$AlCl_3$-Catalyzed transformations of organo(trichloromethyl)silanes

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Reactions of organo(trichloromethyl)silanes RMe_2SiCCl_3 (R = Me, Ph, Me_3Si) with aluminum chloride have been studied. The interaction of trimethyl(trichloromethyl)silane with $AlCl_3$ carried out in cyclohexane or in benzene leads to $Me_3SiCHCl_2$ (in 75 % yield) or $ClMe_2SiCPh_2Me$ (in 70 % yield), respectively; whereas no conversions are observed in *n*-hexane and methylene chloride. Treatment of dimethyl(phenyl)trichloromethyl)silane with aluminum chloride in a n-C_5H_{12}/CH_2Cl_2 mixture gives an aromatic cross-linked insoluble polymer. The reaction of pentamethyl(trichloromethyl)disilane (R = Me_3Si) with $AlCl_3$ in pentane affords the rearrangement product, $Me_3SiCCl_2SiMe_2Cl$, in 65 % yield. In methylene chloride the further cleavage of the disilane occurs to yield Me_2SiCl_2 and CH_2=$CHMe_2SiCl$.

Key words: organosilanes, (trichloromethyl)silanes; $AlCl_3$-catalyzed reactions.

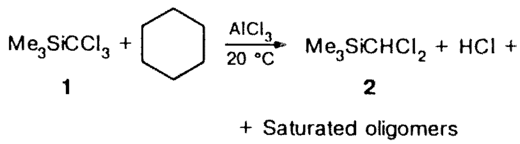
Organochlorosilanes, containing chlorine atoms in the organic moiety, are related to an important class of organosilicon compounds. They are intermediates in the designing and commercial production of different carbofunctional organosilanes and polymers derived from them.[1] Unlike mono- and dichloromethylsilanes,[1,2] until now organo(trichloromethyl)silanes have been expensive and not readily available.

We have developed a convenient method for the synthesis of these compounds by catalytic decarboxylation of the corresponding (trichloroacetoxy)silanes, which makes them available and opens new possibilities of using the trichloromethyl group to modify and functionalize organosilicon compounds.

Conversions of organosilanes containing $ClCH_2$ and Cl_2CH groups attached to silicon atoms through the action of aluminum chloride have been studied earlier.[4–8] It was of interest to compare the reactivity of these compounds with that of their trichloromethyl analogs. In this communication we report the reactions of some organo(trichloromethyl)silanes with $AlCl_3$ that proceed fairly selectively and with good yields of products.

Results and Discussion

Interaction of trimethyl(trichloromethyl)silane (1) with $AlCl_3$ in cyclohexane. Silane **1** is stable towards aluminum chloride in saturated linear hydrocarbons, but readily reacts with $AlCl_3$ in cyclohexane; in this case the trichloromethyl group is selectively converted to the dichloromethyl group to form product **2** in 75 % yield.



(1)

In the course of reaction (1) HCl is vigorously liberated; no other organosilicon compounds are found.* After completion of fractional distillation of the reaction products, a viscous material remains in the still with an IR spectrum identical to that of Vaseline oil. The structure of the products of cyclohexane conversion was not studied comprehensively; probably, the first step of this conversion is the formation of the carbocation $[C_6H_{11}]^+$.

Many examples of the reduction of a trichloromethyl group in organic compounds have been reported in the literature,[10] however, selective methods for conversion of the CCl_3 group to $CHCl_2$ are not numerous. We should mention the systems based on organosilicon hydrides in the presence of various catalysts: R_3SiH/H_2PtCl_6[10] and $HSiCl_3/Bu_3N$.[11] The use of aluminum chloride combined with triethylsilane leads to complete dechlorination of the CCl_3-group in many

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* Note that trimethyl(dichloromethyl)silane under the action of aluminum chloride reacts according to the following scheme:

$$Me_3SiCHCl_2 \xrightarrow{AlCl_3} ClMe_2SiCH(Me)Cl \longrightarrow$$
$$\longrightarrow Me_2SiCl_2 + CH_2{=}CH_2$$

However, this conversion occurs in the absence of solvents and at a higher temperature (85 °C) than in the case of reaction (1) (see Ref. 9).

