

REDUCTION OF ISOCYANATES AND CARBODIIMIDES VIA HYDROSILYLATION

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Summary

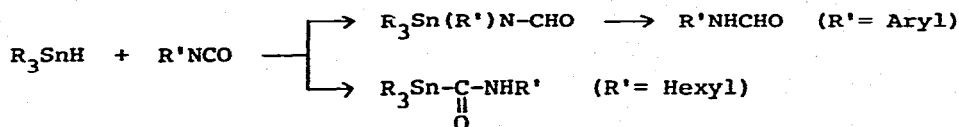
The hydrosilylation of isocyanates is promoted by palladium catalysts and affords N-silylformamides or C-silylamides. The orientation of the reaction depended upon the structure of isocyanates. The reaction of carbodiimides with silicon hydrides, catalyzed by PdCl_2 or $(\text{Ph}_3\text{P})_3\text{RhCl}$, required higher temperatures to give N-silylformamidines. The adducts obtained in these reactions are precursors to formamides, formamidines, and their N-acetyl derivatives.

Introduction

Although the hydrosilylation of carbon-carbon multiple bonds has been studied extensively [1], that of carbon-heteroatom multiple bonds has received less attention. Recently, it has been shown that the hydrosilylation of carbon-heteroatom multiple bonds provides a powerful method for the reduction of carbonyl compounds [2] and imines [3]. However, there have been no reports on the hydrosilylation of heterocumulenes.

Among the hydrides of the Group IV elements, only organotin hydrides were reported to add to the carbon-nitrogen double bond of isocyanates to afford triorgano(N-alkylcarbamoyl)tin or triorgano(N-arylformamido)tin compounds. These can be converted further to N-arylformamide by reaction with an organotin hydride

[4]. It also has been shown that the hydrostannation of carbodiimides using AIBN as initiator gives N-trialkylstannylformamidines [5].



One of the reasons why the corresponding reactions of hydrosilanes have not been reported may be that they lack reactivity toward isocyanates and carbodiimides in the absence of a proper catalyst.

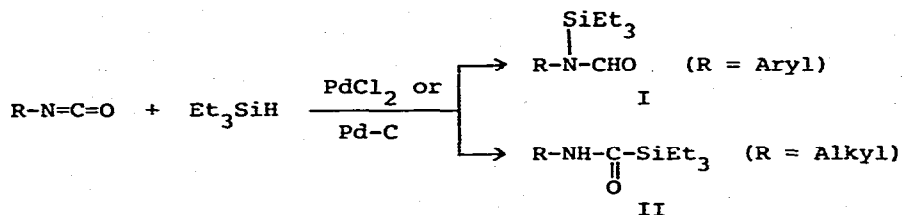
We have found that the hydrosilylation of isocyanates and carbodiimides is promoted by transition metal catalysts such as $PdCl_2$, $Pd-C$, and $(Ph_3P)_3RhCl$, and have reported briefly about these reactions [6]. We provide here a full account of our research on the reactivities of hydrosilanes toward these heterocumulenes in the presence of transition metal catalysts.

Results and Discussion

Hydrosilylation of isocyanates

The hydrosilylation of isocyanates was found to take place in the presence of a catalytic amount of palladium dichloride to afford 1:1 adducts in good yield. It also was found that $Pd-C$ was another effective catalyst for the hydrosilylation of an aryl isocyanate, but it displayed less catalytic activity in analogous reactions with alkyl isocyanates. On the other hand, tris(triphenylphosphine)chlororhodium did not show any catalytic activity in the hydrosilylation of isocyanates, although the rhodium complex had been shown to be an excellent catalyst for the hydrosilylation of carbonyl and imino compounds [2,3]. The hydrosilylation of isocyanates in the presence of the palladium

catalyst, using triethylsilane gave either N-triethylsilylformamides (I) or C-triethylsilylamides (II). Thus, the reaction of aryl isocyanates afforded the former (I) as sole product* *via* normal addition of triethylsilane to the C=N bond of $\text{Ar-N}=\text{C}=\text{O}$, while alkyl isocyanates reacted to give the latter (II) exclusively *via* reverse addition of the hydrosilane to the C=N bond.



