

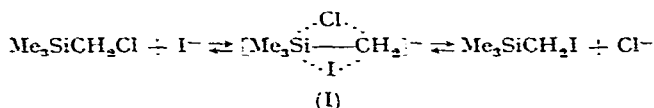
THE REACTIVITIES OF (CHLOROMETHYL)TRIMETHYL-SILANE, -GERMANE, AND -STANNANE TOWARDS IODIDE AND ETHOXIDE ION

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The relatively high reactivity towards iodide ion of (trimethylsilyl)methyl chloride, which is *ca.* 16 times as reactive as *n*-butyl chloride at 50°, has been tentatively attributed to stabilization of the transition state by interaction of the incoming iodide ion with the vacant *d*-orbitals of the silicon atom as well as with the carbon nucleus^{1,2}. The principle of microscopic reversibility requires that the leaving chloride ion should interact similarly with the silicon atom, so that the transition state would have the form shown in (I)^{3,4}.



Such interaction, for convenience referred to below as "bridging", presumably operates also in the reaction of (trimethylsilyl)methyl chloride with thiocyanate ion in acetone⁵ and ethoxide ion in ethanol. Towards ethoxide ion, the chloride is slightly less reactive than *n*-butyl chloride⁶, but it must be remembered that in absence of some special effect such as bridging, the silicon compound would be expected to be markedly less reactive than *n*-butyl chloride, because of a combination of (*a*) the large inductive release of electrons by the Me₃Si group, which hinders the approach of the attacking nucleophile^{1,6,7}, (*b*) the ponderal effect⁷, and (*c*) steric hindrance. (Steric hindrance, while appreciable, would not, of course, be as great as in the true organic analogue, neopentyl chloride, which is abnormally unreactive⁷, and for this reason is not used as the reference compound.)

(Trimethylsilyl)methyl iodide is somewhat less reactive than *n*-butyl iodide towards iodide ion in aqueous ethanol⁸. Again it must be remembered that in absence of special effects the silicon compound would be expected to be much less reactive than the organic iodide, while bridging could be less effective than it is with the chloride in acetone because of greater steric hindrance. It is clear that the transition state (I), in which 6 groups are wholly or partly attached to silicon and 5 to carbon, will be considerably more sterically hindered than the initial state, and replacing the chlorine atom in (I) by a large iodine atom could introduce additional hindrance, and, furthermore, in aqueous ethanol the strongly bound molecules of solvation may also add substantially to the steric hindrance.

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The concept of bridging has been extended to reactions of RHgCH_2Cl and $\text{R}_2\text{B-CH}_2\text{Cl}$ compounds^{15, 16} and to throw further light upon the possible bridging mechanism we measured the reactivities of $\text{Me}_3\text{MCH}_2\text{Cl}$ compounds having M as Si, Ge, or Sn towards iodide ion in acetone and ethoxide ion in ethanol. Since this work was completed Mironov and Kravchenko have shown the germanium compound to be more reactive than the silicon compound towards potassium iodide under unspecified conditions⁹.

REACTIVITY OF $\text{Me}_3\text{MCH}_2\text{Cl}$ COMPOUNDS

(Trimethylsilyl)methyl chloride reacts with ethoxide ion in ethanol to give the expected substitution product, $\text{Me}_3\text{SiCH}_2\text{OEt}$, and the cleavage product, Me_3SiOEt , apparently in a ratio of 86/14, although the substitution product was obtained in only 70% yield¹⁰. From reaction under similar conditions, but on a smaller scale, we obtained 76% of the substitution product $\text{Me}_3\text{GeCH}_2\text{OEt}$ from the germanium compound, and detected no cleavage product. From the tin compound, after a time sufficient for 99.9% production of chloride ion, we obtained the substitution product $\text{Me}_3\text{SnCH}_2\text{OEt}$, in 71% yield and a little ($< 0.5\%$) of a cleavage product. In both cases the amount of substitution product formed was almost certainly higher than that isolated, because of inevitable losses during fractional distillations on a small scale, and it seems likely that cleavage is less favoured with the germanium than with the silicon compound (in line with the observation that the Ge-C bond is normally less readily cleaved by nucleophilic reagents than the Si-C bond), while cleavage of the tin compound is little, if any, more favoured than with the silicon compound.

