Chemistry

V. A. PONOMARENKO, G. V. ODABASHYAN

1960

SovietRxiv

Abstract

Full Text

Chemistry

V. A. PONOMARENKO, G. V. ODABASHYAN
and Corresponding Member of the Academy of Sciences of the USSR **A. D. PETROV**

SYNTHESIS OF ORGANOSILICON MONOMERS FROM METHYLCHLOROSILANE

Investigations in recent years in the field of organosilicon compounds containing Si—H bonds have made it possible to outline new routes (addition reactions, telomerization, thermal condensation, etc.) for obtaining a number of the most important organosilicon monomers: $C_6H_5SiCl_3$, $CH_3Si(C_6H_5)(Cl_2)$, $CH_3Si(Cl)_2CH=CH_2$, $(C_2H_5)_2SiCl_2$, $(C_6H_5)_2SiCl_2$, $(C_6H_5)SiHCl_2$, $CH_3Si(CH_2CH_2CF_3)Cl_2$, and many others ([1]). For their preparation, mainly only halosilicon hydrides containing one Si—H bond were used: Cl_3SiH, CH_3SiCl_2H, $C_2H_5SiHCl_2$, $C_6H_5SiHCl_2$, and certain others. The use of dichlorosilane Cl_2SiH_2, containing two reactive Si—H bonds together with two chlorine atoms, opened up new and very promising possibilities for the synthesis of a wide variety of organosilicon monomers ([2]).

Developing the studies we had begun on the synthesis of monomers based on silicon hydrides, in the present work we used methylchlorosilane CH_3SiH_2Cl, which is readily obtained in good yield by disproportionation of CH_3SiHCl_2 in the presence of cyanamide catalysts ([3]). Carrying out reactions at one or both Si—H bonds of methylchlorosilane made it possible to hope to realize a nonmetalorganic scheme for the synthesis of a number of organosilicon monomers:

$$CH_3SiH_2Cl + RCl \xrightarrow[-HCl]{} (CH_3)(R)SiHCl \xrightarrow{CH\equiv CH} Cl{-}Si(CH_3)(R)CH_2CH_2Si(CH_3)(R){-}Cl \qquad (1)$$

$$CH_3SiH_2Cl + CH_2{=}CHX \nearrow XCH_2CH_2SiHCl(CH_3) \xrightarrow{CH\equiv CH} Cl{-}Si(CH_3)(CH_2CH_2X)CH_2CH_2Si(CH_3)(CH_2C$$

$$\searrow ClSi(CH_3)(CH_2CH_2X)_2 \qquad (2)$$

where $R{-}C_6H_5$, $CH_2=CH{-}$, $X{-}H$, CH_3, CF_3, etc.

To carry out scheme (1), the reaction of thermal condensation of methylchlorosilane with chlorobenzene and vinyl chloride at temperatures of 550-650° and atmospheric pressure was chosen; this reaction had previously been studied by us with dichlorosilane (²). In comparison with dichlorosilane, methylchlorosilane enters into the thermal-condensation reaction with C_6H_5Cl and $CH_2 = CHCl$ with greater difficulty; the yield of products from reaction at the first Si–H bond in this case, under identical conditions, is considerably lower. In this respect the same picture is observed as in the reactions of Cl_3SiH and CH_3SiHCl_2 with chlorobenzene (⁴).

In addition, whereas in the thermal condensation of dichlorosilane with chlorobenzene up to 10% of the product of interaction through two Si–H bonds was isolated, in the case of methylchlorosilane we were unable to isolate methyldiphenylchlorosilane.

Table 1

Addition of silicon hydrides CH_3SiH_2Cl, $(CH_3)(C_2H_5)SiHCl$, and $CH_3(C_6H_5)SiClH$ to unsaturated compounds in the presence of 0.1 M chloroplatinic acid solution in isopropyl alcohol