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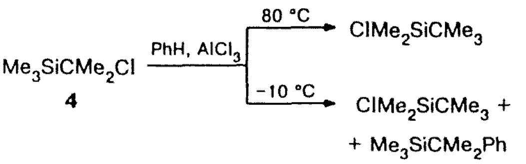
cases.[12] Thus, the cyclohexane—$AlCl_3$ system proved to be a very useful supplement to the already known techniques.

Interaction of trimethyl(trichloromethyl)silane 1 with $AlCl_3$ in benzene proceeds as Friedel—Crafts electrophilic aromatic substitution with migration of the methyl group. In this case dimethyl(1,1-diphenylethyl)chlorosilane (3) is isolated as the ultimate product.

$$\mathbf{1} \xrightarrow{\text{AlCl}_3\text{/PhH, 40 °C}} [Me_3SiCPhCl_2] \longrightarrow [Me_3SiCPh_2Cl] \longrightarrow \underset{\mathbf{3}}{ClMe_2SiCPh_2Me} \qquad (2)$$

Probably, migration of the methyl group occurs after formation of the bisphenylation product — Me_3SiCPh_2Cl. This assumption is supported by the fact that silane **1** does not undergo rearrangement if it is refluxed with $AlCl_3$ in hexane or dichloromethane. At the same time, such a rearrangement is known to be normal for α-chloroalkylsilanes. Thus, trimethyl(dimethylchloromethyl)silane (**4**) rearranges to *tert*-butyldimethylchlorosilane under the action of $AlCl_3$ in benzene, and concurrently it alkylates benzene to form cumyltrimethylsilane.[5] Only the rearrangement is observed at 80 °C; and at −10 °C the yields of the *tert*-butyl and cumyl derivatives are 76 and 24 %, respectively.

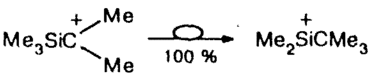


(3)

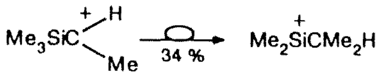
The selectivity of the reactions depends on the substituent at the α-carbon atom of chloromethylsilane. Thus, in the case of compounds **1** and **4** the process occurs very selectively, whereas trimethyl(1-chloroethyl)silane (**5**) concurrently reacts in several directions.[5]

$$\underset{\mathbf{5}}{Me_3SiCMe(H)Cl} + PhH \xrightarrow{AlCl_3} \underset{(25\ \%)}{Me_3SiCMe(H)Ph} + \underset{(34\ \%)}{ClMe_2SiCMe_2H} + \underset{(11\ \%)}{Me_3SiCH_2CH_2Ph} + \underset{(30\ \%)}{Me_3SiCl/C_2H_4} \qquad (4)$$

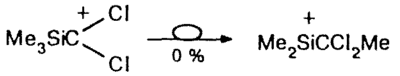
We can easily explain the conversions of chloromethylsilanes if we consider the relative stability of the carbocations and the silicenium ions derived from them as a result of the rearrangement.



$$Me_3Si\overset{+}{C}(Me)Me \xrightarrow[100\ \%]{} Me_2\overset{+}{Si}CMe_3 \qquad (A)$$



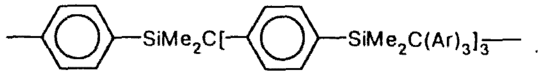
$$Me_3Si\overset{+}{C}(H)Me \xrightarrow[34\ \%]{} Me_2\overset{+}{Si}CMe_2H \qquad (B)$$



