Corresponding Member of the Academy of Sciences of the USSR R. Kh. Freidlina, Tsao I, and E. Ts. Chukovskaya

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR R. Kh. Freidlina, Tsao I, and E. Ts. Chukovskaya

INTERACTION OF HYDRIDOSILANES WITH ACRYLONITRILE IN THE PRESENCE OF IRON PENTACARBONYL AND NICKEL CHLORIDE

As was shown earlier (^{1}), hydridosilanes react with unsaturated compounds in the presence of iron pentacarbonyl with the formation of saturated and unsaturated compounds according to schemes (A) and (B):

$$\mathrm{R'R''R'''SiH + CH_2 = CHR \rightarrow R'R''R'''SiCH_2CH_2R}; \tag{A}$$

$$\mathrm{R'R''R'''SiH + CH_2 = CHR \rightarrow R'R''R'''SiCH = CHR}, \tag{B}$$

where R′R″R‴ are, respectively, alkyl, chlorine, ethoxy groups; R = alkyl, OC_2H_5. The predominance of one or the other of these reactions depends on the nature of the silane and olefin, as well as on the reaction conditions.

In the present work we investigated the reaction between hydridosilanes and acrylonitrile in the presence of iron pentacarbonyl. Since 1956 a considerable number of works have been devoted to the reaction of hydridosilanes with acrylonitrile ($^{2-11}$). Organic bases, acid amides, platinum on carbon, chloroplatinic acid, and Raney nickel have been used as reaction catalysts. Peroxides cannot be used in this reaction, since they cause polymerization of acrylonitrile (^{3}).

Organic bases and acid amides catalyze only the reaction of trichlorosilane with acrylonitrile and are inactive in the reaction of methyldichlorosilane with acrylonitrile ($^{5-7}$). In the presence of platinum catalysts and Raney nickel, methyldichlorosilane reacts with acrylonitrile; however, a mixture of α- and β-methyldichlorosilylpropionitriles is formed.

Nozakura and Konotsune (^{2}) showed that, under the influence of various catalysts, cyanoethylation of trichlorosilane proceeds in different directions. Thus, in glass tubes in the presence of catalytic amounts of pyridine, β-trichlorosilylpropionitrile is formed. Under the same conditions in an autoclave, α-trichlorosilylpropionitrile is formed. This is connected with the formation in the autoclave of tetrapyridinenickel chloride (owing to reaction of trichlorosilane with the metal wall of the autoclave). Thus, if the cyanoethylation of trichlorosilane can be directed both toward the formation of β-trichlorosilylpropionitrile and toward the α-isomer, then in the case of methyldichlorosilane, under all conditions studied up to the present, mixtures of the α- and β-isomers are formed.

We have studied the interaction of methyldichlorosilane and triethylsilane with acrylonitrile. The reaction was carried out in a stainless-steel autoclave or in sealed glass ampoules at 120–150° in the absence of additives or in the presence of iron pentacarbonyl, nickel chloride, or a mixture of both additives; the results obtained are summarized in Table 1. As is seen from Table 1, in the absence of additives the reaction does not proceed (experiment 6); upon addition of nickel chloride alone the reaction likewise does not take place (experiments 7 and 10). Triethylsilane does not react with acrylonitrile in the presence of iron pentacarbonyl in an autoclave (experiment 13). Methyldichlorosilane does not react with acrylonitrile in the presence of iron pentacarbonyl in a sealed glass ...

Table 1

Experiment no.	Silane	Molar ratio: silane : acrylonitrile	Reaction vessel	Additives	Temp., °C	Yield from theory, %
1	CH_3SiCl_2H	2 : 1	Autoclave of stainless steel *	$Fe(CO)_5$ (1 ml)	140–150	0
2	Same	1 : 1	Same	$Fe(CO)_5$ (1 ml)	140–150	12
3	Same	1 : 2	Same	$Fe(CO)_5$ (1 ml)	140–150	39
4	Same	1 : 3	Same	$Fe(CO)_5$ (1 ml)	140–150	46
5	Same	1 : 5	Same	$Fe(CO)_5$ (1 ml)	140–150	42
6	Same	1 : 3	Same	No additives	140–150	0
7	Same	1 : 3	Same	$NiCl_2$ (0.15 g)	140–150	0
8	Same	1 : 3	Same	$Fe(CO)_5$ (1 ml)$NiCl_2$ (0.15 g)+	120–130	60

