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REACTION OF TRIMETHYLSILYL CYANIDE WITH ISOCYANATES AND CARBODIIMIDES

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Summary

Trimethylsilyl cyanide reacts with isocyanates to give 1/2 cycloadducts, 5-(trimethylsilylimino)imidazolidine-2,4-diones, in high yield. The reaction of trimethylsilyl cyanide with carbodiimides proceeded in the presence of a catalytic amount of aluminum trichloride to afford 1/1 adducts, *N*-trimethylsilyl-1-cyanoformamidines. At rather high temperatures, the reaction also proceeded without catalyst. The adducts were further allowed to react with isocyanates and carbodiimides to yield 4-imino-5-(trimethylsilylimino)imidazolidin-2-ones and 2,4-diimino-5-(trimethylsilylimino)imidazolidines, respectively. On the other hand, the reaction of trimethylsilyl cyanide with methyl isothiocyanate gave a novel cycloadduct, 4-cyano-5-bis(trimethylsilyl)aminoimidazolidine-2-thione.

Introduction

Recently, trimethylsilyl cyanide has been shown to be a good reagent for the preparation of *O*-trimethylsilylcyanohydrin derivatives [1], which can be used as a selective carbonyl protective group for substituted *p*-benzoquinones [2] or as a masked carbanion precursor [3] in organic synthesis. It also has been used for the synthesis of β-amino alcohols [4]. The cyanosilylation of Schiff bases has provided a novel route to α-amino nitriles [5] or α-amino acids [6]. However, little attention has been devoted to the reaction of trimethylsilyl cyanide with heterocumulenes, and only the cyanosilylation of ketene [7] has been reported (except our preliminary reports on the cyanosilylation of isocyanates [8a] and carbodiimides [8b]).

We describe here a full account of our research on the reactions of trimethylsilyl cyanide with isocyanates and carbodiimides, which give 5-(trimethylsilylimino)imidazolidine-2,4-diones and *N*-trimethylsilyl-1-cyanoformamidines, respectively. The latter was found to be a good precursor for the synthesis of

4,5-diiminoimidazolidin-2-ones and 2,4,5-triiminoimidazolidines. The reaction of trimethylsilyl cyanide with methyl isothiocyanate also is described.

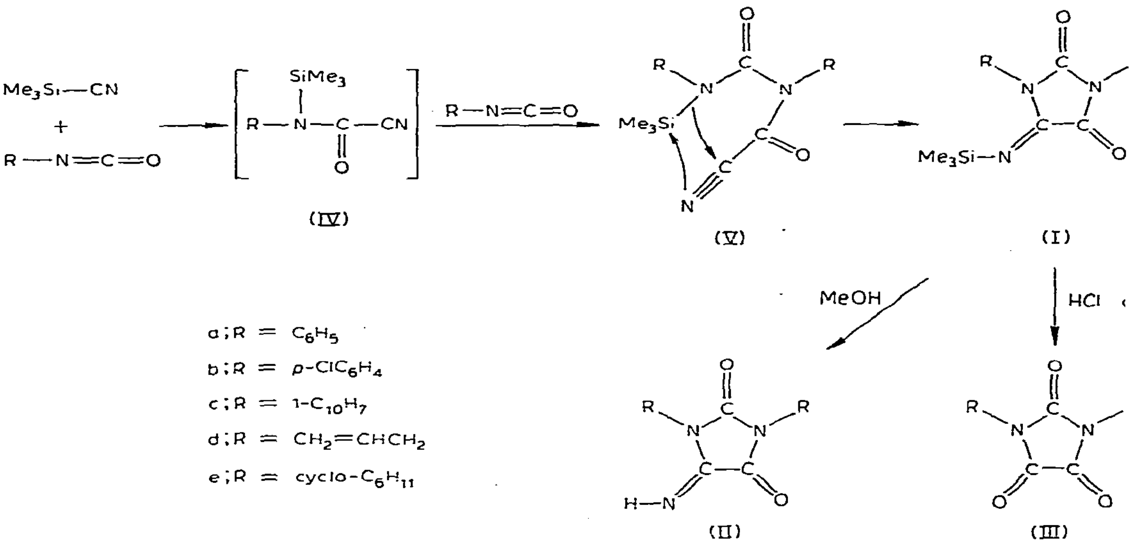
Results and discussion

Reaction of trimethylsilyl cyanide with isocyanates

The reaction of trimethylsilyl cyanide with aryl isocyanates was found to proceed on gentle heating without any catalyst to give 1/2 cycloadducts, 1,3-diaryl-5-(trimethylsilylimino)imidazolidine-2,4-diones (Ia—Ic), in excellent yields.

In the case of alkyl isocyanates, such as allyl and cyclohexyl isocyanates, more drastic conditions, e.g., 170°C for 12 h, were necessary to promote the reaction. The results are listed in Table 1. It is noteworthy that no cyanosilylation of the carbon—carbon double bond of the allyl group was observed with allyl isocyanate.

SCHEME 1



The 1,3-disubstituted-5-(trimethylsilylamino)imidazolidines (I) thus obtained were easily desilylated by methanol to give the corresponding 5-iminoimidazolidine-2,4-diones (II) in 97—98% yields. Hydrolysis of Ia with hydrochloric acid gave 1,3-diphenylimidazolidine-2,4,5-trione (IIIa; 1,3-diphenylparabanic acid) in 75% yield.

Besides such chemical identification, the structures of I and II were confirmed by their IR spectra which display three characteristic absorptions assigned to 2- and 4-carbonyl and 5-imino groups in the 1800—1675 cm^{-1} region. These assignments follow Patton's work on the structure of imidazolidinediones [9]. The NMR and mass spectra and analytical data for these heterocyclic compounds also support the assigned structures. These data for I and II are summarized in Table 2.

