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THERMAL TELOMERISATION OF SILANES WITH OLEFINS*

A. N. Nesmeyanov, R. Kh. Freidlina, and E. C. Chukovskaya
Academy of Sciences of the U.S.S.R., Moscow

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Abstract—(1) Thermal telomerisation reaction of methyldichlorosilane with ethylene at 260–275° and pressure of 560 atm. has been effected. The resulting mixture gave on fractionation pure compounds $CH_3SiCl_2(CH_2CH_2)_nH$, with $n = 1$–6.

(2) Thermal telomerisation reaction of trichlorosilane with ethylene has been effected at 270–285° and 200 atm. pressure. The resulting mixture gave on fractionation pure compounds $Cl_3Si(CH_2CH_2)_nH$ with $n = 1$–5.

(3) Preliminary data obtained show methyldichlorosilane and propylene also to undergo the telomerisation reaction at 260–275° and pressures of 100–120 atm.

Silicon hydrides $HSiCl_3$, $HSiBr_3$, $HSiCl_2R$, $HSiClR_2$, $RSiH_3$ are known to add to double or triple bonds of unsaturated compounds[1–11] under the action of acyl and alkyl peroxides, ultra-violet light as well as on platinum.

Reactions initiated by peroxides or irradiation appear to be of a radical character. The reaction of trichlorosilane with olefins in the presence of acetyl peroxide is suggested to proceed according to the following mechanism:[1]

$$(CH_3COO)_2 \rightarrow 2CH_3COO\cdot \rightarrow \dot{C}H_3 + CO_2$$

$$\dot{C}H_3 + HSiCl_3 \rightarrow CH_4 + Si\dot{C}l_3$$

$$RCH{=}CH_2 + Si\dot{C}l_3 \rightarrow R\dot{C}HCH_2SiCl_3$$

$$R\dot{C}HCH_2SiCl_3 + HSiCl_3 \rightarrow RCH_2CH_2SiCl_3 + Si\dot{C}l_3$$

The photochemical telomerisation reaction of trichlorosilane with perfluoroethylene giving a mixture of products of the composition $SiCl_3(CF_2{\cdot}CF_2)_nH$ where n varies from 1 to 3 has recently been reported, and when carried out thermally the reaction gave perfluorocyclobutane together with small quantities of organosilicon compounds.[7]

The addition of trichlorosilane to the double bond of acrylonitrile, 2-vinylpyridine

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* *Translated by* A. L. Pumpiansky.

[1] L. Sommer, E. W. Pietrutza, and F. C. Whitmore *J. Amer. Chem. Soc.* **69**, 188 (1947).

[2] C. Burkhard and R. Kriebe *J. Amer. Chem. Soc.* **69**, 2687 (1947).

[3] A. J. Barry, L. De Pree, J. W. Gylkey, and D. E. Hook *J. Amer. Chem. Soc.* **69**, 2916 (1947).

[4] E. W. Pietrutza, L. Sommer, and F. C. Whitmore *J. Amer. Chem. Soc.* **70**, 484 (1948).

[5] G. Schott and H. Berge *Chem.-Ing.-Tech.* **6**, 503 (1954).

[6] C. N. Gadsby *Research* **3**, 338 (1950).

[7] R. N. Haszeldine and R. J. Markloy *J. Chem. Soc.* 962 (1956).

[8] J. Spier, R. Zimmerman, and J. Webster *J. Amer. Chem. Soc.* **78**, 2278 (1956).

[9] V. A. Ponomarenko, B. A. Sokolov, X. M. Mironov, and A. D. Petrov *Dokl. Akad. Nauk SSSR* **106**, 76 (1956).

[10] N. S. Nametkin, A. V. Topchiev, and T. I. Chernycheva *Dokl. Akad. Nauk SSSR* **111**, 1260 (1956).

[11] L. L. Stchukovskaya, A. D. Petrov, and Yu. P. Egorov *Zh. Obshch. Khim.* XXVI, 3338 (1956).

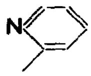
and allyl cyanide in the presence of organic bases has been reported and the following ionic mechanism for these reactions has been suggested.[12,13]

$$Cl_3SiH + B \rightarrow Cl_3Si^- + BH^+$$

$$CH_2{=}CHR + Cl_3Si^- \rightarrow Cl_3SiCH_2\bar{C}HR$$

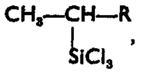
$$Cl_3SiCH_2\bar{C}HR + BH^+ \rightarrow B + Cl_3SiCH_2CH_2R$$

where B is an organic base, R=CN, CH$_2$CN,



Nozakura[13,14] has found tetrapyridinenickel chloride to catalyse the addition of chlorosilane to vinyltrichlorosilane, 1-octene and styrol. The addition product in each case is a mixture of 2 isomers:

SiCl$_3$CH$_2$CH$_2$R and

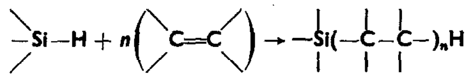


$$\underset{\displaystyle SiCl_3}{CH_3{-}CH}{-}R$$

, where R = SiCl$_3$; C$_6$H$_{13}$; C$_6$H$_5$.