Experiment no.	Silane	Molar ratio: silane : acrylonitrile	Reaction vessel	Additives	Temp., °C	Yield from theory, %
9	Same	1 : 3	Sealed glass ampoule **	+Fe(CO)$_5$ (0.2 g)	140–150	0
10	Same	1 : 3	Same	NiCl$_2$ (0.1 g)	140–150	0
11	Same	1 : 3	Same	Fe(CO)$_5$ (0.2 ml)NiCl$_2$ (0.1 g)	120–130	56
12	$(C_2H_5)_3SiH$	1 : 3	Autoclave of stainless steel *	Fe(CO)$_5$ (1 ml)++NiCl$_2$ (0.15 g)	120–130	73
13	Same	1 : 3	Same	Fe(CO)$_5$ (1 ml)	140–150	30
14	CH_3SiCl_2H ***	2 : 1	Same	Fe(CO)$_5$ (1 ml)	140–150	4

* The experiments were carried out in a half-liter rotating autoclave with charges of silane and acrylonitrile of 200–300 g, calculated for the mixture of reagents. Air was displaced from the autoclave with nitrogen, after which nitrogen was introduced into the autoclave to a pressure of 30 atm. The duration of heating in all experiments was 5 h.
** The experiments were carried out with charges of 17.2 g of silane and 24.3 g of acrylonitrile. The duration of heating was 5 h.
*** The reaction was conducted in the presence of 150 ml of acetonitrile.

ampoule (experiment 9), but under the same conditions, when the experiments are carried out in an autoclave, formation of the adduct takes place, the yield of which increases with increasing excess of acrylonitrile (experiments 1–5). These data made it possible to assume that the reaction is effected under conditions in which, in addition to iron carbonyl, traces of salts of heavy metals are present in the mixture, formed on the walls of the autoclave under the action of chlorosilanes.

Indeed, in the simultaneous presence of small amounts of iron pentacarbonyl and nickel chloride, acrylonitrile adds both methyldichlorosilane and triethylsilane. The reactions proceed equally well both in the autoclave (experiments 8, 12) and in sealed ampoules (experiment 11). The addition leads to α-methyldichlorosilylpropionitrile ($CH_3SiCl_2CH(CH_3)CN$) in the case of methyldichlorosilane and to α-triethylsilylpropionitrile ($(C_2H_5)_3SiCH(CH_3)CN$) in the case of triethylsilane. Apparently, the action of the mixed catalyst found by us directs the reaction by an ionic mechanism. The following arguments can be given in favor of this view: a) the reaction proceeds only in the presence of an excess of acrylonitrile (experiments 4-5) or in the medium of another polar solvent, for example acetonitrile (experiment 14); b) the participation of nickel chloride is necessary; c) the formation of α-isomers is usually associated with the ionic course of the cyanoethylation reaction of hydrosilanes (^{9}).

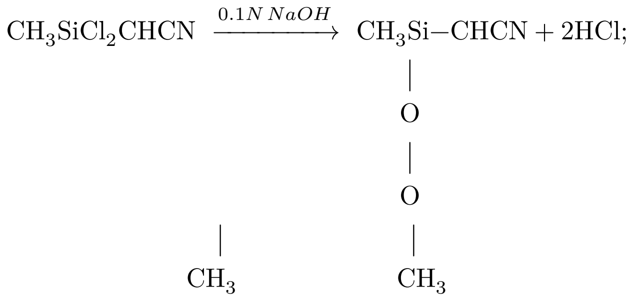
Experimental section

We give a description of experiments 8 and 12 and the evidence for the structure of the adducts obtained.

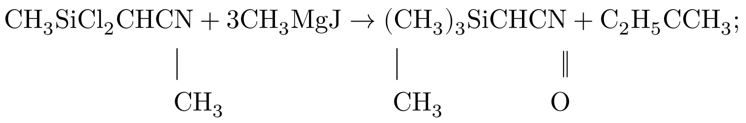
Reaction of methyldichlorosilane with acrylonitrile in the presence of $Fe(CO)_5$ and $NiCl_2$ (experiment 8). Into a half-liter rotating stainless-steel autoclave were placed 115 g (1 mol)

CH_3SiCl_2H, 160 g (3 mol) $CH_2{=}CH{-}CN$, 1 ml $Fe(CO)_5$, and 0.15 g $NiCl_2$. The air was displaced from the autoclave with nitrogen, after which nitrogen was introduced to a pressure of 30 atm. After 5 h of heating at 120—130°, the reaction mixture was fractionated in vacuo. This gave 102 g (60% of theory) of α-methyldichlorosilylpropionitrile (I), b.p. 59—60° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.1635. Found MR 38.74; for $C_4H_7SiCl_2N$ calculated 38.62. Found, %: Si 17.21, 16.88. Calculated, %: Si 16.71. By titration with 0.1 N NaOH found, %: Cl 42.49; 42.41. For $C_4H_7SiCl_2N$ calculated, %: Cl 43.17.