Although aryl and alkyl isocyanates afforded the corresponding cycloadducts

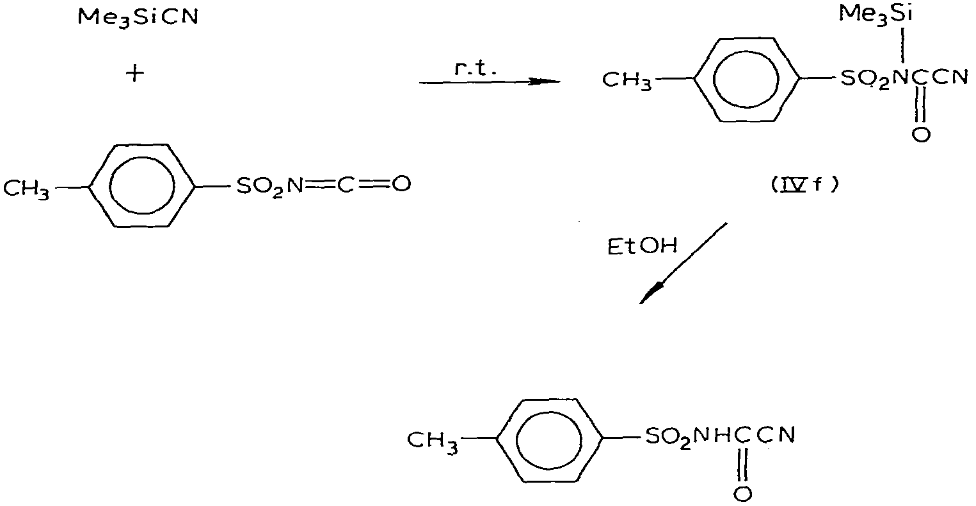
TABLE 1

REACTION OF TRIMETHYLSILYL CYANIDE WITH ISOCYANATES

	R	Conditions	Yield of I (%)
a	Ph	80°C/24 h	91
b	p-ClC_6H_4	55°C/6 h	94
c	1-$C_{10}H_7$ [a]	80°C/18 h	82
d	$CH_2{=}CHCH_2$	170°C/12 h	90
e	cyclo-C_6H_{11}	170°C/12 h	90

[a] 1-$C_{10}H_7$ = 1-naphthyl.

(I), *p*-toluenesulfonyl isocyanate gave only the 1/1 adduct. The reaction of trimethylsilyl cyanide with *p*-toluenesulfonyl isocyanate proceeded exothermally at ambient temperature to give *N*-(*p*-toluenesulfonyl)-*N*-trimethylsilyl-1-cyanoformamide (IVf) even when an excess of the isocyanate was used. The product was easily desilylated by ethanol to afford *N*-(*p*-toluenesulfonyl)-1-cyanoformamide (VI) in 95% yield. The lack of reactivity of IVf toward *p*-toluenesulfonyl isocyanate may be due to the electron-attracting effects of the substituents on the nitrogen atom of the silylamine moiety of IVf, which prevent electrophilic attack by another *p*-toluenesulfonyl isocyanate molecule.



(VI)

This result strongly suggests that the cyanosilylation of aryl and alkyl isocyanates proceeds through the corresponding *N*-trimethylsilyl-1-cyanoformamides (IV) as intermediates. Thus, the first step of the reaction is a nucleophilic addition of trimethylsilyl cyanide to the C=N bond of an isocyanate to form a 1/1 adduct, *N*-trimethylsilyl-1-cyanoformamide (IV), which further adds to another molecule of the isocyanate to give 1/2 adduct (V). Then, an intramolecular addition of the silylamine moiety of V to the cyano group proceeds

TABLE 2

PHYSICAL PROPERTIES AND SPECTRAL AND ANALYTICAL DATA FOR 5-TRIMETHYLSILYLIMINOIMIDAZOLIDINE-2,4-DIONES (I) AND 5-IMINOIMIDAZOLIDINE-2,4-DIONES (II)

Compound	M.p. (°C) or (b.p. (°C/Torr))	IR (cm^{-1})[a]					NMR (δ, ppm)[b]		Mass (m/e) M^+	Analysis (found (calcd.) (%))		
		ν(NH)	$\nu(^2C{=}O)$	$\nu(^4C{=}O)$	$\nu(^5C{=}N)$	δ(SiMe)	SiMe	NH		C	H	N
Ia	118–120	—	1790	1740	1705	1245	0.28	—	337	63.92 (64.07)	5.39 (5.68)	12.68 (12.45)
Ib	192–193	—	1785	1750	1710	1250	0.30	—	333	52.92 (53.21)	4.04 (4.22)	10.33 (10.34)
Ic	175–177	—	1800	1750	1710	1260	0.23	—	437	71.40 (71.37)	5.33 (5.30)	9.74 (9.60)
Id	(86/0.35)	—	1790	1750	1710	1250[c]	0.27	—	265	54.29 (54.31)	7.22 (7.22)	16.11 (15.83)
Ie	(139/0.3)	—	1780	1730	1690	1245[c]	0.24	—	349	61.82 (61.85)	8.74 (8.94)	12.18 (12.02)
IIa	137–138[d]	3220	1795	1750	1675	—	—	9.23	265			
IIb	234–235	3230	1790	1750	1680	—	—	9.57[e]	333	53.63 (53.92)	2.51 (2.71)	12.43 (12.57)
IIc	210–212	3240	1800	1745	1680	—	—	9.23	365	75.35 (75.60)	4.16 (4.14)	11.32 (11.50)
IId	78–80	3230	1790	1735	1675	—	—	8.83	193	55.92 (55.95)	5.63 (5.74)	21.80 (21.75)
IIe	76–77	3230	1785	1735	1675	—	—	8.81	277	64.89 (64.96)	8.33 (8.36)	15.17 (15.15)

[a] Measured as KBr disk unless otherwise noted. [b] Measured in $CDCl_3$. [c] Measured as neat liquid. [d] Lit. [9] m.p. 137°C. [e] Measured in acetone-d_6.

