THE PREPARATION AND SOME REACTIONS OF (CHLOROMETHYL)-*tert*-BUTYLDIMETHYLSILANE

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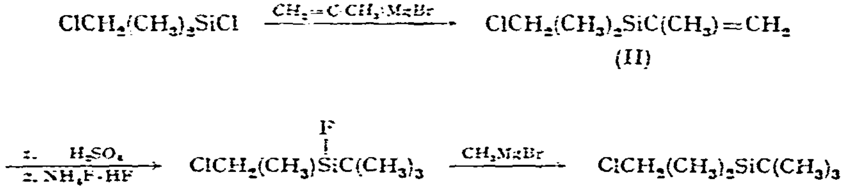
INTRODUCTION

Previous work[1,2] demonstrated that (chloromethyl)pentamethyldisilane, $ClCH_2(CH_3)_2SiSi(CH_3)_3$, undergoes intramolecular rearrangement with anhydrous aluminum chloride and also with sodium ethoxide in ethanol to give disilylmethane derivatives, thus indicating that the trimethylsilyl group migrates from silicon to carbon with great ease. In connection with the investigation of $ClCH_2(CH_3)_2SiSi(CH_3)_3$, it was of considerable interest to study the chemistry of (chloromethyl)-*tert*-butyldimethylsilane (I), in which a $(CH_3)_3C$– group is substituted for $(CH_3)_3Si$– in the disilane. In the present paper we report the preparation and some reactions of this compound.

RESULTS AND DISCUSSION

Synthesis

The following sequence of reactions represents an approach to the synthesis of compound (I) which has been carried out.

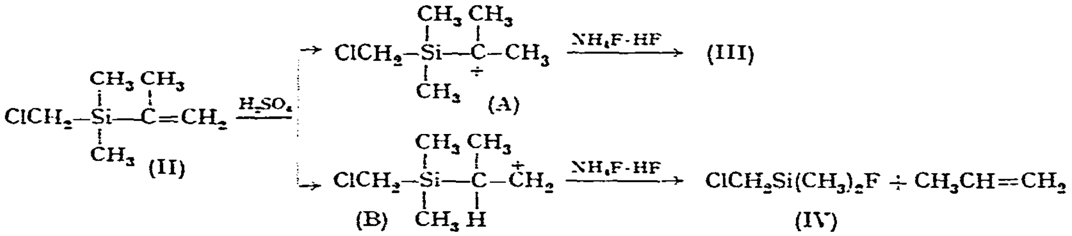


$$ClCH_2(CH_3)_2SiCl \xrightarrow{CH_2=C(CH_3)MgBr} \underset{\text{(II)}}{ClCH_2(CH_3)_2SiC(CH_3)=CH_2}$$

$$\xrightarrow[\text{2. } NH_4F\cdot HF]{\text{1. } H_2SO_4} \underset{\text{(III)}}{ClCH_2(CH_3)\overset{F}{\overset{|}{S}}iC(CH_3)_3} \xrightarrow{CH_3MgBr} \underset{\text{(I)}}{ClCH_2(CH_3)_2SiC(CH_3)_3}$$

This route was chosen because while considerable difficulty is encountered in replacing the chlorine atom of R_3SiCl compounds by a *tert*-butyl group using organometallic compounds[3], the *tert*-butylsilyl structure can easily be produced by intramolecular rearrangement of isopropenylmethylsilanes with concentrated sulfuric acid[4,5].

(Chloromethyl)isopropenyldimethylsilane (II) was obtained in satisfactory yields (60–70 %). Compound (II) underwent intramolecular rearrangement with cold concentrated sulfuric acid and after treatment with ammonium hydrogen fluoride gave (chloromethyl)-*tert*-butylmethylfluorosilane (III) (in about 18 % yield). The rearrangement product cannot be an isomer, $ClCH_2(CH_3)_2CSi(CH_3)_2F$, because this compound would be too unstable to be isolated under the reaction conditions owing to its Cl-C-C-Si structure (see, for example, ref. 6). In the above reaction, however, extensive cleavage of the isopropenyl group from silicon was observed to occur to produce (chloromethyl)dimethylfluorosilane (IV). Whereas compound (III) is a result of intramolecular rearrangement which proceeds probably via an α-carbonium ion intermediate (A), compound (IV) is a product of cleavage which occur probably via a β-carbonium ion intermediate (B).