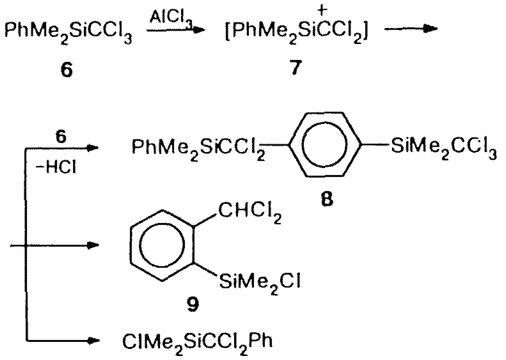
$$Me_3Si\overset{+}{C}(Cl)Cl \xrightarrow[0\ \%]{} Me_2\overset{+}{Si}CCl_2Me \qquad (C)$$

In the examples **A**, **B**, and **C** cited above the *tert*-butyl substituent (**A**; reaction (3)) stabilizes the positive charge on the silicon atom to a maximum extent, to favor migration of the methyl group. The *iso*-propyl substituent (**B**) stabilizes the positive charge to a lesser extent; silicenium and carbenium ions are in equilibrium, which results in a mixture of products (reaction (4)). In the reactions of trichloride **1**, on the other hand, the 1,1-dichloroethyl group exerts a destabilizing effect and does not favor the formation of the silicenium ion. In this case (**C**; reaction (2)) we do not observe migration of the methyl group. The carbocation $[Me_3SiCCl_2]^+$ enters into the normal reaction of electrophilic substitution with benzene. Obviously, the second step of reaction (2) — repeated alkylation leading to the replacement of the second chlorine atom by a phenyl group — also proceeds rapidly, because we failed to isolate the intermediate product, $Me_3SiC(Ph)Cl_2$. Therefore, migration of the methyl group is more probable at the last step of reaction (2).

Interaction of dimethyl(phenyl)(trichloromethyl)silane 6 with aluminum chloride. The above-mentioned data indicate that compound **1** primarily enters into the Friedel—Crafts reaction in the presence of $AlCl_3$ in benzene, whereas 1,2-(Si—C)-migration of the methyl group occurs only at the final step of the process. In this connection studying the reaction of trichloride **6** with aluminum chloride was of interest, because this compounds meets Flory's requirements for a monomer that is capable of reacting to form a dendrite polymer:



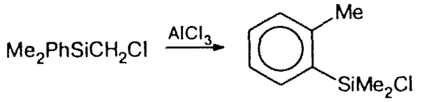
The reaction was carried out in a pentane—dichloromethane mixture (10 : 1). The mixture of solvents was chosen because tar formation occurs in the reaction mixture occurs in pure dichloromethane, and the catalyst is rapidly deactivated if pure pentane is used. The addition of $AlCl_3$ to a solution of trichloride **6** results in the formation of a solid, which gradually occupies the whole volume of the flask. At 35 °C the process is completed within 2 h. The elemental analysis data indicates that the insoluble polymer formed consists of carbon and hydrogen, in the main, and contains 6 % silicon and traces of chlorine. The IR spectrum contains bands at 1240, 840 (Si—Me) and 1580, 730, 690, and 470 cm^{-1} (typical of aromatic groups). The absence of a band at 1100 cm^{-1} indicates that all Ph—Si bonds are destroyed. In the liquid part of the reaction mixture Me_2SiCl_2, CCl_3SiMe_2Cl, and PhH were found. These data confirm that the condensation of trichloride by the Friedel-Crafts reaction is accompanied by the rearrangement and cleavage of the Si—C$_{aryl}$ bond. The carbocation **7** formed at the first step can then react both with molecule **6** and intramolecularly (reactions (6, 7)):


(5)

(6)

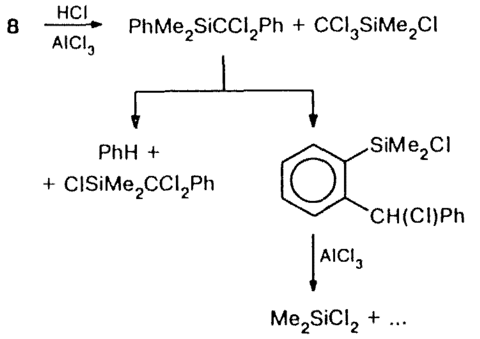
(7)