TABLE 3

REACTION OF TRIMETHYLSILYL CYANIDE WITH CARBODIIMIDES FOLLOWED BY HYDROLYSIS

R	Conditions	Catalyst	Yield of VIII (%)
a, iso-C_3H_7	r.t./4 h	$AlCl_3$ (5 mol%)	95
	190°C/24 h	—	80
b, cyclo-C_6H_{11}	r.t./12 h	$AlCl_3$ (5 mol%)	98
	190°C/24 h	—	54
c, p-$CH_3C_6H_4$	55°C/5 h	$AlCl_3$ (5 mol%)	96
	150°C/20 h	—	32 [a]

[a] Formation of 1/2 cycloadduct (XId, 42% yield based on the carbodiimide) was also observed.

to afford the cycloadduct (I). Attempted isolation of the 1/1 adduct using a large excess of trimethylsilyl cyanide has failed. Thus, the second step may be much faster than the initial 1/1 adduct formation. Accordingly, the cycloaddition most likely is a stepwise process as shown in Scheme 1.

Reaction of trimethylsilyl cyanide with carbodiimides

N,*N*′-Disubstituted carbodiimides were allowed to react with trimethylsilyl cyanide in the presence of a catalytic amount of aluminum trichloride at ambient temperature, which gave 1/1 adducts, *N*,*N*′-disubstituted-*N*-trimethylsilyl-1-cyanoformamidines (VII) in excellent yields.

Even in the absence of catalyst, trimethylsilyl cyanide reacted with carbodiimides under more drastic conditions, i.e., at 190°C for 24 h, to give the 1/1 adducts VII, in moderate to good yields. These adducts were easily converted to the corresponding 1-cyanoformamidines (VIII) by methanol or H_2O/ether in nearly quantitative yields. Results are summarized in Table 3.

The *N*-trimethylsilyl-1-cyanoformamidines (VII) thus obtained were easily converted to the corresponding *N*-acetyl-1-cyanoformamidines (IX) by treatment with an equimolar amount of acetyl chloride at ambient temperature (Scheme 2).

SCHEME 2

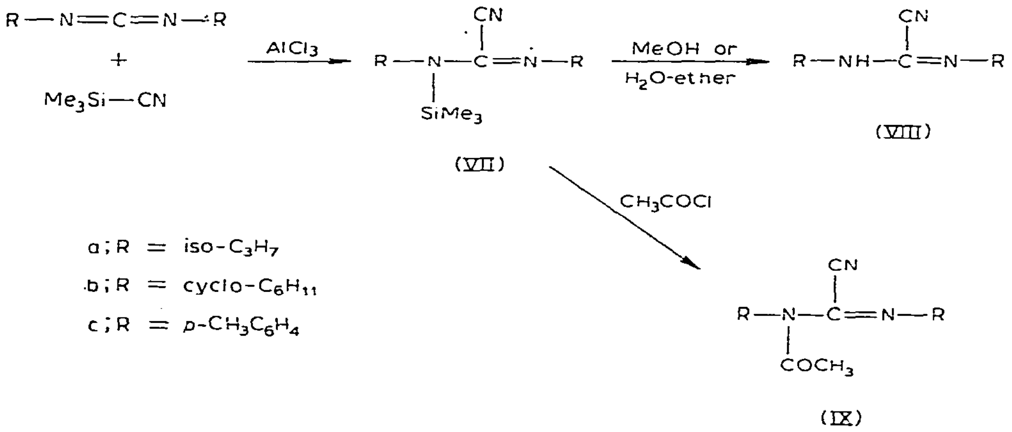


TABLE 4

PHYSICAL PROPERTIES AND SPECTRAL AND ANALYTICAL DATA FOR *N*-TRIMETHYLSILYL-1-CYANOFORMAMIDINES (VII) AND THEIR DESILYLATED AND ACETYLATED DERIVATIVES (VIII AND IX)

Compound	B.p. (°C/Torr) (m.p. (°C))	IR (cm^{-1})[a]				NMR (δ, ppm)[b]			Mass (*m/e*) M^+	Analysis (found (calcd.) (%))		
		ν(NH)	ν(C≡N)	ν(C=N)	ν(C=O)	SiMe	NH	MeCO		C	H	N
VIIa	53/1.3	—	2210	1605	—	0.26	—	—	225	58.83 (58.61)	10.26 (10.28)	18.94 (18.64)
VIIb	116/0.25	—	2220	1600	—	0.25	—	—	305	67.17 (66.83)	9.94 (10.23)	14.11 (13.75)
VIIc	oil	—	2220	1600	—	0.23[d]	—	—	321	70.72 (70.98)	7.03 (7.22)	13.12 (13.07)
VIIIa	85/17	3360	2210	1640	—	—	4.39	—	153	62.85 (62.71)	9.73 (9.87)	27.65 (27.42)
VIIIb	(88–89)	3400	2230	1645[c]	—	—	4.10[d]	—	233	72.15 (72.06)	9.65 (9.93)	17.97 (18.01)
VIIIc	(126–127)	3360	2230	1640[c]	—	—	6.64[d]	—	249	76.98 (77.08)	5.78 (6.06)	16.58 (16.85)
IXa	65/0.45	—	2210	1630	1690	—	—	2.08	195	61.46 (61.51)	8.52 (8.78)	21.62 (21.52)
IXb	(54–55)	—	2220	1630[c]	1670	—	—	2.21[d]	275	69.55 (69.78)	8.90 (9.15)	15.03 (15.26)
IXc	(105–106)	—	2220	1620[c]	1710	—	—	2.07[d]	291	74.15 (74.21)	5.74 (5.88)	14.43 (14.42)