The results are summarized in Table 1. The data on the characterization of the adducts are listed in Table 2. As Table 2 shows, the IR spectrum of N-silylformamide (I) does not show any NH stretching band in the $3100\text{--}3400\text{ cm}^{-1}$ region, while that of the C-silylamide (II) shows both an NH stretching band in the $3250\text{--}3300\text{ cm}^{-1}$ region and an amide II band at 1530 cm^{-1} . It should be noted that the C-silylamide (II) shows an amide I band in the ordinary region, although silyl ketones are known to show a characteristic C=O stretching band in the lower frequency region [7].

The IR spectra of N-silylformamides (I) show two absorption bands in the $1600\text{--}1700\text{ cm}^{-1}$ range and their NMR spectra display two singlets in the $\delta 7\text{--}9$ ppm region. Similarly, the NMR spectrum of the C-silylamide, IIe, shows two singlets around $\delta 8$ ppm, whereas that of IIId does only one singlet at $\delta 7.37$

* In our preliminary communication [6a] we reported an erroneous structure about adduct (Ic) from phenyl isocyanate. A careful reinvestigation revealed that the adduct was N-phenyl-N-triethylsilylformamide. Our mistaken structural assignment is due mainly to the hydrolysis of Ic during the measurement of its IR spectrum.

Table 1. The Reactions of Isocyanates with Triethylsilane Catalyzed by PdCl_2 or Pd-C

	R	Conditions	Catalyst ^{a)}	Product	Yield (%)	bp (°C/Torr)
a	1-Naphthyl	80°, 6 hr	PdCl_2	Ia	97	152/0.17
b	p-Chlorophenyl	80°, 12 hr	PdCl_2	Ib	85	110/0.5
c	Phenyl	130°, 12 hr	PdCl_2	Ic	95	90/0.45
		130°, 48 hr ^{b)}	Pd-C	Ic	88	
d	Cyclohexyl	80°, 12 hr	PdCl_2	IIId	90	72/0.2
		180°, 48 hr ^{b)}	Pd-C	IIId	10	
e	n-Butyl	130°, 12 hr	PdCl_2	IIe	46	82/1.0

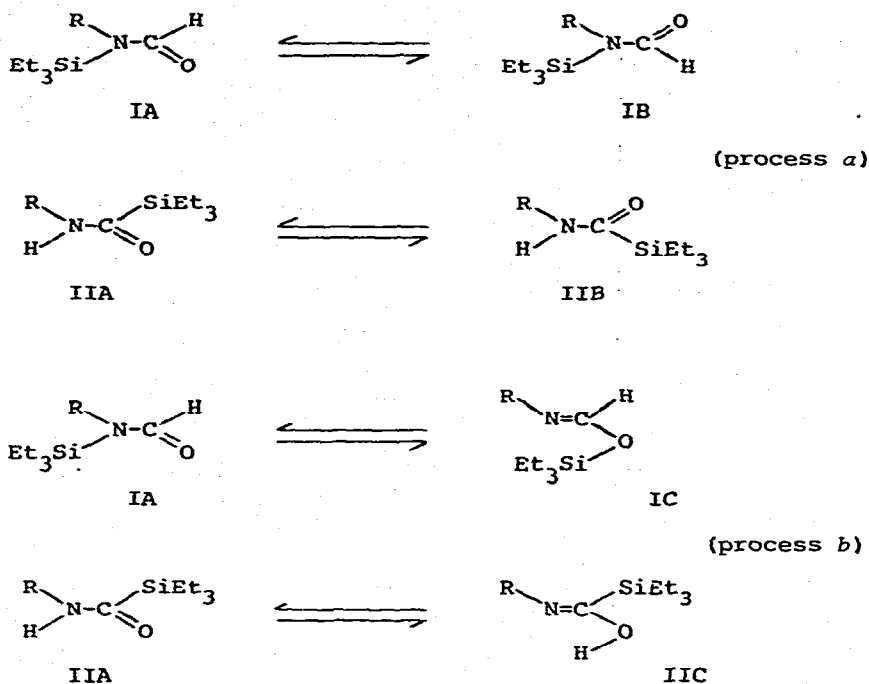
a) All reactions were run with 20 mmol of isocyanate, and 20 mmol of triethylsilane in the presence of 35 mg of PdCl_2 or 30 mg of 10% Pd-C without solvent. b) Reaction was carried out in a sealed tube.