$$ClCH_2Si(CH_3)_2C(CH_3){=}CH_2 \text{ (II)} \xrightarrow{H_2SO_4} ClCH_2Si(CH_3)_2\overset{+}{C}(CH_3)_2 \text{ (A)} \xrightarrow{NH_4F\cdot HF} \text{(III)}$$

$$\xrightarrow{H_2SO_4} ClCH_2Si(CH_3)_2CH(CH_3)\overset{+}{C}H_2 \text{ (B)} \xrightarrow{NH_4F\cdot HF} ClCH_2Si(CH_3)_2F + CH_3CH{=}CH_2 \text{ (IV)}$$

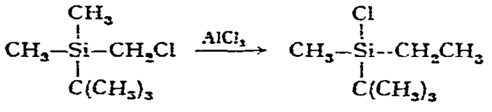
It is well known that vinyl silicon compounds[7], such as $(CH_3)_3SiCH{=}CH_2$, exclusively undergo cleavage with concentrated sulfuric acid, whereas isopropenyl silicon compounds, such as $(CH_3)_3SiC(CH_3){=}CH_2$ and $(CH_3)_3SiSi(CH_3)_2C(CH_3){=}CH_2$[4,5], are substantially converted into products of intramolecular rearrangement. An explanation for this difference is given as follows[4]. In the former case, protonation by sulfuric acid occurs at the α-carbon atom because some conjugation exists between the vinyl π-bond and a *d*-orbital of the silicon atom, which causes the β-carbon to be more positive than the α-carbon. In the latter case, on the other hand, the hyperconjugative effect of the α-methyl group, overcomes the conjugative effect of silicon, and directs protonation to the β-carbon atom.

The extensive cleavage observed with compound (II) may be understood on the same basis. If an electron-withdrawing chloromethyl group is substituted for a methyl attached to silicon in $(CH_3)_3SiC(CH_3){=}CH_2$, the *d*-orbital availability of the silicon atom will be enhanced; accordingly, protonation at the α-carbon will be increased, to give a increased amount of cleavage.

Methylation of compound (III) by the Grignard reaction proceeded smoothly to give the required compound in good yield.

Intramolecular rearrangement

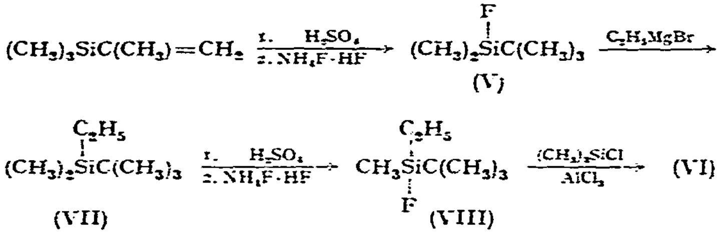
It was found that compound (I) easily undergoes intramolecular rearrangement with anhydrous aluminum chloride to produce *tert*-butylethylmethylchlorosilane (VI), substantially as a single product, thus indicating that a methyl group almost exclusively migrates from silicon to carbon.



$$CH_3Si(CH_3)(CH_2Cl)C(CH_3)_3 \text{ (I)} \xrightarrow{AlCl_3} CH_3Si(Cl)(CH_2CH_3)C(CH_3)_3 \text{ (VI)}$$

(I) (VI)

Evidence for structure (VI), and against the isomeric $(CH_3)_2Si(Cl)CH_2C(CH_3)_3$, was afforded by the following facts. First, physical properties for the rearrangement product were in good agreement with those for the product obtained by a different, unequivocal preparative method as shown below.



$$(CH_3)_3SiC(CH_3){=}CH_2 \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} \underset{(V)}{(CH_3)_2\overset{F}{Si}C(CH_3)_3} \xrightarrow{C_2H_5MgBr}$$

$$\underset{(VII)}{(CH_3)_2\overset{C_2H_5}{Si}C(CH_3)_3} \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} \underset{(VIII)}{CH_3\underset{F}{\overset{C_2H_5}{Si}}C(CH_3)_3} \xrightarrow[AlCl_3]{(CH_3)_3SiCl} (VI)$$

This sequence of reactions involves only the known processes, *i.e.*, intramolecular rearrangement of isopropenyltrimethylsilane[4] followed by treatment with ammonium hydrogen fluoride[5] to give *tert*-butyldimethylfluorosilane (V), ethylation in the usual way to give *tert*-butylethyldimethylsilane (VII), demethylation with concentrated sulfuric acid[6] followed by treatment with ammonium hydrogen fluoride[7] to give *tert*-butylethylmethylfluorosilane (VIII), and metathesis between (VIII) and trimethylchlorosilane[8] in the presence of aluminum chloride to give compound (VI).

