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PREPARATION OF CERTAIN CHLOROMETHYL- AND DICHLOROMETHYL-SUBSTITUTED CHLORODISILANES AND THEIR BEHAVIOR TOWARD ALUMINUM HALIDES

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SUMMARY

Four new (chloromethyl)disilanes, $(ClCH_2)Cl_2SiSiCl_2Me$ (I), $(Cl_2CH)Cl_2SiSiCl_2Me$ (II), $(ClCH_2)MeClSiSiClMe_2$ (III) and $(ClCH_2)Me_2SiSiCl_3$ (IV), have been prepared and studied as to their attitude toward intramolecular rearrangement with aluminum chloride. The reactivity decreases in the order: (III) > (IV) > (II) ≫ (I). Similar reactivity to rearrangement of $Me_3SiSiMe_2(CH_2Br)$ (V), $ClMe_2SiSiMe_2(CH_2Br)$ (VI) and $Me_3SiSiMeCl(CH_2Br)$ (VII) in the presence of aluminum bromide has been found to decrease in the order: (V) > (VI) > (VII). The results are discussed in terms of a mechanism favoring initial rate-determining step of ionization of the carbon–halogen bond in which the migrating group plays a minor role, if any, followed by migration of a silyl group from silicon to carbon. Disilanes (I) and (II) enter into the Friedel–Crafts reaction with benzene to give, after methylation, $PhCH_2SiMe_2SiMe_3$ and $Ph_2CHSiMe_2SiMe_3$, respectively.

INTRODUCTION

In previous papers[1,2] we reported the preparation of (chloromethyl)- and (dichloromethyl)pentamethyldisilane through the photochemical chlorination of the "disilane fraction" of the methylchlorosilane distillation residue, followed by treatment with a methyl Grignard reagent. However, intermediate chloromethyl derivatives that still contain chlorine atoms bonded to silicon could not be isolated in the pure state because the starting substance employed at that time was a rather complex mixture of methylchlorodisilanes of the general formula $Me_nSi_2Cl_{6-n}$. Recently, we have succeeded in preparing 1,2-dimethyltetrachlorodisilane in the pure state very easily from the disilane fraction by treating it with acetyl chloride and anhydrous aluminum chloride at reflux temperature[3]. The ready accessibility of this substance encouraged us to isolate 1-(chloromethyl)-2-methyltetrachlorodisilane (I) and 1-(dichloromethyl)-2-methyltetrachlorodisilane (II), and study some of their reactions. In this connection, we have prepared two further hitherto unknown chloromethyl-substituted chlorodisilanes, *i.e.*, 1-(chloromethyl)-1,2-dichlorotrimethyldisilane (III) and 2-(chloromethyl)-1,1,1-trichlorodimethyldisilane (IV), and examined the action of anhydrous aluminum chloride on all of them and also the action of anhydrous aluminum bromide on three (bromomethyl)disilanes (V)–(VII) recently prepared[4].

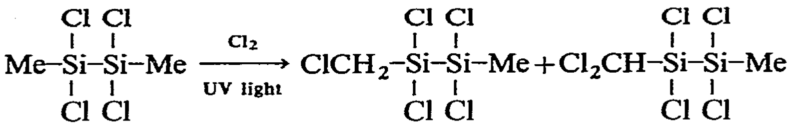
$\mathrm{Cl_2MeSiSiCl_2(CH_2Cl)}$	(I)	$\mathrm{Me_3SiSiMe_2(CH_2Br)}$	(V)
$\mathrm{Cl_2MeSiSiCl_2(CHCl_2)}$	(II)	$\mathrm{ClMe_2SiSiMe_2(CH_2Br)}$	(VI)
$\mathrm{ClMe_2SiSiMeCl(CH_2Cl)}$	(III)	$\mathrm{Me_3SiSiMeCl(CH_2Br)}$	(VII)
$\mathrm{Cl_3SiSiMe_2(CH_2Cl)}$	(IV)		

