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Radical Chain Reactions of Halomethyldimethylsilanes

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Chloromethyldimethylsilyl or bromomethyldimethylsilyl radicals have been generated by photolysis of the corresponding silanes in the presence of mercury or thermolysis with di-*tert*-butyl peroxide. No products of coupling of the silyl radicals [XCH_2–$\dot{S}i(CH_3)_2$] were observed. The products of radical reactions of chloromethyldimethylsilane are time dependent. At short reaction time trimethylsilane and chloromethyldimethylchlorosilane are the major products, while the major product at long reaction time is trimethylchlorosilane. The radical reactions of bromomethyldimethylsilane are faster than those of chloromethyldimethylsilane. No time dependence of the products of radical reaction of bromomethyldimethylsilane was observed. Trimethylbromosilane was the major product of radical reaction of bromomethyldimethylsilane. These results can be explained by two consecutive radical chain processes rather than by a 1,2-halogen shift in the radical intermediates.

The hydrosilation reaction is perhaps the best studied example of a radical chain process involving silyl radicals as intermediates. Thus, the addition of trichlorosilane to 1-octene catalyzed by acetyl peroxide yields trichloro-*n*-octylsilane.[1] This reaction has been proposed to occur by the following mechanism.[1–4]

$$Cl_3Si\text{-}H + In\cdot \rightarrow Cl_3Si\cdot + In\text{-}H$$

$$Cl_3Si\cdot + R\text{-}CH{=}CH_2 \rightarrow Cl_3Si\text{-}CH_2\text{-}\dot{C}H\text{-}R$$

$$Cl_3Si\text{-}CH_2\text{-}\dot{C}H\text{-}R + Cl_3Si\text{-}H \rightarrow Cl_3Si\text{-}CH_2\text{-}CH_2\text{-}R + Cl_3Si\cdot$$

We should like to report a new radical chain process involving silyl radicals as intermediates. The reaction is the conversion of chloromethyldimethylsilane into trimethylchlorosilane under radical initiation. At first this reaction might appear to be a 1,2-radical rearrangement. Few examples of 1,2-radical rearrangements are known in organosilicon chemistry.[5–11] However, on examination this reaction appears to occur by two consecutive radical chain processes both of which involve silyl radical intermediates. The reaction was discovered quite by accident.

Photolysis of trimethylsilane in the vapor phase in the presence of mercury yields hexamethyldisilane and hydrogen.[12] The reaction is believed to involve silyl radicals formed by homolytic cleavage of the Si–H bond. Despite numerous possible complications, both the chemical and quantum yields for the reaction are high. In fact, the reaction has proved a valuable synthetic method to prepare disilanes.[13,14] However, if chloromethyldimethylsilane is photolyzed in the gas phase in the presence of mercury, the products are not the expected disilane, but rather trimethylchlorosilane, trimethylsilane, chloromethyldimethylchlorosilane, and small amounts of hexamethyldisiloxane and chloromethylpentamethyldisiloxane. A small amount of mercury is converted to mercuric chloride. The possibility that mercuric chloride, a weak Lewis acid, catalyzed these transformations was eliminated by control experiments. Thus, chloromethyldimethylsilane was recovered unchanged after refluxing with mercuric chloride. The alternative possibility that this reaction involved a free-radical process was supported by the following experiment. Heating chloromethyldimethylsilane at 136 °C in the presence of a catalytic amount of di-*tert*-butyl peroxide (2%) leads to a similar product mixture. Di-*tert*-butyl peroxide has been previously used to generate silyl radicals by hydrogen abstraction from silanes.[15–17]

The ratio of products is time dependent. (See Figure 1 and Table I). After 20 min at 136° the reaction of chloromethyldimethylsilane initiated by di-*tert*-butyl peroxide (2%) has already consumed almost 40% of the starting material. At this time, the major products were trimethylsilane (~20%) and chloromethyldimethylchlorosilane (~20%). Trimethylchlorosilane was present in small amount (1%). However, if the reaction mixture was heated for longer periods of time, the amounts of trimethylsilane and chloromethyldimethylchlorosilane decreased while the yield of trimethylchlorosilane increased. These results can be explained by a sequence of two radical chain reactions.

