml of tetrahydrofuran was added over a 30-min period. After work-up as above, **1a** was obtained as a pure colorless liquid in 35% yield.

Preparation of 2-(Dichloromethyl)heptamethyltrisilane (1b).—Essentially by the same procedure as for **1a**, **1b** was prepared from 2-chloroheptamethyltrisilane in 50% yield.

Reactions of 1a with Anhydrous Aluminum Chloride.—To 8.5 g (0.031 mol) of **1a**, stirred and protected from moisture, was added anhydrous aluminum chloride in small portions with cooling by ice bath. A vigorous, exothermic reaction took place. After a total of about 20 mg of aluminum chloride was added, no further noticeable change accurred at ice-bath temperature with an addition of catalyst. Then an additional 60 mg of catalyst was added and the mixture was warmed gradually. At about 40°, a second exothermic reaction took place vigorously. When the reaction subsided, gentle heat was applied with an additional 450 mg of aluminum chloride. The mixture was stirred at 60–80° for 8 hr and was flash distilled under reduced pressure to separate the products from the catalyst. A crystalline material, bp 53–62° (1 mm), was obtained, yield 7 g (83%). This material consists of four components (on glpc), two of which were identified as tris(trimethylsilyl)methane and tris(dimethylchlorosilyl)methane. The mixture was analyzed by titrating the hydrolyzable chlorine (bonded to silicon atoms) and so estimated to contain 27.23% (weight %) of chlorine. This figure corresponds to 2.1 chlorines in a molecule assuming that the mixture had the same molecular weight on an average as **1a** (273.43). By refluxing with a 0.1-mol solution of methylmagnesium bromide in ether, 6 g (0.022 mol) of the mixture gave after work-up 4.5 g (0.019 mol) of tris(trimethylsilyl)methane, 96–102° (20 mm).

Attempts to Isolate an Intermediate in the Reaction of 1a with Aluminum Chloride.—To 3.8 g of **1a** was added a total of 180 mg of anhydrous aluminum chloride essentially by the same procedure as above except for additional warming. To this mixture, 1 ml of acetone was added to deactivate the catalyst.[17] The mixture was then flash distilled under reduced pressure to give 2 g of the mixed product boiling at 30–45° (4 mm). An examination by glpc disclosed that the mixture was composed of six components, four of which had the same retention times as those of the product from **1a** with aluminum chloride (*vide supra*). Another peak was identified as the starting material. Methylation of the mixture gave 1 g of product, boiling up to 38° (4 mm). It consists mainly of tris(trimethylsilyl)methane with some higher boiling products. The ir spectra of this mixture exhibited bands at 1040 and 800 cm^{-1} in addition to those observed for tris(trimethylsilyl)methane. These observations suggest the existence of an intermediate such as $(CH_3)_3SiCHClSi(CH_3)_2Si(CH_3)_3$ (after methylation); however, no further attempt to isolate the compound was made because of an extensive decompositon on gas chromatographic separation.

Reaction of 1b with Anhydrous Aluminum Chloride.—2-(Dichloromethyl)heptamethyltrisilane (2.5 g, 0.01 mol) was subjected to the reaction with 100 mg of anhydrous aluminum chloride essentially by the same procedure to give 1.5 g of a mix-

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(13) M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, **23**, 292 (1958).

(14) M. Kumada, M. Ishikawa, and K. Tamao, *J. Organometal. Chem.*, **5**, 226 (1966).

(15) H. Sakurai, M. Kira, and M. Kumada, *Chem. Commun.*, 889 (1967).

(16) M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.*, **2**, 478 (1964).

(17) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, **39**, 1820 (1966).

ture boiling at 65–72° (2.5 mm). The mixture exhibited a gas chromatogram almost identical with that for the reaction product of **1a**, with slight differences in relative peak areas. The mixture gave tris(trimethylsilyl)methane with a small amount of an unidentified compound by methylation. The latter compound had OH absorption at 3400 cm^{-1} (silanol), being presumably $((CH_3)_3Si)_2CHSi(CH_3)_2OH$.

Aluminum Chloride Catalyzed Redistribution between 4 and 5.—In a 50-ml three-necked flask fitted with an air-tight stirrer, a calcium chloride tube, and a stopper, 2 g (0.0095 mol) of **4**, 2.5 g (0.0095 mol) of **5**, and 0.3 g of freshly sublimed aluminum were placed. The mixture was heated at 70–80° for 9 hr and was flash distilled to give 2.5 g of crystalline materials boiling at 70–115° (24 mm). The product was found to consist only of the same four components as those of the reaction mixture from **1a** or **1b**. The relative peak area of **4**:**6**:**7**:**5** (on silicone DC 550) was 1:9.3:11:2.4.

