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METAL-CATALYZED ADDITION OF HCN TO OLEFINIC SILANES*

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SUMMARY

Addition of HCN to vinyltriethoxysilane, vinylmethyldiethoxysilane, vinyldimethylethoxysilane and 1,3-divinyltetramethyldisiloxane affords the corresponding (cyanoethyl)silane in each case. The additions are catalyzed by tetrakis(triphenylphosphite)palladium (0) and give yields in the range 30–80 %. In each of the palladium-catalyzed reactions, the (2-cyanoethyl)silane isomer is the major addition product.

Soluble transition metal complexes have been employed as catalysts in the synthesis of nitriles from non-conjugated olefins and hydrogen cyanide[1–8]. The utility of the reaction has often been impaired, however, by the large catalyst requirement[1–6]. In addition to dicobalt octacarbonyl[1], complexes of zerovalent palladium and nickel have been demonstrated to be effective as catalysts for the reaction[2–8].

From previous evidence apparently only olefins which bond well with low-valent metals readily undergo HCN addition in the presence of zerovalent palladium or nickel complexes. For example, the tetracyanonickelate(0) ion is reported to catalyze HCN addition only to olefins containing electron-withdrawing substituents[9], while $Pd[P(OC_6H_5)_3]_4$ is most effective with olefins such as ethylene and those related to norbornene.

Vinyl- and allylsilanes act as typical olefins in reactions such as hydrogen halide addition[10], and radical additions of halomethanes[11]. More importantly, vinylsilanes behave in certain reactions as if they are conjugated (activated) olefins[12,13]. Therefore, we wished to determine whether vinyl and allyl silicon compounds would undergo metal-catalyzed HCN addition. We wish to report results of this investigation.

Vinyltriethoxysilane failed to react with HCN in the presence of KCN. It did react with excess HCN at atmospheric pressure in the presence of tetrakis(triphenylphosphite)palladium(0) (2 mol %) to afford (cyanoethyl)triethoxysilane (Table 1) in

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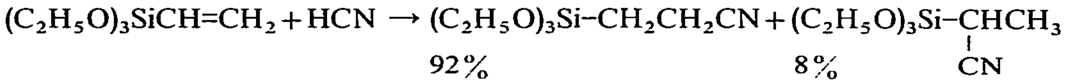
TABLE 1

ADDITION OF HCN TO VINYL SILANES

Olefinic silane (mol)	*Product(s)*	(%)	*Pd[P(OC$_6$H$_5$)$_3$]$_4$ (mol %)*^{a}	*HCN (mol)*	*Temp. (°C)*	*Time (h)*	*Yield (%)*
$CH_2=CH-Si(OC_2H_5)_3$ (0.1)	$NC-CH_2CH_2-Si(OC_2H_5)_3$	92	2.4	0.31	135	6.5	73.3
	$CH_3CH(CN)Si(OC_2H_5)_3$	8					
$CH_2=CH-Si(CH_3)(OC_2H_5)_2$ (0.1)	$NCCH_2CH_2Si(CH_3)(OC_2H_5)_2$	>95	2.0	0.38	135	7.0	30.5
	$CH_3CH(CN)Si(CH_3)(OC_2H_5)_2$	<5					
$CH_2=CH-Si(CH_3)_2(OC_2H_5)$ (0.1)	$NCCH_2CH_2Si(CH_3)_2(OC_2H_5)$	>95	2.0	0.62	130	17.5	30.6
	$CH_3CH(CN)Si(CH_3)_2(OC_2H_5)$	<5					
$[CH_2=CH-Si(CH_3)_2]_2O$ (0.1)	$[NCCH_2CH_2Si(CH_3)_2]_2O^b$	>98	2.0	0.52	135	21	84.5
$CH_2=CH-CH_2Si(OC_2H_5)_3$ (0.075)	$NC(CH_2)_3Si(OC_2H_5)_3$	50	2.0	0.13	120	21	49.1
	$CH_3CH(CN)CH_2Si(OC_2H_5)_3$	50					
$CH_3-CH=CH-Si(OC_2H_5)_3$ (0.045)	No reaction		2.0	0.13	120	21	
$CH_2=CH-Si(OC_2H_5)_3$ (0.05)	$NCCH_2CH_2Si(OC_2H_5)_3$	68	2.0^c	0.26	135	20	32.8
	$CH_3CH(CN)Si(OC_2H_5)_3$	32					

[a] Calcd. on olefin. [b] No detectable α-isomer by NMR. [c] Tetrakis(triphenylphosphite)nickel used as catalyst.

