Photobromination of Alkyltrichlorosilanes

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Photobromination of *n*-butyl, *n*-propyl, ethyl, 2-propyl, and cyclopentyl groups in butyl-, propyl-, ethyl-, and cyclopentyltrichlorosilanes and 2-propylmethyldichlorosilane was studied. The trichlorosilyl group activated the adjacent position toward bromination and had very little effect upon other positions in the alkyl groups. In contrast, the trichlorosilyl group deactivates the adjacent position toward chlorination. Stabilization of a free radical α to silicon by delocalization of the electron between the carbon and the adjacent silicon atom is suggested to explain these results.

Data concerned with the chlorination of alkylchlorosilanes have been collected and summarized.[1,2] The directive effects of various substituted silyl groups have been studied using sulfuryl chloride as the reagent for chlorination.[3-7] Trimethylsilyl, Me_2ClSi, $MeCl_2Si$, and Cl_3Si groups show an effect upon the near positions of an alkyl group that varies from one of activation by Me_3Si to deactivation by Cl_3Si–. Recent experiments using toluene as a standard for measurement of relative rates.[8,9] verified the above conclusions.

The only example of direct bromination of an alkylsilane in which the distribution of products is known is that of tetraethylsilane which brominated only at the position adjacent to silicon.[10] The results obtained by using mixtures of bromine and chlorine to brominate ethyltrichlorosilane and 1-methylethyltrichlorosilane[11] are best compared with those of chlorination since the chlorine radical abstracts the hydrogen in both cases.[12] This paper reports results of the bromination of several alkyltrichlorosilanes.

Results

The apparatus used for the brominations has been described.[13] In this apparatus a volatile conpound is continually fractionated so that the high boiling halogenated products are collected in a receiver and the unhalogenated compound is refluxed through an illuminated chamber. Halogen is admitted to this chamber in which a large molar ratio of compound to halogen is always maintained. This permits a very high yield of monohalogenated products in most cases.

The results of the bromination of various alkylchlorosilanes are summarized in Table I. The mole fractions of the isomeric monobrominated species were corrected by the appropriate statistical factors for the number of hydrogens at the position of substitution. The amount of the most abundant product in each case was set equal to unity and the amounts of other products shown in Table I are then relative to the most abundant one. No products were detected that could have arisen from skeletal rearrangements or from replacement of chlorine by bromine on silicon.

TABLE I

RELATIVE REACTIVITIES PER C–H BOND IN THE BROMINATION OF ALKYLCHLOROSILANES

Substrate	Registry no.	Position[a] 1	2	3	4
$Cl_3SiCH_2CH_2CH_2CH_2H$	7521-80-4	0.00	1.00	0.96	0.00
$Cl_3SiCH_2CH_2CH_2H$	141-57-1	0.00	1.00	0.00	
$Cl_3SiCH_2CH_2H$	115-21-9	1.00[b]	0.22		
$Cl_3SiCH(CH_3)_2$	4170-46-1	1.00	0.00		
$CH_3Cl_2SiCH(CH_3)_2$	18236-89-0	1.00	0.00		
$Cl_3SiCH\underset{\underset{(CH_2)_3}{\vert}}{C}HH$	14579-03-4	1.00	0.04	0.00	

[a] The silyl group is at position 1. [b] The amount of the 1-bromo isomer was corrected for that consumed by formation of 1,1-dibromoethyltrichlorosilane.

Discussion

Butyltrichlorosilane was brominated only in the 2 and 3 positions and nearly equally in each position. *n*-Butane under comparable conditions yielded essentially only 2-bromobutane.[14] These results indicate that the orienting effects of a CH_3 group or of a CH_2SiCl_3 group are nearly identical during bromination.

The chlorination of butyltrichlorosilane with sulfuryl chloride in carbon tetrachloride and toluene showed that the 3 position was more reactive than the 2 position and Nagai concluded that this was because of the inductive effect of the trichlorosilyl group removing electron density from the 2 position.[8,9] However, Mironov's[15] study of the same reaction showed that the 2 position was equally or more reactive than the 3 position. The differences in these two reports[9,15] are likely to be not due to the better analyses as suggested by Nagai[9] but due to the effects of carbon tetrachloride and toluene used as solvents by Nagai. Walling and Miller[16] have shown that the presence of carbon tetrachloride alters the selectivity of the chlorine radical and Russell[17] has demonstrated that the presence of aromatic solvents can change the selectivity of the chlorine radical by

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(1) C. Eaborn, "Organosilicon Compounds," Butterworths and Co. Ltd., London, 1960, p 379.