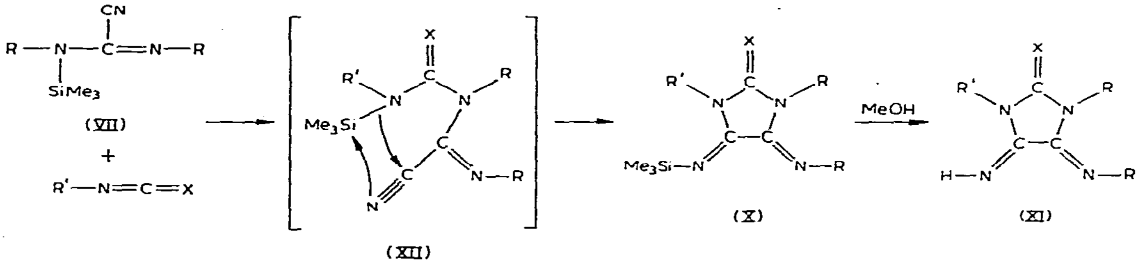
[a] Measured as neat liquid unless otherwise noted. [b] Measured in CCl_4 unless otherwise noted. [c] Measured as KBr disk. [d] Measured in $CDCl_3$.

Physical properties and spectral data for 1-cyanoformamidine derivatives (VII—IX) are summarized in Table 4.

Reaction of N-trimethylsilyl-1-cyanoformamidines (VII) with isocyanates and carbodiimides

Next, we performed a cycloaddition of *N*-trimethylsilyl-1-cyanoformamidines (VII) with isocyanates and carbodiimides in connection with the reaction of trimethylsilyl cyanide with isocyanates, which gave cyclic 1/2 adducts (Scheme 3). When *N*,*N'*-diisopropyl-*N*-trimethylsilyl-1-cyanoformamidine (VIIa) was treated with *p*-toluenesulfonyl isocyanate, an exothermic reaction took place to give 1-(*p*-toluenesulfonyl)-3-isopropyl-4-isopropylimino-5-(trimethylsilylimino)imidazolidin-2-one (Xa), in 99% yield. The reaction of phenyl isocyanate with VIIa required heating at 80°C for 14 h to produce the cycloadduct (Xb) in 87% yield. In the presence of aluminum trichloride (5 mol%), however, the latter cycloaddition took place smoothly at ambient temperature to give Xb in 86% yield.

SCHEME 3



a; R = iso-C_3H_7, R' = p-$CH_3C_6H_4SO_2$, X = O

b; R = iso-C_3H_7, R' = Ph, X = O

c; R = R' = cyclo-C_6H_{11}, X = cyclo-$C_6H_{11}N$

d; R = R' = p-$CH_3C_6H_4$, X = p-$CH_3C_6H_4N$

In the case of carbodiimides, the cycloaddition required more drastic conditions. The reaction of *N*,*N'*-dicyclohexyl-*N*-trimethylsilyl-1-cyanoformamidine (VIIb) with *N*,*N'*-dicyclohexylcarbodiimide proceeded at 190°C for 60 h to afford 1,3-dicyclohexyl-2,4-bis(cyclohexylimino)-5-(trimethylsilylimino)imidazolidine (Xc) in 56% yield. The addition of a catalytic amount of aluminum trichloride to the reaction system did not display a significant effect, in contrast with the case of phenyl isocyanate. 1,3-Di-*p*-tolyl-2,4-bis(*p*-tolylimino)-5-(trimethylsilylimino)imidazolidine (Xd) also was obtained by the reaction of VIIc with *N*,*N'*-bis(*p*-tolyl)carbodiimide at 190°C for 24 h in 43% yield.

The 4-imino-5-(trimethylsilylimino)imidazolidin-2-ones (Xa, Xb) and 2,4-diimino-5-(trimethylsilylimino)imidazolidines (Xc, Xd) thus obtained were easily desilylated by methanol to give the corresponding 4,5-diiminoimidazolidin-2-ones (XIa, XIb) and 2,4,5-triiminoimidazolidines (XIc, XId) in quantitative yields.

Physical properties and spectral data for imidazolidine derivatives (X and XI) are listed in Table 5. The IR spectra of these imidazolidine derivatives

TABLE 5

PHYSICAL PROPERTIES AND SPECTRAL AND ANALYTICAL DATA FOR 5-(TRIMETHYLSILYLIMINO)IMIDAZOLIDIN-2-ONES (Xa, Xb) AND 5-(TRIMETHYLSILYLIMINO)IMIDAZOLIDINES (Xc, Xd) AND THEIR DESILYLATED DERIVATIVES (XI)