Since the first work by Whitmore, Sommer and Gold[5], many papers have been devoted to the studies, particularly from a mechanistic point of view[6,7], of aluminum chloride-catalyzed intramolecular rearrangement of (chloromethyl)triorganosilanes, $\mathrm{RMe_2SiCH_2Cl}$, R being an alkyl or aryl group, and (dichloromethyl)trimethylsilane, $\mathrm{Me_3SiCHCl_2}$[8]. It has been well established that all of these compounds readily undergo rearrangement involving migration, from silicon to carbon, of a methyl or R group, depending upon the nature of R, but replacement of just one alkyl group on silicon by chlorine prevents the rearrangement (the compounds $\mathrm{Me_2ClSiCH_2Cl}$ and $\mathrm{Me_2ClSiCHCl_2}$ do not react with aluminum chloride[9]). In a previous paper, we reported that the trimethylsilyl and chlorodimethylsilyl group in the (chloromethyl)-disilanes $\mathrm{XMe_2SiSiMe_2(CH_2Cl)}$, where X = Me or Cl, migrate much more readily than methyl groups to give $\mathrm{XMe_2SiCH_2SiMe_2Cl}$ compounds[1].

RESULTS AND DISCUSSION

Preparation

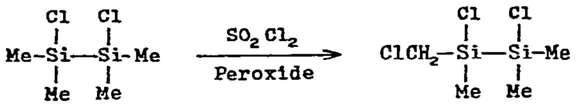
Photochemical chlorination of 1,2-dimethyltetrachlorodisilane[3] in the liquid phase followed by fractional distillation under reduced pressure gave very readily both (I) and (II):



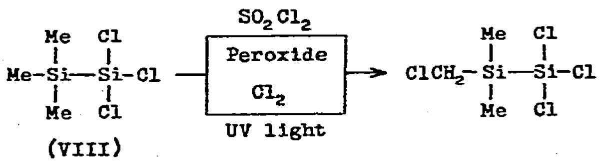
$$\mathrm{Me{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}Me} \xrightarrow[\text{UV light}]{\mathrm{Cl_2}} \mathrm{ClCH_2{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}Me} + \mathrm{Cl_2CH{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Si}}}\mathrm{{-}Me}$$

(I) (II)

Peroxide-initiated chlorination with sulfuryl chloride of 1,2-dichlorotetramethyldisilane[10,11] gave (III) in a satisfactory yield.



(III)



(VIII) (IV)

Compound (IV) was prepared in a similar way in 17% yield from 1,1,1-trimethyltrichlorodisilane (VIII), but photochemical chlorination of (VIII) in carbon tetrachloride proved to be more convenient and gave a better yield (31%). The trichlorotrimethyldisilane (VIII)* used here was prepared through aluminum chloride-catalyzed chlorodephenylation of 1,1,1-trimethyltriphenyldisilane[13] with dry hydrogen chloride in benzene.

The action of methylmagnesium bromide on (I) and (II) proceeded in the normal way and formed the known (chloromethyl)pentamethyldisilane[1,2] and (dichloromethyl)pentamethyldisilane[2] in 89 and 88% yield, respectively.

Some physical constants and ^1H NMR and analytical data for the chloromethyl-containing disilanes are listed in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND NMR AND ANALYTICAL DATA FOR (CHLOROMETHYL)DISILANES

Compound		B.p. (°C/mm)	τ(CH)[a]			Analysis found (calcd.) (%)	
No.	Formula		H^a	H^b	H^c	Cl	Si
(I)	$(CH^a_3)Cl_2SiSiCl_2(CH^c_2Cl)$	80–84/19[b]	8.90		6.70	67.65 (67.53)[c]	21.83 (21.40)
(II)	$(CH^a_3)Cl_2SiSiCl_2(CH^cCl_2)$	100/16	8.86		4.45	47.44 (47.75)[d]	19.00 (18.92)
(III)	$(CH^a_3)_2ClSiSi(CH^b_3)(Cl)(CH^c_2Cl)$[e]	84–85/20	9.33	9.30	6.93	31.88 (31.99)[d] 47.12 (47.98)[c]	24.95 (25.34)
(IV)	$Cl_3SiSi(CH^b_3)_2(CH^c_2Cl)$[f]	86/21		9.51	6.99	44.48 (43.93)[d]	22.84 (23.20)

[a] Spectra were determined on a JEOL Model C-60H apparatus in carbon tetrachloride. [b] M.p., 30–32°. [c] Total chlorine content (see text). [d] Content of chlorine bonded only to silicon. [e] Found: C, 22.65; H, 5.12. $C_4H_{11}Cl_3Si_2$ calcd.: C, 21.67; H, 5.00%. [f] Found: C, 15.04; H, 3.40. $C_3H_8Cl_4Si_2$ calcd.: C, 14.82; H, 3.31%.