Table 2. Spectral and Analytical Data for N-Triethylsilylformamides (I) and C-Triethylsilylamides

Compound	IR (cm^{-1})			NMR (δ , CCl_4)		Analysis, found (calcd.) (%)	
	ν_{NH}	$\nu_{\text{C=O}}$	Amide II	$\text{NH}^{\text{a)}$	$\text{CHO}^{\text{a)}$	C	H
Ia	---	1670 1630	---	---	--- ^{b)}	71.27 (71.53)	8.11 (8.12)
Ib	---	1680 1630	---	---	7.59(4) 8.23(1)	57.93 (57.86)	7.40 (7.47)
Ic	---	1675 1630	---	---	7.64(2) 8.27(1)	66.08 (66.33)	8.66 (8.91)
IIId	3250	1650	1530	7.37	---	64.85 (64.67)	11.09 (11.27)
IIe	3300	1670	1530	8.12(3) 8.17(1)	---	61.05 (61.33)	11.53 (11.70)

a) The value in the parentheses represents the relative peak area b) A signal of the aldehyde proton of this compound overlaps in aromatic protons

ppm. These phenomena can be interpreted by either hindered rotation around C-N bond (process a) or amide-imide exchange (process b). According to the conclusions of Yoder and Belber, who carried out NMR studies on the structure of N-trimethylsilyl-anilides [8], the two species observed in the NMR spectrum of



an N-trimethylsilylanilide at ambient temperature should be assigned to the amide form and the imidate form. Consequently, it is strongly suggested that N-silylformamide (I) exists as a mixture of the tautomers IA and IC. On the other hand, in the case of N-monosubstituted amides, such a phenomenon has been explained by the existence of two rotamers caused by the hindered rotation around the C-N bond [9]. Thus, it is reasonable to assume that the C-silylamide, IIe, exists as a mixture of the rotamers IIA and IIB. As for the C-silylamide, IID, the severe steric repulsion between the cyclohexyl group and the triethylsilyl group may force the equilibrium to the side of the *trans* form, and this may be the reason why only one singlet due to an

NH proton could be observed in its NMR spectrum[‡].

Reactions of hydrosilylated products with methanol and acetyl chloride

The N-triethylsilylformamides (I) thus obtained were easily desilylated by methanol at room temperature to give N-arylformamides (IIIa-c) in quantitative yields. Similarly, the C-triethylsilylamides (II) also reacted with methanol to give N-alkylformamides (IIIId,e). The data for identification of these formamides (III) are listed in Table 3. These results are distinctly different from those obtained in the reduction of isocyanates with LiAlH_4 , which produces N-methylamines [10]. Accordingly, the hydrosilylation followed by methanolysis, which gives N-substituted formamides provides a new method for the reduction of isocyanates.

Table 3. Spectral and Physical Data for Formamides (III)

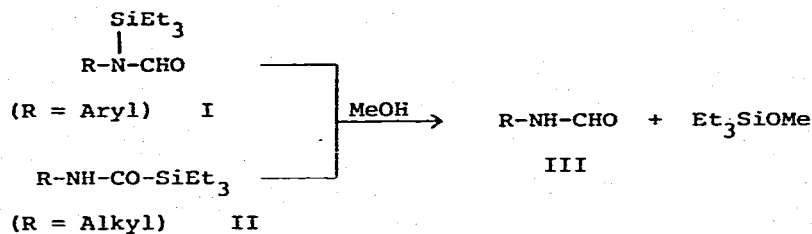
Compound	IR (cm^{-1})			NMR (δ)		mp($^{\circ}\text{C}$) or bp($^{\circ}\text{C}/\text{Torr}$)
	ν_{NH}	Amide I	Amide II	NH ^{b)}	CHO	
IIIa	3200	1655	1535	8.63	8.63	141-143 (lit.[12], 137)
IIIb	3230	1655	1535	7.92 8.69	8.30 8.69	101-102 (lit.[13], 100-102)
IIIc	3240	1670	1555	8.61 9.00	8.35 8.79	42-44 (lit.[14], 47.5)
IIId	3250	1660	1530	7.77	7.79 ^{c)} 8.02	89/0.4 (lit.[15], 155-157/22)
IIIe	3260	1660	1530	7.05	7.80 ^{c)} 8.03	110/26 (lit.[15], 122-123/16)

