solved in benzene and chromatographed over Florisil. Elution with benzene yielded 4.0 g (75%) of yellow solid, mp 115–116°.

Anal. Calcd for $C_{17}H_{13}NS$: C, 77.5; H, 4.95; N, 5.33. Found: C, 77.8; H, 5.12; N, 5.42.

11H-Benzo[*a*]carbazole.—Treatment of 12-methylbenzo[*a*]-phenothiazine with lithium in tetrahydrofuran was in similar fashion to the reaction described above. The product was eluted from a Florisil chromatographic column with a 1:1 mixture of ligroin (bp 60–80°) and benzene. The yield was 0.41 g (24%) of light tan solid, mp 222–223°, identical (melting point and infrared spectrum) with an authentic sample[15] of 11H-benzo[*a*]-carbazole.

2-Ethyl-12-methylbenzo[*a*]phenothiazine.—A solution of 4.0 g (14 mmoles) of 2-ethyl-12H-benzo[*a*]phenothiazine in 20 ml of dry ether was added to a suspension of approximately 30 mmoles of sodium amide in 20 ml of dry ether. An excess of methyl iodide was added and the resulting solution was stirred at room temperature for 6 hr. The ether was removed by evaporation and 100 ml of water was added to the residue. The mixture was warmed on a steam bath for 30 min. The aqueous suspension was extracted with benzene and the extract was dried over magnesium sulfate. Chromatographic separation of the benzene solution over Woelm neutral alumina, using benzene as the eluent, yielded 1.8 g (44%) of viscous oil.

Anal.[14] Calcd for $C_{19}H_{17}NS$: C, 78.36; H, 5.84; N, 4.81. Found: C, 78.16; H, 5.74; N, 4.75.

Desulfurization of 2-Carboxy-12H-benzo[*a*]phenothiazine (XIV) with Raney Nickel.—The desulfurization of 2-carboxy-12H-benzo[*a*]phenothiazine was accomplished in 42% yield by the procedure described for the desulfurization of 10-carboxy-12H-benzo[*b*]phenothiazine. The product was recrystallized from ethanol to yield yellow crystals, mp 220–222°.

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.5; H, 4.94; N, 5.32. Found: C, 77.69, 77.75; H, 5.08, 5.05; N, 5.08, 5.28.

(15) Prepared by C. J. Campbell following procedures of Ng. Ph. Buu-Hoi, Ng. Hoan, and Ng. Khoi, *Rec. Trav. Chim.*, **69**, 1053 (1949); Ng. Ph. Buu-Hoi, Ng. Hoan, and Ng. Khoi, *J. Org. Chem.*, **14**, 492 (1949).

Registry No.—VII, 7775-60-2; 7-chloroacetylbenzo-[*c*]phenothiazine, 3640-00-4; XIV, 7731-92-2; VIII, 7731-93-3; II, 7731-94-4; VI, 7731-95-5; XII, 7731-96-6; XXI, 7731-97-7; 10-chloroacetyl-12H-benzo[*b*]phenothiazine, 7731-98-8; 5-chloroacetyl-7H-benzo[*c*]phenothiazine, 7731-79-5; XV, 7771-19-9; 5-acetyl-7H-benzo-[*c*]phenothiazine, 7775-58-8; XVI, 7775-59-9; IX, 7731-80-8; 10-carbomethoxy-12H-benzo[*b*]phenothiazine, 7731-81-9; X, 7731-82-0; III, 7731-83-1; 5-carbomethoxy-7H-benzo[*c*]phenothiazine, 7731-84-2; IV, 7731-85-3; XVII, 7731-86-4; XVIII, 7731-87-5; 12-methylbenzo[*a*]phenothiazine, 6937-18-4; 2-ethyl-12-methylbenzo[*a*]phenothiazine, 7731-89-7; XXII, 7731-90-0.