Titration of compounds (II) and (IV) with 0.1 *N* alkali at room temperature gave neutral equivalents corresponding to the quantitative hydrolysis of only the Si–Cl bonds. In striking contrast, titration of compound (I) gave a neutral equivalent corresponding to the total chlorine under the same conditions. With compound (III), only unreliable neutral equivalents were obtained upon titration at room temperature. However, titration with cooling in an ice bath gave the exact neutral equivalents corresponding to the Si–Cl bonds. Back titration of (III) after allowing it to stand with an excess of 0.1 *N* alkali for 50 h and then heating at 50° for 5 h gave the neutral equivalent corresponding to the total chlorine (see Table 1). The similar behavior was previously found for 1-(bromomethyl)-1-chlorotetramethyldisilane (VII)[4]. The unusual reactivity of the carbon–halogen bond in these compounds will be discussed elsewhere[14].

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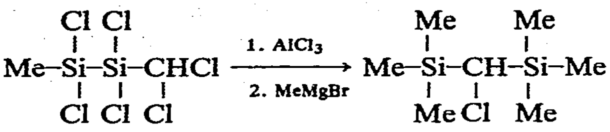
* This compound has been prepared by an alternative route by Urry[12].

Aluminum halide-catalyzed intramolecular rearrangement

It was of interest to determine the relative ease with which compounds (I)–(IV) and (V)–(VII) undergo the aluminum halide-catalyzed intramolecular rearrangement involving migration of a silyl group from silicon to carbon. The extents of the rearrangement were estimated by GLC after methylation, *e.g.*,



$$\mathrm{Me{-}\underset{Cl}{\overset{Cl}{Si}}{-}\underset{Cl}{\overset{Cl}{Si}}{-}\underset{Cl}{CHCl}} \xrightarrow[\text{2. MeMgBr}]{\text{1. AlCl}_3} \mathrm{Me{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Cl}{CH}{-}\underset{Me}{\overset{Me}{Si}}{-}Me}$$

The results are summarized in Tables 2 and 3.

A rapid redistribution of methylchlorodisilanes by the action of aluminum chloride has been observed[15]. If such an undesirable reaction should occur in the present cases, comparison of the reactivity among these compounds toward the aluminum halide would become meaningless. GLC analysis of the reaction mixture of

TABLE 2

THE ACTION OF ALUMINUM CHLORIDE ON COMPOUNDS (I)–(IV)[a]

Compound No.	Reaction conditions					
	20°		50°	80°		100°
	1 h	15 h	1 h	1 h	7 h	14 h
(I)					Trace	Trace
(II)					Trace	21
(III)	Trace	6	56	100		
(IV)	Trace	Trace	6	92		

[a] The extents of rearrangement are given in per cent.

TABLE 3

ALUMINUM BROMIDE-CATALYZED REARRANGEMENT OF (V)–(VII)[a]

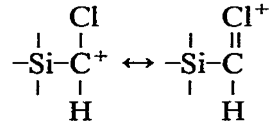
Compound[b] (mole/l)	$AlBr_3$ (mole/l)	Rearrangement (%)	
		1 min	10 min
$SiSiCH_2Br$ (V)			
0.146	0.032	99	
$ClSiSiCH_2Br$(VI)			
0.153	0.045	91	96
$SiSi(Cl)CH_2Br$(VII)			
0.146	0.032	4	12
0.153	0.045	6	28

[a] In a benzene solution at 5°. [b] For clarity, methyl groups are omitted.

compounds (I), however, showed no such a redistribution reaction.

The data clearly show that the ease with which the rearrangement occurs falls in the order: (III) > (IV) > (II) ≫ (I), and (V) > (VI) > (VII). Thus it will well be said that, in general, the greater the total number of Si–Cl bonds in the molecule, the less readily the rearrangement takes place. Moreover, comparison of (VI) with (VII) on the one hand and (I) with (II) on the other, in either pair the total number of Si–Cl bonds being equal, reveals that a compound in which the silicon atom bearing a halomethyl group is less highly substituted by chlorine undergoes the rearrangement more easily than a compound having the similar silicon atom which is more highly substituted by chlorine, and that a compound having a dichloromethyl group is, other things being equal, more reactive than a compound having a chloromethyl group.

