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HOMOLYTIC CHLORINATION OF ALIPHATIC COMPOUNDS—V[1, 2]

PHOTOCHLORINATION OF METHYLSILANES, METHYL(CHLOROMETHYL)-SILANES, ETHYLSILANES AND THEIR CARBON ANALOGUES

Y. NAGAI, M. KOSUGI, K. TAKEUCHI and T. MIGITA
Department of Chemistry, Gunma University, Kiryu, Gunma, Japan

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Abstract—The relative reactivities of various C—H bonds of eleven different alkylchlorosilanes in photochlorination were compared with those of the corresponding carbon analogues. Results show that the C—H bonds attached to carbon are more activated than would be expected on the basis of the inductive effect only. It is also shown that the relative reactivities of various C—H bonds are correlated with the ^{13}C—H coupling constants. The Hammett-Taft equation applies to the correlations and the magnitudes of resonance effects associated with the substituents attached to the point of attack have been estimated.

IN EARLIER studies[3, 4] on chlorination of alkylchlorosilanes, the electronic effects of substituted silyl groups were discussed. As a marked decrease in the reactivity of hydrogens on carbons alpha to silicon was found, it seemed of interest to compare the relative site reactivities of alkylchlorosilanes with those of their carbon analogues.

Such a comparison employing methylsilanes has been previously made and Speier[5] found that trimethylchlorosilane and t-butyl chloride were chlorinated photochemically at 55–60° at about the same rate. Recent results obtained by Russell[6] also indicate that the reactivity of a Me group in tetramethylsilane toward photochemical chlorination is almost the same as that of a Me group in 2,3-dimethylbutane. Furthermore, progressive decrease of reactivity with increasing number of Cl atoms on silicon was noticed in reactions of tetramethyl-, trimethylchloro-, and dimethyldichlorosilane. It was then mentioned that neighboring silicon appears to have much the same effect as neighboring carbon.[7] The situation is mildly different in the case of the hydrogen abstraction by the trifluoromethyl radical, since Cheng and Szwarc[8] recently reported that tetramethylsilane reacted about three times as rapidly as neopentane.

In the present paper a comparison is made between the rates of methylsilanes, chloromethyl methylsilanes and ethylsilanes toward the chlorine radical with those of their carbon analogues, in order to obtain a better understanding of the controlling factors of the silicon atom in the free radical chlorination. Furthermore, the present paper discloses several correlations between the relative site reactivities and the respective NMR ^{13}C-H coupling constants which seem to constitute a useful theoretical tool in elucidating the reactivities of a variety of C-H bonds for the hydrogen abstraction by free radicals.

RESULTS

All the compounds used were competitively photochlorinated at 40° with an insufficient amount of the chlorinating agent. Product analysis was made by VPC. Relative rates were calculated using the equation of Ingold and Shaw[9] from concentrations of reactants or products as described previously.[4, 10] For convenience all relative rates are referred to 2,2-dichloropropane as standard. Relative site reactivities of various C-H bonds were calculated from the relative rates thus obtained together with relative amounts of the chlorinated isomers and the statistical factor for the respective position. Unit reactivity was assigned to one of the six available hydrogens of 2,2-dichloropropane. Each pure sample of the chlorination products was obtained either by VPC from the respective chlorination mixture or by independent synthesis. The structures of these materials were unequivocally characterized by means of NMR spectroscopy (Experimental).

Calculation of relative site reactivities for the positions of tetraethylsilane and triethylchlorosilane was found to require precautions. Actually, a vapor phase chromatogram of the chlorination mixture of tetraethylsilane showed complete absence of a peak for 2-chloroethyltriethylsilane. Instead, a peak for triethylchlorosilane was noticed. The formation of this compound may be accounted for by the unusual ease with which 2-chloroethyltriethylsilane decomposes when heated to give ethylene and triethylchlorisilane.[11, 12] Thus, the extent of the formation of

$$ClCH_2CH_2SiEt_3 \rightarrow ClSiEt_3 + CH_2{=}CH_2$$

triethylchlorosilane was considered to be a direct measure of the β-substitution. On this basis the relative reactivity of the 2-position was obtained by determining the relative amount of triethylchlorosilane. Likewise, a chlorination mixture was found to afford diethyldichlorosilane together with 2-chloroethyldiethylchlorosilane besides the 1-chlorination product. For the same reason as above the total amount of these two compounds was assumed to be equal to the extent of the β-attack by the chlorine radical. The relative reactivities thus determined are listed in Table 1.