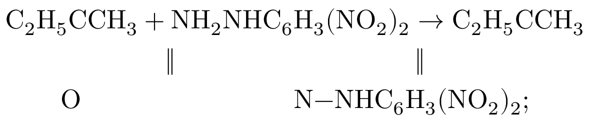
Proof of the structure of the adduct was carried out according to the known scheme (^{2,4})



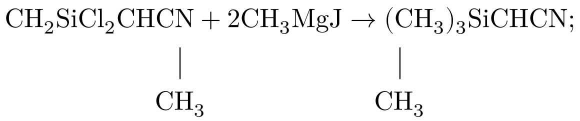
$$CH_3SiCl_2\underset{\underset{CH_3}{|}}{CH}CN \xrightarrow{0.1N\,NaOH} CH_3\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{O}}{|}}{O}}{\underset{|}{Si}}-CHCN + 2HCl; \qquad (1)$$



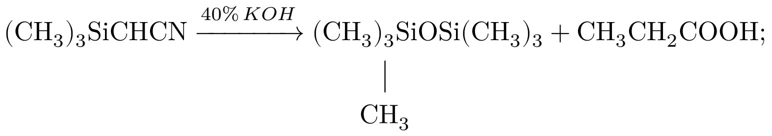
$$CH_3SiCl_2\underset{\underset{CH_3}{|}}{CH}CN + 3CH_3MgJ \rightarrow (CH_3)_3Si\underset{\underset{CH_3}{|}}{CH}CN + C_2H_5\underset{\underset{O}{\|}}{C}CH_3; \qquad (2)$$



$$C_2H_5\underset{\underset{O}{\|}}{C}CH_3 + NH_2NHC_6H_3(NO_2)_2 \rightarrow C_2H_5\underset{\underset{N-NHC_6H_3(NO_2)_2}{\|}}{C}CH_3; \qquad (2')$$

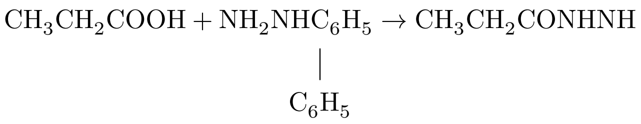


$$\underset{\underset{CH_3}{|}}{CH_2SiCl_2CH}CN + 2CH_3MgJ \rightarrow (CH_3)_3Si\underset{\underset{CH_3}{|}}{CH}CN; \qquad (3)$$



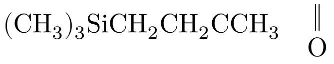
$$(CH_3)_3SiCHCN \xrightarrow{40\%\,KOH} (CH_3)_3SiOSi(CH_3)_3 + CH_3CH_2COOH; \qquad (4)$$

(II)



$$CH_3CH_2COOH + NH_2NHC_6H_5 \rightarrow CH_3CH_2CONH\underset{\underset{C_6H_5}{|}}{N}H \qquad (4')$$

Since, in carrying out reaction (2), no



$$(CH_3)_3SiCH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$$

was detected, and in carrying out reaction (4) no acid of the structure $(CH_3)_3SiCH_2CH_2COOH$ was formed, even an admixture of β-methyldichlorosilylpropionitrile is absent.

In the Raman spectrum of trimethylsilylpropionitrile there is a frequency of 2212 cm^{-1}, and in the infrared spectrum of this substance an absorption band at 2205 $cm^{-1} \pm 10\ cm^{-1}$, characteristic of α-nitriles*.

Preparation of α-trimethylsilylpropionitrile. From 16 g of (I), on methylation with a Grignard reagent prepared from 4.8 g Mg, 8.8 g (70% of theory) of α-trimethylsilylpropionitrile (II) was obtained, b.p. 71.5°/20 mm; n_D^{20} 1.4245; d_4^{20} 0.8303. Found MR 39.14; for $C_6H_{13}SiN$ calculated 39.09. Literature data (^{2}): n_D^{25} 1.4232; d_4^{25} 0.8254.

Found, %: C 56.64; 56.55; H 10.47; 10.37; Si 22.08; 22.39
$C_6H_{13}SiN$. Calculated, %: C 56.63; H 10.30; Si 22.05

* The spectra were recorded and interpreted by L. A. Leites (Institute of Organic Chemistry, Academy of Sciences of the USSR), for which the authors express their sincere gratitude to her.

