Organosilicon Compounds. Part X. The Reaction between Organosilylmethyl Chlorides and Iodide Ion.*

By C. Eaborn and J. C. Jeffrey.

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The reaction between iodide ion and trimethylsilylmethyl chloride and related chlorides in acetone has been studied kinetically. The chlorides are more reactive under these conditions than ethyl and higher-alkyl chlorides, and possible reasons for this are discussed.

Trimethylsilylmethyl chloride, $Me_3Si{\cdot}CH_2Cl$, has been examined by Whitmore and Sommer (*J. Amer. Chem. Soc.*, 1946, **68**, 481), who showed that, while it is much more reactive than the analogous *neo*pentyl chloride towards nucleophilic reagents, it is less reactive than *n*-hexyl chloride towards sodium ethoxide in ethanol and somewhat less reactive towards other basic reagents. The same authors showed that interaction of trimethylsilylmethyl chloride and iodide ion in acetone gave trimethylsilylmethyl iodide, and we now report a kinetic study of this reaction and of the similar reactions involving (aryldimethylsilyl)methyl chlorides. So that the rates of reaction may be related to those of alkyl chlorides we have examined also *n*-butyl chloride, with respect to which the reactivities of other alkyl chlorides are known (Conant and Hussey, *ibid.*, 1925, **47**, 476).

The following data refer to the interaction of RCH_2Cl compounds with iodide ion

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* Part IX, *J.*, 1954, 3169.

(initially *ca.* 0·018M) in acetone at 49·7°; the values of k_2, the second-order rate constant, are probably accurate to within ±2%, as based on estimated titration errors and reproducibility:

R	Pr^n	$SiMe_3$	$SiPhMe_2$	$SiMe_2 \cdot C_6H_4 \cdot Me$-*p*	$SiMe_2 \cdot C_6H_4 \cdot OMe$-*p*	$SiMe_2 \cdot C_6H_4Cl$-*p*
k_2, hr.$^{-1}$ mole^{-1} l.	0·127	2·00	1·13	0·88	0·87	2·58
E, kcal.	23·4	20·7	19·5	20·6	21·5	20·9

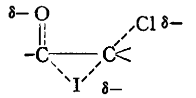
(The Arrhenius activation energies, *E*, were deduced from measurements at only two temperatures, and may be considerably in error, but it may safely be concluded that the lower reactivity of the *n*-butyl chloride is due to the higher activation energy involved. The variations in *E* within the group of organosilylmethyl chlorides are probably not significant.)

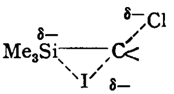
The reactivity of trimethylsilylmethyl chloride is *ca.* 16 times that of *n*-butyl chloride, and thus *ca.* 15 times that of *n*-propyl chloride and *ca.* 8 times that of ethyl chloride (Conant and Hussey, *loc. cit.*). Methyl chloride has not been examined in this reaction, but from figures for other halogen-exchange reactions of alkyl halides (Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Son, London, 1953, p. 323) methyl chloride is probably more reactive than trimethylsilylmethyl chloride.

A trimethylsilyl group, when attached to a saturated carbon atom, has a stronger +*I* effect even than the *tert.*-butyl group (Sommer, Gold, Goldberg, and Marans, *J. Amer. Chem. Soc.*, 1949, **71**, 1509). The increase in reactivity which occurs, in spite of the increase in steric hindrance, when the trimethylsilyl group replaces the methyl group in ethyl chloride might, then, be thought to arise from the increased electron supply to the central carbon atom, since such electron supply can facilitate this type of reaction; 4-methylbenzyl chloride, for example, is more reactive than benzyl chloride towards iodide ion in acetone (Ingold, *op. cit.*, p. 327). That this is unlikely to be the explanation, however, is shown by the decrease of reactivity with increasing electron release of the organosilyl group as R in *p*-$R \cdot C_6H_4 \cdot SiMe_2 \cdot CH_2Cl$ changes in the series Cl, H, Me, MeO.

The increase in reactivity when a trimethylsilyl group replaces a methyl group may originate in the ability of a silicon atom to expand its valency shell. Winstein has suggested that the high reactivity of α-halogeno-ketones towards nucleophilic reagents may be due to partial bonding of the attacking reagents with the carbonyl carbon in the transition state, as in (I) (see Bartlett, in Gilman's "Organic Chemistry," Wiley and Son, New York, 1953, p. 35; also, Eaborn, *Chem. and Ind.*, 1954, 930). By analogy, a transition state such as (II) may be postulated to explain the activating effect of a neighbouring silicon atom.* In the extreme, one might imagine a complex, in which iodide ion attached to silicon would be favourably placed for a displacement at the neighbouring carbon atom, but such an intermediate need not exist for (II) to be possible. Electron supply to the silicon atom would hinder its interaction with the iodide ion and reduce its activating influence, in agreement with the observed effects. The activation would probably be greater in the absence of steric hindrance, which must be appreciable in (II).