The ^{13}C—H spin–spin coupling constants, $J(^{13}C—H)$, determined for the majority of compounds used in this study are listed in Table 2 together with those reported by other workers. Table 2 includes data for ethane, ethyl chloride, n-propyl chloride, ethylidene chloride, 1,2-dichloroethane and 1,1,2-trichloroethane the relative rate data of which have been obtained previously.[10, 13] Coupling constants were evaluated from the satelite bands produced by the ^{13}C in natural abundance which are symmetrically disposed about the main proton signals.

DISCUSSION

Comparison of chlorination rates between Methylsilanes and their carbon analogues. As expected from the electron seeking character of the attacking chlorine radical,[19] relative reactivities in both silicon and carbon series decrease with successive introduction of chlorine substituents on the central atom.

A Me group in the silicon series reacts at almost the same rate as does the respective Me group in the carbon series and this finding is in keeping with earlier studies.[5, 6] This trend cannot be explained, however, by the simple conception of induction, because a silyl group should be more electron-releasing in nature than the analogous carbon group[20] and therefore a methylsilane would be expected to react faster toward

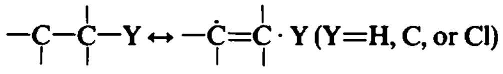
TABLE 1. RELATIVE REACTIVITIES FOR THE PHOTOCHLORINATION OF VARIOUS SILANES AND THEIR CARBON ANALOGUES (40°)[a, b]

CH_3—$SiCl_3$	0·13	CH_3—CCl_3	0·07
CH_3—$SiMeCl_2$	1.2	CH_3—$CMeCl_2$	1·00
CH_3—$SiMe_2Cl$	12	CH_3—CMe_2Cl	9·8
CH_3—$SiMe_3$	118	CH_3—CMe_3	(56)[b]
CH_3—$SiCl_2$—$CHCl$	— 6·4	CH_3—CCl_2—$CHCl$	0·36 1·5
$(CH_3)_2$—$SiCl$—CH_2Cl	4·4 24	$(CH_3)_2$—CCl—CH_2Cl	3·4 5·9
$(CH_3)_3$—Si—CH_2Cl	22 58	$(CH_3)_3$—C—CH_2Cl	20 20
CH_3—CH_2—$SiCl_3$	12 7·6	CH_3—CH_2—CCl_3	3·1 2·6
CH_3—CH_2—$SiCl_2Et$	21 24	CH_3—CH_2—CCl_2Et	4·4 7·2
CH_3—CH_2—$SiClEt_2$	25 48	CH_3—CH_2—$CClEt_2$	9·3 19
CH_3—CH_2—$SiEt_3$	40 66	CH_3—CH_2—CEt_3	27 39

[a] The values are relative to the reactivity of a C—H bond of 2,2-dichloropropane

[b] Calculated from the rate constants of vapor phase photochlorination of neopentane and ethyl chloride[14]

the chlorine radical than the respective carbon analogue. Accordingly, it is possible to conclude that the methyl hydrogens in the carbon series are actually more activated than would be expected on the basis of the inductive effect only. Should this be the case, the increased reactivity for the carbon series can be ascribed to the stabilization of the intermediate radicals by hyperconjugation[3, 4, 21] involving C—H, C—C or C—Cl bonds. Stabilization of this



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Y \leftrightarrow -\overset{\cdot}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}\cdot Y\ (Y=H, C, \text{or } Cl)$$

type is hardly expected for the silicon series, since the contributing hybrid structure requires an effective $p_\pi(C)$-$p_\pi(Si)$ orbital overlap which is as yet unqualified, at least in the ground states.[22] Conflicting with this explanation, resonance stabilization of the intermediate free radicals by delocalizing an electron in the vacant d orbitals of silicon has recently been suggested[23] to explain the results of bromination of alkylchlorosilanes. However, an effect of this kind is not likely to be operative in our case

