

Reaction of Unsaturated Nitriles with Hydrosilanes

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Received June 25, 2009

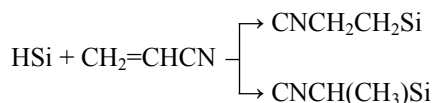
Abstract—Reaction of acrylonitrile and 1,4-dicyanobut-1-ene with hydrosilanes in the presence of various catalysts was studied. In the presence of triallylamine, allyl-bis(triethoxypropyl)amine, diallylamino-propyltriethoxysilane, HMPA, $\text{NiCl}_2 + 2\text{MePh}_2\text{PO}$, $\text{CuCl} + 2\text{MePh}_2\text{PO}$, $[(\text{Me}_2\text{N})_2\text{CCl}]_2\text{CuCl}_4$, and $[(\text{Me}_2\text{N})_2\text{CCl}]_2\text{PtCl}_6$, the addition of trichlorosilane to acrylonitrile proceeded with the yield of 36 to 97%. Triethoxy- and tributoxysilane were added to acrylonitrile in the presence of rhodium dicarbonyl acetylacetonate with the formation of α -isomer in 56–58% yield. Attempted addition of hydrosilanes to 1,4-dicyanobutene failed.

DOI: 10.1134/S1070363210050105

Owing to practical value of silicon monomers containing nitrile groups the interest to the search for new catalysts of hydrosilylation of cyanoalkenes, the most useful reaction for the synthesis of such compounds, remains continuously unabated.

While hydrosilylation of allyl cyanide proceeds smoothly in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, hydro-silylation of acrylonitrile, the most accessible among the unsaturated nitriles, is not practicable in these conditions. In this communication we report on the results of the search of catalysts for the hydrosilylation of acrylonitrile.

As known, the addition of hydrosilanes to acrylonitrile may result in the formation of both α - and β -isomers, and basic catalysts (amines, phosphine) promote formation of a more valuable β -isomer.



We found that in the presence of triallylamine, allylbis(triethoxysililpropyl)amine, diallylamino-propyltriethoxysilane and HMPA, acrylonitrile added trichlorosilane with the formation of only β -cyanoethyltrichlorosilane; in the presence of triallylamine and HMPA the yield reaches 97 and 75% respectively (see the table, nos. 1–4). The reaction proceeds at heating the mixture of components to boiling. All four new

catalyst can be easily separated from the adduct by distillation, and provide a pure β -cyanoethyltrichlorosilane.

In the literature a catalytic system for hydro-silylation of simple olefins, $\text{NiX}_2 + 2\text{R}_3\text{P}=\text{O}$, has been described [1]. We carried out reaction of trichlorosilane with acrylonitrile in the presence of the mixtures $\text{NiCl}_2 + 2\text{MePh}_2\text{P}=\text{O}$ and $\text{CuCl} + 2\text{MePh}_2\text{P}=\text{O}$, by heating the reagents in a sealed ampule at 90–95°C. In contrast to the reactions catalyzed by phosphines, in both cases formed a mixture of β - and α -isomers. It seems that this is due to the change in the polarization of the double bond in acrylonitrile under the action of phosphine oxide, which is of more acid nature (see the table).

Addition to the acrylonitrile of trichlorosilane occurs also in the presence of dimethylaminochloro-carbenium tetrachlorocuprate and hexachloroplatinate. The yield of β -cyanoethyltrichlorosilane is 60 and 20% respectively. Analogous Co, Ni, and Mn salts are not active. Attempts of applying any of the above-mentioned catalysts except bisdimethylaminochloro-carbenium hexachloroplatinate in the reaction of methylchlorosilane and dimethylchlorosilane addition to acrylonitrile failed. In the presence of $[(\text{Me}_2\text{N})_2\text{SCl}]_2\text{PtCl}_6$, methylchlorosilane is added to acrylonitrile in 12% yield (see the table). There are practically no published data on the addition to acrylonitrile of hydroalkoxysilanes. A formation of β -