Table 1 lists second-order rate constants, k_2 , for the reactions of the $\text{Me}_3\text{MCH}_2\text{Cl}$ compounds with ethoxide ion in ethanol at 70°. Second-order rate constants vary somewhat with the initial ethoxide ion concentration in accordance with the expected

TABLE 1

REACTION OF $\text{Me}_3\text{MCH}_2\text{Cl}$ WITH SODIUM ETHOXIDE IN ETHANOL AT 70.0°

M	Si	Ge	Sn	Sn	Sn
$[\text{NaOEt}] \text{ (M)}^a$	0.45	0.45	0.45	0.13	0.045
$k_2 \text{ (l. mole}^{-1}\text{. h}^{-1}\text{)}$	0.045	0.062	3.35	3.60	4.20
k_{rel}	1.00	1.38	74.5		

^a Initial concentration.

salt effects⁶. The relative rates, k_{rel} , are taken below to apply to the substitution reaction; that is, no corrections are made for the concurrent cleavage, which is justified because such corrections would be relatively small and, in any case, would probably only accentuate the differences to be discussed.

Reactions of $\text{Me}_3\text{MCH}_2\text{Cl}$ compounds with sodium or potassium iodide in acetone are not complicated by cleavage and the substitution products have been isolated in yields of 70% (M = Si)²⁸, 84% (M = Ge), and 78% (M = Sn)²⁴. Table 2 lists observed second-order rate constants, k_2 , and relative rates, k_{rel} , at 50°, the very small salt effect¹ being neglected. In the case of the tin compound, the relative rate has been calculated by extrapolation of rate constants from lower temperatures.

TABLE 2

REACTION OF $\text{Me}_3\text{MCH}_2\text{Cl}$ WITH POTASSIUM IODIDE IN ACETONE

<i>M</i>	<i>Temp.</i>	$[\text{KI}]^a$ (<i>M</i>)	k_2 ($\text{l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$)	k_{rel}	<i>E</i> (kcal/mole)	$\log A$
Si	50.00	0.022	2.06 ^b	1.00	20.7 ^c	14.3
Ge	50.00	0.029	3.63	1.76	19.6	13.8
Ge	34.94	0.029	0.82			
Sn	34.94	0.015	165	360	17.2	14.4
Sn	24.95	0.015	64.2			

^a Initial concn. ^b Compare the value of $2.00 \text{ l} \cdot \text{mole}^{-1} \cdot \text{h}^{-1}$ at 49.7° recorded in ref. 1. ^c Value from ref. 1.

It will be seen that towards ethoxide ion and iodide ion, the reactivities of the $\text{Me}_3\text{MCH}_2\text{Cl}$ compounds rise slightly from the silicon to the germanium compound, and then markedly to the tin compound. Since electron-release to the CH_2Cl group should lower the rate, this order is the opposite of that expected from polar effects, the order of inductive electron release towards a saturated carbon atom being $\text{Me}_3\text{Si} < \text{Me}_3\text{Ge} < \text{Me}_3\text{Sn}^{11,12}$. Ponderal effects⁷ would also tend to give a rate sequence opposite to that observed.

The high reactivity of the tin compounds is readily understandable in terms of bridging, since (a) the power to form penta- and hexa-co-ordinate complexes is greatest with tin¹³, (b) nucleophilic attack at tin is generally easier than that at silicon or germanium, and (c) steric hindrance is at a minimum with the large tin atom. The reactivity of the tin compound is more marked in reaction with iodide ion, in which bridging appears to be more effective.

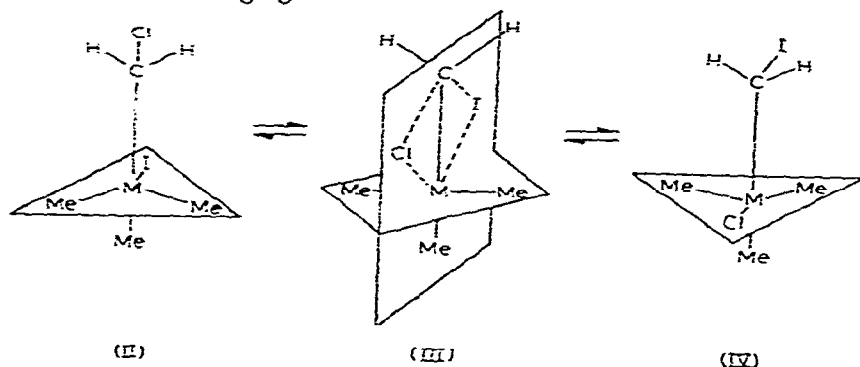
The order of reactivity of the silicon and germanium compounds could not have been predicted, but it is not inconsistent with the bridging mechanism. Although nucleophilic attack on the metalloid atom (some degree of such attack being involved in the bridging) seems to be commonly easier for silicon than germanium¹⁴, this is not always the case (for example, organogermanium alkoxides seem to undergo solvolysis faster than the corresponding organosilicon alkoxides), and, furthermore, formation of hexa-co-ordinate complexes is thought to be easier with germanium than silicon¹³. There will also be less steric hindrance with the germanium compound.