Starting reagents	Amount, g (mol.)	Amount of catalyst, ml	Reaction temperature, °C	Max. pressure, atm	Duration of reaction, h	Weight of reaction products, g	Reaction products	Yield, g	Yield, % of theory
CH_3SiClH_2 $CH_2=CH_2$	20.2 (0.25) 5.6 (0.20)	0.3	20	20	0.5	21.5	$CH_3(C_2H_5)SiClH$	9.1	42.0
CH_3SiClH_2 $CH_2=CH_2$	16.5 (0.21) 11.8 (0.42)	0.2	20	20	1.0	24.0	$CH_3(C_2H_5)_2SiCl$	5.0 19.5	18.0 69.0
CH_3SiClH_2 $CH_2=CHCH_3$	10.0 (0.12) 5.5 (0.12)	0.2	40	8	2.0	11.0	$CH_3(C_3H_7)SiClH$	8.0	53.0
CH_3SiClH_2 $CH_2=CHCF_3$	16.1 (0.2) 18.2 (0.19)	0.4	150	22.1	3.5	26.2	$CH_3(CF_3CH_2CH_2)SiClH$ $CH_3(CF_3CH_2CH_2)_2SiCl$	5.0 15.0	7.0 27.0
CH_3SiClH_2 $CH_2=CHCF_3$	8.1 (0.1) 20.0 (0.21)	0.5	138	22.6	5.0	26.4	$CH_3(C_2H_5)(Cl)SiCH_2CH_2CF_3$	27.5	67.0
$CH_3(C_2H_5)SiClH$ $CH_2=CHCF_3$	21.6 (0.2) 20.0 (0.2)	0.4	167	12.5	2.5	40.0	Cl	Cl| 6.5 |$CH_3(C_2H_5)SiCH_2CH_2Si(C_2H_5)CH_3$|	56.0
$CH_3(C_2H_5)SiClH$ CH CH	10.3 (0.1)	0.5	20	10	2.0	10.0	$CH_3(C_6H_5)SiClCH_2CH_2Si(C_6H_5)CH_3$	9.4	61.0

$CH_3(C_6H_5)SiClH$	14.1 (0.09)	0.5	CH CH	20	15	0.1	15.0	$CH_3(C_6H_5)SiCH_2CH_2Si(C_6H_5)CH_3$	9.4	61.0

Unlike scheme (1), scheme (2), as is evident from the data in Table 1, is carried out considerably more easily. Methylchlorosilane reacts almost as readily with ethylene and propylene as dichlorosilane does. This applies equally to reaction through one and through two Si–H bonds of methylchlorosilane. The $(CH_3)(C_2H_5)SiHCl$ formed in fairly good yield in the reaction with acetylene is readily converted, in the presence of H_2PtCl_6, into $CH_3(C_2H_5)(Cl)SiCH_2CH_2Si(Cl)(C_2H_5)CH_3$. $(CH_3)(C_2H_5)SiHCl$ also reacts with $CH_2{=}CHCF_3$ under the same conditions, giving a fluorine-containing compound of the $RR'R''SiCl$ type.

Methylchlorosilane adds to trifluoropropylene with more difficulty than to propylene. In this respect CH_3SiH_2Cl behaves similarly to Cl_2SiH_2.

As a result of the work carried out, it was possible to outline a completely nonmetal-organic scheme for the synthesis of such alkyl-(aryl)-silane- and disilane chlorides as $(CH_3)(R)SiHCl$, $(CH_3)(R)_2SiCl$, $(CH_3)(R')(R'')SiCl$, $(CH_3)(Cl)(R)SiCH_2CH_2Si(R)(Cl)(CH_3)$, where R, R′, and R″ are the groups $CH_2{=}CH{-}$, $C_6H_5{-}$, $C_2H_5{-}$, $C_3H_7{-}$, $CF_3CH_2CH_2{-}$, and others.

Experimental Part

1. Preparation of methylchlorosilane. CH_3SiClH_2 is obtained by disproportionation of CH_3SiCl_2H* in the presence of dimethylcyanamide ([3]). Into a flask of a rectification column packed with nichrome packing (35–50 theoretical plates), 200 g of CH_3SiCl_2H and 14 g of previously activated dimethylcyanamide were placed. Methylchlorosilane was taken off continuously and condensed in a trap cooled with solid CO_2 and acetone. The reaction time was 5-6 h. The starting CH_3SiCl_2H and CH_3SiCl_3 were distilled from the same flask. To the residue containing the catalyst and a little CH_3SiCl_3, a fresh portion of CH_3SiCl_2H was added, and the reaction was repeated in exactly the same way

* For the rearrangement it is necessary to take methyldichlorosilane carefully purified from Cl_3SiH.

as described above. The yield of methylchlorosilane was 50-60% of theory. In all, from 700 g of CH_3SiHCl_2, 290 g of pure CH_3SiH_2Cl was obtained. The catalyst does not lose its activity upon repeated repetition of the experiment.