73% yield. Also, 0.1 mol% of tetrakis(triphenylphosphite)palladium afforded 278 mol of (cyanoethyl)triethoxysilane per mole of complex during 72 h. 2-(Cyanoethyl)-triethoxysilane was the predominant isomer formed. When tetrakis(triphenylphosphite)nickel(0) was employed as catalyst under comparable conditions, a lower yield of (cyanoethyl)triethoxysilanes was obtained. Furthermore, the ratic of (2-cyanoethyl)- to (1-cyanoethyl)triethoxysilane was only 2.1/1.



$$(C_2H_5O)_3SiCH{=}CH_2 + HCN \rightarrow \underset{92\%}{(C_2H_5O)_3Si{-}CH_2CH_2CN} + \underset{8\%}{(C_2H_5O)_3Si{-}\underset{\displaystyle CN}{\underset{|}{C}}HCH_3}$$

To determine the generality of the reaction and to gain some insight as to structural effects upon reactivity, addition of HCN to several different vinylsilanes was carried out using $Pd[P(OC_6H_5)_3]_4$ as catalyst (Table 1).

The addition of HCN to 1,3-divinyltetramethyldisiloxane gave first the mononitrile and subsequently the dinitrile in high yield (84%). At less than 50% conversion, the intermediate mononitrile 1-vinyl-3-(2-cyanoethyl)tetramethyldisiloxane could be recovered in good yield. At 50% conversion the mixture contained 50% mononitrile, 25% dinitrile and 25% starting material. This showed that the vinyl groups are equally reactive.

Allyltriethoxysilane with HCN in the presence of $Pd[P(OC_6H_5)_3]_4$ gave a 1/1 mixture of 4-(triethoxysilyl)butyronitrile and 2-methyl-3-(triethoxysilyl)propionitrile in 49% overall yield. Concurrently, isomerization of allyltriethoxysilane to *trans*-propenyltriethoxysilane occurred. The latter fails to add HCN under these conditions.

The predominance of (2-cyanoethyl)silane products in the reactions investigated may be partially a consequence of the conjugative interaction of the vinyl substituent with silicon. Other factors, *e.g.* the nature of the metal, may be of equal importance in determining the structure of the nitrile product.

EXPERIMENTAL

Reagents

All of the unsaturated silanes were obtained from Peninsula ChemResearch, Inc., and redistilled prior to use.

Each of the (cyanoalkyl)silanes was distilled on a 24" Nester–Faust spinning band distillation apparatus. All boiling points are uncorrected.

Product purities and isomer distributions were determined by gas chromatography.

Tetrakis(triphenylphosphite)palladium[14] and tetrakis(triphenylphosphite)-nickel[15] were prepared by known methods.

Preparation of (2-cyanoethyl)- and (1-cyanoethyl)triethoxysilane

Vinyltriethoxysilane (20 g, 0.105 mol), nonane (20 ml) and tetrakis(triphenylphosphite)palladium(0) (3.39 g, 0.0025 mol) were charged to a flask fitted with reflux condenser, thermometer and gas inlet. The mixture was stirred and heated to 135° under an inert atmosphere (argon). Gaseous HCN was introduced by passing argon first through a wash bottle containing liquid HCN, thereby saturating the argon with

HCN vapors, and then into the reaction vessel. The wash bottle was thermostatted at −5° and the argon flow was adjusted to provide an HCN feed of about 0.05 mol/h. A total of 0.31 mol of HCN was passed through the reaction vessel in 6½ h.