a) Measured in CDCl_3 unless otherwise noted. b) The signal(s) disappeared on treatment with D_2O

c) Measured in CCl_4

[‡] The following possible explanations for the presence of only one NH peak in the NMR spectrum of IId cannot be excluded:

a) exchange of NH protons, b) coincidental equivalence of the chemical shifts of the two rotamers, and c) rapid rotation about the C(O)-N bond.



On the other hand, both the N-silylformamide (I) and the C-silylamide (II) were found to be excellent precursors for N-acetylformamide (IV), as the reactions of these silylamides with acetyl chloride proceeded very smoothly at room temperature to give N-acetylformamides (IV) in nearly quantitative yields. The data for identification of N-acetylformamides (IV) are presented in Table 4. The acetylation of I may proceed *via* a four center transition state which affords IV and triethylchlorosilane, while the formation of an N-acetyl-C-silylamide

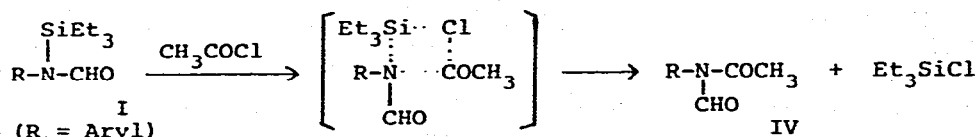
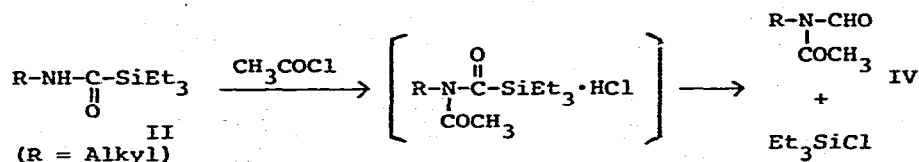


Table 4. Spectral and Physical Data for N-Acetylformamides (IV)

Compound	IR (cm ⁻¹)	NMR (δ) ^{a)}		mp(°C) or bp(°C/Torr)	Analysis, found (calcd.)(%)	
	ν _{C=O}	CH ₃ CO	CHO		C	H
IVa	1725 1685	1.94	10.60	79-81	73.51 (72.23)	5.04 (5.20)
IVb	1725 1695	2.02	9.30	78-80	54.80 (54.70)	4.04 (4.08)
IVc	1720 1685	2.05	9.40	50-53 (lit.[16], 55)		
IVd	1720 1670	2.40	9.07 ^{b)}	89-90/0.8 (lit.[16], 74-75/0.2)		
IVe	1730 1670	2.41	9.17 ^{b)}	117/26 (lit.[16], 74.5-75.5/0.70-0.75)		

a) Measured in CDCl₃ unless otherwise noted b) Measured in CCl₄



which is further converted to IV and triethylchlorosilane by the action of *in situ* generated hydrogen chloride may be the first step in the acetylation of II.

