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A Convenient Method for the Synthesis of Alkylsilyl Cyanides Using Potassium or Sodium Cyanide Impregnated on Amberlite XAD Resin

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Synopsis. Potassium and sodium cyanide impregnated on Amberlite XAD resin were found to be effective for converting alkylsilyl chloride to the corresponding alkylsilyl cyanide under mild conditions.

Alkylsilyl cyanides are versatile and important reagents for organic synthesis. Among these, trimethylsilyl cyanide (Me_3SiCN) has been most widely used for preparing useful nitriles and isonitriles: Carbonyl compounds[1)] and imines[2)] react with Me_3SiCN to give silylated cyanohydrins and aminonitriles, respectively. The reaction of acetals and orthoesters with Me_3SiCN gives alkoxynitriles.[3)] The reaction of oxiranes with Me_3SiCN produces trimethylsilyloxynitriles in the presence of aluminium chloride[4)] or diethylaluminium chloride,[5)] whereas in the presence of zinc iodide it gives the corresponding isonitriles.[6)] On the other hand, other alkylsilyl cyanides, *t*-butyldimethylsilyl cyanide (*t*-$BuMe_2SiCN$)[7)] and dimethylsilyl dicyanide ($Me_2Si(CN)_2$),[8)] also have recently been employed as cyanation agents.

A number of methods for the synthesis of Me_3SiCN have been reported.[1d,9)] In many reported methods, however, there seem to be few methods that can be utilized for preparing other alkylsilyl cyanides in satisfactory yields. Although only the method reported by Mai and Patil[10)] affords good yields of alkylsilyl cyanides, it requires the use of lithium cyanide which is prepared by the reaction of butyllithium and Me_3SiCN[10)] or by the reaction of lithium hydride with hydrogen cyanide[1d)] or acetone cyanohydrin.[9e)]

In previous papers, it has been shown that potassium and sodium cyanide impregnated on macroporous polymer resins such as Amberlite XAD resins (KCN/XAD, NaCN/XAD) are effective reagents for some reactions.[11)] This paper shows that the reaction of alkylsilyl chlorides with KCN/XAD or NaCN/XAD gives alkylsilyl cyanides in good yields under mild conditions.

$$R_{4-n}SiCl_n \xrightarrow{\text{KCN or NaCN/XAD}} R_{4-n}Si(CN)_n$$

In a preliminary experiment, the reaction of trimethylsilyl chloride (Me_3SiCl) with KCN/XAD-4 was carried out in various solvents. Table 1 shows the results. In *N*-methylpyrrolidone (NMP), the reaction was so fast that the complete conversion of Me_3SiCl occured within 0.5 h at room temperature giving Me_3SiCN in 92—94% yields (GLC). In acetonitrile, the reaction afforded 94—95% yield of Me_3SiCN at 60 °C after 1.5 h. Contrary to expectations, the yields in 1,2-dimethoxyethane (DME) and in tetrahydrofuran (THF) were very similar to that without any solvent. In a nonpolar solvent such as benzene or hexane, the

Table 1. Preparation of Me_3SiCN Using KCN/XAD-4 in Various Solvents[a)]

Solvent	Time/h	Temp/°C	Yield/%[b)]
NMP	<0.5	25	92[d)]
c)	<0.5	25	94[d)]
Acetonitrile	1.5	60	94[d)]
c)	1.5	60	95[d)]
DME	8.0	60	18
THF	8.0	60	22
Benzene	6.0	60	10
Hexane	8.0	60	11
None	8.0	60	19

a) Unless otherwise noted, reactions were carried out with KCN (15 mmol)/XAD-4 (3.75 g), Me_3SiCl (7.5 mmol), and a solvent (20 ml). b) Determined by GLC using toluene as the internal standard. c) NaCN (15 mmol)/XAD-4 (3.75 g) was used. d) The conversion of Me_3SiCl was completed.

Table 2. Alkylsilyl Cyanides[a)]

Alkylsilyl cyanide	Alkali metal cyanide	Temp	Time	Yield[b)]	Bp/mmHg (mp)		IR
		°C	h	%	Found	Reported	cm⁻¹
Me_3SiCN[c)]	NaCN	25	0.5	61(94)	114—118/760	117—118/760[1d)]	2190
$PhMe_2SiCN$	KCN	60	3.0	79(95)	79—81/3	228—235/760[10)]	2185
t-$BuMe_2SiCN$	KCN	60	4.0	80(95)	77—79/45	163—167/760[10)]	2185
	NaCN	60	4.0	85(95)	(79—81)	(82—84)[10)]	
$Me_2Si(CN)_2$	KCN	60	6.0	73(85)	109—112/55	166—170/760[10)]	2195
d)	NaCN	40	4.0	71(95)	(82—84)	(82—85)[10)]	
$Et_2Si(CN)_2$	KCN	60	4.0	75(90)	89—92/9.5	210—215/760[10)]	2195
d)	NaCN	40	4.0	77(95)	(35—37)		
$Ph_2Si(CN)_2$[d)]	NaCN	40	4.0	70	121—122/0.35 (44—47)	110—115/0.1[10)] (45—47)[10)]	2185

a) Unless otherwise noted, reactions were carried out with alkylsilyl chloride (15 mmol), alkali metal cyanide (30 mmol)/XAD-4 (7.5 g), and acetonitrile (40 ml). b) Isolated yields. The values in parentheses are the yields determined by GLC. c) Me_3SiCl (24 mmol) and NMP (20 ml) were used. d) R_2SiCl_2 (10 mmol) was used.

reaction was very slow. The reaction of Me_3SiCl with KCN impregnated on alumina or silica gel was also performed. No Me_3SiCN was obtained, though the coversion of Me_3SiCl was very fast. Although NMP is an appropriate solvent for Me_3SiCN because of the ease in separating the product from the solvent, its use is limited in the preparation of other alkylsilyl cyanides having high boiling points. Table 1 shows that acetonitrile, which has a low boiling point, can be used for this purpose though the reaction is slower than that in NMP.