Thermal addition of trichlorosilane and alkylchlorosilane to olefins at 160–400° has also been reported,[3] and the authors believe the reaction proceeds through a transition state, the electron attracting silicon bonding to the methylene group of the olefin RCH=CH$_2$ and the chlorine atom to the adjacent carbon atom, the end product resulting from the exchange of the chlorine atom with the labile hydrogen atom of the silane.

It would be reasonable to expect that the reaction between silanes and olefins can be effected by telomerisation yielding a mixture of compounds, according to the following scheme:



$$\rangle Si{-}H + n\left(\rangle C{=}C\langle\right) \rightarrow {-}Si({-}C{-}C{-})_nH$$

Carrying out this reaction under pressure with an excess of olefins appeared to favour this course of the reaction. The reactions of methyldichlorosilane, ethyldichlorosilane, triethylsilane with ethylene and propylene respectively in the presence of benzoyl peroxide or tertiary butyl peroxide at 100–140° and 100–300 atm, carried out in a stainless steel autoclave, failed, however, to give a positive result. We succeeded in carrying out telomerisation when methyldichlorosilane and trichlorosilane reacted with ethylene and methyldichlorosilane with propylene at 260–285° under pressure, compounds $CH_3SiCl_2(CH_2CH_2)_nH$, $Cl_3Si(CH_2CH_2)_nH$ and $CH_3SiCl_2(C_3H_6)_nH$ respectively having been obtained.[20]

Since dialkyldichlorosilanes and alkyltrichlorosilanes are not capable of reacting with olefins,[3] the formation of a mixture of compounds excludes the thermal reaction mechanism mentioned above. It is thus evident that the thermal reaction investigated

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[12] S. Nozakura and S. Konotsune *Bull. Chem. Soc. Japan* **29**, 322, 326 (1956).

[13] S. Nozakura *Bull. Chem. Soc. Japan* **29**, 785 (1956).

[14] S. Nozakura *Bull. Chem. Soc. Japan* **29**, 660 (1956).

[15] O. K. Johanson *Chem. Abstr.* **42**, 922 (1948).

[16] J. A. Vogel, W. T. Cresswell, and J. Leicester *J. Phys. Chem.* **58**, 174 (1956).

[17] R. N. Meals *J. Amer. Chem. Soc.* **68**, 1880 (1946).

[18] R. N. Lewis *J. Amer. Chem. Soc.* **69**, 717 (1947).

[19] F. C. Whitmore and L. H. Sommer *J. Amer. Chem. Soc.* **68**, 475 (1946).

[20] A. N. Nesmeyanov, R. Kh. Freidlina, and E. C. Chukovskaya *Dokl. Acad. Nauk SSSR* **112**, 271 (1957); **113**, 120 (1957).

TABLE 1

$(CH_3SiCl_2/CH_2CH_2/_nH)$

n	Yields (Per cent of the sum of all products).	n_D^{20}	d_4^{20}	MR Found	MR Calc.*	B.p.(°C)	B.p.(°C) lit.	Ref.	C		H		Si		Cl	
									Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1	23·6	—				100	100	15								
2	25·6	1·4312	1·0427	43·48	43·26	147–148	147·5–148	2	35·08	35·20 35·37	7·01	7·00 7·08	16·40	16·60 16·64	41·52	41·44 40·52
3	17·7	1·4390	0·9931	52·75	52·59	91 (32 mm)	192	2	42·21	42·64 42·71	8·10	8·24 8·33				
4	13·4	1·4440	0·9761	61·83	61·88	94 (6 mm)	100–110 (20 mm)	2	47·57	47·73 47·76	8·81	9·01 9·00				
5	4·7	1·4490	0·9600	71·32	71·18	111–114 (3 mm)	—	—	51·76	51·67 51·79	9·41	9·36 9·45	11·00	11·00 10·99	27·83	27·64 27·25
6	3·8	1·4532	0·9552	80·20	80·47	124–127 (3 mm)	—	—	55·12	55·28 55·32	9·83	9·90 9·93	9·91	9·80 9·57	25·08	25·22 24·70
$n > 6$	8·5															

* Calculated refraction value has been obtained based on bond refraction data due to Vogel *et al.*[16]

by us is of a chain character. The telomerisation reaction studied in the present investigation as well as addition reactions reported in the literature are the result of a cleavage of the Si—H bond, as evidenced by the absence of this bond in the compounds obtained (the test for the Si—H bond with potassium hydroxide in water being negative). The structures of the resulting methylalkyldichlorosilanes and alkyltrichlorosilanes are also substantiated by the determination of the molecular refraction of these compounds and the formation of corresponding trimethyl derivatives by the Grignard reaction.