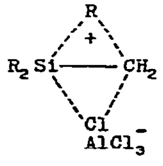
If we confine our consideration to the migratory aptitudes of the groups, it might be expected that they decrease in the order $Me_3Si- > ClMe_2Si- > Cl_2MeSi- > Cl_3Si-$. The fact is that (IV) is more reactive than (I) on the one hand and (VI) rearranges more readily than (VII) on the other, and so it is very likely that the most important will be the stabilization, by electronic effects of substituents, of an incipient carbonium ion (or an electron-deficient transition state) brought about by complexation of the halomethyl group with the aluminum halide catalyst. Thus, the incipient carbonium ion (or the transition state) arising from compound (VI) is reasonably considered to be more strongly stabilized than that from compound (VII) and so the former undergoes the rearrangement more easily than the latter despite the migratory aptitude of $ClMe_2Si$–group is, other things being equal, smaller than that of Me_3Si–group. Further, the fact that (II) is much more reactive than (I) toward aluminum chloride may be explained in terms of the stabilization of the carbonium ion intermediate (or transition state) by an electromeric electron-donating effect of the chlorine atom directly bonded to it, as formulated below:



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{\overset{\mathrm{Cl}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}^+}} \leftrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{\overset{\mathrm{Cl}^+}{\|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}$$

Analogously stabilized halocarbonium ions have been described by Olah *et al.*[16]

On the basis of kinetic studies on the aluminum chloride-catalyzed rearrangement of p-$XC_6H_4SiMe_2(CH_2Cl)$ (X = H, Me, and Cl) and Me_3SiCH_2Cl in 1,2-dichloroethane at −20°, Bott, Eaborn, and Rushton[6] proposed a mechanism involving synchronous intramolecular migration of the organic group and the chlorine atom (A). Thus, the rate-determining step involves the direct participation of the migrating organic group rather than the simple ionization of the C–Cl bond. Recently, Steward *et al.*[7] compared the migratory aptitudes of alkyl groups in (chloromethyl)-trialkylsilanes under the action of aluminum chloride and favored a two step mechan-



(A)

ism involving an unstable intermediate (A), in which the first step involves heterolytic cleavage of the alkyl–Si bond and the second step the formation of the C–C bond.

For the rearrangement of (α-hydroxyalkyl)triphenylsilanes with boron trifluoride, Brook *et al.*[17] suggested a mechanism involving the initial formation of the α-silylcarbonium ions and subsequent attack of fluoride ion on silicon and migration of phenyl group from silicon to carbon. Most recently, Hairston and O'Brien[18] followed the reaction of (α-haloalkyl)silanes with antimony pentafluoride by NMR and found the reaction to proceed stepwise; the initial ionization and subsequent rearrangement of the organic group from silicon to carbon.

From our results described above, it seems more likely that a mechanism for aluminum halide-catalyzed rearrangement of (halomethyl)disilanes involves initial slow, rate-determining step of ionization of the carbon–halogen bond where the migrating group plays a minor if any role, and subsequent, synchronous, fast step of nucleophilic attack of the halide ion on the silicon atom and migration of the silyl group from silicon to carbon.

Friedel–Crafts reaction of (I) and (II) with benzene

α- and β-Chloroethyltrichlorosilane and chloromethyltrichlorosilane have been shown to enter into the Friedel–Crafts reaction with benzene and its derivatives[19,20]. An analogous reaction was found to occur between both (I) and (II) and benzene. Thus the reaction of (I) with benzene in the presence of aluminum chloride as catalyst at reflux temperature for 4 days, followed by treatment with methylmagnesium bromide gave 43% yield of benzylpentamethyldisilane (IX), whilst the reaction of (II) under similar conditions gave (diphenylmethyl)pentamethyldisilane (X) in 84.5% yield.

$$(\mathrm{I}) + C_6H_6 \xrightarrow[\text{2. MeMgBr}]{\text{1. AlCl}_3} \underset{(\mathrm{IX})}{C_6H_5CH_2SiMe_2SiMe_3}$$

$$(\mathrm{II}) + 2C_6H_6 \xrightarrow[\text{2. MeMgBr}]{\text{1. AlCl}_3} \underset{(\mathrm{X})}{(C_6H_5)_2CHSiMe_2SiMe_3}$$

Here again we find that (II) is much more reactive than (I).