Compound	M.p. (°C)	IR (cm^{-1})[a]			NMR (δ, ppm)[b]		Mass (m/e) M^+	Analysis (found (%) (calcd.))			
		ν(NH)	ν(C=O)	ν(C=N)	$SiCH_3$	NH		C	H	N	S
Xa	90—92	—	1805	1750, 1670	0.33	—	—[c]	54.02 (54.00)	6.91 (7.16)	13.19 (13.26)	7.73 (7.59)
Xb	103—104	—	1740	1710, 1670	—0.20	—	334	62.99 (62.75)	8.02 (8.19)	16.55 (16.26)	
Xc	157—159	—	—	1735, 1690, 1655	0.23	—	511	70.12 (70.39)	10.32 (10.44)	13.79 (13.68)	
Xd	152—154	—	—	1760, 1700, 1655	0.12	—	543	75.33 (75.10)	6.56 (6.86)	12.87 (12.88)	
XIa	108—110	3330	1760	1760, 1670	—	9.96	—[d]	54.56 (54.84)	6.31 (6.33)	15.82 (15.99)	9.03 (9.15)
XIb	100—102	3220	1760	1675, 1655	—	8.14	272	66.34 (66.15)	7.19 (7.40)	20.65 (20.57)	
XIc	107—108	3400	—	1700, 1670, 1630	—	7.13	439	73.94 (73.76)	10.36 (10.32)	15.98 (15.93)	
XId	169—170	3320	—	1715, 1680, 1645	—	—[e]	471	79.07 (78.95)	5.91 (6.20)	14.91 (14.85)	

[a] Measured as a KBr disk. [b] Measured in $CDCl_3$. [c] Instead of M^+, m/e 267 ($M^+ - CH_3C_6H_4SO_2$) was observed. [d] Instead of M^+, m/e 195 ($M^+ - CH_3C_6H_4SO_2$) was observed. [e] NH signal overlapped over the aromatic ones.

show characteristic absorption bands assigned to C=O and/or C=N stretching in the region 1805—1630 cm^{-1}.

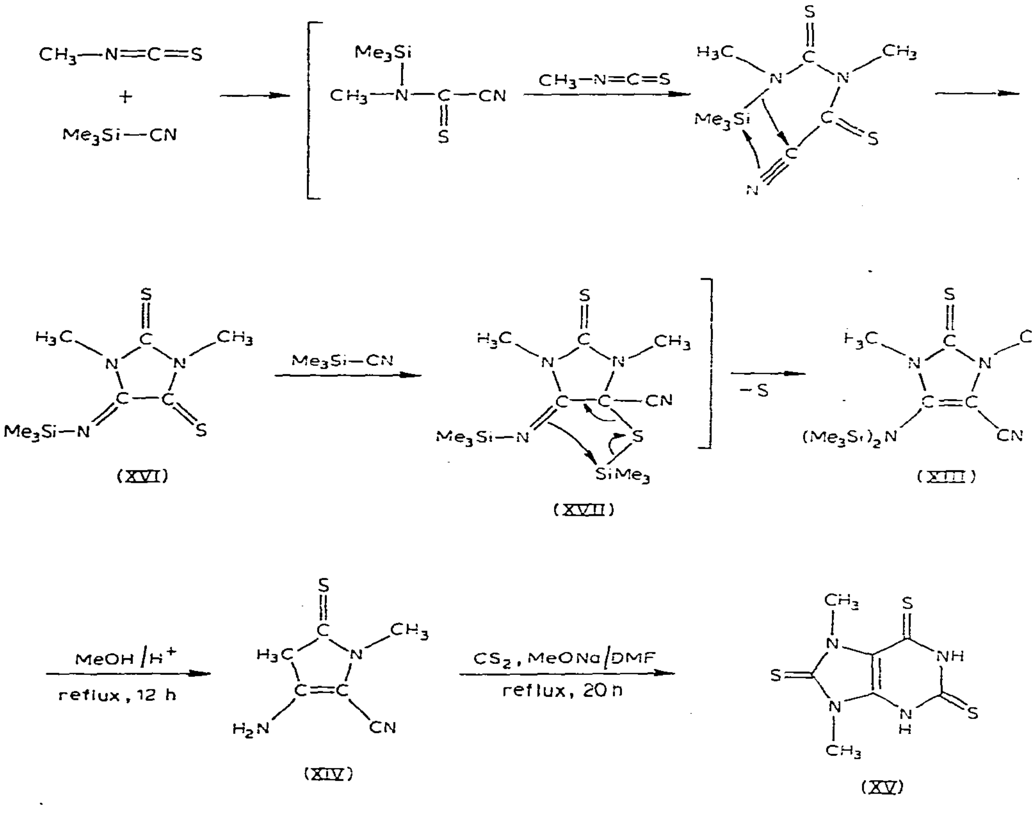
As Scheme 3 shows, the cycloaddition may not be a concerted process, but a stepwise one through the nucleophilic attack of the silylamine moiety of VI to the C=N bond of isocyanates (or carbodiimides) to form the open chain intermediate (XII), which may lead to the production of the cycloadduct (X) via an intramolecular addition of the silylamine moiety of XII to the cyano group.

Reaction of trimethylsilyl cyanide with methyl isothiocyanate

When methyl isothiocyanate was employed as substrate, another type of cycloadduct was obtained. The reaction of trimethylsilyl cyanide with methyl isothiocyanate was found to proceed without any catalyst under reflux for 26 h to give the cycloadduct, 1,3-dimethyl-4-cyano-5-bis(trimethylsilyl)aminoimidazolidine-2-thione (XIII) in 54% yield. The structure of XIII was elucidated on the basis of NMR, IR and mass spectra and elemental analyses.

The new heterocyclic compound (XIII) thus obtained was easily desilylated by methanol containing *p*-toluenesulfonic acid to give 1,3-dimethyl-4-cyano-5-aminoimidazolidine-2-thione (XIV), in quantitative yield.