Preparation of (Chloromethyl)pentamethyldisilane.—To 3.0 g (0.43 g-atom) of dispersed lithium metal in 100 ml of dry ether was added 33 g (0.2 mol) of chloropentamethyldisilane in one portion at 0° under a nitrogen stream and then 25 g (0.19 mol) of bromochloromethane was added over a period of 30 min. After the addition was complete, the mixture was stirred for 2 hr at 0°. The mixture was then kept at room temperature overnight and hydrolyzed with saturated ammonium chloride solution. After work-up, the mixture was fractionated to give 6 g (18%) of (chloromethyl)pentamethyldisilane, 12 g of bis(pentamethyldisilanyl) ether, and 7 ml of mixture containing bis(pentamethyldisilanyl)methane, decamethyltetrasilane, and other unidentified materials. The (chloromethyl)pentamethyldisilane thus obtained was identified by comparing its ir spectrum and gas chromatogram with those of authentic sample.

Preparation of 1-(Chloromethyl)heptamethyltrisilane.—By the same procedure as above, 12 g of a mixture containing mainly 1-(chloromethyl)heptamethyltrisilane was obtained from 2 g (0.28 g-atom) of lithium, 15 g (0.066 mol) of 1-chloroheptamethyltrisilane, and 40 g (0.3 mol) of bromochloromethane. Pure 1-(chloromethyl)heptamethyltrisilane was isolated from the mixture by preparative glpc.

Registry No.—1, 2344-80-1; 2, 5181-46-4; 3, 15816-06-5; 4, 5926-38-5; 5, 15816-03-2; 6, 15816-04-3; 7, 15816-05-4.

The Reactions of Trichloroacetyl Chloride with 2-Picoline N-Oxide and Pyridylcarbinols

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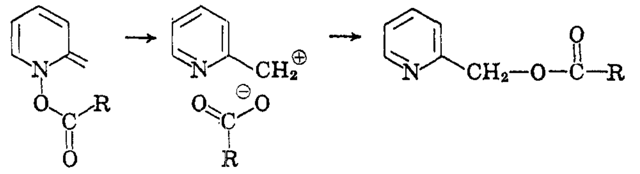
Received September 26, 1967

The reaction of trichloroacetyl chloride with 2-picoline N-oxide gives 2-pyridylmethyl chloride and carbon dioxide in high yields. This is shown to be a result of a reaction of the expected trichloroacetate ester with chloride ion. The formation of pyridyl chlorides from trichloroacetyl chloride and the corresponding alcohols is a general reaction.

The concerted decompositions of the *t*-butyl per esters of acids such as pivalic,[2,3] phenylacetic,[2–4] and trichloroacetic[2] seem to be well-established processes. If such behavior is general for any X–O bond homolysis, then the incorporation of such a structural feature into an acyloxy side chain should serve as a useful method for making the difficult choice between intramolecular radical-pair and ion-pair reactions. When the radical path is operative, nearly quantitative amounts of carbon dioxide should be obtained no matter how efficient the cage combination, which might explain the normal products, is proposed to be.

We have recently[5] applied this criterion to the cleavage of the –N–O– bond in the rearrangement of the anhydro bases thought to be involved in the reaction



of 2-picoline N-oxide with acid anhydrides. The results of this study indicated that this cleavage was ionic since the carbon dioxide yields were not significantly increased on going from acetic to phenylacetic or trichloroacetic anhydride as reagent. During the course of these investigations we also examined the reaction of 2-picoline N-oxide with trichloroacetyl chloride. This reaction gave the qualitatively conflicting result that carbon dioxide is produced in high yield at a fairly rapid rate. We now wish to report the results of further studies of this reaction which indicate that trichloroacetate esters are susceptible to displacement by chloride ion under these relatively mild conditions.

Results and Discussion

When trichloroacetyl chloride is added into a refluxing chloroform solution of 2-picoline N-oxide (2 *M*), a rapid evolution of carbon dioxide (20% yield in 1 hr) occurs. The nmr spectrum of the solution after 1 hr shows the presence of the 2-picolylmethyl trichloroacetate ester (I) (singlet at 5.8 ppm) in about 40% yield. An additional singlet is also present at 5.1 ppm and continued reflux of the original solution leads to continued carbon dioxide formation and a decrease in the 5.8-ppm singlet accompanied by an increase in the 5.1-ppm peak. After a 12-hr reflux, the carbon dioxide yield is 83% and the trichloroacetate ester is nearly completely consumed. The nmr spectrum of the final solution indicated the new product to be present in 70% yield. The isolated yield of this compound is 30–40% after distillation. The product was identified as α-chloro-2-picoline (II) by its spectral properties, boiling point, and picrate.

The ester I, obtained in pure form from 2-pyridylcarbinol and trichloroacetic anhydride, gives II and carbon dioxide on treatment with hydrogen chloride, followed by reflux in chloroform or acetonitrile. When

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[2] P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

[3] T. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2773 (1965); T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **89**, 2948 (1967).

[4] R. Neuman and J. Behar, *ibid.*, **89**, 4549 (1967).

[5] T. Koenig, *ibid.*, **88**, 4045 (1966).