(2) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. 1, Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965, p 269.

(3) L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 485 (1946).

(4) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *ibid.*, **68**, 488 (1946).

(5) L. H. Sommer, D. L. Bailey, W. A. Strong, and F. C. Whitmore, *ibid.*, **68**, 1881 (1946).

(6) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

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(8) Y. Nagai, N. Machida, and T.Migita, *Bull. Chem. Soc. Jap.*, **39**, 412 (1966).

(9) Y. Nagai, N. Machida, K. Kono, and T. Migita, *J. Org. Chem.*, **32**, 1194 (1967).

(10) E. Larsson and L. O. Knopp, *Acta Chim. Scand.*, **1**, 268 (1947).

(11) V. Mironov, V. Nepomnina, and L. Leites, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **3**, 461 (1960); 428 CB translation.

(12) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, Chapter 8 and references cited therein.

(13) J. L. Speier, U. S. Patent 2,510,148, and U. S. Patent 2,510,149 (June 6, 1950).

(14) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, **25**, 144 (1960).

(15) V. F. Mironov and U. V. Nepomnina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 182 (1955).

(16) C. Walling and B. Miller, *J. Amer. Chem. Soc.*, **29**, 4181 (1957).

(17) G. A. Russell, *ibid.*, **79**, 2977 (1957).

more than a power of ten.[18] Until the nature of these changes[16-19] are understood, evaluation of data obtained in such solvents in terms of only simple inductive effects as done by Nagai[8,9] is unwarranted.

The bromination of propyltrichlorosilane gave mostly 2-bromopropyltrichlorosilane along with a small amount of 2,2-dibromopropyltrichlorosilane. Chlorination has also shown that the 2 position was the most reactive one in propyltrichlorosilane.[4,8,9,20]

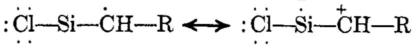
Ethyltrichlorosilane was much less reactive than either propyl- or butyltrichlorosilane. Both positions on the ethyl group were slow to brominate, but the CH_3 group was slower than the Cl_3SiCH_2 group by a factor of about five. Chlorination by sulfuryl chloride showed that the CH_3 was more reactive than the Cl_3SiCH_2-group.[3,8,9] Chlorination with chlorine gave a ratio of 2-chloroethyl to 1-chloroethyltrichlorosilane of about 1.7.[21,22] Correction for the number of hydrogens at each position gives the reactivity at the 2 position as 1.3 times that of the 1 position for chlorination,[23] whereas this study found the 1 position was about 5 times as reactive as the 2 position for bromination.

2-Propyltrichlorosilane and 2-propylmethyldichlorosilane were both brominated exclusively in the 2 position. These results are as expected from the preceding data which indicate a slight activating influence of the silyl groups upon the position adjacent to the silicon atom and the known difficulty of brominating methyl groups in such molecules.

Cyclopentyltrichlorosilane, as expected from the preceding examples, brominated almost entirely in the 1 position with a small amount in the 2 position. The extent of activation of the 1 position may be surprising in this example. The chlorination of cyclopentyltrichlorosilane by sulfuryl chloride has been described[24] as yielding at least 50% 2-chlorocyclopentyltrichlorosilane.