SCHEME 4



As heterocyclic *ortho*-aminonitriles are known to be converted to the corresponding fused pyrimidinethiones by reaction with carbon disulfide [10], we treated XIV with carbon disulfide to afford the expected fused pyrimidinedithione, 2,4,6(5*H*,7*H*)-1,3-dimethylimidazo(4,5-*d*)pyrimidinetrithione (XV). Accordingly, the result clearly indicates that XIV has the *ortho*-aminonitrile structure. The structure of XIV was further confirmed by a positive Feigl's spot test, which indicates the existence of C=S group [11].

As for the formation of XIII, the following pathway is plausible. First, the reaction of trimethylsilyl cyanide with methyl isothiocyanate may proceed, in a manner similar to that described in the reaction with isocyanate, giving an intermediate, 5-(trimethylsilylimino)imidazolidine-2,4-dithione (XVI). However, the 4-thione group of XVI may be reactive toward nucleophilic attack by another molecule of trimethylsilyl cyanide to form a trimethylsilylthiocyanohydrin (XVII). Then, sigmatropic migration of the trimethylsilyl group from the sulfur to the nitrogen atom via a five-membered transition state would occur to give XIII.

Experimental

Measurement

Boiling points and melting points were uncorrected. The infrared spectra were measured on a Hitachi Model EPI-G3 or Model 285 spectrophotometer using samples as neat liquid or KBr disks. Nuclear magnetic resonance spectra were obtained by the use of a Varian HA 100 or T 60 spectrometer with TMS as the internal standard. Mass spectra were recorded on a Hitachi EMU-6E or EMU-6M spectrometer. Analytical gas chromatography was carried out on a Shimadzu GC-3BT using a column packed with 3% or 10% SE-30.

Materials

Trimethylsilyl cyanide was prepared by the reaction of silver cyanide with an excess of trimethylsilyl chloride [2a]. All other reagents were obtained from commercial sources and were purified by distillation or recrystallization before use.

Reaction of trimethylsilyl cyanide with aryl and alkyl isocyanates

A typical procedure is described for the reaction of trimethylsilyl cyanide with phenyl isocyanate: A mixture of trimethylsilyl cyanide (1.10 g, 11 mmol) and phenyl isocyanate (2.38 g, 20 mmol) was heated at 80°C for 24 h with stirring under nitrogen. After cooling to ambient temperature, the addition of n-pentane (5 ml) resulted in formation of pale yellow crystals which were washed with 5 ml of n-pentane to give Ia (3.07 g, 91%) as colorless needles. The sample was of satisfactory analytical purity; m.p. 118—120°C.

In similar manner, the reactions of trimethylsilyl cyanide with *p*-chlorophenyl and 1-naphthyl isocyanates gave the corresponding adducts. In the case of allyl and cyclohexyl isocyanates, the reaction was carried out in a sealed pyrex tube at 170°C for 12 h and the adduct was purified by distillation. Physical properties and spectral and analytical data for 5-(trimethylsilylimino)imidazolidine-2,4-diones (I) are summarized in Table 2.

Methanolysis of 5-(trimethylsilylimino)imidazolidine-2,4-diones

Typically, 1,3-diphenyl-5-(trimethylsilylimino)imidazolidine (Ia, 2.0 g, 5.9 mmol) was added to methanol (5 ml) and the mixture was stirred for 1 h at ambient temperature. After the removal of an excess of methanol and methoxytrimethylsilane formed under reduced pressure, the resulting crystalline product was recrystallized from ether to give colorless needles (IIa, 1.52 g, 97%); m.p. 137—138°C (lit. [9] m.p. 137°C).

Physical properties and spectral and analytical data for 5-iminoimidazolidine-2,4-diones (II) thus obtained are listed in Table 2.

Hydrolysis of 1,3-diphenyl-5-(trimethylsilylimino)imidazolidine-2,4-dione (Ia)

A solution of 1,3-diphenyl-5-(trimethylsilylimino)imidazolidine-2,4-dione (Ia, 1.0 g, 3 mmol) in 10 ml of 3 *N* hydrochloric acid was heated under reflux for 2 h. Precipitated crystals were gathered and recrystallized from ethanol to give 1,3-diphenylimidazolidine-2,4,5-trione (IIIa, 0.60 g, 75%); m.p. 205°C (lit. [9] m.p. 206—207°C).

Reaction of trimethylsilyl cyanide with p-toluenesulfonyl isocyanate

To *p*-toluenesulfonyl isocyanate (1.97 g, 10 mmol) was added dropwise trimethylsilyl cyanide (1.0 g, 10 mmol) with stirring over a period of 30 min at ambient temperature. The reaction completed to give the 1/1 adduct as viscous liquid. *N*-(*p*-Toluenesulfonyl)-*N*-trimethylsilyl-1-cyanoformamide (IVf) thus obtained was not stable enough to be distilled. NMR ($CDCl_3$): δ 0.35 (s, 9H, $SiCH_3$), 2.47 (s, 3H, CH_3), and 7.55 ppm (AB quartet, 4H, Arom). IR (neat): 1610 (ν(C=O)), 1340 and 1165 ($\nu(SO_2)$), and 1260 cm^{-1} (δ(SiMe)).