The preliminary data concerning the reaction between methyldichlorosilane and propylene showed that the reaction is complicated; the fractional distillation of the mixture from the reaction gave fractions boiling over a range of 10–20° from which methyl alkyldichlorosilanes, n=1–3, were isolated, the structures of which were not investigated.

The yields, both of methylalkyldichlorosilanes and of alkyltrichlorosilanes of different molecular weight exhibit a regularity characteristic of the telomerisation reaction, namely, compounds with $n = 2$ were obtained in a maximum yield, that of other compounds decreasing with increasing n, amounting for $n = 5$ to 4–4, 5 per cent of the reaction products.

The reaction of methyldichlorosilane with ethylene was carried out in a 500 cm^3 stainless autoclave. After CH_3SiCl_2H(123 g) had been fed into the autoclave and air driven out by nitrogen, ethylene was introduced. The reaction mixture was heated up to 260°, pressure rising to 560 atm. The reaction was maintained at 260–270° for 2 hr, pressure dropping to 50 atm. After three runs the reaction products were collected and subjected to fractional distillation, the overall feed amounting to 381 g of methyldichlorosilane yielding 499 g of reaction products. Distillation gave 51 g of recovered methyldichlorosilane. The reaction products were fractionated in a Vigreux column to give pure methylalkyldichlorosilanes $CH_3SiCl_2(CH_2CH_2)_nH$, with $n = 1$–6, their properties and yields being summarised in Table 1.

The reaction of trichlorosilane with ethylene was carried out at 270–285° for 2 hr with the maximum pressure of 200 atm. Four runs yielded 353 g of reaction product, the overall feed of trichlorosilane being 261 g. The reaction product was

Table 2

($SiCl_3(CH_2CH_2)_nH$)

n	Yield (grams)	Yield (per cent to the sum of all products)	n^{20}_D	d^{20}_4	MR Found	MR Calc.	B.p. (°C)	B.p.(°C) lit	Ref.	Si Found	Si Calc.
1	69	20·1					98	97–100	(17)		
2	87	25·3	1·4352	1·1577	43·19	42·82	146–147	147–151	(18)	14·72 14·45	14·65
3	54	15·4	1·4440	1·1094	52·51	52·12	87–89/30	127/38	(19)	12·83 12·59	12·78
4	45	13·1	1·4490	1·0744	61·76	61·41	96·5/10	119/28 231–232/731	(19)	11·26 11·67	11·33
5*	14	4·0	1·4547	1·0501	71·17	70·71	76/2	183/84	(19)	10·55 10·58	10·17
$n > 5$	42	12·2									

* For $SiCl_3C_{10}H_{21}$	Calculated	C—43·56 per cent	H—7·67 per cent	Cl—38.62 per cent
	Found	C—43·68 per cent	H—7·79 per cent	Cl—38·21 per cent
		43·71 per cent	7·71 per cent	38·03 per cent

TABLE 3

n	Formula*	B.p.°/mm	n_D^{20}	d_4^{20}	MR Calc.	MR Found	C		H		Si	
							Calc.	Found	Calc.	Found	Calc.	Found
1	$C_4H_9Si/CH_3/_3$	114°	1·4030	0·7203	44·14	44·12	64·66	64·44 64·47	13·85	13·83 13·87	21·57	21·29 21·46
2	$C_6H_{13}Si/CH_3/_3$	163°	1·4160	0·7412	53·35	53·58	68·30	68·48 68·28	14·01	14·02 14·02	17·73	17·56 17·61
3	$C_8H_{17}Si/CH_3/_3$	75°/10 mm	1·4242	0·7646	62·58	62·21	70·89	71·03 71·14	14·07	14·03 14·18	15·05	14·59 14·53

* For literature values see reference.[19]

distilled on a column (15 theoretical plates), 10 g of the starting trichlorosilane being isolated. The mixture on fractionation produced pure alkyltrichlorosilanes $SiCl_3(CH_2CH_2)_nH$, with $n = 1$–5, their properties and yields being listed in Table 2. The properties of trimethyl derivatives produced from our alkyltrichlorosilanes by Grignard reaction are given in Table 3.

TABLE 4

($CH_3SiCl_2(C_3H_6)_nH$)

n*	n_D^{20}	B.p. (°C)	Si	
			Found	Calc.
1	1·4240	123–124*†		
2	1·4400	82 (32 mm)	14·01 14·07	14·10
3	1·4540	80–82 (2mm)	11·77 11·82	11·64

* Products with $n > 3$, amounting to 10 per cent of the sum of all products, have also been obtained.

*† Literature 3: b.p. 123–124°.

The reaction of methyldichlorosilane with propylene was carried out at 260–275° for 3 hr (maximum pressure being 100 atm). Two runs yielded 216 g of reaction products with 151 g overall feed of methyldichlorosilane. Distillation of the mixture yielded 21 g of recovered methyldichlorosilane and resulted in methylalkyldichlorosilanes $CH_3SiCl_2(C_3H_6)_nH$ with $n = 1$–3; the properties of methylalkyldichlorosilanes produced from propylene are given in Table 4.