The rearrangement, which is similar to reaction (6), was observed earlier [13] in the reaction of aluminum chloride with dimethyl(phenyl)(chloromethyl)silane.*


(8)

The hydrogen chloride formed in the course of electrophilic substitution (reaction (5)) is capable of cleaving Si—Ar bonds in the presence of $AlCl_3$, thus removing silicon in the form of Me_2SiCl_2 from the polymer formed.

$$\mathbf{9} \xrightarrow[AlCl_3]{HCl} Me_2SiCl_2 + PhCHCl \qquad (9)$$


(10)

The CCl_3 and CCl_2 groups remain the centers of condensation during the formation of cross-linked aromatic polymers of irregular structure.

Interaction of pentamethyl(trichloromethyl)disilane (10) with aluminum chloride was studied in pentane and dichloromethane, and the compositions of products were different in these two cases. When the reaction was carried out in pentane, the rearrangement product — 1,1,1,3,3-pentamethyl-2,2,3-trichloro-1,3-disilapropane (**11**) — was formed in 85 % yield.

$$\underset{\mathbf{10}}{Me_3SiSiMe_2CCl_3} \xrightarrow[C_5H_{12}]{AlCl_3} \underset{\mathbf{11}}{Me_3SiCCl_2SiMe_2Cl} \qquad (11)$$

The action of ultrasound (22 kHz, 150 Wt) within 10 min results in the same product yield. Similar rearrangements of α-mono- and α,α-dichloromethyldisilanes have been studied by Japanese authors.[6–8] They showed that the rearrangement of pentamethyl(chloromethyl)disilane in the presence of $AlCl_3$ proceeds easily and with high conversion (82 %), to yield trimethylsilyl(dimethylchlorosilyl)methane.[8] An increase in the number of electro-negative substituents (chlorine atoms) attached to the silicon atom retards the reaction. The yield of the corresponding carbosilane decreases in the series $ClMe_2SiSiMe(Cl)CH_2Cl$, $Cl_3SiSiMe_2(CH_2Cl)$, $Cl_2MeSiSiCl_2(CHCl_2)$, and $Cl_2MeSiSiCl_2(CH_2Cl)$, in spite of the more and more drastic conditions used.[6]

Dichloromethylsilanes undergo two succesive rearrangements. Migration of the trimethylsilyl group initially occurs, followed by migration of the methyl group.[7]

$$Me_3SiSiMe_2CHCl_2 \xrightarrow[75\ ^\circ C]{AlCl_3} ClMe_2SiCH(Cl)SiMe_3 \longrightarrow$$

$$\xrightarrow[140\ ^\circ C]{AlCl_3} ClMe_2SiCH(Me)SiMe_2Cl \qquad (12)$$

The end product in reaction (12) is formed in a fairly high yield (70 %).

The presence of three chlorine atoms attached to the α-carbon atom of disilane **10** suggest that this compound can basically undergo three successive rearrangements in the presence of $AlCl_3$. Actually, if pentane is replaced by more polar methylene chloride, the process does not cease at the first step. Dimethyldichlorosilane and vinyldimethylchlorosilane are the end products in this case (34 °C, 10 min). We can explain their formation by considering the chain of successive rearrangements.

Migration of the trichloromethylsilyl group (**12**→**13**) is the first and the last rearrangement in this chain if the reaction is carried out in pentane (Equation. (11)). In dichloromethane the reaction does not cease at this step, and compound **11** forms carbocation **14** with $AlCl_3$. In the latter, migration of the methyl group occurs (**14**→**15**) to lead to trichloride **16**. The third carbocation **17**, formed from the product **16** is stabilized