The resulting mixture was filtered and the filtrate was fractionally distilled. After removing unreacted vinyltriethoxysilane, 16.8 g (71% yield) of (cyanoethyl)triethoxysilane, b.p. 91°/4 mm (lit.[16]: b.p. 114°/12 mm). (Found: C, 49.34; H, 8.61; N, 6.19. $C_9H_{19}NO_3Si$ calcd.: C, 49.73; H, 8.81; N, 6.44%.)

The distillate was subjected to VPC analysis on a 10′ 5% OV-17 column (100–225° at 10°/min). The presence of two products in a ratio of 11/1 was indicated. Comparison of retention times of the products with that of authentic (2-cyanoethyl)triethoxysilane[16] indicated that this material predominated in the distillate. The PMR spectrum of the distillate substantiated the isomer composition.

Preparation of 1,3-*bis*(2-*cyanoethyl*)*tetramethyldisiloxane*

To a mixture of 1,3-divinyltetramethyldisiloxane (18.6 g, 0.1 mol), tetrakis(triphenylphosphite)palladium(0) (2.7 g, 0.002 mol) and anisole (18.6 g) gaseous HCN was introduced at the rate of 0.025–0.05 mol/h. In about 20 h a total of 0.5 mol of HCN had been added. The mixture was fractionally distilled to give 20.3 g of 1,3-bis(2-cyanoethyl)tetramethyldisiloxane (84.5% yield based on olefin) b.p. 77°/0.03 mm (lit.[17]: b.p. 153–155°/3 mm). (Found: C, 49.85; H, 8.09. $C_{10}H_{20}N_2OSi_2$ calcd.: C, 49.95; H, 8.38%.)

Preparation of 1-(2-*cyanoethyl*)-3-*vinyltetramethyldisiloxane*

1,3-Divinyltetramethyldisiloxane (18.6 g, 0.1 mol) reacted with HCN in the presence of tetrakis(triphenylphosphite)palladium(0) (2.7 g, 0.002 mol) in anisole (18.6 g) at 130° in the manner described previously. During 1.5 h, a total of 0.25 mol HCN was passed through the vessel. Distillation of the mixture afforded, in addition to unreacted starting material and some dinitriles, 7.6 g of 1-(2-cyanoethyl)-3-vinyltetramethyldisiloxane, b.p. 41°/1 mm. (Found: C, 50.79; H, 9.09; N, 6.22. $C_9H_{19}NOSi_2$ calcd.: C, 50.65; H, 8.97; N, 6.56%.)

Preparation of (2-*cyanoethyl*)- *and* (1-*cyanoethyl*)*methyldiethoxysilane*

To a mixture of vinylmethyldiethoxysilane (16 g, 0.1 mol) and tetrakis(triphenylphosphite)palladium(0) (2.7 g, 0.002 mol) heated at 135°, gaseous HCN was introduced at the rate of 0.054 mol/h. After 7 h the mixture was cooled, filtered and the filtrate distilled to give 5.7 g (30.5% yield, based on silane) of predominantly (2-cyanoethyl)methyldiethoxysilane, as shown by its PMR spectrum; b.p. 43°/1 mm (lit.[18]: b.p. 123–123.5°/30 mm). (Found: C, 51.10; H, 8.93; N, 7.03. $C_8H_{17}NO_2Si$ calcd.: C, 51.12; H, 9.11; N, 7.45%.)

Preparation of (2-*cyanoethyl*)*dimethylethoxysilane*

Vinyldimethylethoxysilane (13.0 g, 0.1 mol) and tetrakis(triphenylphosphite)palladium(0) (2.7 g, 0.002 mol) were heated to 130° in anisole (13 ml). Gaseous HCN was introduced at the rate of about 0.025 mol/h. After 18 h the mixture was filtered and fractionally distilled to give 4.8 g (30.6% yield, based on silane) of (2-cyanoethyl)dimethylethoxysilane, b.p. 55–70°/5–10 mm (lit.[18]: b.p. 106–108°/30 mm). The product was identified by its PMR spectrum (Table 2).