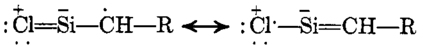
During photohalogenation or other halogenations that proceed by a free-radical mechanism, several factors may determine the distribution of products. The electrophilic halogen atom tends to attack a C–H bond of greatest electron density to form hydrogen halide and an organic free radical.[12] Structural effects upon orientation are greater during brominations than during chlorination for several reasons. Abstraction of a hydrogen atom by a bromine atom is usually endothermic, whereas the corresponding process with a chlorine atom is strongly exothermic.[12] Substituents which influence the stability of the organic radical in these processes will greatly lower the energy of the transition state during brominations, but will have little effect during chlorination.[12] Russell and Brown[25] recognized this when they found that the methyl C–H bonds of toluene were only one-third as reactive as the C–H bonds in cyclohexane toward chlorination, but 230 times as reactive toward bromination. Resonance stabilization of the benzyl free radical is thought to lead to this result in bromination but to have slight effect upon chlorination. Similar effects have been ascribed to halogen substituents during halogenation of haloalkanes.[14,26,27]

No activating influence for bromination having a magnitude comparable with that of an aromatic ring on a methyl group is found in Cl_3Si, Cl_2MeSi, or $ClMe_2Si$ groups as evidenced by the fact that Cl_3SiCH_3, $Cl_2MeSiCH_3$, and $ClMe_2SiCH_3$ are difficult to photobrominate with bromine.[28] However, a small effect of this kind is useful to explain the products obtained in this work. The inductive effect of the Cl_3Si or Cl_2MeSi groups is electron withdrawing leading to deactivation of the positions near silicon during chlorination of alkylsilanes. Resonance stabilization of the intermediate free radicals by delocalizing an electron in the vacant d orbitals of silicon can explain the results of bromination. Delocalization can be thought of in terms of structures such as



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}-\mathrm{Si}-\overset{\cdot}{\mathrm{C}}\mathrm{H}-\mathrm{R} \longleftrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}-\overset{\overset{-}{\cdot}}{\mathrm{Si}}-\overset{+}{\mathrm{C}}\mathrm{H}-\mathrm{R}$$

Because the silicon chlorine bond has double-bond character,[29] stabilization may also be thought of as involving the chlorine as in structures such as



$$:\underset{\cdot\cdot}{\overset{+}{\mathrm{Cl}}}=\overset{-}{\mathrm{Si}}-\overset{\cdot}{\mathrm{C}}\mathrm{H}-\mathrm{R} \longleftrightarrow :\underset{\cdot\cdot}{\overset{+}{\mathrm{Cl}}}\cdot-\overset{-}{\mathrm{Si}}=\mathrm{CH}-\mathrm{R}$$

Experimental Section

A Varan Associates Model A-60 was used to obtain nmr spectra using tetramethylsilane as an internal standard. Analyses by vapor phase chromatography (vpc) were obtained on an F & M Model 720 dual column programmed temperature gas chromatograph equipped with 4 ft × 0.25 in. stainless steel columns packed with 16% Dow Corning® FS-1265 on Chromosorb P.

Materials.—Bromine (Baker Analyzed Reagent), 2-chloropropane (Eastman Organic Chemicals), cyclopentene (Columbia Organic Chemicals), and N-bromosuccinimide (Eastman Organic Chemicals) were used as obtained. Propyltrichlorosilane (bp 123°), methyltrichlorosilane (bp 66.4°), silicon tetrachloride (bp 57.6°), trichlorosilane (bp 31°), and ethyltrichlorosilane (bp 99°) were products of Dow Corning Corp.

1-Methylethyltrichlorosilane was prepared by the method of Sommer and Evans[30] by the reaction of isopropylmagnesium chloride wih silicon tetrachloride.

(1-Methylethyl)methyldichlorosilane was prepared by the reaction of isopropylmagnesium chloride with methyltrichlorosilane and had $n^{25}D$ 1.4250 and $d^{25}{}_4$ 1.0333 (lit.[31] $n^{20}D$ 1.4270 and $d^{20}{}_4$ 1.0385).

Cyclopentyltrichlorosilane was prepared by the following method. Cyclopentene (95.7 g, 1.40 mol), trichlorosilane (191 g, 1.40 mol), and chloroplatinic acid (0.1 N in isopropyl alcohol, 1.0 ml) were heated at 145–155° for 19 hr in a 1.4-l. strainless steel bomb. Analysis by vpc showed a 75% yield. Distillation gave pure cyclopentyltrichlorosilane, bp 181° (756 mm), $n^{25}D$ 1.4687, $d^{25}{}_4$ 1.2414 (lit.[32] $n^{25}D$ 1.4688).