TABLE 2. ^{13}C—H COUPLING CONSTANTS FOR THE RELEVANT COMPOUNDS

Compound[a]	$J(^{13}C—H)$, c/s	Ref
$C\underline{H}_3SiCl_3$	125·5	15
$(C\underline{H}_3)_2SiCl_2$	124	15
$(C\underline{H}_3)_3SiCl$	121	15
$(C\underline{H}_3)_4Si$	118	15
$C\underline{H}_3CH_3$	126	18
$C\underline{H}_3CH_2Cl$	127	18
$C\underline{H}_3CHCl_2$	132	18
$C\underline{H}_3CCl_3$	134	16
$(C\underline{H}_3)_2CCl_2$	132	16
$(C\underline{H}_3)_3CCl$	128	*b*
$(C\underline{H}_3)_4C$	124	17
$C\underline{H}_3SiCl_2(CH_2Cl)$	124	*b*
$CH_3SiCl_2(C\underline{H}_2Cl)$	144	*b*
$(C\underline{H}_3)_2SiCl(CH_2Cl)$	122	*b*
$(CH_3)_2SiCl(C\underline{H}_2Cl)$	141	*b*
$(C\underline{H}_3)_3Si(CH_2Cl)$	120	*b*
$(CH_3)_3Si(C\underline{H}_2Cl)$	137	*b*
$C\underline{H}_3CCl_2(CH_2Cl)$	132	*b*
$CH_3CCl_2(C\underline{H}_2Cl)$	156	*b*
$(C\underline{H}_3)_2CCl(CH_2Cl)$	129	*b*
$(CH_3)_2CCl(C\underline{H}_2Cl)$	153	*b*
$(C\underline{H}_3)_3C(CH_2Cl)$	126	*b*
$(CH_3)_3C(C\underline{H}_2Cl)$	148·5	*b*
$C\underline{H}_3CH_2CCl_3$	130	*b*
$(C\underline{H}_3CH_2)_2CCl_2$	128	*b*
$(C\underline{H}_3CH_2)_3CCl$	127	*b*
$(C\underline{H}_3CH_2)_4C$	126	*b*
$CH_3CH_2C\underline{H}_2Cl$	150	*b*
$C\underline{H}_2ClCH_2Cl$	154	18
$C\underline{H}_2ClCHCl_2$	157	*b*

[a] $J(^{13}C—H)$ for protons underlined

[b] The present work

since its magnitude is small even in bromination where the resonance effects of substituents are exceedingly important.[7] Moreover, since it has been demonstrated[24] that in bromination the ratio of products which are finally formed is not the result of a kinetically controlled substitution reaction, kinetic elucidation based upon the bromination results without special precautions could be of limited theoretical significance.

Interestingly, the chloromethyl groups on silicon are much more reactive than the corresponding groups on carbon. A possible explanation can be advanced for this trend when the effects of the α-chlorine substituent are considered. Instead of the hyperconjugation discussed above, it can be argued that the resonance stabilization by the α-Cl atom as depicted by the hybrid radical structures below[25] could be very important.[10, 26] Hence, the greater reactivity

$$\dot{C}—\underset{\cdot\cdot}{\ddot{Cl}}: \leftrightarrow \overset{(-)}{\ddot{C}}—\underset{\cdot\cdot}{\overset{(+)}{Cl}}:$$

for an CH_2Cl-Si group over that for the corresponding CH_2Cl-C group is perhaps not unexpected, since the hyperconjugation cannot make as large a contribution as the activating resonance effect of the Cl atom[27] and the polar nature of the groups attached to the reaction site is likely to be responsible for the difference in reactivity between two types of the chloromethyl group.

Comparison of chlorination rates between ethylsilanes and their carbon analogues. Sommer *et al.* studied the sulfuryl chloride chlorination of the ethylsilanes and determined the isomer distribution based upon the amounts of isolated products.[28] A progressive change was found in the directive effects of silicon, with $SiCl_3$ directing strongly to the β-carbon and $SiEt_3$ being strongly α-directing. This statement is qualitatively true, but as discussed earlier, the relative reactivities of ethylsilane should take into account the occurrence of β-elimination involving silicon and this was done when tabulating the data in Table 1.