Hydrosilylation of carbodiimides

The hydrosilylation of carbodiimides proceeded at higher temperature in the presence of catalytic amounts of either palladium dichloride or tris(triphenylphosphine)chlororhodium to afford N-silylformamidines (V) in high yield. The formation of C-silylamidines was not observed. The yield of the product in the palladium dichloride-catalyzed reaction depended on the reaction conditions and good results were obtained at relatively high temperature (200°C), although the reaction proceeded even at 120°C. In the case of the rhodium catalyst, the most suit-

Table 5. Hydrosilylation of Carbodiimides Catalyzed by PdCl_2 or $(\text{Ph}_3\text{P})_3\text{RhCl}$

Carbodiimide	Hydrosilane ^{a)}	Catalyst ^{b)}	Conditions	Conversion ^{c)} (%)	Yield ^{d)} (%)
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	Et_3SiH	PdCl_2	140°, 15 hr	84	98
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	EtMe_2SiH	PdCl_2	140°, 15 hr	75	93
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	EtMe_2SiH	PdCl_2	200°, 48 hr	92	97
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	PhMe_2SiH	PdCl_2	200°, 48 hr	100	83
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	EtMe_2SiH	$(\text{Ph}_3\text{P})_3\text{RhCl}$	140°, 15 hr	80	60
$\text{Pr}^i-\text{N}=\text{C}=\text{N}-\text{Pr}^i$	PhMe_2SiH	$(\text{Ph}_3\text{P})_3\text{RhCl}$	150°, 36 hr	100	80
$\text{C}_6\text{H}_{11}-\text{N}=\text{C}=\text{N}-\text{C}_6\text{H}_{11}$ ^{e)}	Et_3SiH	PdCl_2	200°, 48 hr	96	96
$\text{C}_6\text{H}_{11}-\text{N}=\text{C}=\text{N}-\text{C}_6\text{H}_{11}$ ^{e)}	EtMe_2SiH	PdCl_2	200°, 48 hr	64	95
$\text{C}_6\text{H}_{11}-\text{N}=\text{C}=\text{N}-\text{C}_6\text{H}_{11}$ ^{e)}	Et_3SiH	$(\text{Ph}_3\text{P})_3\text{RhCl}$	140°, 15 hr	60	75

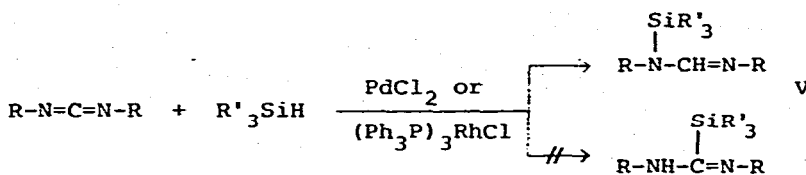
a) 10-50% excess hydrosilane was used b) 1 mol% of PdCl_2 or 0.5 mol% of $(\text{Ph}_3\text{P})_3\text{RhCl}$ was used based on a carbodiimide c) Conversion based on a carbodiimide was determined by GLC analysis d) Yield was determined by GLC analysis based on a carbodiimide consumed e) C_6H_{11} = cyclohexyl

Table 6. Spectral and Analytical Data for N-Silylformamidines (V)

N-Silylformamidine	bp (°C/Torr)	IR (cm ⁻¹) ν _{C=N}	NMR (δ) CH=N	Analysis, found (calcd.)(%)	
				C	H
a Pr ⁱ (Et ₃ Si)N-CH=N-Pr ⁱ	75/1.1	1630	7.43	64.12 (64.39)	12.31 (12.47)
b Pr ⁱ (EtMe ₂ Si)N-CH=N-Pr ⁱ	58/4	1640	7.49	61.64 (61.62)	11.95 (12.22)
c Pr ⁱ (PhMe ₂ Si)N-CH=N-Pr ⁱ	80/0.4	1635	--- ^{a)}	68.57 (68.64)	9.75 (9.98)
d C ₆ H ₁₁ (Et ₃ Si)N-CH=N-C ₆ H ₁₁	133/0.4	1630	7.53	70.95 (70.74)	12.07 (11.87)
e C ₆ H ₁₁ (EtMe ₂ Si)N-CH=N-C ₆ H ₁₁	96/0.1	1640	7.50	69.27 (69.32)	11.37 (11.63)

a) A signal of the methine proton of this compound overlaps in phenyl protons b) C₆H₁₁ = cyclohexyl

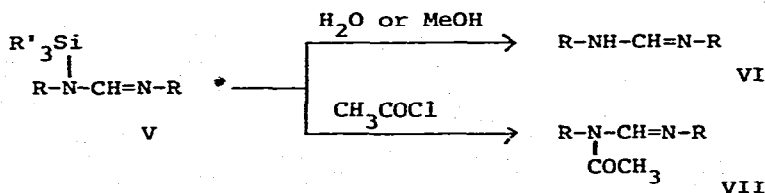
able temperature range was 130–150°C. In the absence of these catalysts, the hydrosilane did not add to the carbodiimides, even at 200°C for 36 hr.