Table 2 shows the results of the preparation of alkylsilyl cyanides using KCN/XAD-4 or NaCN/XAD-4 in acetonitrile. These results are comparable to that using LiCN[10] and indicates that KCN/XAD-4 and NaCN/XAD-4 are very effective reagents for the synthesis of alkylsilyl cyanides. On the other hand, a small amount of siloxanes was produced because of the incomplete drying of the system. In particular, since the boiling points of Me_3SiCN and the byproduct, hexamethyldisiloxane, are very similar, the isolated yield of Me_3SiCN was considerably lower than those of the other alkylsilyl cyanides.

For certain cyanosilylation, the use of isolated silyl cyanides will not be necessary. In fact, the one-pot cyanosilylation of aldehydes and ketones was found to proceed smoothly under mild conditions using KCN/XAD or NaCN/XAD producing silylated cyanohydrins in good yields.[12]

Experimental

Materials. Solvents were dried with molecular sieves 3A or 4A. Dimethylsilyl dichloride and Me_3SiCl (Toray Silicone Co.), *t*-$BuMe_2SiCl$, phenyldimethylsilyl chloride, diethylsilyl dichloride (Shin-Etsu Chemical Industries) and diphenylsilyl dichloride (Wako Pure Chemical Industries) were used without further purification. KCN/XAD and NaCN/XAD were prepared according to the method previously reported,[11] dried at 90 °C and 0.1 mmHg (1 mmHg=133.322Pa) for 5 h.

Typical Procedure for the Reaction of Alkylsilyl Chloride with KCN or NaCN/XAD-4. In all reactions, alkylsilyl chloride was added directly to the flask in which the KCN or NaCN/XAD-4 had been made and dried. All the products were known compounds.

The Reaction of Me_3SiCl with KCN/XAD-4 in Various Solvents. A mixture of KCN/XAD-4 made from KCN (15 mmol) and XAD-4 (3.75 g), Me_3SiCl (7.5 mmol), and a solvent (20 ml) was stirred under the conditions presented in Table 1. The yield of Me_3SiCN was determined by GLC using toluene as the internal standard.

Me_3SiCN: A mixture of NaCN (1.47 g, 30 mmol)/XAD-4 (7.5 g), Me_3SiCl (2.60 g, 24 mmol), and NMP (20 ml) was stirred for 0.5 h at 25 °C. The solid material was filtered and meticulously washed with dichloromethane. The filtrate and washings were combined. After the dichloromethane had been carefully removed, the residual solution was carefully distilled under reduced pressure ($\approx$120 mmHg) giving the crude product. The total crude product obtained from triplicates was carefully redistilled with a 15 cm Vigreaux column, giving 4.33 g (61%) of Me_3SiCN, bp 114—118 °C (lit,[1d] bp 117—118 °C); IR (CCl_4) 2190 cm^{-1}.

***t*-$BuMe_2SiCN$:** A mixture of NaCN (1.47 g, 30 mmol)/ XAD-4 (7.5 g), *t*-$BuMe_2SiCl$ (2.26 g, 15 mmol), and acetonitrile (40 ml) was stirred at 60 °C for 4 h. The solid material was filtered and meticulously washed with 100 ml of benzene-dichloromethane (2 : 1). The filtrate and the washings were combined. After removal of the solvent, the residual solid was distilled under reduced pressure, giving 1.80 g (85%) of *t*-$BuMe_2SiCN$, bp 77—79 °C/45 mmHg, mp 79—81 °C (lit,[10] bp 163—167 °C, mp 82—83 °C); IR (CCl_4) 2185 cm^{-1}.

Diethylsilyl Dicyanide ($Et_2Si(CN)_2$): A mixture of KCN (1.95 g, 30 mmol)/XAD-4 (7.5 g), diethylsilyl dichloride (2.36 g, 15 mmol) and acetonitrile (40 ml) was stirred at 60 °C for 4 h. The resulting mixture was treated according to the same method as *t*-$BuMe_2SiCN$. After removal of the solvent, the residual solid was distilled under reduced pressure giving 1.56 g (75%) of $Et_2Si(CN)_2$, bp 89—92 °C/9.5 mmHg, mp 35—37 °C (lit,[10] bp 210—215 °C); IR (CCl_4) 2195 cm^{-1}.

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12) For example, the one-pot cyanosilylation of benzaldehyde with KCN/XAD and Me_3SiCl in acetonitrile gave the corresponding trimethylsilylated cyanohydrin in 98% yield (GLC) under mild conditions. The study of this reaction is now in progress.