Both the 1- and 2-positions of the ethylsilanes are more reactive than the corresponding positions in the carbon series. This trend is reasonable from the consideration of the electron-releasing property of silicon. Intermediate radicals derived from methylene groups in the ethylsilanes are stabilized by hyperconjugation due to the adjacent Me groups, so that the additional resonance effects which might be expected from the replacement of silicon by carbon would be only of secondary importance. Instead, the change in the electron density around hydrogens of the methylene groups seems to be more important. The case is quite different with the methylsilanes.

Correlation of reactivities of various C—H *bonds with the* ^{13}C—H *coupling constants.* With a view to structure-reactivity relationship, free radical chlorination has been treated within the framework of the linear free energy relationships. Typically, relative rates of hydrogen abstraction by halogen atoms from benzylic C—H bonds have been frequently quoted to correlate with the Hammett substituent constants.[29] Also, we were first to report a relationship between free radical chlorination rates and the Taft polar substituent constants in a purely aliphatic system[10, 13] and a similar treatment has been reported by Mack.[30] Since, however, substituent constants of groups containing silicon are ill-defined, the similar Hammett treatment cannot be applied to a large range of organosilicon compounds. Nevertheless, information now available provides a good measure of the electron density around hydrogens in a variety of C—H bonds. It has been shown that the ^{13}C—H coupling constants are related to the fraction of s character employed by carbon in its bonds to hydrogen[31] which is in turn related to the electron density around that hydrogen.[32] It is apparent, therefore, that the change in the $J(^{13}C—H)$ is reflected[33, 34] in the kinetic data for a reaction of C—H bonds where the polar factor is important.

Relative rate data given in Table 1 are plotted in Fig 1 against $J(^{13}C—H)$ available (Table 2). The reactivities of the C—H bonds investigated can be grouped under four categories, since there are four satisfactory correlations represented by lines a–d. Therefore, within a limited type of C—H bonds, the reactivities are chiefly governed by the electron density around hydrogen. Such linear relationships should be observed when the resonance stabilization by substituents is absent, nearly constant or varies linearly for a set of the intermediate radicals resulting from the hydrogen abstraction. Thus, plots for the fourteen C—H bonds of Me groups attached to carbon afford an excellent correlation (line b) with a slope of -0.285 and a correlation coefficient of 0·964. A linear correlation also shown in Fig 1 (line a) is found for the six CH_3-Si

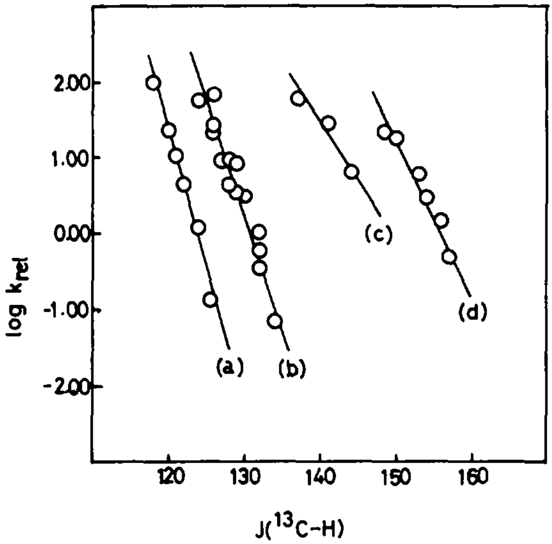


FIG 1. Relationship between log k_{rel} and $J(^{13}C—H)$ (c/s)

groups of compounds listed in Table 1. In this relationship the slope is equal to −0·369 with a correlation coefficient of 0·990. Similar correlations (line C and line d) are found for the six CH_2Cl-C groups with a slope of −0·185 and a correlation coefficient of 0·972 and for the three CH_2Cl-Si groups with a slope of −0·132 and a correlation coefficient of 0·956. The negative signs of the slopes for these lines are expected, since the electron-seeking chlorine radical tends to attack a C—H bond of greater electron density[19] where the s character employed by carbon will be diminished.