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Free-Radical Chlorination of Alkylsilanes. II.[1] The Controlling Factors in the Sulfuryl Chloride Chlorination of Alkylchlorosilanes

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The relative reactivities of various carbon–hydrogen bonds of seven different alkylchlorosilanes toward the sulfuryl chloride chlorination have been determined in carbon tetrachloride solvent in the presence of toluene as standard. The reactivity data indicate that the trichlorosilyl group exhibits a negative ($-I$) inductive effect, whereas the dimethylchlorosilyl group displays a positive ($+I$) inductive effect. It is also concluded that the polar effect of the methyldichlorosilyl group is very small in magnitude. The decrease in reactivity of carbon–hydrogen bonds adjacent to a silicon atom is observed and ascribed to the reduced possibilities of the incipient radicals for hyperconjugation.

The free-radical chlorination of alkylchlorosilanes, R_nSiCl_{4-n}, has received extensive attention in the field of synthetic organosilicon chemistry,[2] but studies of the directing effects of the changes in the silane structure on chlorination have been rather semiquantitative. Thus, Sommer and co-workers studied the sulfuryl chloride chlorination of ethyltrichloro-,[3] diethyldichloro-,[4] triethylchloro-,[5] tetraethyl-,[6] and *n*-propyltrichlorosilane,[7] and determined isomer distributions based upon the amounts of the isolated products. Their results show a progressive change in the directive effects of silicon, with $SiCl_3$ directing strongly to the β carbon and $SiEt_3$ being strongly α directing. They also noticed deactivation of the α positions in ethyltrichlorosilane[3] and *n*-propyltrichlorosilane[7] by proximity of the $SiCl_3$ group. More recently, Steward and Pierce[8] chlorinated 3,3,3-trifluoropropyltrichlorosilane using chlorine gas and ultraviolet light to determine the effect of the trifluoromethyl and trichlorosilyl groups on the product distribution. In this instance the carbon–hydrogen bonds in the α position to silicon were found to be about 6.2 times more susceptible to attack by a chlorine radical than the carbon–hydrogen bonds in the β position.

Unfortunately, however, the detailed analysis of much of earlier data concerning the chlorination of alkylchlorosilanes[3–13] was hampered by the lack of the

(1) Part I: Y. Nagai, N. Machida, and T. Migita, *Bull. Chem. Soc. Japan*, **39**, 412 (1966).

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

(4) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *ibid.*, **76**, 1613 (1954).

(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).

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

(8) O. W. Steward and O. R. Pierce, *J. Organometal. Chem.* (Amsterdam), **4**, 138 (1965).

(9) V. F. Mironov and N. A. Pogonkina, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 182 (1955).

(10) V. F. Mironov and V. V. Nepomnina, *ibid.*, 1231 (1959).

(11) S. Munkelt and R. Muller, *Chem. Ber.*, **92**, 1012 (1959).

(12) E. A. Chernyshev, M. E. Dolgaya, and Y. P. Egorov, *Zh. Obshch. Khim.*, **28**, 2829 (1958).

(13) A. D. Petrov, V. F. Mironov, and D. Mashantsker, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 550 (1956).

competitive experiments employing a standard substrate to which the relative reactivities may be referred. Accordingly, comparison of the relative susceptibility of a certain carbon–hydrogen bond in one type of molecule with those of others in another type of molecule was hardly possible.

The present paper describes a study of the sulfuryl chloride chlorination of ethyltrichloro-, ethylmethyldichloro-, ethyldimethylchloro-, *n*-propyltrichloro-, *n*-propylmethyldichloro-, *n*-butyltrichloro-, and *n*-butylmethyldichlorosilane utilizing the competitive chlorination technique[1] in the presence of toluene as standard. By this means, the relative reactivities for those silanes can conveniently be determined.

Results

The chlorination reactions were carried out in carbon tetrachloride using sulfuryl chloride in the presence of benzoyl peroxide as a chlorinating agent. Thus relative reactivities of the above silanes can be calculated by the usual relation for competitive chain-carrying steps in radical chain reactions involving the same attacking radicals

$$\frac{\log [R_1H]_0/[R_1H]}{\log [R_2H]_0/[R_2H]} = \frac{k_1}{k_2} \quad (1)$$

where $[R_1H]_0$ and $[R_2H]_0$ are the initial concentrations of two substrates, $[R_1H]$ and $[R_2H]$ final concentrations, and k_1/k_2 the ratio of rate constants for the attack of the chlorinating reagent on the two species.