TABLE 2

PMR DATA FOR CYANOALKYLSILANES[a]

	Compound	*Chemical shift* (*δ*, *ppm*)
(I)	NC–CH$_2$CH$_2$–Si(OCH$_2$CH$_3$)$_3$ c a d b	a 0.94 (m) b 1.22 (t, $J_{b,d}$ 7.0 Hz) c 2.36 (m) d 3.85 (q, $J_{b,d}$ 7.0 Hz)
(II)	NC–CH$_2$CH$_2$–Si(OCH$_2$CH$_3$)$_2$(CH$_3$) d b e c a	a 0.22 b 0.96 (m) c 1.28 (t, $J_{c,e}$ 7.0 Hz) d 2.45 (m) e 3.83 (q, $J_{c,e}$ 7.0 Hz)
(III)	[NC–CH$_2$CH$_2$–Si(CH$_3$)$_2$]$_2$O c b a	a 0.41 b 0.89 (m) c 2.32 (m)
(IV)	CH$_2$=CH–Si(CH$_3$)$_2$–O–Si(CH$_3$)$_2$CH$_2$CH$_2$CN d a a b c	a 0.2 (s) b 1.21 (m) c 2.63 (m) d 5.95 (m)
(V)	NC–CH$_2$CH$_2$CH$_2$Si(OCH$_2$CH$_3$)$_3$ d c a e b	a 0.69 (m) b 1.18 (t, $J_{b,e}$ 7.0 Hz) c 1.70 (m) d 2.36 (m) e 3.80 (q, $J_{b,e}$ 7.0 Hz)
(VI)	CH$_3$CH(CN)CH$_2$–Si(OCH$_2$CH$_3$)$_3$ c d a e b	a 1.0 b 1.18 } (m) c 1.22 d 2.67 (m) e 3.80 (q, $J_{b,e}$ 7.0 Hz)

[a] The PMR spectra were recorded on a Varian A-60 spectrometer in CDCl$_3$ relative to tetramethylsilane; s singlet; t triplet; q quartet; m multiplet.

Preparation of 4-(triethoxysilyl)butyronitrile and 2-methyl-3-(triethoxysilyl)propionitrile

Allyltriethoxysilane (15.3 g, 0.075 mol) was treated with HCN in the presence of tetrakis(triphenylphosphite)palladium(0) (2.02 g, 0.0015 mol) at 120° in the manner described. During 20 h a total of 0.5 mol of HCN was passed into the vessel. Distillation afforded 8.5 g (49.1% yield) of (triethoxysilyl)butyronitriles, b.p. 42–50°/0.02 mm (lit.: b.p. 117–119°/6 mm).

VPC analysis on a 10′ 5% OV-17 column (100–225° at 10°/min) showed that the product consisted of two components in a 1/1 ratio. Each component could be obtained in pure form by further careful distillation. One component was identified by its PMR spectrum as 4-(triethoxysilyl)butyronitrile. (Found: C, 52.00; H, 9.06; N, 5.59. $C_{10}H_{21}NO_3Si$ calcd.: C, 51.91; H, 9.15; N, 6.05%.) The second component was identified as 2-methyl-3-(triethoxysilyl)propionitrile. (Found: C, 51.80; H, 8.88; N, 5.85. $C_{10}H_{21}NO_3Si$ calcd.: C, 51.91; H, 9.15; N, 6.05%.)

Preparation of (2-cyanoethyl)- and (1-cyanoethyl)triethoxysilane catalyzed by tetrakis(triphenylphosphite)nickel(0)

Vinyltriethoxysilane (10 g, 0.05 mol), anisole (10 g) and tetrakis(triphenylphosphite)nickel(0) (1.299 g, 0.001 mol) and gaseous HCN, fed at an average rate of 0.013 mol per hour for 20 h, were reacted. At the end of this time VPC analysis showed a 32.8% yield of (cyanoethyl)triethoxysilanes. The product consisted of 68.1% (2-cyanoethyl)triethoxysilane and 31.9% (1-cyanoethyl)triethoxysilane.

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