THE STEREOCHEMISTRY OF THE BRIDGING MECHANISM

For simplicity we can consider the reaction as entering and leaving the transition state (III) (which would have some hexa-co-ordinate character) via the penta-co-ordinate complexes (II) and (IV), respectively, but we stress that there is no reason to believe that these complexes have discrete existence^{1,2}. This sequence would lead to inversion of configuration at the metal atom. It is possible, however, that the *d*-orbitals of the metal are involved without general rehybridization, and thus that inversion of configuration does not occur; the probability of discrete existence of penta-co-ordinate intermediates, and thus of inversion, is greatest with the tin compound*.

* Optically active organotin compounds are not available for such a study. Attempts²⁹ to repeat the reported³⁰ resolution of ethylmethyl-*n*-propyltin iodide have not only been unsuccessful but also indicate clearly that the original reports are in error.

Inversion will occur at the carbon atom of the CH_2Cl group, and since this would also be the result of straightforward $\text{S}_{\text{N}}2$ reaction at carbon, optical studies of stereochemical effects at the carbon atom would apparently provide no evidence on the existence of a bridging mechanism.



RELATIVE ELECTRONEGATIVITIES OF Me_3Si AND Me_3Ge GROUPS

We have assumed that the Me_3Ge group releases electrons more effectively than the Me_3Si group towards the saturated carbon atom of the attached CH_2Cl group. We favour this order mainly because the compound $p\text{-Me}_3\text{GeCH}_2\text{C}_6\text{H}_4\text{SiMe}_3$ undergoes acid cleavage of the aryl-Si bond (an electrophilic aromatic substitution, facilitated by electron releasing substituents in the ring) faster than the compound $p\text{-Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{SiMe}_3$ ¹¹, but a supporting piece of evidence¹⁷ is that thiocyanogenation of the double bond of the compounds $\text{Me}_3\text{MCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, an electrophilic addition facilitated by electron supply to the double bond, is faster with $\text{M} = \text{Ge}$ than $\text{M} = \text{Si}$. It is relevant then to examine the reasoning which led Mironov and Kravchenko to conclude that the Me_3Ge group is more electronegative than the Me_3Si group^{9*}, and the three separate aspects of their argument⁹ are considered below.

(a) Since the chloride $\text{Me}_3\text{GeCH}_2\text{Cl}$ is more reactive towards various nucleophilic reagents than the chloride $\text{Me}_3\text{SiCH}_2\text{Cl}$ it is argued that the Me_3Ge must be more electronegative than the Me_3Si group. If this reasoning, which attributes the reactivity differences entirely to polar effects, were correct, then it would follow that the Me_3Sn group must be markedly more electronegative than the Me_3Ge and Me_3Si groups, and that all three of these groups are more electronegative than the Me_3C or $n\text{-Bu}$ groups, which is clearly not the case. It is because the reactivities of the $\text{Me}_3\text{MCH}_2\text{Cl}$ compounds cannot be satisfactorily interpreted in terms of polar effects that we proposed the bridging mechanism.

(b) The compound $\text{Me}_3\text{SiCH}_2\text{HgCH}_2\text{GeMe}_3$ is cleaved by hydrogen chloride to give the compounds Me_4Ge and $\text{Me}_3\text{SiCH}_2\text{HgCl}$, and it is argued that since the Me_3GeCH_2 group acquires the proton it is more electronegative than the Me_3SiCH_2

* We use the term electronegativity here because Mironov and Kravchenko⁹ do so. We should prefer not to use such a general term or to enter the discussion on the relative electronegativities of germanium and silicon¹⁸, since it seems to us that the order of electronegativity may vary with the definition of electronegativity adopted, and thus often with the property used to measure it, and furthermore it is possible that the order also varies with the nature of the group to which the silicon and germanium are attached. All we suggest is that towards a saturated, sp^3 -hybridized, carbon atom the Me_3Ge group releases electrons more strongly than the Me_3Si group.

group. This reasoning is the basis of the Kharasch series of electronegativities¹⁹, which we and others have shown to be unsound²⁰. The cleavage of the mercury-carbon bond involves electrophilic attack on carbon, and thus occurs particularly readily, for example, with Hg-aryl bonds. Other factors, such as steric effects, being absent, the Hg-CH₂X bond is cleaved more readily the higher the electron density at the carbon atom, or the greater the electron release in X, or, in other words, the *lower* the electronegativity of the CH₂X group. The direction of cleavage of the compound Me₃GeCH₂-HgCH₂SiMe₃ thus provides further evidence that the Me₃Ge group releases electrons more readily than Me₃Si group towards a saturated carbon atom.