Several good approximations can be made in this equation. If we neglect the dichlorination compared with the monochlorination, we obtain

$$\frac{k_1}{k_2} = \frac{\log [R_1H]_0/([R_1H]_0 - [R_1H]_x)}{\log [R_2H]_0/([R_2H]_0 - [R_2H]_x)} \quad (2)$$

where $[R_1H]_x$ and $[R_2H]_x$ are the final concentrations of the monochlorination products. Hence

$$\frac{k_1}{k_2} = \frac{\log \{1 - ([R_1H]_x/[R_1H]_0)\}}{\log \{1 - ([R_2H]_x/[R_2H]_0)\}} \quad (3)$$

When the concentration of the chlorinating reagent is small relative to the initial concentration of the respective substrate, $[RH]_x << [RH]_0$. Therefore, we can expand

$$\log \{1 - ([RH]_x/[RH]_0)\} = -\left\{\frac{[RH]_x}{[RH]_0}\right\} - \left\{\frac{[RH]_x}{[RH]_0}\right\}^2 - \cdots$$

Since the second and higher terms can be neglected compared to the first term, application of the series expansion to eq 3 gives

$$\frac{k_1}{k_2} = \frac{[R_1H]_x/[R_1H]_0}{[R_2H]_x/[R_2H]_0} \quad (4)[14]$$

For convenience all reactivities are referred to toluene as standard. Relative site reactivities of different carbon–hydrogen bonds in a given substrate were calculated from the relative reactivity thus obtained together with relative amounts of the chlorinated isomers and the statistical factor of each position.

The chlorination mixtures were conveniently separated in vapor phase chromatography with the aid of judicious selection of suitable column materials and also of prior conditioning of the columns employed.[15] Pure samples of the chlorinated products were obtained by vapor phase chromatography collection and structures of these materials unambiguously determined by the inspection of their nuclear magnetic resonance (nmr) spectra (see Table I).

TABLE I
NMR SPECTRA[a] OF MONOCHLORINATED ALKYLCHLOROSILANES

	Values[b]
$\overset{2}{C}H_3\overset{1}{C}HClSiCl_3$	6.42 (H^1 quartet), 8.31 (H^2 doublet)
$\overset{2}{C}H_2Cl\overset{1}{C}H_2SiCl_3$	6.23 (H^2 triplet), 7.98 (H^1 triplet)
$\overset{3}{C}H_3\overset{2}{C}HCl\overset{1}{Si}(CH_3)Cl_2$	6.47 (H^2 quartet), 8.35 (H^3 doublet), 9.10 (H^1 singlet)
$\overset{3}{C}H_2Cl\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	6.26 (H^3 triplet), 8.24 (H^2 triplet), 9.13 (H^1 singlet)
$\overset{3}{C}H_3\overset{2}{C}HCl\overset{1}{Si}(CH_3)_2Cl$	6.58 (H^2 quartet), 8.42 (H^3 doublet), 9.47 (H^1 singlet)
$\overset{3}{C}H_3\overset{2}{C}HCl\overset{1}{Si}(CH_3)_3$	6.73 (H^2 quartet), 8.53 (H^3 doublet), 9.91 (H^1 singlet)
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}HClSiCl_3$	6.48 (H^1 two doublets), 8.02 (H^2 multiplet), 8.79 (H^3 doublet)
$\overset{3}{C}H_3\overset{2}{C}HCl\overset{1}{C}H_2SiCl_3$	5.64 (H^2 sextet), 7.43 (H^1 two doublets), 8.33 (H^3 doublet)
$\overset{3}{C}H_2Cl\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	6.44 (H^3 triplet), 8.20 (H^1 and H^2 multiplet)
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{Si}(CH_3)Cl_2$	6.67 (H^2 two doublets), 8.02 (H^3 multiplet), 8.84 (H^4 triplet), 9.10 (H^1 singlet)
$\overset{4}{C}H_3\overset{3}{C}HCl\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	5.66 (H^3 sextet), 8.37 (H^2 and H^4 multiplet), 9.12 (H^1 singlet)
$\overset{4}{C}H_2Cl\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	6.49 (H^4 triplet), 8.06 (H^3 multiplet), 8.79 (H^2 multiplet), 9.20 (H^1 singlet)
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{C}H_2SiCl_3$	5.84 (H^2 multiplet), 8.07 (H^1 and H^3 multiplet), 8.92 (H^4 triplet)
$\overset{4}{C}H_3\overset{3}{C}HCl\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	5.99 (H^3 sextet), 8.26 (H^1, H^2, and H^4 multiplet)
$\overset{4}{C}H_2Cl\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	6.47 (H^4 triplet), 8.37 (H^1, H^2, and H^3 multiplet)
$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{Si}(CH_3)Cl_2$	6.60 (H^2 multiplet), 8.23 (H^3 and H^4 multiplet), 8.96 (H_5 multiplet), 9.10 (H^1 singlet)
$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}HCl\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	5.90 (H^3 quintet), 8.18 (H^2 and H^4 multiplet), 8.94 (H_5 triplet), 9.10 (H^1 singlet)
$\overset{5}{C}H_3\overset{4}{C}HCl\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	5.02 (H^4 sextet), 7.9–9.0 (H^2 and H^4 multiplet), 8.45 (H_5 doublet), 9.19 (H^1 singlet)
$\overset{5}{C}H_2Cl\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{Si}(CH_3)Cl_2$	6.51 (H^5 triplet), 8.1–9.1 (H^2, H^3, and H^4 multiplet), 9.20 (H^1 singlet)