Secondly, the proton nuclear magnetic resonance spectrum (Fig. 1) of a sample (VI) obtained by rearrangement indicates that only one $CH_3Si\equiv$ structure is present, and areas (a) assignable to $CH_3Si\equiv$ and (b) + (c) assignable to $(CH_3)_3C-$ and C_2H_5- are approximately in the ratio 3:14, as expected for the proposed structure.

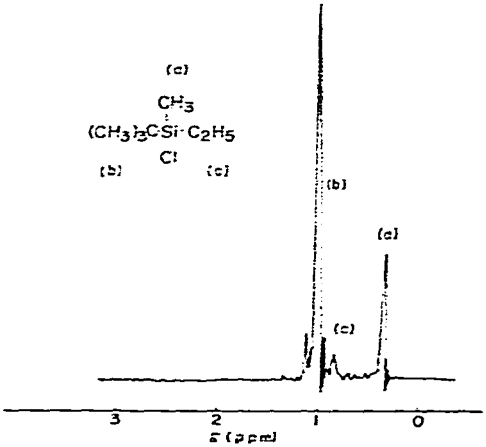
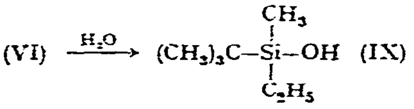


Fig. 1. The NMR spectrum of *tert*-butylethylmethylchlorosilane (VI).

Hydrolysis of compound (VI) gave *tert*-butylethylmethylsilanol (IX) in 80% yield. No formation of the disiloxane was observed.



$$(VI) \xrightarrow{H_2O} (CH_3)_3C-\underset{C_2H_5}{\overset{CH_3}{Si}}-OH \quad (IX)$$

Reaction with sodium methoxide in methanol

It was found that compound (I) is not only much less reactive than, but also behaves itself in a different manner from (chloromethyl)pentamethyldisilane toward alkoxide ion in alcohol. Thus, the reaction of (I) with sodium methoxide at the reflux temperature of methanol over a 100-h period led exclusively to substitution of the chlorine atom by methoxyl group to give (methoxymethyl)-*tert*-butyldimethylsilane (X). No intramolecular rearrangement took place.

$$\text{(I)} \xrightarrow[CH_3OH]{CH_3ONa} CH_3OCH_2Si(CH_3)_2C(CH_3)_3 \quad \text{(X)}$$

Proof of the structure of the product (X) was afforded by its infrared spectrum, which showed an intensive absorption band characteristic of C–O–C stretching at 1110 cm^{-1} and no absorption of Si–O–C structure. The NMR spectrum shown in Fig. 2 is also consistent with the structure (X).

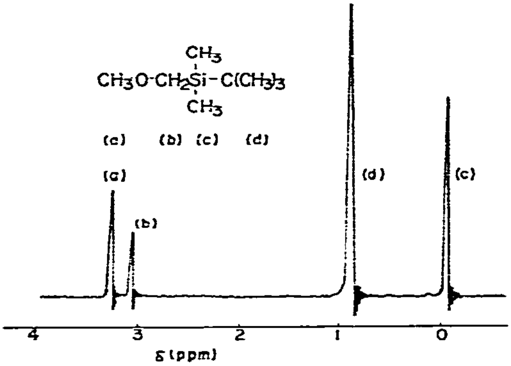


Fig. 2. The NMR spectrum of (methoxymethyl)-*tert*-butyldimethylsilane (X).