(I)





(II)

There is no obvious reason why the silicon atom should not similarly activate trimethylsilylmethyl chloride towards attack by sodium ethoxide in ethanol. In this case the greater nucleophilic power of the attacking reagent may cause the bond-making influences at the central carbon atom to be so dominant compared with bond-breaking influences that deactivation by the +*I* effect of the trimethylsilyl group more than outweighs activation by interaction similar to that in (II).

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* We understand that this type of transition state has been discussed by Drs. Cooper and Prober at the Kansas City meeting of the American Chemical Society, March 1954.

EXPERIMENTAL

Organosilylmethyl Chlorides.—Interaction of chloromethyldimethylchlorosilane with the Grignard reagents from methyl iodide, bromobenzene, *p*-bromotoluene, *p*-bromoanisole, and *p*-bromochlorobenzene gave 60—70% yields of, respectively, chloromethyl-trimethylsilane, b. p. 97·5°, n_D^{20}, 1·4180; -dimethylphenylsilane, b. p. 123°/25 mm., n_D^{20} 1·5214; *-dimethyl-*p*-tolylsilane*, b. p. 138—140°/12 mm., 243°/750 mm., n_D^{25} 1·5182 (Found: C, 61·0; H, 7·6. $C_{10}H_{15}ClSi$ requires C, 60·5; H, 7·6%); *-dimethyl-*p*-methoxyphenylsilane*, b. p. 143°/5 mm., 270°/755 mm., n_D^{25} 1·5282 (Found: C, 56·2; H, 7·0. $C_{10}H_{15}OClSi$ requires C, 56·0; H, 7·0%); and *-*p*-chlorophenyldimethylsilane*, b. p. 133°/3 mm., 260·5°/755 mm., n_D^{25} 1·5350 (Found: C, 49·7; H, 5·8. $C_9H_{12}Cl_2Si$ requires C, 49·3; H, 5·5%). Except with the first-named product, fractionations were at reduced pressure; b. p.'s (corr.) at atmospheric pressure were taken quickly with rapidly heated samples, and there were no signs of decomposition.

Materials.—Acetone was purified by Conant and Kirner's method (*J. Amer. Chem. Soc.*, 1924, **46**, 232). Potassium iodide was several times recrystallised from distilled water and was dried at 120° for 2 hr.

Kinetic Measurements.—Separate solutions of the organic chloride and of potassium iodide were prepared by dissolving weighed quantities in acetone at room temperature. Portions (5 ml.) of the chloride solution were introduced into small Pyrex test-tubes and cooled to *ca.* −80°. Then the iodide solution (5 ml.) was added, and the tubes were sealed and kept at −80° until required; they were then immersed in a thermostat for known times. "Zero" time readings were determined by analysis after the samples had been in the thermostat long enough to reach bath-temperature. The iodide-ion content on withdrawal was determined by Dostrovsky and Hughes's method (*J.*, 1946, **161**) since Conant and Hussey's method is inaccurate (Senior, Hetrick, and Miller, *J. Amer. Chem. Soc.*, 1944, **66**, 1987). Thermostats were constant to ±0·02°, and methylene-blue was dissolved in the bath water to protect the reaction mixture from light. For determinations of activation energies runs involving similar initial iodide concentrations were carried out at 49·7° and 40·6°.

The following typical run refers to the interaction of (dimethylphenylsilyl)methyl chloride (initially 0·04548M) at 49·7°; k_2 is the second-order rate constant. An 0·00404M-potassium iodate solution was used in titrating the iodide ion.

Time, hr.	0	4	6·5	12·5	18·5	23·5	30	43
Titre, ml.	21·32	17·58	15·70	12·15	9·40	7·70	6·30	3·82
10^2[RCl],* M	4·407	4·117	3·971	3·696	3·483	3·352	3·243	3·051
10^3[KI],* M	16·52	13·62	12·16	9·412	7·283	5·967	4·881	2·960
k_2, hr.$^{-1}$ mole^{-1} l.	—	1·13	1·13	1·12	1·15	1·15	1·11	1·14

* Corrected for expansion of the acetone between room and bath temperature (factor, 1·043).

The reaction is of second order within a run, and is of first order in organic chloride since the rate-constant was independent of the organic chloride concentration, which was usually 2—4 times that of the potassium iodide. As is usual for this type of reaction, the rate constant fell slightly with increasing salt concentration: *e.g.*, k_2 for (dimethyl-*p*-tolylsilyl)methyl chloride was 0·85(6) and 0·88(2) hr.$^{-1}$ mole^{-1} l. for initial potassium iodide concentrations of 0·030 and 0·019M, respectively.

UNIVERSITY COLLEGE, LEICESTER.

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