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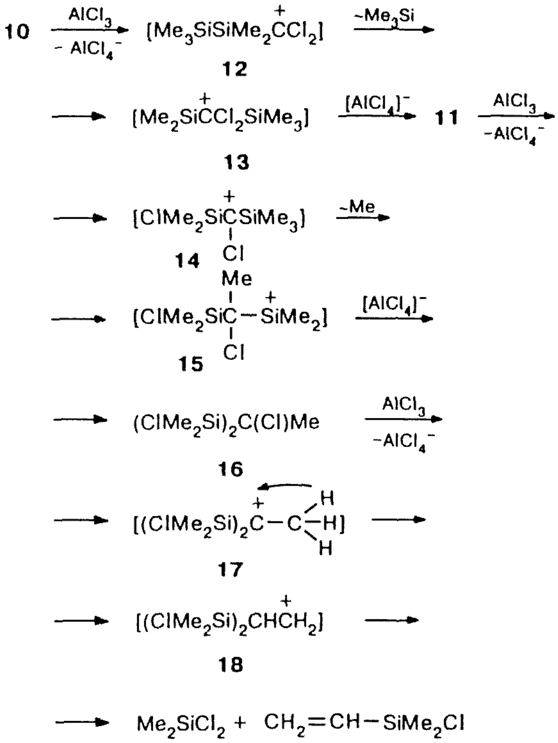
* However, other data were reported[14] on the migration of the phenyl group resulting in benzylsilanes in this reaction. There is not sufficient information in the publications under consideration to unambiguously conclude whether *o*-tolyl- or benzylsilanes are formed. The ^{1}H and ^{13}C NMR spectra reported for dimethyl(*o*-tolyl)chlorosilane[13] can be also assigned to dimethyl(benzyl)chlorosilane.[15]

by migration of the β-hydrogen atom (**17**→**18**). The carbocation **18**, the last one in this chain, decomposes to form two products — dimethyldichlorosilane and vinyldimethylchlorosilane. We should note that the starting disilane **10** is quantitatively converted to these compounds. Similar migration of β-hydrogen atoms was observed in the reaction of diethyl(1-chloroethyl)chlorosilane with aluminum chloride leading to diethyldichlorosilane and ethylene.[9]



(14)

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Tesla-BS-567-A (100 and 25 MHz) instrument in $CDCl_3$ using HMDS and $CDCl_3$ as internal standards, respectively. GLC was carried out on a Tsvet-500 chromatograph (stainless steel column 0.4×200 cm, sorbent — 5 % SE-30 on Chromaton-N-Super, detector — catharometer, carrier gas — helium). IR spectra were measured on a Perkin-Elmer-577 spectrophotometer (thin layer between KBr plates).

The solvents (cyclohexane, pentane, benzene, and dichloromethane) were distilled over P_2O_5 prior to use. The starting organo(trichloromethyl)silanes **1**, **6**, and **13** were obtained by the well known procedure.[3]

Interaction of trimethyl(trichloromethyl)silane 1 with aluminum chloride. ***A*. In cyclohexane.** A mixture of silane **1** (4.90 g, 30 mmol) and anhydrous $AlCl_3$ (0.20 g, 1.5 mmol) was vigorously stirred at 20 °C for 5 h in 40 mL of a cyclohexane—dichloromethane (5 : 1) mixture (methylene chloride was added to accelerate the reaction). The course of the process was monitored by GLC and by the amount of HCl liberated. The reaction mixture was filtered and 1 drop of acetonitrile was added to the filtrate to remove the remaining $AlCl_3$. The solvent was distilled off, and the residue fractionated *in vacuo*. Trimethyl(dichloromethyl)silane **2** was obtained (3.53 g, 75 %), b.p. 136—137 °C (760 Torr), n_D^{20} 1.4435, d_4^{20} 1.0430. IR, ν/cm^{-1}: 2900, 2830, 1435, 1390 (C—H); 1240, 840 (Si—Me); 750, 680, 620 (Si—C); 700 (CCl_2) (*cf.* Refs. 16 and 17: b.p. 133 °C (730 Torr); n_D^{25} 1.4430, d_4^{25} 1.0400).