Vapor Phase Bromination of Alkylchlorosilanes.—An apparatus described for the chlorination of alkylsilanes was used.[13] Refluxing alkylsilane and bromine were mixed in a chamber illuminated with a 200-W incandescent lamp. Brominated prod-

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(18) Walling has also reported significant influences in the presence of carbon disulfide or oxygen.[19]

(19) C. Walling and M. F. Mayahi, *J. Amer. Chem. Soc.*, **81**, 1485 (1959).

(20) S. Munkett and R. Muller, *Chem. Ber.*, **92**, 1012 (1959).

(21) A. D. Petrov, V. F. Mironov. V. A. Ponomarenko, and E. A. Chernyshev, *Dokl. Akad. Nauk SSSR*, **97**, 687 (1954).

(22) C. F. Mironov and V. A. Ponomarenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 199 (1957).

(23) E. P. Mikheev [*Dokl. Akad. Nauk SSSR*, **117**, 821 (1957)] reports that this reaction at 15–20° in the liquid phase had a reactivity at the 2 position 1.9 times that of the 1 position.

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(26) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 3520 (1960).

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(28) J. L. Speier, *ibid.*, **73**, 826 (1951).

(29) C. Eaborn, "Organosilicon Compounds," Butterworths and Co. Ltd., London, 1960, p 96.

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(32) H. M. El-Abbady and L. C. Anderson, *J. Amer. Chem. Soc.*, **80**, 1737 (1958).

ucts were continuously separated by a distillation column. Hydrogen bromide passed the condenser and was vented from the system.

Bromination of Butyltrichlorosilane.—Bromine (335 g, 2.09 mol) and butyltrichlorosilane (534 g, 2.79 mol) gave 675 g of crude product. Analysis by vpc (area per cent) showed 40% butyltrichlorosilane, 30% 2-bromobutyltrichlorosilane, 28% 3-bromobutyltrichlorosilane, and 2% unknowns. The 3-bromobutyltrichlorosilane was isolated by preparatory vpc. The nmr gave a sextet at τ 5.9 for BrCH due to adjacent CH_3 and CH_2 and a doublet at 8.25 for CH_3 in the ratio of 1:2.9. The methylene region was not resolved. The nmr of a fraction obtained by distillation [bp 65° (60 mm)] which was by vpc 80% 2-bromo- and 20% 3-bromobutyltrichlorosilane showed a quintet for BrCH at τ 5.71 due to two CH_2 groups, a triplet for CH_3 at 8.90, and a doublet at 7.74 for $SiCH_2$ in the ratio of 1.0:3.0:2.0 for the 2-bromo isomer. The other methylene unit was not resolved. The neutralization equivalent of this fraction was 71.3 (theoretical value for the 80:20 ratio is 71.6).

Bromination of Propyltrichlorosilane.—Propyltrichlorosilane (1084 g, 6.11 mol) and bromine (719 g, 4.49 mol) gave 1397 g of crude product. Analysis by vpc (area per cent) showed 35% unreacted propyltrichlorosilane, 63% 2-bromopropyltrichlorosilane, and 2,2-dibromopropyltrichlorosilane. Distillation gave 2-bromopropyltrichlorosilane, bp 178.8° (751 mm), $n^{25}D$ 1.4871, $d^{25}{}_4$ 1.4976, 99% pure by vpc with a neutralization equivalent of 64.3 (theoretical value 64.2). The nmr showed a sextet for BrCH at τ 5.52, $SiCH_2$ at 7.7–7.9, and CH_3 as a doublet at 8.12 in the proton ratio of 1.0:2.0:3.0. The 2,2-dibromopropyltrichlorosilane was identified in a fraction containing 14.5% 2-bromopropyltrichlorosilane from the nmr spectrum which gave a single peak for CH_2CBr_2 at τ 6.75 and a single peak for CBr_2CH_3 at 7.72 in the ratio of 2.0:3.0.

Propyltrichlorosilane (27 g, 0.15 mol) was also brominated with N-bromosuccinimide (18 g, 0.10 mol) in refluxing carbon tetrachloride (75 ml). The color of bromine was stable in the absence of illumination with a 200-W incandescent lamp. After 40 min of illumination, solid succinimide (9.5 g, theoretical value 9.9 g) was removed by filtration. Analysis by vpc showed 2-bromopropyltrichlorosilane as the only significant product. Traces of higher eluting materials were present.