Magnesium and mercury compounds

Compound (I) could easily be converted into the Grignard reagent in ether, and subsequently into [(*tert*-butyldimethylsilyl)methyl]mercuric chloride (XI), upon treatment with mercuric chloride, in 64.5 % over-all yield.

$$\text{(I)} \xrightarrow[\text{ether}]{Mg} (CH_3)_3C(CH_3)_2SiCH_2MgCl \xrightarrow{HgCl_2} (CH_3)_3C(CH_3)_2SiCH_2HgCl \quad \text{(XI)}$$

EXPERIMENTAL

All organosilicon compounds reported here were fractionally distilled through a Stedman-type column rated at about 20 theoretical plates, and were gas-chromatographically homogeneous, unless otherwise stated. Boiling and melting points were uncorrected. NMR spectra were obtained by Dr. K. TORI of Shionogi Research Laboratory in carbon tetrachloride solutions containing cyclohexane (Varian A-60, 60 Mc/sec). Chemical shifts are expressed as δ values in ppm relative to tetramethylsilane as internal standard. To obtain δ values we have taken 1.43 ppm as the signal difference between cyclohexane and tetramethylsilane.

(Chloromethyl)isopropenyldimethylsilane (II)

To a stirred solution of isopropenylmagnesium bromide prepared from 40 g (1.65 g-atoms) of magnesium, 200 g (1.65 moles) of isopropenyl bromide in 600 ml of tetrahydrofuran was added dropwise 177 g (1.24 moles) of (chloromethyl)dimethylchlorosilane[9]. The reaction mixture was heated to reflux over a 20-h period and was then hydrolyzed with aqueous solution of ammonium chloride. Fractional distillation of the organic layer gave 123 g (67 % yield) of (chloromethyl)isopropenyldimethylsilane, b.p. 141–143°, n_D^{20} 1.4546, d_4^{20} 0.9360, MR_D 43.07 (calcd. 43.44). (Found: Si, 18.87. $C_6H_{13}ClSi$ calcd.: Si, 18.92 %.)

(Chloromethyl)-tert-butylmethylfluorosilane (III)

To 130 g of concentrated sulfuric acid stirred and cooled to 0° was added dropwise 185 g (1.25 moles) of compound (II) over a 1-h period. After an additional 1-h stirring at the same temperature, to the solution was added 107 g (1.87 moles) of ammonium hydrogen fluoride in portions. The upper organic layer was separated and fractionally distilled to give two fractions: (*1*) (chloromethyl)dimethylfluorosilane, b.p. 84°, n_D^{25} 1.4000, d_4^{25} 1.0234, MR_D 29.20 (calcd. 30.00), 73 g; (Found: F, 14.81. C_3H_8ClFSi calcd.: F, 15.01 %.) (*2*) (chloromethyl)-*tert*-butylmethylfluorosilane, b.p. 143–145°, n_D^{20} 1.4222, d_4^{20} 0.9829, MR_D 43.64 (calcd. 43.73), 38 g (18 % yield). (Found: F, 11.07. $C_6H_{14}ClFSi$ calcd.: F, 11.26 %.)

Yields from several runs conducted in essentially the same manner as above were between 15 and 20 %.

(Chloromethyl)-tert-butyldimethylsilane (I)

To an ether solution containing 0.5 mole of methylmagnesium bromide was added 35 g (0.21 mole) of compound (III). The reaction mixture was heated to reflux over a 20-h period and then worked up in the usual manner. Simple distillation gave 27 g of a mixture of liquid and crystals, boiling over the range of 155–164°. This mixture was dissolved in petroleum ether (b.p. 45–55°) and then treated with concentrated sulfuric acid at 0° to remove any silanol or siloxane. The organic layer was separated, washed until neutral, and distilled to give 26 g (75 % yield) of colorless, readily sublimed crystals of (chloromethyl)-*tert*-butyldimethylsilane, m.p. 52.5–53° (from 90 % ethanol). (Found: Cl, 20.05; Si, 16.67. $C_7H_{17}ClSi$ calcd.: Cl, 20.06; Si, 17.05 %.)