Ethanol (0.7 g) was added to the crude adduct (VIf, 10 mmol) dropwise (ice-water bath) with stirring. After the additional stirring for 1 h at ambient temperature, n-pentane (10 ml) was added to the reaction mixture to precipitate the crystalline product. The latter was collected and washed with n-pentane (10 ml) to afford *N*-(*p*-toluenesulfonyl)-1-cyanoformamide (VI, 2.20 g, 98%). M.p. 120—123°C (from ether/n-hexane). NMR ($CDCl_3$): δ 2.48 (s, 3H, CH_3), 7.53 (broad s, 1H, NH), and 7.60 ppm (AB quartet, 4H, Arom.). IR (KBr disk): 3220 (ν(NH)), 2230 (ν(C≡N)), 1740 (ν(C=O)), 1360 and 1160 cm^{-1} ($\nu(SO_2)$). (Found: C, 48.10; H, 3.88; N, 12.27; S, 14.14. $C_9H_8N_2O_3S$ calcd.: C, 48.21; H, 3.60; N, 12.49; S, 14.30%.)

Reaction of trimethylsilyl cyanide with carbodiimides

N,N'-Diisopropyl-N-trimethylsilyl-1-cyanoformamidine (VIIa). A mixture of trimethylsilyl cyanide (2.40 g, 24 mmol), aluminum trichloride (134 mg, 5 mol%) and *N,N'*-diisopropylcarbodiimide (2.52 g, 20 mmol) was stirred at ambient temperature for 4 h. n-Hexane was added to the reaction mixture to cause the precipitation of aluminum trichloride, which was filtered off. Distillation of the filtrate under reduced pressure afforded VIIa (3.78 g) in 84% yield; b.p. 74°C/4 Torr.

N,N'-Dicyclohexyl-N-trimethylsilyl-1-cyanoformamidine (VIIb). The reaction was carried out in similar manner as described above. However, distillation of the filtered reaction mixture resulted in partial decomposition (b.p. 118°C/0.3 Torr). The resulting precipitate of aluminum trichloride was filtered with G4-

glass filter under argon at —10°C and the filtrate was concentrated in vacuo. The oil obtained was pure enough to satisfy elemental analyses.

N,N'-Di-p-tolyl-N-trimethylsilyl-1-cyanoformamidine (VIIc). The reaction was carried out in similar manner as described above at 55°C for 5 h. Then, n-hexane (20 ml) was added to the reaction mixture and the solution was cooled to —10°C. The resulting precipitate was filtered (G4-glass filter) under argon. The filtrate was cooled to —78°C, giving a crystalline product. These crystals were collected (G4-glass filter) but became an oil on warming to ambient temperature. The oil was pure enough to give satisfactory elemental analyses.

Spectral and analytical data for *N*-trimethylsilyl-1-cyanoformamidines (VII) are listed in Table 4.

Reaction of N-trimethylsilyl-1-cyanoformamidines (VII) with methanol or acetyl chloride

Typically, *N,N'*-diisopropyl-*N*-trimethylsilyl-1-cyanoformamidine (VIIa, 1.13 g, 5 mmol) was allowed to react with methanol (1 ml) at ambient temperature with stirring. After the exothermic reaction had ceased, stirring was continued for 15 min. Distillation of the reaction mixture gave *N,N'*-diisopropyl-1-cyanoformamidine (VIIIa, 0.75 g) in 98% yield.

Methanolysis of VIIb and VIIc was carried out in a manner similar to that described above and the crude product was recrystallized from ether and ether/n-hexane, respectively.

A procedure for the reaction with acetyl chloride is as follows: *N*-Trimethylsilyl-1-cyanoformamidines (VII) in ether were allowed to react with 1 equivalent of acetyl chloride with stirring for 1 h and the reaction mixture was either distilled under reduced pressure or recrystallized from ether to give *N*-acetyl-1-cyanoformamidines (IX). The data for the characterization of the 1-cyanoformamidines (VIII) and *N*-acetyl-1-cyanoformamidines (IX) thus obtained are summarized in Table 4.

Reaction of N-trimethylsilyl-1-cyanoformamidines (VII) with isocyanates and carbodiimides

The reaction of *N,N'*-diisopropyl-*N*-trimethylsilyl-1-cyanoformamidine and *p*-toluenesulfonyl isocyanate is described: *p*-Toluenesulfonyl isocyanate (1.97 g, 10 mmol) was added dropwise to *N,N'*-diisopropyl-*N*-trimethylsilyl-1-cyanoformamidine (VIIa, 2.25 g, 10 mmol) in ether (10 ml) at ambient temperature. After the exothermic reaction had ceased, stirring was continued for 30 min. The addition of n-pentane (10 ml) to the reaction mixture resulted in the precipitation of the crystalline product, 1-(*p*-toluenesulfonyl)-3-isopropyl-4-isopropylimino-5-(trimethylsilylimino)imidazolidin-2-one (Xa, 4.18 g, 99%), which was pure enough to give satisfactory elemental analyses; m.p. 90—92°C.

In similar manner, the reaction of VIIa with phenyl isocyanate was performed without solvent at 80°C for 14 h to yield the corresponding cycloadduct (Xb) as colorless leaflets in 87% yield.

In the case of the reaction with diisopropyl- and di-*p*-tolyl carbodiimides, the reaction was carried out in a sealed tube at 190°C for 60 h and 34 h, respectively.

Methanolysis of Xa—Xd thus obtained was carried out using an excess of methanol at ambient temperature for 1 h, and the resulting crystalline product was purified by recrystallization from ether or methanol to give 4,5-diiminoimidazolidin-2-ones (XIa, XIb) or 2,4,5-triiminoimidazolidines (XIc, XId).

Physical properties and spectral and analytical data for 5-(trimethylsilylimino)imidazolidin-2-ones (Xa, Xb), 5-(trimethylsilylimino)imidazolidines (Xc, Xd) and their desilylated derivatives (XI) are summarized in Table 5.