Bromination of Ethyltrichlorosilane.—Bromine (60 g, 0.38 mol) and ethyltrichlorosilane (81.8 g, 0.50 mol) gave 109 g of crude product. The reaction was very slow and it was difficult to avoid excess bromine in the illuminated chamber. Analysis by vpc (area per cent) showed 48% ethyltrichlorosilane, 27% 1-bromoethyltrichlorosilane, 12% 2-bromoethyltrichlorosilane, and 13% 1,1-dibromoethyltrichlorosilane. The material was distilled. The nmr of a fraction which was by vpc 85% 1-bromo- and 15% 2-bromoethyltrichlorosilane, neut equiv 76.2 (theoretical value for 85:15 ratio is 77.7), showed BrCH as a quartet at τ 6.45 and CCH_3 as a doublet at 8.13 in the ratio of 1.0:2.9 for the 1-bromoethyltrichlorosilane. A fraction which was 34% 1-bromo and 66% 2-bromo isomer gave CH_2Br as a triplet at τ 6.46 and CH_2Si as a multiplet at 7.87 in the ratio of 2.0:2.0 for the 2-bromo isomr. The 1,1-dibromoethyltrichlorosilane was a solid (mp 150–153°) with a neutralization equivalent of 107 (theoretical value 107). The nmr showed CCH_3 as a singlet at τ 7.58.

Bromination of 1-Methylethyltrichlorosilane.—Bromine (60 g, 0.38 mol) and 1-methylethyltrichlorosilane (88.8 g, 0.50 mol) gave 118 g of crude product. Analysis by vpc (area per cent) showed 22% unreacted 1-methylethyltrichlorosilane and 77% 1-bromo-1-methylethyltrichlorosilane along with traces of higher eluting materials. Distillation gave pure 1-bromo-1-methylethyltrichlorosilane, mp 100–110°,[33] with a neutralization equivalent of 85.2 (theoretical value 85.5). The nmr showed only a single peak at τ 8.10.

Anal. Calcd for $C_3H_6BrCl_3Si$: C, 14.1; H, 2.23; Si, 10.9. Found: C, 14.2; H, 2.33; Si, 11.0.

Bromination of (1-Methylethyl)methyldichlorosilane.—Bromine (85 g, 0.53 mol) and (1-methylethyl)methyldichlorosilane (100 g, 0.64 mol) gave 142 g of curde product. Distillation gave 98.5 g (0.42 mol, 79% yield) of the monobrominated product as a waxy solid. The nmr showed only (1-bromo-1-methylethyl)-methyldichlorosilane with $SiCH_3$ as a singlet at τ 9.06 and CCH_3 as a singlet at 8.16 in the ratio of 3.0:5.9.

Anal. Calcd for $C_4H_9BrCl_2Si$: C, 20.3; H, 3.81; Si, 11.9. Found: C, 20.5; H, 3.92; Si, 11.9.

Bromination of Cyclopentyltrichlorosilane.—Bromine (24 g, 0.15 mol) and cyclopentyltrichlorosilane (41 g, 0.20 mol) at 98 mm gave 53 g of crude product. Distillation gave unreacted cyclopentyltrichlorosilane (13 g, 0.065 mol) and bromocyclopentyltrichlorosilane (35 g, 0.12 mol), bp 110° (49 mm), which had a neutralization equivalent of 90.2 (theoretical value for 83% 1- and 3-bromocyclopentyltrichlorosilane and 17% 2-bromocyclopentyltrichlorosilane, 90). The nmr of the bromocyclopentyltrichlorosilane showed CHBr at τ 5.56 and broad alkyl in the approximate ratio of 1:62. The ratio of CHBr to CH_2 plus SiCH was determined by nmr. Bromocyclopentyltrichlorosilane (6.71 mmol) in 2.30 mmol of chloroform gave a ratio of CHBr to $HCCl_3$ of 0.441 showing that 15% was 2- and 3-bromocyclopentyltrichlorosilane and 85% was 1-bromocyclopentyltrichlorosilane.

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[33] The solid underwent a change of structure making the melting point difficult to determine on a Fisher-Johns apparatus.