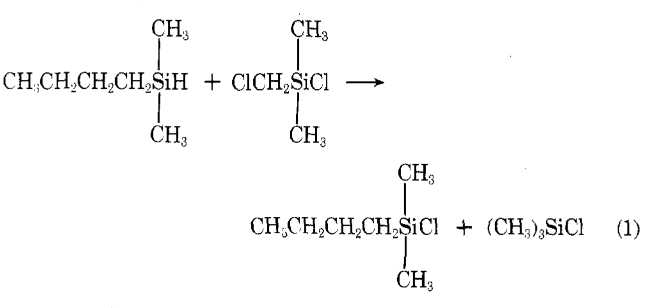
The reaction is initiated by abstraction of a hydrogen atom from the Si–H bond by a *tert*-butoxy radical to form the chloromethyldimethylsilyl radical. Abstraction of a chlorine atom from the starting material by this radical leads to chloromethyldimethylchlorosilane and the dimeth-

Table I. Time Dependence of Products from Chloromethyldimethylsilane + *t*-BuO•

Reaction time, min	$HSi(CH_3)_2$-CH_2Cl, %	$(CH_3)_3$-SiH, %	$ClSi(CH_3)_2$-CH_2Cl, %	$(CH_3)_3$-SiCl, %
10	91.2	4.4	3.5	0.9
20	60.3	20.9	15.6	1.2
40	41.0	23.9	24.0	10.3
80	28.5	28.8	25.2	17.3
160	23.9	27.6	28.4	20.1
400	8.5	22.6	22.6	46.3
900	0.0	4.1	4.3	91.0

ylsilylmethyl radical [$(CH_3)_2SiH$–CH_2•]. Silyl radicals are known to abstract halogen atoms from alkyl halides.[15,18–22] Abstraction of a hydrogen atom from the Si–H bond of the starting material by the dimethylsilylmethyl radical [$(CH_3)_2SiH$–CH_2•] leads to trimethylsilane and the chloromethyldimethylsilyl radical. This constitutes the initial radical chain reaction. It predicts that trimethylsilane and chloromethyldimethylchlorosilane will be produced in equal amounts as is observed. The second chain reaction sequence results from the buildup of trimethylsilane. Thus, the dimethylsilylmethyl radical [$(CH_3)_2SiH$–CH_2•] can abstract a hydrogen atom from either the starting material or from trimethylsilane. Abstraction of a hydrogen atom from trimethylsilane yields the trimethylsilyl radical and trimethylsilane. The trimethylsilyl radical will abstract a chlorine atom from the chloromethyldimethylchlorosilane to yield trimethylchlorosilane and the dimethylchlorosilylmethyl radical [$(CH_3)_2ClSi$–CH_2•]. The dimethylchlorosilylmethyl radical [$(CH_3)_2ClSi$–CH_2•] will abstract a hydrogen atom from trimethylsilane to yield trimethylchlorosilane and the trimethylsilyl radical. The trimethylsilyl radical may also abstract chlorine from chloromethyldimethylsilane. This sequence of reactions constitutes the second radical chain process. The second radical chain process depends on the concentration of trimethylsilane and chloromethyldimethylchlorosilane, which are the products of the first radical chain process. (See Figure 2.)

This second radical chain process was independently verified. Thus heating *n*-butyldimethylsilane and chloromethyldimethylchlorosilane together in the presence of a catalytic amount of di-*tert*-butyl peroxide leads to trimethylchlorosilane and *n*-butyldimethylchlorosilane in equal amounts (eq 1).



$$CH_3CH_2CH_2CH_2Si(CH_3)_2H + ClCH_2Si(CH_3)_2Cl \longrightarrow CH_3CH_2CH_2CH_2Si(CH_3)_2Cl + (CH_3)_3SiCl \quad (1)$$

Two other products formed, hexamethyldisiloxane and chloromethylpentamethyldisiloxane, can be minimized if care is taken to exclude moisture. Thus it is assumed that they are secondary products of hydrolysis of trimethylchlorosilane and chloromethyldimethylchlorosilane.