Reaction of trimethylsilyl cyanide with methyl isothiocyanate

A mixture of trimethylsilyl cyanide (2.0 g, 20 mmol) and methyl isothiocyanate (1.46 g, 20 mmol) was heated under reflux for 26 h. After the reaction mixture had been cooled to ambient temperature, n-hexane (3 ml) was added. The resulting precipitate was recrystallized from ether to give 1,3-dimethyl-4-cyano-5-bis(trimethylsilyl)aminoimidazolidine-2-thione (XIII, 1.68 g) as colorless needles in 54% yield. M.p. 132—135°C. IR (KBr disk): 2220 (ν(C≡N)), 1600 (ν(C=C)), and 1250 cm^{-1} (δ(SiMe)). NMR ($CDCl_3$): δ 0.23 (s, 18H, SiMe), 3.40 (s, 3H, CH_3), and 3.67 ppm (s, 3H, CH_3). Mass spectrum (100°C, 70 eV): *m/e* 312 (M^+). (Found: C, 46.08; H, 7.66; N, 17.96; S, 10.26. $C_{12}H_{24}N_4SSi_2$ calcd.: C, 46.11; H, 7.74; N, 17.92; S, 10.26%.)

XIII thus obtained was desilylated as follows: A mixture of XIII (1.0 g, 3.21 mmol) and *p*-toluenesulfonic acid (60 mg) in methanol was heated at reflux for 12 h, and the resulting precipitates were recrystallized from acetone to give 1,3-dimethyl-4-cyano-5-aminoimidazolidine-2-thione (XIV, 0.54 g, 100%) as pale yellow needles. M.p. 252—254°C. IR (KBr disk): 2220 (ν(C≡N)) and 1670 cm^{-1} (ν(C=C)). NMR (acetone-d_6): δ 3.47 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), and 6.13 ppm (broad s, 2H, NH_2). Mass spectrum (150°C, 70 eV): *m/e* 168 (M^+, base peak). (Found: C, 43.10; H, 4.59; N, 33.38; S, 18.81. $C_6H_8N_4S$ calcd.: C, 42.84; H, 4.79; N, 33.31; S, 19.06%.)

2,4,6(5H,7H)-1,3-Dimethylimidazo(4,5-d)pyrimidinetrithione (XV). A mixture of XIV (0.76 g, 4.5 mmol), carbon disulfide (8.5 ml) and sodium methoxide (0.43 g) in *N,N*-dimethylformamide (20 ml) was heated at reflux for 20 h. The solvents were removed by distillation under reduced pressure and the residue was dissolved in diluted NaOH, and filtered with G-3 glass filter. The filtrate was acidified with aqueous hydrochloric acid to afford the precipitate, which was recrystallized from ethanol to give XV (0.62 g) as yellow needles in 56% yield; m.p. >300°C. IR (KBr disk): 3200—2500 (ν(NH) and ν(SH)) and 1530 cm^{-1} (δ(NH)). NMR (DMSO-d_6): δ 3.53 (s, 3H, CH_3), 3.97 (s, 3H, CH_3) and 6.13 ppm (broad s, 2H, NH and SH). Mass spectrum (100°C, 70 eV): *m/e* 244 (M^+, base peak). (Found: C, 34.54; H, 3.23; N, 23.06; S, 38.98. $C_7H_8N_4S_3$ calcd.: C, 34.41; H, 3.30; N, 22.93; S, 39.36%.)

References

1 W. Lidy and W. Sundermeyer, Chem. Ber., 106 (1973) 587; H. Neef and R. Müller, J. Prakt. Chem., 315 (1973) 367; H. Neef, ibid., 316 (1974) 817; D.A. Evans, L.K. Truesdale, and G.L. Carroll, J. Chem. Soc. Chem. Commun., (1973) 55; D.A. Evans and L.K. Truesdale, Tetrahedron Lett., (1973) 4929.

2 (a) D.A. Evans, J.M. Hoffman, and L.K. Truesdale, J. Amer. Chem. Soc., 95 (1973) 5822; (b) D.A. Evans and J.M. Hoffman, ibid., 98 (1976) 1983; (c) D.A. Evans and R.Y. Wong, J. Org. Chem., 42

(1977) 350; (d) D.J. Hart, P.A. Cain and D.A. Evans, J. Amer. Chem. Soc., 100 (1978) 1548.
3 K. Deuchert, U. Hertenstein and S. Hünig, Synthesis, (1973) 777; S. Hünig and G. Wenner, ibid., (1975) 180, 391.
4 D.A. Evans, G.L. Carroll and L.K. Truesdale, J. Org. Chem., 39 (1974) 914.
5 I. Ojima, S. Inaba, K. Nakatsugawa and Y. Nagai, Chem. Lett., (1975) 331; I. Ojima, S. Inaba and Y. Nagai, ibid., (1975) 737.
6 Y. Nakajima, T. Makino, J. Oda and Y. Inouye, Agr. Biol. Chem., 39 (1975) 571.
7 U. Hertenstein and S. Hünig, Angew. Chem., 87 (1975) 195.
8 (a) I. Ojima, S. Inaba and Y. Nagai, J. Chem. Soc. Chem. Commun., (1974) 826; (b) idem, J. Organometal. Chem., 99 (1975) C5.
9 T.L. Patton, J. Org. Chem., 32 (1967) 383.
10 E.C. Taylor, A. McKillop,and R.N. Warrender, Tetrahedron, 23 (1967) 891.
11 F. Feigl, Spot Test in Organic Chemistry, 6th ed., Elsevier, Amsterdam, 1960, p. 242.