***B*. In benzene** A solution of silane **1** (7.66 g, 40 mmol) in 20 mL of benzene was slowly added dropwise to a suspension of anhydrous aluminum chloride (0.53 g, 4 mmol) in 20 mL of benzene with vigorous stirring. The temperature of the reaction mixture did not exceed 30 °C. The course of the reaction was monitored by GLC and by the amount of HCl liberated. The main part of the solvent (80 %) was removed *in vacuo*. Acetonitrile (0.5 mL) was added to bind $AlCl_3$. Benzene was replaced by hexane, the reaction mixture was filtered, and the filtrate fractionated *in vacuo* (hexane was distilled off in advance). Dimethyl(1,1-diphenylethyl) chlorosilane **3** (7.70 g, 70 %) was obtained, b.p. 140—142 °C (0.5 Torr). ^{1}H NMR ($CDCl_3$), δ : 0.33 (s, 6 H, Me_2Si, $^2J_{H,^{29}Si}$ = 6.67 Hz); 1.76 (s, 3 H, C—Me); 7.21 (s, 10 H, Ph). IR, ν/cm^{-1}: 3040, 2940 (C—H); 1590 (Ph); 1250, 840 (Si—Me); 700, 650 (Ph); 510 (Si—Cl). Found (%): C, 69.34; H, 7.03; Si, 10.55; Cl, 12.67. $C_{16}H_{19}SiCl$. Calculated (%): C, 69.92; H, 6.97; Si, 10.22; Cl, 12.90.

Interaction of dimethylphenyl(trichloromethyl)silane (6) with aluminum chloride. Anhydrous $AlCl_3$ (0.40 g, 3.0 mmol) was added to a mixture of trichloride **6** (7.61 g, 30 mmol), 20 mL of pentane, and 1 mL of dichloromethane. The reaction was carried out at 35 °C with vigorous stirring. The amount of the precipitate formed gradually increased, and after 2 h a viscous,difficult-to-stir material was formed. The precipitate was separated by centrifugation, washed five times with 10 % acetonitrile solution in benzene to remove $AlCl_3$, and dried *in vacuo* to yield a powdered light brown polymer (2.50 g), which is insoluble in organic solvents. Found (%): C, 85.27; H, 7.02; Si, 6.30; Cl, 1.03. IR, ν/cm^{-1}: 1580, 730, 690, 470 (aryl), 1240, 840 (Si—Me). Benzene, Me_2SiCl_2, and CCl_3SiMe_2Cl were found in the liquid phase after centrifugation by GLC. A minor amount of HCl was liberated during the reaction.

Interaction of pentamethyl(trichloromethyl)disilane (10) with aluminum chloride. ***A*. In pentane.** Anhydrous $AlCl_3$ (0.40 g, 3.0 mmol) was added to a solution of disilane **10** (7.49 g, 30 mmol) in 50 mL of pentane. The reaction mixture was vigorously stirred for 5 h at 20 °C and filtered. The pentane was distilled off, and the residue fractionated *in vacuo* to give compound **11** (4.85 g, 65 %), b.p. 48—50 °C (0.1 Torr); n_D^{20} 1.4781, d_4^{20} 1.1357; MR_D 62.25, calculated 62.91. ^{1}H NMR ($CDCl_3$), δ : 0.30 (s, 9 H, $SiMe_3$, $^2J_{H,^{29}Si}$ = 6.76 Hz); 0.65 (s, 6 H, $SiMe_2$, $^2J_{H,^{29}Si}$ = 7.70 Hz). ^{13}C NMR ($CDCl_3$), δ : 71.9 (CCl_2), −2.46 ($SiMe_3$), +0.18 ($SiMe_2$). IR, ν/cm^{-1}: 2940, 2880, 1430, 1400 (C—H); 1250, 850 (SiMe); 740, 670, 620 (Si—C), 700 (CCl_2), 500 (Si—Cl) (*cf.* Ref. 18: ^{13}C NMR (CCl_4), δ : 71.3 (CCl_3), −2.1 ($SiMe_3$), +0.7 ($SiMe_2$)).