EXPERIMENTAL

Photochlorination of 1,2-dimethyltetrachlorodisilane

1,2-Dimethyltetrachlorodisilane[3] (456 g, 2.0 mole) was chlorinated under irradiation of UV light, in essentially the same manner as reported previously[1]. Fractional distillation of the reaction mixture under reduced pressure gave 85 g of compound (I) and 59 g of (II), along with 202 g of the unchanged starting material and 103 g of residue. Attempts to isolate any individual compound from the higher boiling material failed.

Methylation of (I) and (II)

The action of methylmagnesium bromide in ether on compound (I) (13.1 g, 50 mmole) followed by the usual work-up afforded 8 g (89% yield) of (chloromethyl)-pentamethyldisilane[1,2] as a crystallizable material. Similarly, methylation of (II)

(14.9 g, 50 mmole) gave 9.5 g (88%) of (dichloromethyl)pentamethyldisilane[1].

1-(*Chloromethyl*)-1,2-*dichlorotrimethyldisilane* (*III*)

In a 100-ml three-necked flask equipped with a reflux condenser, a stirrer and a pressure-equalizing addition funnel, was placed a solution of 40 g (0.214 mole) of 1,2-dichlorotetramethyldisilane[10,11] and 0.1 g of benzoyl peroxide. Sulfuryl chloride (43.5 g; 0.32 mole) was added to it with stirring at 80–85° over a period of 0.5 h. After 3-h heating, a second portion of sulfuryl chloride (20 g; 0.15 mole) was added and then the mixture was heated for an additional 5 h. After flash distillation, fractionation through a short column packed with glass helices gave 11 g (23% yield) of (III), in addition to 14 g of the unchanged starting material.

2-(*Chloromethyl*)-1,1,1-*trichlorodimethyldisilane* (*IV*)

(*a*). In essentially the same manner as described above, 46 g (0.22 mole) of 1,1,1-trichlorotrimethyldisilane (VIII) was treated with 61.2 g (0.45 mole) of sulfuryl chloride in the presence of 0.2 g of benzoyl peroxide. Fractional distillation gave 9 g (17% yield) of (IV) in the pure state.

(*b*). Compound (VIII) (93 g; 0.4 mole) diluted with 100 ml of carbon tetrachloride was chlorinated by passing chlorine under irradiation of UV light in the usual manner[1]. Without any external heating the reaction occurred. After a theoretical amount of hydrogen chloride was generated, the reaction mixture was distilled fractionally to give 30.5 g (31% yield) of (IV), together with 22.5 g of the unchanged starting material and 33 g of residue.

1,1,1-*Trichlorotrimethyldisilane* (*VIII*)

In a 1-l three-necked flask fitted with a gas-inlet tube, a stirrer and a reflux condenser the top of which was protected with a drying tube was placed a mixture of 280 g (0.84 mole) of 1,1,1-triphenyltrimethyldisilane[13], 800 ml of dry benzene and about 2 g of anhydrous aluminum chloride. Dry hydrogen chloride was passed through the stirred mixture at room temperature for 11 h. The extent of the reaction was followed by GLC analysis of small samples of the reaction mixture. Acetone (ca. 10 ml) was added to deactivate aluminum chloride. After filtration and removal of solvent, fractional distillation gave 132 g (75% yield) of (VIII) as a crystallizable material, b.p. 65–66°/40 mm, m.p. 23.5–24.5°. (Found: C, 17.65; H, 4.26; Cl, 50.48. $C_3H_9Cl_3Si_2$ calcd.: C, 17.35; H, 4.37; Cl, 51.22%.)

Action of aluminum chloride on (*I*)–(*IV*)

A mixture of about 50 mg of a (chloromethyl)- or (dichloromethyl)chlorodisilane and a catalytic amount of anhydrous $AlCl_3$ was sealed in a small glass ampoule and maintained at a given temperature for a given period of time. After methylation of the reaction mixture with a methyl Grignard reagent, the extent of rearrangement was estimated by GLC by comparing an amount of $Me_3SiCH_2SiMe_3$ (or $Me_3SiCHClSiMe_3$) with that of (chloromethyl)pentamethyldisilane [or (dichloromethyl)pentamethyldisilane]. The results are listed in Table 2.