A similar radical reaction has been observed in the case of heating bromomethyldimethylsilane at 136° in the presence of a catalytic amount of di-*tert*-butyl peroxide. However, this reaction is faster than that of chloromethyldimethylsilane and so we were unable to observe a time dependence on the product ratios. At even 10 min the reaction was virtually complete. The following products were obtained: trimethylbromosilane, bromomethyldimethylbromosilane, trimethylsilane, hexamethyldisiloxane, and bromomethylpentamethyldisiloxane.

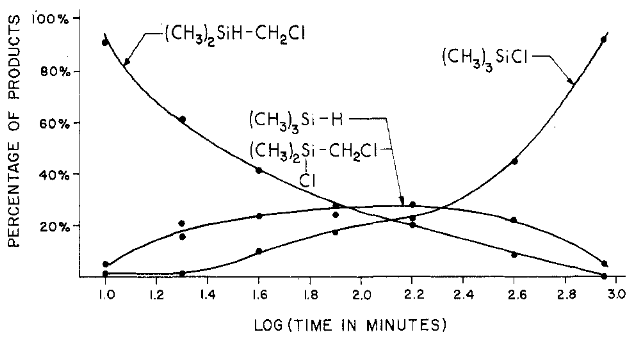


Figure 1. Time dependence of the product ratios in the radical chain reactions of chloromethyldimethylsilane initiated by di-*tert*-butyl peroxide.

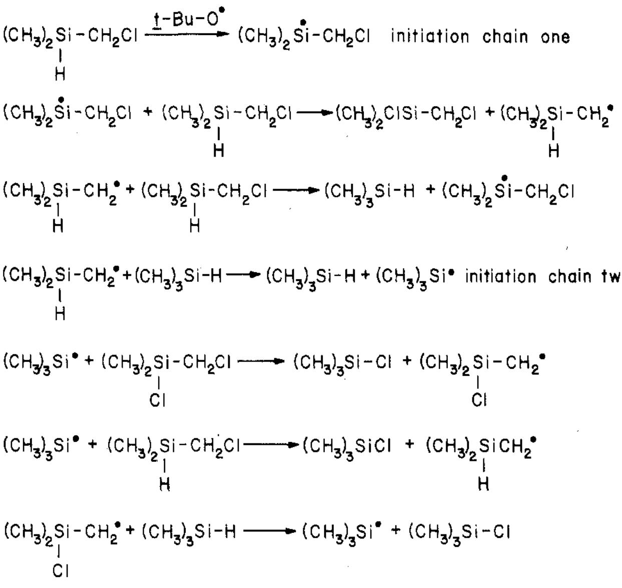


Figure 2. Radical chain reactions of chloromethyldimethylchlorosilane initated by di-*tert*-butyl peroxide.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian T-60 spectrometer. Ten percent solutions in carbon tetrachloride with methylene chloride as internal standard (δ 5.28) were used. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer at an ionizing voltage of 70 eV. Vapor phase chromatography was carried out on a Hewlett-Packard F & M 700 using a 20% polyphenyl ether on Chromosorb P 4 ft × 0.25 in. column. Microanalysis was performed by Elek Microanalytical Laboratories, Torrance, Calif. Boiling points were not corrected.

Bromination of Trimethylchlorosilane. Bromine (454 g, 2.8 mol) was slowly added to a solution of trimethylchlorosilane (1200 g, 11 mol) through which chlorine was being bubbled. The solution was illuminated with a 60-W incandescent lamp. This procedure involves in situ formation of bromine chloride.[23] The product was purified by distillation through a 20-cm Vigreux column. A fraction (510 g), bp 120–140 °C, was collected. In contrast to the literature report, this product was a 1:2 mixture of chloromethyldimethylchlorosilane[24] and bromomethyldimethylchlorosilane[23] as determined by NMR integration.