The fact that four independent correlations exist between the kinetic data and $J(^{13}C—H)$ implies that resonance stabilization by substituents is nearly constant for a given set of C—H bonds. Contrary to this expectation, there is a trend of slopes* for the correlations which decrease going from line a through line b to line d, supporting Russell's interpretation[35] that in chlorination the sensitivity of the transition state to resonance stabilization depends on the reactivity of a C—H bond to be abstracted. To the first approximation, however, the difference in the degree of bond breaking involved in chlorination is not so large that it can be assumed that the sensitivity to resonance is nearly equal for the range of C—H bonds investigated. Thus, if we accept a hypothesis that a silyl group has no ability to delocalyze an odd electron placed on an adjacent C atom,† the deviations from the correlation from the CH_3-Si groups (line a) are implied to be measures of resonance effects of the substituents. The vertical deviations for the experimental points from this line can be divided into three classes and average deviations of 2·5, 7·6 and 11·4 are found for the CH_3-C (line b), CH_2Cl-Si (line c) and CH_2Cl-C (line d) groups, respectively. Since

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* The slope of the correlation for $CH_2Cl—Si$ (line c) was omitted from the consideration because it includes only three experimental points.

† This hypothesis received a further support from the fact that the relative reactivity of a methane hydrogen (0·226) calculated from the rate constant of methane[14] falls on the correlation for the $CH_3—Si$ groups (line a).

these deviations correspond to the resonance effects of the groups to which the reacting C—H bonds are attached, it is clear that the hydrogen abstraction rates follow an equation that relates the rates to the sum of polar and resonance effects.[20] This relationship is represented by the equation

$$\log k_{rel} = \rho^{*} J(^{13}C{-}H) + M \qquad (1)$$

where M is the resonance effect. A deviation of 2·5 log unit found for the CH_3—C groups is a measure of resonance effects of the substituted Me groups attached to the reacting methyls (designates as M_C). Likewise, the deviation of 7·6 log unit represents the magnitude of the resonance effect of the α-Cl atom (designated as M_{Cl}). A deviation of 11·4 log unit found for the CH_3Cl—C groups correspond the resonance effects concurrently exerted by the two independent substituents, the Cl and a substituted Me group (designated as $M_{C,\,Cl}$). From the above rationalization, it is expected that the value of $M_{C,\,Cl}$ is equal to the sum of the values of M_C and M_{Cl}. We feel that the agreement is satisfactory, since the M_{Cl} value derived as above is subjected to rather large experimental error. Apart from this point, using parameters obtained above, Eq. (1) is followed by the rates of twenty-nine C—H bonds toward the chlorine radical with a correlation coefficient of 0·995 as shown in Fig 2. Two conclusions, in addition to the additivity rule regarding the resonance and inductive effects, can be drawn from the success of Eq. (1) in correlating the hydrogen abstraction rates:

(a) The resonance effects of all the substituted Me groups are nearly the same in the magnitude.

(b) The resonance effect of the α-Cl atom is much larger than hyperconjugation effects.

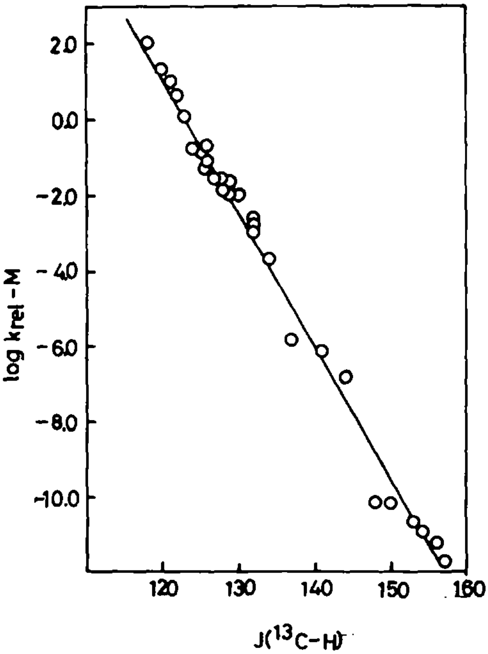

FIG 2. Relationship between (log k_{rel}-M) and J(^{13}C—H) (c/s)

TABLE 3. NMR CHEMICAL SHIFTS (τ VALUE) OF VARIOUS COMPOUNDS[a, b]