[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Hitachi H-60 nmr spectrometer was used. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed, the peak areas were consistent with proton assignments made.

Interestingly, in all cases examined, the order of increasing retention times (vpc) of monochlorinated

(14) Such a way of approximations for calculating the relative site reactivities has been frequently used in the literature. See, for example, D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2094 (1952); J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959); P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960); R. A. Benkeser, Y. Nagai, and Hooz, *J. Am. Chem. Soc.*, **86**, 3742 (1964).

(15) B. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *ibid.*, **86**, 2446 (1964).

isomers within a given set was found to be invariably $\alpha < \beta < \gamma < \delta$.

In order to test the validity of our method of determining the relative site reactivity for each position of alkylchlorosilanes toward the free-radical chlorination, methyl-*n*-propyldichlorosilane was chlorinated with sulfuryl chloride under slightly different conditions. The data are summarized in Table II in which the reasonably satisfactory constancy of relative site reactivity for each position is evident.

TABLE II

RELATIVE REACTIVITIES FOR THE SULFURYL CHLORIDE CHLORINATION OF METHYL-*n*-PROPYLDICHLOROSILANE IN THE PRESENCE OF BENZOYL PEROXIDE

n-PrSiMeCl$_2$, g	Toluene, g	SO_2Cl_2, g	CCl_4, g	Reflux, hr	Relative reactivity[a,b] α	β	γ
3.14	1.0	1.00	12.3	4	0.40	0.87	0.31
3.14	1.0	1.00	12.3	6	0.40	0.95	0.32
3.14	1.0	0.90	12.3	6	0.34	0.89	0.29
1.57	0.5	0.40	3.1	2	0.34	0.82	0.27
1.57	0.5	0.20	3.1	3	0.41	1.00	0.28
3.14	1.0	0.40	6.2	2	0.40	0.97	0.31
3.14	1.0	0.20	6.2	3	0.35	0.94	0.27

[a] The values listed are relative to one of the three aliphatic hydrogens of toluene which is assigned unit. [b] Product analyses were made by means of vapor phase chromatography (QF-1, 3 m, 100°, 40 ml/min).

The data thus obtained are summarized in Table III which lists the relative site reactivities per hydrogen atom at each carbon atom of those silanes, an aliphatic hydrogen atom in toluene being taken as unity.

Earlier data on isomer distribution in the sulfuryl chloride chlorination are given in Table IV together with our data for comparison. As will be seen from the table, the present results are not always in complete agreement with the earlier data reported by other workers. Such discrepancies are not surprising, however, since earlier data were obtained with far less sensitive analytical techniques.