(c) The acid Me₃GeCH₂CO₂H is stronger than the acid Me₃SiCH₂CO₂H (*cf.* ref. 11) and the base Me₃GeCH₂NEt₂ is weaker than the base Me₃SiCH₂NEt₂. These facts would indicate the order of electron release Me₃Ge < Me₃Si if polar effects were the only factors operating. However, steric effects can be serious in compounds of this type²¹ and, furthermore, it is known²² that with the acids XCH₂COOH the effect of the substituent X on the strength is exerted almost entirely through the entropy of ionization, which makes simple conclusions difficult to reach. It must be recognised, however, that with the amines, the obvious steric effect, *viz.* hindrance to solvation of the ammonium ion, would probably be greater for the silicon than for the germanium compound (though quantitative analysis might reveal the contrary to be true), and this would tend to make the silicon-containing base the weaker. Because of the complications, this one possible anomaly cannot be taken to cast serious doubt on the validity of the reasons above for suggesting that the Me₃Ge is more electron-releasing than the Me₃Si group.

It is clear that, whichever is the order of effectiveness, the Me₃Si and Me₃Ge groups differ very little in their ability to release electrons to a saturated carbon atom. Our discussions of the reactivities of Me₃MCH₂Cl compounds above would not be changed significantly if the order were proved to be the opposite of that we think it to be.

EXPERIMENTAL

Preparation of Me₃MCH₂Cl compounds

(Chloromethyl)trimethylsilane, b.p. 97.5°/742 mm, n_D^{20} 1.4175, was made by Eaborn and Jeffrey's method¹, (chloromethyl)trimethylgermane, b.p. 113.6°/735 mm, n_D^{20} 1.4420, by Seyferth and Rochow's method²³ and (chloromethyl)trimethylstannane²⁴, b.p. 52.0°/25 mm, n_D^{25} 1.4869, was made in 78 % yield from (chloromethyl)-trichlorostannane²⁵ and methylmagnesium bromide in ether.

Reaction of (chloromethyl)trimethylgermane with ethoxide ion

(Chloromethyl)trimethylgermane (5.97 g, 0.0357 mole) was refluxed under anhydrous conditions with a solution of sodium (1.01 g, 0.0439 g-atom) in ethanol (15 ml) for 25 h. The mixture was treated with water (25 ml) and extracted three times with ether. The combined ethereal layers were washed with water, dried (Na₂SO₄), and fractionally distilled to give a little ethanol, b.p. 78-79°, and then (ethoxymethyl)trimethylgermane (4.46 g, 71 %), b.p. 118°/755 mm, n_D^{20} 1.4173. (Found: C, 40.9; H, 9.1. C₆H₁₆GeO calcd.: C, 40.8; H, 9.1 %.) No higher-boiling material could be isolated. The ethanol fraction on dilution with water followed by ether-extraction and

distillation, gave further (ethoxymethyl)trimethylgermane (0.38 g), bringing the total yield of this compound to 76 %.

Reaction of (chloromethyl)trimethylstannane with ethoxide ion

Sodium (1.01 g, 0.0439 g-atom) was dissolved in anhydrous ethanol (100 ml) and (chloromethyl)trimethylstannane (7.43 g, 0.0349 mole) was added. The mixture was kept at 70° for 20 h (the time for 99.9 % production of chloride ion), and water (600 ml) was then added. Ether-extraction, followed by washing to remove ethanol, drying (Na_2SO_4), and fractionation of the extracts gave a liquid (5.52 g, 71 %), b.p. 63.5°/43 mm, which on standing deposited needles of trimethyltin hydroxide (0.04 g, < 0.5 %). The mother liquor was washed with water, dried (Na_2SO_4) and redistilled from a little charcoal in micro-fractionation apparatus, to give (ethoxymethyl)-trimethylstannane, b.p. 64°/45 mm, n_D^{25} 1.4553. (Found: C, 32.6; H, 7.3. $\text{C}_6\text{H}_{16}\text{OSn}$ calcd.: C, 32.3; H, 7.2 %.)