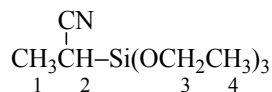
Hydrosilylation of acrylonitrile

Run no.	Hydrosilane moles per 1 mol of acrylonitrile	Catalysts moles per 1 mol of acrylonitrile	Reaction conditions		Addition product	
			temperature, °C	duration, h	formula	yield, %
1	HSiCl ₃ , 1.5	Triallylamine, 0.05	120	36	NCCH ₂ CH ₂ SiCl ₃	97
2	HSiCl ₃ , 1.5	Allylbis(triethoxypropyl)amine, 0.05	120	36	NCCH ₂ CH ₂ SiCl ₃	49
3	HSiCl ₃ , 1.5	Diallylaminopropyltriethoxysilane, 0.05	120	36	NCCH ₂ CH ₂ SiCl ₃	40
4	HSiCl ₃ , 1.3	HMPA	120	3	NCCH ₂ CH ₂ SiCl ₃	75
5 ^a	HSiCl ₃ , 1.0	NiCl ₂ +2MePh ₂ PO, 0.015 + 0.02	90–95	10	NCCH ₂ CH ₂ SiCl ₃ NCCHMeSiCl ₃	32.0 23.0
6 ^a	HSiCl ₃ , 1.0	CuCl+2MePh ₂ PO, 0.006 + 0.02	90–95	10	NCCH ₂ CH ₂ SiCl ₃ NCCHMeSiCl ₃	14.0 22.0
7 ^a	HSiCl ₃ , 1.0	[(Me ₂ N) ₂ CCl] ₂ CuCl ₄ , 0.01	100	10 24	NCCH ₂ CH ₂ SiCl ₃	35.0 60.0
8 ^a	HSiCl ₃ , 1.0	[(Me ₂ N) ₂ CCl] ₂ PtCl ₆ , 1×10 ⁻⁵	100	20	NCCH ₂ CH ₂ SiCl ₃	20.1
9 ^a	MeSiHCl ₂ , 1.0	[(Me ₂ N) ₂ CCl] ₂ PtCl ₆ , 1×10 ⁻⁵	100	16	NCCHMeSiMeCl ₂	12.1
10	HSi(OEt) ₃ , 1.0	Rh(acac) ₂ (CO) ₂ , 3×10 ⁻²	120	3	NCCHMeSi(OEt) ₃ ^b	56.0
11	HSi(OBu) ₃ , 1.0	Rh(acac) ₂ (CO) ₂ , 3×10 ⁻²	120	3	NCCHMeSi(OBu) ₃ ^c	58.0

^a In a sealed ampule. ^b bp. 70–73°C (3 mm Hg), n_D^{20} 1.4100. ^c bp 122–123°C (3.5 mm Hg), n_D^{20} 1.4205.

cianoethyltriethoxysilane in the presence of poly(*p*-diphenylphosphinostyrene)bis(triphenylphosphine)-rhodium with 10% yield has been described [2] and of α -cyanoethyltriethoxysilane in the presence of Ph₃PRhCl in 66% yield [3].

Applying as a catalyst rhodium dicarbonyl acetylacetonate, we performed addition of triethoxysilane to acrylonitriles and obtained α -isomer with 56% yield.



In the NMR spectrum was detected: (a) a protons, (b) a quadruplet at 1.9–2.4 ppm of CH² protons, and (c) a complex signal in the region of 1.2–1.6 ppm from the doublet of CH¹ protons and triplet of CH⁴ protons. The ratio of integral intensities of the signals is a:b:c = 1:6:12. Since the reaction is accompanied by strong spontaneous heating it is recommended to perform it by means of gradual adding acrylonitrile to a mixture of silane and catalyst. Similarly was prepared α -cyanoethyltributoxysilane (see the table).

An attempt was made to obtain cyano-containing silicon monomers by addition of hydrosilanes to 1,4-dicyanobut-2-ene. The following catalysts were tested:

H₂PtCl₆, H₂O, Pd/C, tetramethylethylenediamine, benzoyl peroxide, and *tert*-butyl peroxides. However, in the presence of the first three catalysts formed an isomeric compound, 1,4-dicyanobut-1-ene; in the presence of the last two catalysts interactions did not proceed.

EXPERIMENTAL

Chromatographic analysis was carried out on a Color-100 chromatograph with a detector on the thermal conductivity, a glass column 3 x 3000 mm and with evaporator containing a glass tube. Phase 15% E-301 on the carrier "Cromaton-N-AW." Evaporator temperature 150°C, detector temperature 180°C, column temperature from 30 to 130°C, the programmed increase rate 20°C per 1 min. The detector current 130 mA, the rate of helium flow 60 ml min⁻¹. The NMR spectra were registered on a Varian spectrometer with an operating frequency 60 MHz.

Hydrosilylation with trichlorosilane in the presence of amines. A mixture of acrylonitrile and trichlorosilane (mole ratio 1:1) with a catalyst in a flask with reflux condenser was boiled for 18 h, the remaining trichlorosilane was then added, and the boiling was continued for another 18 h. The

temperature of the mixture reached 120°C. After cooling, dry HCl was passed to precipitate the amine. The mixture was filtered and filtrate was subjected to the fractional distillation.

Hydrosilylation in the presence of HMPA. To the catalyst 1/10 part of a mixture of trichlorosilane with acrylonitrile was added, the mixture was heated to boiling and then at of 80–90°C the remaining mixture was added over 3 hours. The boiling was continued until the temperature of the mixture reached 120°C. The mixture was maintained at this temperature for 1 h and then it was distilled.

Hydrosilylation in the presence of salts of nickel and copper and phosphinioxides, as well as in the presence of carbenium salts was carried out in ampules.

Hydrosilylation in the presence of rhodium dicarbonyl acetylacetonate. To a mixture of trialkoxysilane and a catalyst heated to 95–100°C acrylonitrile was slowly added over 0.5 h. At the beginning of the additions there was a sharp rise in temperature to 150°C. The remaining acrylonitrile was added at a temperature of 120°C, and after adding the mixture was maintained at this temperature for 1 h.

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