Intramolecular rearrangement of (I) with aluminum chloride

In a 50-ml three-necked flask equipped with a stirrer, dropping funnel and reflux condenser we placed 1.5 g of freshly sublimed, anhydrous aluminum chloride. A solution of 25 g (0.15 mole) of compound (I) in 10 ml of *n*-pentane was added dropwise at room temperature over a 40-min period, a vigorous exothermic reaction taking place. After addition was complete, the mixture was heated to reflux for 8 h, at which time no appreciable change occurred if an additional small amount of aluminum chloride was introduced. Flash distillation *in vacuo* gave a catalyst-free distillate (20 g), which was then fractionated to give 15.4 g (61.5 % yield) of gas-chromatographically homogeneous *tert*-butylethylmethylchlorosilane (VI), b.p. 152°, n_D^{20} 1.4380, d_4^{20} 0.8877, MR_D 48.72 (calcd. 48.35). (Found: Cl, 21.16. $C_7H_{17}ClSi$ calcd.: Cl, 21.52 %.)

tert-Butyldimethylfluorosilane (*V*)

Isopropenyltrimethylsilane[4] was prepared from isopropenylmagnesium bromide and trimethylchlorosilane in tetrahydrofuran, in 53 % yield. To 800 g of concentrated sulfuric acid stirred and cooled to —10° was added dropwise 120 g (0.52 mole) of isopropenyltrimethylsilane over a 1-h period. After an additional 2.5-h stirring, 90 g (1.6 mole) of ammonium hydrogen fluoride was added in portions to the reaction mixture. The resulting organic layer was separated and fractionally distilled to give 95 g (69 % yield) of compound (V), b.p. 89°, n_D^{25} 1.3817, d_4^{25} 0.8061, MR_D 38.74 (calc. 38.29). (Found: F, 14.05. $C_6H_{15}FSi$ calcd.: F, 14.15 %.) From the fore-run 9 g of trimethylfluorosilane was isolated.

tert-Butylethyldimethylsilane (*VII*)

To a stirred ether solution containing 0.57 mole of ethylmagnesium bromide was added dropwise 51.7 g (0.38 mole) of compound (V). After addition was complete, the solvent was distilled off through a column and the residual mass was heated on a steam bath for 12 h. It was then worked up in the usual way to give, in addition to 16 g of unchanged starting material, 19 g (34 % yield) of compound (VII), b.p. 136°, n_D^{20} 1.4240, d_4^{20} 0.7531, MR_D 48.87 (calcd. 48.78). (Found: C, 66.47; H, 13.73. $C_8H_{20}Si$ calcd.: C, 66.99; H, 13.97 %.)

tert-Butylethylmethylfluorosilane (*VIII*)

In a 500-ml three-necked flask fitted with a stirrer, a thermometer and a reflux condenser leading to a gas collector was stirred vigorously a mixture of 19 g (0.13 mole) of compound (VII) with 200 g of concd. sulfuric acid at about 28°. After 2 h, 2 l of gas (theory 3.2 l) was collected and no more evolution was observed on further stirring. Fractional distillation of the organic layer gave 10 g (57 % yield) of compound (VIII), b.p. 118–119°, n_D^{20} 1.3990, d_4^{20} 0.8310, MR_D 43.03 (calcd. 42.94). (Found: F, 12.92. $C_7H_{17}FSi$ calcd.: F, 12.81 %.)

tert-Butylethylmethylchlorosilane (*VI*)

A mixture of 10 g (0.068 mole) of compound (VIII), 9.2 g (0.084 mole) of trimethylchlorosilane and 0.5 g of anhydrous aluminum chloride was heated in a distillation apparatus fitted with a small Stedman column, from the top of which trimethylfluorosilane was collected as it formed. After 8 h 4.5 g (73 % yield) of trimethylfluorosilane was obtained. The residue was flash-distilled *in vacuo*, and the catalyst-free distillate was redistilled to give 5 g (50 % yield) of compound (VI), b.p. 154°, n_D^{20} 1.4375, d_4^{20} 0.8883, MR_D 48.64 (calcd. 48.35). (Found: Cl, 21.36. $C_7H_{17}ClSi$ calcd.: Cl, 21.52 %.) This product was shown to be identical with the rearranged product of (I) by gas-chromatographic analysis as well as by comparison of physical properties.

tert-Butylethylmethylsilanol (*IX*)

In a 500-ml flask, equipped with a stirrer and a dropping-funnel, and surrounded by ice-water, was placed a solution of 10 g (0.06 mole) of compound (VI) in 100 ml of ether. A few drops of phenolphthalein indicator was then added. To the stirred solution was added dropwise a solution of 2.5 g (0.063 mole) of sodium hydroxide in 100 ml of water over a 30-min period. The organic layer was separated and the water layer was extracted with ether. The combined ether solution was washed to neutral, dried over potassium carbonate and distilled to give 8 g (80 % yield) of compound (IX), b.p. 158°, n_D^{20} 1.4400, d_4^{20} 0.8606, MR_D 44.79 (calcd. 44.77). (Found: Si, 19.23. $C_7H_{18}OSi$ calcd.: Si, 19.20 %.) The infrared spectrum showed an intensive absorption band at 3350 cm^{-1} characteristic of OH group.