***B*. In methylene chloride.** A solution of disilane **10** (7.49 g, 30 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a suspension of anhydrous $AlCl_3$ (0.4 g, 3.0 mmol) in 10 mL of CH_2Cl_2. The reaction was carried out at 30—50 °C (evolution of heat) with vigorous stirring. An efficient reflux condenser was required to prevent loss of Me_2SiCl, liberated in the reaction. After completion of the exothermic reaction the reaction mixture was stirred for an additional 1 h. The reaction mixture was separated from $AlCl_3$ by filtration. Two products — Me_2SiCl_2 and $CH_2{=}CHMe_2SiCl$ — were determined in equivalent amounts (GLC). Products containing

CH_2=CH groups were not found. The filtrate was completely distilled off and gave no residue.

References

1. G. V. Motsarev, M. V. Sobolevskii, V. R. Rosenberg, *Karbofunktsional'nye organosilany i organosiloksany* [*Carbofunctional Organosilanes and Organosiloxanes*], Khimiya, Moscow, 1990 (in Russian).
2. R. Anderson, *Synthesis*, 1985, **8**, 717.
3. A. N. Kornev, V. V. Semenov, O. C. Donnikova, and Yu. A. Kurskii, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 150 [*Russ. Chem. Bull.*, 1995, **44**, 145 (Engl. Transl.)].
4. K. A. Petrov, V. A. Chausov, I. V. Pastukhova, and N. V. Pakhitnova, *Zh. Obshch Khim.*, 1978, **48**, 1377 [*J. Appl. Chem. USSR*, 1978, **48** (Engl. Transl.)].
5. T. J. Hairston and D. H. O'Brien, *J. Organomet. Chem.*, 1971, **29**, 79.
6. K. Tamao and M. Kumada, *J. Organomet. Chem.*, 1971, **30**, 339.
7. M. Kumada and M. Jshikava, *J. Organomet. Chem.*, 1964, **1**, 411.
8. M. Kumada, J.-I. Nakajima, M. Ishikava, and Y. Yamamoto, *J. Org. Chem.*, 1958, **23**, 292.
9. L. H. Sommer, D. L. Bailey, J. R. Gould, and F. C. Whitmore, *J. Am. Chem. Soc.*, 1954, **76**, 801.
10. *Metody elementoorganicheskoi khimii: khlor. Alifaticheskiye soedineniya* [*Methods of Organoelement Compounds: Chlorine, Aliphatic Compounds*], Ed. by A. N. Nesmeyanov and K. A. Kocheshkov, Nauka, Moscow, 1973 (in Russian).
11. R. A. Benkeser and W. E. Smith, *J. Am. Chem. Soc.*, 1968, **90**, 5307.
12. V. S. Romanova, Z. N. Parnes, and M. E. Vol'pin, *VII Vsesoyuzn. konf. po khimii, tekhnologii proizvodstva i prakticheskomu primeneniyu kremneorganicheskikh soedinenii* [*VII All-Union Conf. on Chemistry, Production Technology and Applications of Organosilicon Compounds*], Tbilisi, 1990, part 1, 104 (in Russian).
13. V. I. Zhun, O. L. Ustinova, V. D. Sheludyakov, G. N. Turkel'taub, T. F. Slyusarenko, S. N. Tandura, and S. I. Androsenko, *Zh. Obshch. Khim.*, 1990, **60**, 1111 [*J. Appl. Chem. USSR*, 1990, **60** (Engl. Transl.)].
14. R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organomet. Chem.*, 1965, **3**, 455.
15. C. Eaborn, A. R. Hancock, and W. A. Stanczyk, *J. Organomet. Chem.*, 1981, **218**, 147.
16. *Organometallic Compounds of Silicon*, Ed. by D. R. M. Walton, London, New York, 1985, 48.
17. D. R. Dimel, C. A. Wilke, and F. Ramon, *J. Org. Chem.*, 1972, **37**, 2662.
18. G. Fritz, and W. Himmes, *Z. Anorg. Allg. Chem.*, 1979, **448**, 55.

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