2. **Addition of CH_3SiClH_2 and $CH_3(C_2H_5)SiClH$ to unsaturated compounds.** The conditions and results of all experiments on the catalytic addition of methylchlorosilane and methylethylchlorosilane to unsaturated compounds in the presence of chloroplatinic acid are given in Table 1, and some physical constants of the substances obtained in Table 2.

3. **Preparation of methylphenylchlorosilane $CH_3(C_6H_5)SiClH$.** A mixture of 24.2 g (0.3 mole) of methylchlorosilane and 39.5 g (0.35 mole) of chlorobenzene was passed, over 2 h 40 min, through a glass tube with an internal diameter of 23 mm and a reaction-zone length of 600 mm, heated to 635–645°.

Table 2

Physical properties of the compounds obtained

Compounds	B.p., °C/mm	d_4^{20}	n_D^{20}	MR found	MR calcd.
CH_3SiClH_2	8–9°/745	–	–	–	–
$CH_3(CH_2{=}CH)SiClH$	60.5°/761	0.9125	1.4140	29.21	29.70
$CH_3(C_2H_5)SiClH$	176°/740	1.0540	1.5171	44.99	45.22
$CH_3(C_6H_5)SiCl_2$	197°/740	1.1814	1.5194	49.13	49.16
$CH_3(CF_3CH_2CH_2)SiClH$ *	96.5°/746	1.1565	1.3651	34.14	34.89
$CH_3(CF_3CH_2CH_2)_2SiCl$ *	45.5–47°/6	1.2791	1.3699	48.21	48.61
$CH_3(C_2H_5)(CF_3CH_2CH_2)SiCl$ *	140°/758	1.1044	1.3871	43.65	43.77
$CH_3(C_2H_5)(Cl)SiCH_2CH_2Si(Cl)(C_2H_5)CH_3$	100.5–101.5°/10	0.9981	1.4580	66.53	66.71
$CH_3(C_6H_5)(Cl)SiCH_2CH_2Si(Cl)(C_6H_5)CH_3$ **	207–209°/9	–	–	–	–

* These substances were obtained for the first time.
** M.p. 59–60°.

From the resulting condensate the following were isolated by rectification: 7 g of CH_3SiClH_2, b.p. 8–10°; 8 g of CH_3SiCl_2H, b.p. 39–42°; 9.4 g of C_6H_6, b.p. 78–79.5°; 15 g of C_6H_5Cl, b.p. 128–129.5°; 7.4 g (15.5%) of $CH_3(C_6H_5)SiClH$, b.p. 176° (740 mm); d_4^{20} 1.0540; n_D^{20} 1.5171; MR found 44.99, calculated 45.22; 7.1 g (yield 12.5%) of $CH_3(C_6H_5)SiCl_2$, b.p. 197° (740 mm); d_4^{20} 1.1814; n_D^{20} 1.5194; MR found 49.13 (calculated 49.16); 4.1 g—residue boiling above 197°.

4. **Preparation of methylvinylchlorosilane $CH_3(CH_2{=}CH)SiClH$.** A mixture of 23.2 g (0.3 mole) of methylchlorosilane and 41.5 g (0.66 mole) of vinyl chloride was passed, over 3 h, through a glass tube with an internal diameter of 23 mm and a reaction-zone length of 600 mm, heated to 550–560°. From the resulting condensate, 3.7 g (11.5%) of $CH_3(CH_2{=}CH)SiClH$ was isolated, b.p. 60.5° (761 mm); d_4^{20} 0.9125; n_D^{20} 1.4140; MR found 29.21 (calculated 29.70).

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
11 IX 1959

REFERENCES

1. Proceedings of the Second All-Union Conference on the Chemistry and Practical Application of Organosilicon Compounds, vol. 1, Leningrad, 1958.

2. A. D. Petrov, V. A. Ponomarenko, G. V. Odabashyan, *DAN*, **126**, No. 5, 1009 (1959).

3. D. L. Bailey, G. H. Wagner, US patent 2732280 (1956); *RZhKhim.*, 67177 (1957).

4. A. D. Petrov, V. F. Mironov et al., *Izv. AN SSSR, OKhN*, 1958, No. 8, 954.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.