We initially attempted to obtain data on tetraalkylsilanes in addition to the above alkylchlorosilanes. Unfortunately, however, apart from alkyltrichloro- and dialkyldichlorosilanes, tetraalkylsilanes were found to give rise to complex mixtures of chlorination products. Typically, sulfuryl chloride chlorination of ethyltrimethylsilane was shown by vpc analysis to result in the formation of at least seven different compounds, among them trimethylchlorosilane, chloromethyldimethylethylsilane, and 1-chloroethyltrimethylsilane being identified. Though the formation of these can easily be understood by the following sequences,

$$CH_3CH_2SiMe_3 \xrightarrow{SO_2Cl_2} CH_3CHClSiMe_3 + CH_2ClCH_2SiMe_3 + CH_2ClSiMe_2Et$$

$$ClCH_2CH_2SiMe_3 \longrightarrow CH_2{=}CH_2 + Me_3SiCl$$

$$(\text{or } \cdot CH_2CH_2SiMe_3 \longrightarrow CH_2{=}CH_2 + \cdot SiMe_3 \xrightarrow{SO_2Cl_2} ClSiMe_3)$$

there still remain four unidentified products having comparable retention times. More mysterious is that ethyldimethylchlorosilane was found in the distillates, while it was absent in the original mixture. Thus, the complex nature of the reaction seriously prevented us from obtaining relative reactivity at each position of this sort of silanes.

Discussion

It is generally accepted that free-radical attack of a chlorine atom on aliphatic compounds is controlled by two important structural factors,[16] the inductive and resonance effects of the substituent groups. Some aspects of this problem have been discussed in considerable detail recently.[17-20] Similar investigations with silicon containing aliphatic compounds have suffered from insufficient data. In addition, relatively little is known about the electronic effects of silyl groups,[21] so that the interpretation of the data must be done with care. The present investigation of the structural effects on the free-radical chlorination was carried out employing seven different alkylchlorosilanes for the purpose of obtaining more detailed picture in this area.

The results listed in Table III indicate the similarity of values for the terminal methyl groups in *n*-propyltrichloro-, *n*-propylmethyldichloro-, *n*-butyltrichloro-, and *n*-butylmethyldichlorosilane which confirms that the trichlorosilyl and methyldichlorosilyl groups exert only the slightest influence on the γ- and δ-carbon atoms. It is then obvious that the reactivities of these methyl groups are almost the same as those of ordinary primary hydrogens and also that the γ-methylene groups in the above *n*-butylsilanes undergo substitution at almost the same rate as do ordinary methylene groups. The definitely lower reactivity of the methyl group in ethyltrichlorosilane toward the electron-seeking chlorinating species[16] compared with those of ordinary primary hydrogens must be attributed to induction, so that the trichlorosilyl group is concluded to have $-I$ effect. Comparison of values for the β-methylene groups (0.57, 0.49) in *n*-propyl- and *n*-butyltrichlorosilane with those of γ-methylene groups (1.1, 1.2) in the *n*-butylsilanes also supports this conclusion.

From a similar consideration about the β-methyl group in ethylmethyldichlorosilane, the methyldichlorosilyl group might be deemed to possess the electron-releasing inductive effect. In accord with this interpretation, the α-methylene groups in *n*-propyl- and *n*-butylmethyldichlorosilane are found to be more reactive than the terminal methyl groups in all the *n*-propyl- and *n*-butylsilanes examined.[22] However, disturbing are the lower reactivities for the β-methylene groups in *n*-propyl- and *n*-butylmethyldichlorosilane than those of γ-methylene groups in *n*-butyltrichlorosilane and *n*-butylmethyldichlorosilane. If the methyldichlorosilyl group were an electron-supplying group, the reverse should be observed. It is less safe, therefore, to predict the direction of the inductive effect of the methyldichlorosilyl group, but in any case its magnitude should be considered as very small. Then it is quite reasonably deduced that the dimethylchlorosilyl group is definitely electron donating by induction, since in this group an electron-releasing methyl sub-

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 347.
(17) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).
(18) G. A. Russell, *ibid.*, **80**, 4997 (1958).
(19) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).
(20) P. S. Fredricks and J. M. Tedder, *ibid.*, 3520 (1961).
(21) Reference 2, p 98; D. R. M. Walton, *J. Organometal. Chem.* (Amsterdam), **3**, 438 (1965).
(22) For this comparison it should be noted that all of the groups in question possesses two adjacent carbon–hydrogen bonds available for hyperconjugation.