Formula	X:Si	X:C
$CH^1_3XCl_2CH^2_2Cl$	0·19 (H^1 singlet) 6·94 (H^2 singlet)	7·82 (H^1 singlet) 6·03 (H^2 singlet)
$(CH^1_3)_2XClCH^2_2Cl$	9·43 (H^1 singlet) 7·08 (H^3 singlet)	8·35 (H^1 singlet) 6·33 (H^2 singlet)
$(CH^1_3)_3XCH^2_2Cl$	9·87 (H^1 singlet) 7·31 (H^2 singlet)	9·00 (H^1 singlet) 6·74 (H^2 singlet)
$CH^1_3XCl_2CH^2Cl_2$	8·96 (H^1 singlet) 4·60 (H^2 singlet)	7·70 (H^1 singlet) 4·08 (H^2 singlet)
$(CH_2Cl)_2XCl_2$	—	5·89 (singlet)
$(CH^1_3)_2XClCH^2Cl$	9·34 (H^1 singlet) 4·68 (H^2 singlet)	8·21 (H^1 singlet) 4·23 (H^2 singlet)
$CH^1_3XCl(CH^2_2Cl)_2$	9·32 (H^1 singlet) 6·97 (H^1 singlet)	8·28 (H^1 singlet) 6·22 (H^2 singlet)
$(CH^1_3)_3XCH^2Cl_2$	9·78 (H^1 singlet) 4·78 (H^2 singlet)	8·87 (H^1 singlet) 4·47 (H^2 singlet)
$(CH^1_3)_2X(CH^2_2Cl)_2$	9·79 (H^1 singlet) 7·19 (H^2 singlet)	8·92 (H^1 singlet) 6·57 (H^2 singlet)
$CH^1_3CH^2ClXCl_3$	8·31 (H^1 doublet) 6·42 (H^2 quartet)	9·16 (H^1 doublet) 5·50 (H^2 quartet)
$CH^1_2ClCH^2_2XCl_3$	6·23 (H^1 triplet) 7·98 (H^2 triplet)	6·18 (H^1 multiplet) 6·89 (H^2 multiplet)
$CH^1_3CH^2ClX(CH^3_2CH^4_3)Cl_2$	8·43 (H^1 doublet) 6·43 (H^2 quartet) 8·78 (H^3 and H^4 multiplet)	8·21 (H^1 doublet) 5·75 (H^2 quartet) 7·65 (H^3 multiplet) 8·80 (H^4 triplet)
$CH^1_2ClCH^2_2X(CH^3_2CH^4_3)Cl_2$	6·25 (H^1 triplet) 8·27 (H^2 triplet) 8·82 (H^3 and H^4 singlet)	6·20 (H^1 triplet) 7·65 (H^2 and H^3 multiplet) 8·80 (H^4 triplet)
$CH^1_3CH^2ClX(CH^3_2CH^4_3)_2Cl$	8·41 (H^1 doublet) 6·53 (H^2 quartet) 8·95 (H^3 and H^4 multiplet)	8·36 (H^1 doublet) 5·77 (H^2 quartet) 8·08 (H^3 multiplet) 8·95 (H^4 triplet)
$CH^1_2ClCH^2_2X(CH^3_2CH^4_3)_2Cl$	6·36 (H^1 triplet) 8·57 (H^2 triplet) 9·01 (H^3 and H^4 multiplet)	6·42 (H^1 triplet) 7·3–8·6 (H^2 and H^3 multiplet) 9·11 (H^4 multiplet)
$CH^1_3CH^2ClX(CH^3_2CH^4_3)_3$	8·52 (H^1 doublet) 6·63 (H^2 quartet) 9·20 (H^3 and H^4 multiplet)	8·2–8·8 (H^1 and H^3 multiplet) 6·02 (H^2 quartet) 9·11 (H^4 multiplet)
$CH^1_2ClCH^2_2X(CH^3_2CH^4_3)_3$	*c*	6·60 (H^1 triplet) 8·2–9·4 (H^2, H^3 and H^4 multiplet)

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[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. 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