Preparation of Chloromethyldimethylsilane and Bromomethyldimethylsilane. This mixture (220 g) was reduced with lithium aluminum hydride (20.0 g, 1.2 equiv) in ether. Chloromethyldimethylsilane and bromomethyldimethylsilane were separated by fractional distillation through a vacuum jacketed 25-cm spiral wire column. Chloromethyldimethylsilane (38.2 g, 0.35 mol), bp 80 °C (lit. bp 81.5 °C),[24] was obtained. Bromomethyldimethylsilane (78.5 g, 0.51 mol), bp 99 °C (lit. bp 99–101 °C), was obtained.

Photolysis of Chloromethyldimethylsilane. In a dry 500-ml cylindrical quartz flask connected to a reflux condenser were placed 12.0 g of chloromethyldimethylsilane, 2 drops of mercury, and a 0.5-in. Teflon-covered magnetic stirring bar. The flask was placed at the center of a circular array of 16 12-in. G.E. germicidal lamps (2537 Å). The bottom of the flask was heated using a heating mantle. The solution was stirred. The refluxing vapors were photolyzed for 12 h in an inert atmosphere of purified nitrogen. No mercury was left at the end of the reaction. However, some white solid later identified as mercuric chloride had been formed. The solution weighed 9.2 g. There had been a loss of 2.8 g. Yields reported reflect this loss. Since a water-cooled condenser had been used most of the trimethylsilane formed (lit. bp 6.7 °C)[26] would have been slowly lost. The loss of trimethylsilane will limit the second chain reaction. Thus the amount of chloromethyldimethylchlorosilane will be high. The products were analyzed by VPC: trimethylsilane (1.2%), trimethylchlorosilane (45.4%), chloromethyldimethylchlorosilane (23.2%), hexamethyldisiloxane (1.9%), and finally chloromethylpentamethyldisiloxane (3.2%).

Preparative Scale Thermolysis of Chloromethyldimethylsilane and Di-*tert*-butyl Peroxide. Freshly distilled chloromethyldimethylsilane (8.0 g, 0.074 mol) and 0.4 ml of di-*tert*-butyl peroxide were placed in an ampule (2 × 20 cm) which had been carefully dried. The solution in the ampule was degassed, the ampule sealed, and then heated at 136 °C for 15 h in a Haake R20 constant-temperature bath. At the end of this period, the solution was frozen and the ampule opened. The products were analyzed by VPC: trimethylsilane (3.1%), trimethylchlorosilane (84.8%), chloromethyldimethylchlorosilane (3.4%), hexamethyldisiloxane (3.2%), and chloromethylpentamethyldisiloxane (2.9%).

Preparative Scale Thermolysis of Bromomethyldimethylsilane and Di-*tert*-butyl Peroxide. The reaction of bromomethyldimethylsilane and di-*tert*-butyl peroxide was carried out in a similar fashion. The products were analyzed by VPC: trimethylsilane (3.6%), trimethylbromosilane (83.2%), bromomethyldimethylbromosilane (5.1%), hexamethyldisiloxane (4.4%), and bromomethylpentamethyldisiloxane (1.1%).

Time Dependence of the Product Ratios. Thermolysis of Chloromethyldimethylsilane with Di-*tert*-butyl Peroxide. In each of seven NMR tubes was placed 1 ml of chloromethyldimethylsilane and 10 μl of di-*tert*-butyl peroxide. The solution was degassed and the tubes were sealed. The tubes were heated at 136 °C in a constant-temperature bath. The tubes were withdrawn after various times. They were rapidly cooled to 0 °C and analyzed by NMR. See Table I for data.