Reaction of (chloromethyl)trimethylgermane with iodide ion

(Chloromethyl)trimethylgermane (7.53 g, 0.045 mole) was refluxed with dry sodium iodide (11.4 g, 0.076 mole) in anhydrous acetone (75 ml) for 37 h. Sodium chloride was filtered from the cold solution, and washed with more acetone. Most of the acetone was removed by fractional distillation, and the residue was treated with water to remove the remaining salts. Two layers formed and the lower layer was separated and combined with the ether washings of the upper (aqueous) layer. Fractionation at atmospheric pressure gave (iodomethyl)trimethylgermane (9.78 g, 84 %), b.p. 158°, n_D^{25} 1.5148. Refractionation at reduced pressure gave the colourless product, b.p. 72°/42 mm, n_D^{25} 1.5140 (lit.²⁶ b.p. 154°/752 mm, n_D^{20} 1.5112).

Kinetic studies

(a) *Reactions with ethoxide ion in absolute ethanol.* Samples were made up in the manner described by Eaborn and Jeffrey¹, brought rapidly to the reaction temperature ($70.00 \pm 0.02^\circ$) in a thermostat bath, removed singly at appropriate intervals after an arbitrary zero-time, and kept at -80° until required. The free chloride-ion contents of the samples were determined potentiometrically. In the case of the stannane, swift, efficient cooling of the sample after reaction was necessary, and strongly-acidic analytical conditions were avoided.

The typical run shown in Table 3 refers to (chloromethyl)trimethylstannane (initially 0.02489 *M* at 20° and ethoxide ion (initially 0.4586 *M* at 20°). Portions (5.00 ml) were titrated against 0.009949 *N* silver nitrate solution. The values of k_2 are

TABLE 3

Time (min)	0	5	10	15	23	28	33	39	49	57
AgNO ₃ (ml)	1.184	2.454	3.626	4.574	5.926	6.692	7.392	8.048	9.024	9.606
k_2 (l·mole ⁻¹ ·h ⁻¹)		3.33	3.41	3.33	3.34	3.36	3.41	3.39	3.43	3.41

corrected for the expansion of ethanol between 20° and the reaction temperature.

Rate constants were reproducible to within $\pm 2\%$. Rate constants used to determine relative reactivities (Table 1) were the average of two or three independent runs.

(b) *Reactions with iodide ion in acetone.* Aliquots (5.00 ml) of a solution of a weighed amount of the organometallic compound in acetone were placed in constricted test-tubes and chilled to -80° . To these were added aliquots (5.00 ml) of an acetone solution potassium iodide, the air space was flushed with dry nitrogen, and the tubes were sealed. After being immersed in a darkened thermostat bath at the required reaction temperature ($\pm 0.02^\circ$) for chosen intervals, the samples were chilled to -80° and then poured into water (25 ml). The organic matter was taken up immediately in carbon tetrachloride (15 ml). The aqueous layer, and a washing of the organic layer, were acidified with 9 *M* sulphuric acid (10 ml) and there was added a single drop of ferroin indicator, for which an indicator blank had been determined. The free iodide ion was titrated against ceric sulphate solution (*ca.* 0.01 *N*) (see ref. 27), this procedure being better than the "iodine cyanide" method previously employed¹.

Second-order rate coefficients were satisfactorily constant during a run provided the reactant concentrations separately exceeded *ca.* 0.002 *M*; at lower concentrations the proportion of dissolved potassium chloride was sufficient for the reverse reaction to be important. The typical run shown in Table 4 refers to (chloromethyl)trimethyl-

TABLE 4

Time (h)	0	10.50	11.67	12.50	13.55	14.50	15.92	17.75	21.10
Ce(SO ₄) ₂ (ml)	15.406	10.106	9.654	9.398	8.994	8.758	8.314	7.810	6.976
[KI] (M)	0.0288	0.0189	0.0180	0.0175	0.0168	0.0164	0.0155	0.0146	0.0130
<i>k</i> ₂ (l·mole ⁻¹ ·h ⁻¹)		0.810	0.821	0.820	0.825	0.810	0.816	0.815	0.825

germane (initially 0.05640 *M*) and potassium iodide (initially 0.02896 *M*) at 34.94° (concentrations measured at 20°). Titration was against 0.009342 *N* ceric sulphate. The values of *k*₂ are corrected for expansion of the reaction medium between 20° and the reaction temperature. Values of *k*₂ in Table 2 are the means of several runs.

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SUMMARY

Towards ethoxide ion and iodide ion the reactivities of Me₃MCH₂Cl compounds (M = Si, Ge, Sn) rise slightly from the silicon to the germanium compound and then markedly to the tin compound. This order of reactivity is discussed in terms of stabilization of the transition state by interaction of the nucleophile with the vacant *d*-orbitals of the metal concomitant with its attack at carbon.

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