Action of aluminum bromide on (*V*)–(*VII*)

A solution of bromomethyldisilane in benzene was placed in a well dried test tube and cooled to 5°. A solution of aluminum bromide in benzene was then added at once. Small samples were extracted at suitable intervals and methylated with methylmagnesium bromide. The extents of rearrangement were estimated by GLC by comparing the amount of produced bis(trimethylsilyl)methane with that of nonane added as an internal standard.

The reaction conditions and the extents of rearrangement are listed in Table 3.

Reaction of compound (I) with benzene in the presence of $AlCl_3$

A mixture of 26.2 g (0.10 mole) of (I), 115 ml of dry benzene and 3.7 g of $AlCl_3$ was heated to reflux with stirring under a slow stream of dry nitrogen for 4 days. The reaction mixture was treated with a methyl Grignard reagent and worked up in the usual way. Fractional distillation through a short column gave 9.5 g (43% yield) of benzylpentamethyldisilane, b.p. 73–74°/2 mm, n_D^{20} 1.5080 (lit.[21] n_D^{20} 1.5092), along with 1.5 g of uncharacterized material, b.p. 134–135°/2 mm, n_D^{20} 1.5510, d_4^{20} 0.9484.

Reaction of compound (II) with benzene in the presence of $AlCl_3$

A mixture of 15 g (0.05 mole) of (II), 100 g of dry benzene and 2 g of anhydrous $AlCl_3$ was refluxed for 105 h and then worked up similarly. Distillation through a short Vigreux column gave 12.5 g (84.5% yield) of (diphenylmethyl)pentamethyldisilane, b.p. 136–137°/3 mm, n_D^{20} 1.5591, d_4^{20} 0.9626; MR_D found 100.17, calcd. 99.67. (Found: C, 72.17; H, 8.62. $C_{18}H_{26}Si_2$ calcd.: C, 72.40; H, 8.78%.) NMR (τ values): $Si(CH_3)_3$, 10.12; $Si(CH_3)_2$, 9.90; $-CHPh_2$, 6.44; aromatic, 2.83.

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REFERENCES

1 M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, 23 (1958) 292.
2 M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 1 (1964) 411.
3 H. Sakurai, T. Watanabe and M. Kumada, *J. Organometal. Chem.*, 7 (1967) P15.
4 K. Tamao and M. Kumada, *J. Organometal. Chem.*, 30 (1971) 329.
5 F. C. Whitmore, L. H. Sommer and J. Gold, *J. Amer. Chem. Soc.*, 69 (1947) 1976.
6 R. W. Bott, C. Eaborn and B. M. Rushton, *J. Organometal. Chem.*, 3 (1965) 455.
7 O. W. Steward, W. L. Uhl and B. W. Sands, *J. Organometal. Chem.*, 15 (1968) 329.
8 L. H. Sommer, D. L. Bailey, J. R. Gould and F. C. Whitmore, *J. Amer. Chem. Soc.*, 76 (1954) 801.
9 C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, Dekker, New York, 1968, pp. 443–446.
10 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 21 (1956) 1264.
11 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Lett.*, (1966) 5493.
12 G. Urry, *Accounts Chem. Res.*, 3 (1970) 306, and references cited therein.
13 H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.*, 73 (1951) 4031; *J. Org. Chem.*, 18 (1953) 753.
14 K. Tamao and M. Kumada, *J. Organometal. Chem.*, 30 (1971) 349.
15 H. Sakurai, K. Tominaga and M. Kumada, *Bull. Chem. Soc. Jap.*, 39 (1966) 1820.
16 G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 91 (1969) 2955.

17 A. G. Brook, K. H. Pannell, G. E. LeGrow and J. J. Sheeto, *J. Organometal. Chem.*, 2 (1964) 491.
18 T. J. Hairston and D. H. O'Brien, *J. Organometal. Chem.*, 23 (1970) C41.
19 G. H. Wagner, D. L. Bailey, A. Pinos, M. Dunhan and D. McIntire, *Ind. Eng. Chem.*, 45 (1953) 367.
20 A. D. Petrov, V. F. Mironov, V. A. Ponomarenko and E. A. Chernyshev, *Sintez Kremniiorganicheskikh Monomerov*, Akademya Nauk SSSR, Moscow, 1961, pp. 338–343.
21 E. A. Chernyshev, N. G. Tolstikova, A. A. Ivashenko, A. A. Zelenetskaya and L. A. Leites, *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, (1963) 660.