TABLE III

THE RELATIVE REACTIVITIES OF CARBON–HYDROGEN BONDS IN THE SULFURYL CHLORIDE CHLORINATION OF SILANES[a,b]

CH_3—CH_2SiCl_3[c]	CH_3—$CH_2SiMeCl_2$[c]	CH_3—CH_2SiMe_2Cl[c]
0.17 (0.01) 0.15 (0.01)	0.35 (0.01) 0.41 (0.02)	d 0.82 (0.04)

CH_3—CH_2—CH_2SiCl_3[e]	CH_3—CH_2—$CH_2SiMeCl_2$[f]
0.27 (0.01) 0.57 (0.02) 0.19 (0.01)	0.29 (0.01) 0.92 (0.02) 0.38 (0.01)

CH_3—CH_2—CH_2—CH_2SiCl_3[e]	CH_3—CH_2—CH_2—$CH_2SiMeCl_2$[e]
0.25 (0.01) 1.1 (0.06) 0.49 (0.03) 0.09 (0.01)	0.32 (0.01) 1.2 (0.05) 0.84 (0.04) 0.37 (0.03)

[a] All the experiments were carried out in carbon tetrachloride at reflux temperature. Products analyses were made by means of vapor phase chromatography (QF-1, silicone grease, PMPE). [b] The values quoted in parentheses are probable errors. [c] Average of four runs. [d] The β-chloroethyl compound has not yet been characterized. [e] Average of three runs. [f] Average of seven runs.

TABLE IV

ISOMER DISTRIBUTION IN THE SULFURYL CHLORIDE CHLORINATION

Compound	1	2	3	4	Ref
$CH_3CH_2SiMeCl_3$	29	71			3
	37	63			a
$CH_3CH_2SiMeCl_2$	33	67			10
	43	57			a
$CH_3CH_2CH_2SiCl_3$	13	46	41		7
	7	43	50		11
$CH_3CH_2CH_2CH_2SiCl_3$	16	49	35		a
	0	51	(49)		10
	4	24	54	18	a

[a] The present work.

stituent is replaced for an electron-withdrawing chlorine atom. The present data are consistent with this hypothesis. Thus the α-methylene group in ethyldimethylchlorosilane is significantly more reactive than all the α-methylene groups adjacent to methyldichlorosilyl group.

Another significant feature of Table III is the marked decrease in reactivity of hydrogens on carbons α to silicon. For instance, the α-methylene group in ethyldimethylchlorosilane is less reactive than ordinary methylene groups (0.82 *vs.* 1.1, 1.2). Furthermore, the methylene groups bearing the methyldichlorosilyl substituent are about one-third as reactive as ordinary methylene groups (0.41, 0.38, 0.37 *vs.* 1.1, 1.2). In the former case, the α-methylene group might be expected to be much more reactive than ordinary methylene groups because of its proximity to the electron-releasing dimethylchlorosilyl substituent. Similarly, in the latter cases, the α-methylene groups would be expected to be nearly the same in reactivity as ordinary methylene groups, since they possess the methyldichlorosilyl substituent that exerts a very small inductive effect. Although these results can not be predicted on the simple theory of inductive and resonance effects, the concept of hyperconjugation readily explains such low reactivities of the α positions. These methylene groups on silicon have only two or three adjacent carbon–hydrogen bonds capable of stabilizing the incipient radicals by hyperconjugation and the α-methylene hydrogens must be compared with ordinary hydrogens. The effect of this sort must partly be responsible for the very low reactivities of the methylene groups bearing the trichlorosilyl substituent. On this basis the hydrogen abstraction from the α-methylene groups relative to silicon is considerably difficult compared with that from ordinary methylene groups.