Upon methylation with an excess of Grignard reagent, in addition to product (II), methyl ethyl ketone was obtained, b.p. 80-82°, n_D^{20} 1.3885. Literature data (^{12}): b.p. 79.6°; n_D^{20} 1.38071 (^{15,9}).

The ketone was identified as the 2,4-dinitrophenylhydrazone, m.p. 115° (from alcohol). Found, %: N 23.26; 22.92. For $C_{10}H_{12}O_4N_4$ calculated, %: N 22.21. Literature data (^{12}): m.p. 117°.

Alkaline hydrolysis of trimethylsilylpropionitrile. Substance (II) was boiled for 7 h with 45% KOH. As a result, the following substances were obtained: $(CH_3)_3Si-O-Si(CH_3)_3$, b.p. 99°, n_D^{20} 1.3740; d_4^{20} 0.7656. Found *MR* 48.42; for $C_6H_{18}Si_2O$ calculated 48.89. Literature data (^{13}): n_D^{20} 1.3792; d_4^{20} 0.7638.

Found, %:	C 44.43; 44.31;	H 11.37; 11.51		
$C_6H_{18}Si_2O$. Calculated, %:	C 44.38;	H 11.17		

2. CH_3CH_2COOH, b.p. 141°, n_D^{20} 1.3871. Literature data (^{12}): b.p. 141°, n_D^{20} 1.3874. The acid was identified as the phenylhydrazide, m.p. 153-155° (from benzene). Found, %: N 16.68; 16.57. $C_9H_{12}N_2O$ calculated, %: N 17.06. Literature data (^{2}): m.p. 155-156°.

Reaction of triethylsilane with acrylonitrile in the presence of $Fe(CO)_5$ **and** $NiCl_2$ (experiment 12). The experiment was carried out as in the case of methyldichlorosilane. From 87 g (0.75 mole) of triethylsilane, 132 g (2.5 moles) of acrylonitrile, 0.5 ml of $Fe(CO)_5$, and 0.2 g of $NiCl_2$, 92 g (73% of theory) of a substance was obtained, b.p. 97-98° at 8 mm. After redistillation n_D^{20} 1.4525; d_4^{20} 0.8634. Found *MR* 52.95; for $C_9H_{19}SiN$ calculated* 52.88.

Found, %:	C 63.77; 63.49;	H 11.38; 11.33;	Si 16.83; 16.85
$C_9H_{19}SiN$. Calculated, %:	C 63.85;	H 11.31;	Si 16.57

Upon alkaline hydrolysis, carried out analogously to that described above, hexaethyldisiloxane and propionic acid were obtained.

In the IR spectrum of this compound there is a band at 2205 ± 10 cm^{-1}, characteristic of α-nitriles.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
20 I 1960

REFERENCES CITED

1. R. Kh. Freidlina, E. Ts. Chukovskaya, Tsao I, DAN, **127**, 352 (1959).
2. S. Nozakura, S. Konotsune, Bull. Chem. Soc., Japan, **29**, 323, 326 (1956).
3. I. L. Speier, R. Zimmerman, J. Webster, J. Am. Chem. Soc., **78**, 2278 (1956).
4. A. D. Petrov, V. M. Vdovin, Izv. AN SSSR, OKhN, 1957, 1490.
5. M. Prober, S. D. Cooper, Fr. Pat. 1116726, RZhKhim., 1958, 47712.
6. J. C. Saam, U.S. Pat. 2,860,153, November 11, 1958; Chem. Abstr., **53**, 9060 (1959).
7. J. C. Saam, J. L. Speier, J. Org. Chem., **24**, 427 (1959).
8. L. Goodman, R. M. Silverstein, A. Benitz, J. Am. Chem. Soc., **79**, 3073 (1957).
9. L. Goodman, R. M. Silverstein, J. N. Shoolery, J. Am. Chem. Soc., **78**, 4493 (1956).
10. A. D. Petrov, V. F. Mironov, V. M. Vdovin, S. I. Sadykh-Zade, Izv. AN SSSR, OKhN, 1956, 257.
11. V. M. Vdovin, Dissertation, Inst. Org. Chem., AN SSSR, 1957.
12. *Handbook of Chemistry and Physics*, 1, 37th ed., pp. 118, 814 (1955–1956).
13. K. A. Andrianov, *Organosilicon Compounds*, Moscow, 1955, p. 414.
14. V. F. Mironov, E. I. Nikishin, Izv. AN SSSR, OKhN, 1958, 1080.

* The calculation was made using group increments proposed by V. F. Mironov and G. I. Nikishin (14).

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

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