***n*-Butyldimethylsilane.** In a 1-l. three-neck round-bottom flask equipped with a mechanical stirrer and a reflux condenser were placed 60.0 g (0.63 mol) of dimethylchlorosilane (Silar Laboratories, Inc.) and 180 ml of absolute diethyl ether. *n*-Butyllithium (2.1 M) in hexane (300 ml) was injected slowly into the solution with vigorous stirring under a dry nitrogen atmosphere. The solution was stirred overnight. The reaction mixture was poured into 300 g of ice. The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered and the product separated by fractional distillation through a 30-cm vacuum-jacketed Vigreux column. A fraction, bp 99 °C (lit. bp 100.5–100.9 °C),[29] 48.2 g (0.4 mol), 63.5% yield, was obtained, ir Si–H 2095 cm^{-1}.

Cothermolysis of *n*-Butyldimethylsilane and Chloromethyldimethylchlorosilane. One milliliter of a 1:1 mixture (v/v) of *n*-butyldimethylsilane and chloromethyldimethylchlorosilane and 15 μl of di-*tert*-butyl peroxide was placed in an NMR tube. The solution was degassed and sealed. The tube was heated in a constant-temperature bath at 136 °C for 3 h. At the end of this time, the NMR spectrum showed no peak at δ 2.64 due to chloromethyldimethylchlorosilane. The products were analyzed by VPC. The following two compounds were separated by preparative VPC and identified by spectral methods: trimethylchlorosilane and *n*-butyldimethylchlorosilane, NMR s (6 H) δ 0.40, m (4 H) 0.91, m (5 H) 1.36, mass spectrum parent ion at *m/e* 150 and 152 with an intensity ratio 2:1.

Spectral Properties of Products. All of the products are known compounds. However, spectral data for these compounds is meager. For this reason we have chosen to report their NMR spectral data.

Chloromethyldimethylchlorosilane.[24] NMR s (6 H) δ 0.52, s (2 H) 2.64; mass spectra parent ion at *m/e* 142, 144, and 146 with intensity ratio of 9:6:1 indicating two chlorine atoms.

Bromomethyldimethylchlorosilane.[23] NMR s (6 H) δ 0.50, s (2 H) 2.35.

Trimethylsilane.[26] NMR d (9 H) δ 0.07, J = 4 Hz; m (1 H) 4.00, J = 4 Hz.

Chloromethyldimethylsilane.[24] NMR d (6 H) δ 0.22, J = 4 Hz; d (2 H) 2.82, J = 2 Hz; m (1 H) 4.13.

Bromomethyldimethylsilane.[25] NMR d (6 H) δ 0.22, J = 4 Hz; d (2 H) 2.48, J = 2 Hz; m (1 H) 4.09.

Chloromethylpentamethyldisiloxane.[27] NMR s (9 H) δ 0.07, s (6 H) 0.15, s (2 H) 2.62; ir 1055 cm^{-1} (Si–O–Si). Anal. Calcd for $C_6H_{17}ClOSi_2$: C, 36.61; H, 8.71. Found: C, 36.99; H, 8.43.

Bromomethyldimethylbromosilane.[28] NMR s (6 H) δ 0.73, s (2 H) 2.70; mass spectra parent ion at *m/e* 230, 232, and 234 with intensity ratio of 1:2:1 indicating two bromines.

Bromomethylpentamethyldisiloxane.[23] NMR s (9 H) δ 0.10, s (6 H) 0.21, s (2 H) 2.39, ir 1064 cm^{-1} (Si–O–Si). Anal. Calcd for $C_6H_{17}BrOSi_2$: C, 29.87; H, 7.10. Found: C, 29.85; H, 6.97.

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Registry No.—Trimethylchlorosilane, 75-77-4; bromine, 7726-95-6; di-*tert*-butyl peroxide, 110-05-4; *n*-butyldimethylsilane, 1001-52-1; *n*-butyldimethylchlorosilane, 1000-50-6; chloromethyldimethylchlorosilane, 1719-57-9; bromomethyldimethylchlorosilane, 16532-02-8; trimethylsilane, 993-07-7; chloromethyldimethylsilane, 3144-74-9; bromomethyldimethylsilane, 7393-54-6; chloromethylpentamethyldisiloxane, 17201-83-1; bromomethyldimethylbromosilane, 18191-42-9; bromomethylpentamethyldisiloxane, 18143-90-3.

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