The same argument can also be applied to explain why the α positions of 1,1-dichlorosilacyclopentane are quite reluctant to free-radical formation relative to the β positions.[15] Likewise, it has now become easy to elucidate the fact that ethylmethyldichlorosilane undergoes substitution at only the ethyl group in the sulfuryl chloride chlorination.[23] In this case, the radical intermediate derived from the hydrogen abstraction from the methyl group attached to silicon is by no means resonance stabilized by hyperconjugation. The importance of hyperconjugation is also manifest in the high reactivities of the β-methylenes in the *n*-propylsilanes relative to those in the corresponding *n*-butylsilanes.

Experimental Section

Materials.—All the alkylchlorosilanes used were prepared as described in the literature. These were ethyltrichlorosilane[3] (bp 96°), ethylmethyldichlorosilane[10] (bp 98–99°), ethyldimethylchlorosilane[24] (bp 88–89°), ethyltrimethylsilane[25] (bp 62°), *n*-propyltrichlorosilane[7] (bp 122°), *n*-propylmethyldichlorosilane[26] (bp 127°), *n*-butyltrichlorosilane[10] (bp 146°), and *n*-butylmethyldichlorosilane[26] (bp 148.5°). (All the boiling points are uncorrected.)

Procedure for the Competitive Chlorination.—A solution of sulfuryl chloride and benzoyl peroxide in carbon tetrachloride was added dropwise to a solution of an appropriate alkylchlorosilane and toluene in carbon tetrachloride under reflux. After refluxing for 2–6 hr, the resultant reaction mixture was subjected to vpc analysis employing an Ohkura Model 1700 chromatograph. In all competitive experiments conversion of each of the reactants was found at most below 20%. Vpc analysis also showed the extent of dichlorination to be below 5% relative to monochlorination even in the worst cases. It was necessary for obtaining reproducible analysis of a chlorosilane mixture to condition the columns utilized by the prior injection of a large amount of silicon tetrachloride or other volatile chlorosilanes.[15] Analytical procedures were calibrated by the use of prepared samples of the chlorinated products. The vpc analytical method was tested upon known mixtures of the various chlorination products. The results showed that there was no preferential decomposition of one of the products during the analysis. Except for the case of ethyldimethylchlorosilane, the vapor phase chromatograms showed the expected product peaks as well as the starting materials but no other peaks. This fact furnishes evidence of the stability of these chlorination products during the reaction. A noncompetitive chlorination mixture of ethyldimethylchlorosilane yielded four product peaks in a chromatogram (silicone DC 550, 120°) and among them only the first peak was isolated

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by vpc. From its nmr pattern the compound was identified as α-chloroethyldimethylchlorosilane. The remaining three peaks could not be isolated and purified by vpc because of the rather poor resolution obtained for these peaks. Since there must be only three possible monochlorination products, one would imagine some side reaction occurring with this starting material. However, such complications do not preclude obtaining the relative site reactivity for the α position of ethyldimethylchlorosilane in view of the present method of calculation. The possibility for the decomposition of the α-chloro isomer during the vpc analysis could be eliminated by the success of vpc isolation and purification. A typical set of the competitive data is presented in Table II.

Chlorination Products of Ethyltrichlorosilane.[3]—Ethyltrichlorosilane (189 g) was heated under reflux with 187 g of sulfuryl chloride in the presence of 2 g of benzoyl peroxide to give 34 g of α-chloroethyltrichlorosilane (bp 135°) and 48 g of β-chloroethyltrichlorosilane (bp 150°). These were used as authentic samples. Each of the samples collected by vpc from the competitive runs agreed, in every respect (infrared absorptions, retention times, chemical shifts, and refractive indices) with the corresponding authentic sample.

Chlorination Products of Ethylmethyldichlorosilane.[23]—Ethylmethyldichlorosilane (179 g) was chlorinated with 268 g of sulfuryl chloride in the presence of 0.1 g of benzoyl peroxide yielding 49 g of α-chloroethylmethyldichlorosilane (bp 137°) and 63 g of β-chloroethylmethyldichlorosilane (bp 153°). These were used as authentic samples and their physical properties were compared with those of the samples obtained from the competitive chlorination mixtures by vpc.