Reaction of (I) with sodium methoxide in methanol

Sodium (4.5 g, 0.2 g-atom) was dissolved in 40 ml of methanol. To the solution was added 27 g (0.16 mole) of compound (I) dissolved in 40 ml of methanol. No appreciable change occurred. The reaction mixture was then heated to reflux with stirring over a 100-h period. As the reaction proceeded two organic layers appeared and inorganic salt precipitated. Subsequently, 25 ml of *n*-pentane and 50 ml of water were then added, and the upper layer was separated. The lower layer was neutralized with hydrogen chloride gas and then extracted with five portions of 50 ml of *n*-pentane. All *n*-pentane solutions were combined and fractionally distilled to give 8 g (72 % yield on the basis of unrecovered I) of (methoxymethyl)-*tert*-butyldimethylsilane (X), b.p. 147°, n_D^{20} 1.4244, d_4^{20} 0.8028, MR_D 51.00 (calcd. for $CH_3OCH_2Si(CH_3)_2C(CH_3)_3$: 50.51; calcd. for $CH_3OSi(CH_3)(C_2H_5)C(CH_3)_3$: 49.57). (Found: Si, 17.12. $C_8H_{20}OSi$ calcd.: Si, 17.52 %.) Recovered starting material weighed 15.6 g.

[(tert-Butyldimethylsilyl)methyl]mercuric chloride (XI)

A mixture consisting of 6 g (0.036 mole) of compound (I), 0.8 g (0.033 g-atom) of magnesium turnings, one crystal of iodine and 50 ml of dry ether was heated to gentle reflux. The reaction soon set in. After 2-h reaction at room temperature, the magnesium had almost completely disappeared. The mixture was heated for an additional 1 h and then 10 g (0.037 mole) of mercuric chloride suspended in 10 ml of ether was added to it. After heating to reflux over a 5-h period the solvent ether was completely evaporated (initially at atmospheric pressure on a steam-bath; later *in vacuo* at room temperature). To the residual mass was added 40 ml of 98 % ethanol, and the mixture was heated to reflux for 1 h, then filtered while hot, and the precipitate on the filter was washed with 10 ml of hot ethanol. To the combined ethanol solution was added 20 ml of water. The mixture was allowed to stand overnight to give 8 g (64.5 %) of colorless needle crystals, m.p. 82–83° (recrystallized from 90 % ethanol). (Found[10]: Hg, 53.31. $C_7H_{17}ClHgSi$ calcd.: Hg, 53.44 %.)

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SUMMARY

(Chloromethyl)-*tert*-butyldimethylsilane (I) was prepared from (chloromethyl)isopropenyldimethylsilane through a series of reactions: intramolecular rearrangement with sulfuric acid, fluorination with ammonium hydrogen fluoride and methylation with the Grignard reagent. It has been found that compound (I) easily undergoes

intramolecular rearrangement with aluminum chloride, involving migration of a methyl group from silicon to carbon, and that the chlorine atom is replaced by a methoxyl group without rearrangement when the compound is treated with sodium methoxide in methanol.

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 L. J. TYLER, L. H. SOMMER AND F. C. WHITMORE, *J. Am. Chem. Soc.*, 70 (1948) 2876.
4 L. H. SOMMER AND F. J. EVANS, *J. Am. Chem. Soc.*, 76 (1954) 1186.
5 M. KUMADA, K. NAKA AND M. ISHIKAWA, *J. Organometal. Chem.*, 2 (1964) 136.
6 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, p. 133.
7 M. KANAZASHI, *Bull. Chem. Soc. Japan*, 28 (1955) 4450.
8 B. A. BLUESTEIN, *J. Am. Chem. Soc.*, 70 (1948) 3068.
9 R. H. KRIEBLE AND J. R. ELLIOTT, *J. Am. Chem. Soc.*, 67 (1945) 1810.
10 F. C. WHITMORE AND R. J. SABATZKI, *J. Am. Chem. Soc.*, 55 (1933) 1128.