[c] The compound was too unstable to be measured

EXPERIMENTAL

Starting materials. The methylchlorosilanes and 1,1,1-trichloroethane were available commercially. 2,2-Dichloropropane, t-butyl chloride and 1,1,2-trichloropropane were obtained as before.[10] Ethyltrichlorosilane (b.p. 96°, lit[26] 100°), diethyldichlorosilane (b.p. 129°, lit[26] 129·1°), triethylchlorosilane (b.p. 144·5°, lit[26] 146·5°), tetraethylsilane (b.p. 152°, lit[26] 153°), 1,1,1-trichloropropane (b.p. 107°, lit[24] 108·5°), 3,3-dichloropentane (b.p. 132°, lit[36] 135°), 3-chloro-3-ethylpentane (b.p. 72°/50 mm, lit[37] 73·5°/50 mm), 3,3-diethylpentane (b.p. 143°, lit[38] 147·6°) and neopentyl chloride (b.p. 83°, lit[39] 82·5°) were prepared as described. Methyldichloro(chloromethyl)silane (b.p. 121°, lit[40] 122°), dimethylchloro(chloromethyl)silane (b.p. 112°, lit[40] 115°), trimethyl(chloromethyl)silane (b.p. 97°, lit[5] 97·2°) and 1,2-dichloro-2-methylpropane (b.p. 106°, lit[41] 106·1°) were obtained by the chlorination of the respective parent compounds. All the materials thus obtained were purified by fractional distillation until VPC analysis showed negligible impurities.

Chlorination products. Authentic samples of 1-chloroethylethyldichlorosilane (b.p. 75°/43 mm, lit[26] 76°/43 mm), 2-chloroethylethyldichlorosilane (b.p. 92°/43 mm, lit[26] 92°/42 mm), 1-chloroethyldiethylchlorosilane (b.p. 112°/100 mm, lit[26] 114°/100 mm), 2-chloroethyldiethylchlorosilane (b.p. 132°/100 mm, lit[26] (132°/100 mm), 1-chloroethyltriethylsilane (b.p. 195°, lit[42] 112°/58 mm) were obtained by fractionation of the chlorination mixture from the parent ethylsilanes. Dimethylchloro(dichloromethyl)silane (b.p. 147°, lit[40] 149°) and methylchlorobis(chloromethyl)silane (b.p. 172°, lit[40] 172°) were prepared by chlorination of dimethylchloro(chloromethyl)silane. Trimethyl(dichloromethyl)silane (b.p. 133°, lit[5] 134°) and dimethylbis-(chloroethyl)silane (b.p. 161°, lit[5] 161°) were obtained by the action of MeMgBr with dimethylchloro-(dichloromethyl)silane and methylchlorobis(chloromethyl)silane, respectively. An authentic sample of 1,2,2,3-tetrachloropropane was isolated from a chlorination mixture of 1,2,3-trichloropropane by VPC collection. (Found: C, 19·38; H, 2·27. Calc for $C_3H_4Cl_4$: C, 19·81; H, 2·22%).

1,2,3-Trichloro-2-methylpropane was isolated from a chlorination mixture of 1,3-dichloro-2-methylpropane by VPC and its refactive index (n_D^{25} 1·4740) was compared with a reported value (n_D^{25} 1·4736).

Isolation and characterization of samples of other materials necessary for the present investigation had been reported before.[10, 43]

Competitive chlorination procedures. A 2 ml portion of a binary mixture of two appropriate substrates was introduced into a reaction tube attached to vacuum line and the mixture was degassed. A measured amount of chlorine was condensed in the tube through a gas buret. The tube was sealed and immersed in a thermostat and irradiated with a 200W tungsten lamp until the chlorine color disappeared.

Product analyses were carried out using column materials such as Apiezon L, QF-1, XF-1105, Silicon DC550 and so on. Under the conditions employed, separations of the product peaks were satisfactory. It was shown by VPC analysis that with all the competitive experiments polychlorination occurred to the smallest extent. Also, in all cases the conversion was estimated to be less than 10% and it was believed that complications which might arise from the reaction of alkyl radicals with hydrogen chloride[44] were eliminated. The data listed in Table 1 were calculated as shown by a sample calculation that was given previously.[10]

NMR data. Table 3 lists the NMR spectra of all the compounds reported in this paper.

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