Chlorination of Ethyldimethylchlorosilane.—A chlorination mixture of ethyldimethylchlorosilane was subjected to vpc analysis (silicone DC 550, 120°), there being noticed four product peaks in a ratio of 53:18:22:7. The compound responsible for the largest peak was obtained by vpc collection and identified as α-chloroethyldimethylchlorosilane by its nmr spectrum (Table I).

Chlorination Products of *n*-Propyltrichlorosilane.—There were three peaks on the chromatogram (QF-1, 120°). Each of the compounds was obtained by vpc collection and identified by nmr measurement. The first was (1-chloropropyl)trichlorosilane, the second the 2-chloro isomer, the last the 3-chloro isomer.

Chlorination Products of *n*-Propylmethyldichlorosilane.—There were again three product peaks on the chromatogram (QF-1, 120°). The compounds were separately collected by vpc; the structures were determined based on their nmr spectra (Table I). The order of retention times was found to be 1-chloro < 2-chloro < 3-chloro isomer.

Chlorination Products of *n*-Butyltrichlorosilane.—Vpc analysis (Versilube F-50, 135°) of a chlorination mixture of the silane disclosed four product peaks. Pure samples of the second, third, and fourth compounds were obtained by vpc collection. These were the 2-chloro, 3-chloro, and 4-chloro isomers, respectively (Table I). The first peak was, therefore, due to the 1-chloro isomer.

Chlorination Products of *n*-Butylmethyldichlorosilane.—Vpc analysis (QF-1, 125°) of a noncompetitive chlorination mixture of *n*-butylmethyldichlorosilane disclosed four product peaks. Each of pure samples of these products was isolated and purified by preparative scale vpc. Nmr determination of these compounds (Table I) confirmed the identity of the first peak as the 1-chloro isomer, the second as the 2-chloro isomer, the third as the 3-chloro isomer, and the fourth as the 4-chloro isomer.

Registry No.—**1**, 7787-82-8; **2**, 6233-20-1; **3**, 7787-84-0; **4**, 7787-85-1; **5**, 7787-86-2; **6**, 7787-87-3; **7**, 7787-88-4; **8**, 7787-89-5; **9**, 2550-06-3; **10**, 7787-91-9; **11**, 7787-92-0; **12**, 7787-93-1; **13**, 7787-94-2; **14**, 1000-58-4; **15**, 2322-28-3; **16**, 7787-97-5; **17**, 7787-98-6; **18**, 1591-20-4; **19**, 1591-21-5.

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The Chemiluminescence of Some Monoacylhydrazides

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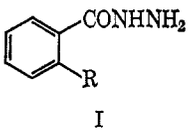
Some correlations between the structures of acylhydrazines and N,N′-diacylhydrazines and their chemiluminescence efficiencies have been determined. A comparison of the chemiluminescence spectra of the hydrazides of 1-hydroxy-2-naphthoic acid and of 1-hydroxy-2-anthroic acid and the fluorescence spectra of the corresponding carboxylate ions in dimethyl sulfoxide indicates that the latter compounds may be the emitters in the chemiluminescent reaction. A hydrazide related to firefly luciferin was prepared and shown not to be efficient in chemiluminescence.

Because of the low intensity of their chemiluminescence, monoacylhydrazides have not been studied by many workers with the purpose of establishing a relationship between structure and chemiluminescent reactivity. In aqueous systems, some *ortho*-substituted benzhydrazides (I, R = OH, NH_2) are weakly chemiluminescent.[3,4] Recrystallized *o*-, *m*-, and *p*-nitrobenzhydrazides do not emit light, although the crude materials (possibly containing the aminohydrazides) do in aqueous systems.[5] Among disubstituted hydrazines, N,N′-dianthranoylhydrazine was found to be weakly chemiluminescent.[3] The hydrazide of benzenesulfonic acid is not chemiluminescent[6] and so resembles benzhydrazide, which is nonchemiluminescent.[5] Other references to earlier work have been summarized.[7] This paper reports the results of a search for efficient acyclic hydrazides.



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From the observations above, it appeared that chemiluminescent activity was conferred on linear hydrazides by electron-supplying substituents. This correlation had been noted for derivatives of phthalic hydrazide by Drew and Pearman.[8] Accordingly, examination of substituent effects was directed toward the amino, hydroxy, and methoxy substituents.

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