The results of the hydrosilylation of N,N'-diisopropyl- and N,N'-dicyclohexylcarbodiimides using various hydrosilanes are illustrated in Table 5. The data for identification of the adducts are listed in Table 6. The IR spectra of the adducts show no band due to NH stretching, and their NMR spectra display a singlet in the δ 7.4–7.5 ppm region, which is reliably assigned to the vinylogous proton.

The N-silylformamidines (V) reacted exothermally with water or methanol to give formamidines (VI) in quantitative yield. Thus, the hydrosilylation of carbodiimides, followed by hydrolysis, provides a novel route to formamidines. In a manner

similar to that of N-silylformamides, the reaction of V with an equimolar amount of acetyl chloride at room temperature resulted in the production of N-acetylformamidine (VII) in nearly quantitative yield.



Experimental

Measurement

Boiling points and melting points were uncorrected. The infrared spectra were measured on a Hitachi EPI-G3 spectrophotometer using samples as neat liquid or in KBr disks. The nuclear magnetic resonance spectra were obtained using a Varian T-60 or a Hitachi R-20B spectrometer, with TMS as the internal standard. Analytical gas chromatography (GLC) was carried out on a Shimadzu GC-3BT using a column packed with 3% or 20% SE-30.

Materials

Hydrosilanes were prepared by known methods. Tris(triphenylphosphine)chlororhodium was prepared from rhodium trichloride trihydrate and triphenylphosphine [11]. Palladium dichloride and 10% palladium-on-carbon were obtained commercially from Wako Pure Chemical Industries LTD and Nippon Engelhard, respectively. Isocyanates and carbodiimides were obtained from commercial sources and were purified by distillation or recrystallization before use.

Hydrosilylation of aryl and alkyl isocyanates

A typical procedure is described for the hydrosilylation

of 1-naphthyl isocyanate with triethylsilane. A mixture of triethylsilane (2.34 g, 20 mmol), 1-naphthyl isocyanate (3.38 g, 20 mmol) and palladium dichloride (35 mg, 1 mol%) was heated at 80°C for 6 hr with stirring under nitrogen. The progress of the reaction was checked by GLC analysis (3% SE-30, 1m, 200°C). After the reaction mixture had been cooled to ambient temperature, dry ether (5 ml) was added and the precipitated catalyst was filtered. The filtrate was distilled under reduced pressure to give 5.07 g of N-(1-naphthyl)-N-triethylsilylformamide (Ia, 89%). (GLC yield 97%).

The results employing different isocyanates are summarized in Table 1 and the characterization data of N-silylformamides (Ia-Ic) and C-silylamides (IIId and IIe) are listed in Table 2.

Methanolysis of N-triethylsilylformamides (I) and C-triethylsilylamides (II)

Typically, N-(1-naphthyl)-N-triethylsilylformamide (Ia, 0.7 g, 2.5 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. The addition of hexane (10 ml) to the reaction mixture resulted in the formation of prisms of N-(1-naphthyl)formamide (IIIa), which were collected on a glass filter (0.4 g, 94%).

Physical properties and spectral data of the formamides (III) thus obtained are summarized in Table 3.

Reaction of N-triethylsilylformamides (I) and C-silylformamides (II) with acetyl chloride

A typical procedure is as follows: N-(1-naphthyl)-N-triethylsilylformamide (Ia, 1.0 g, 3.5 mmol) was added to acetyl chloride (0.28 g, 3.6 mmol) at room temperature. After the exothermic reaction had ceased, stirring was continued for 15 min.

The addition of hexane (15 ml) to the reaction mixture resulted in the precipitation of the colorless needles of N-(1-naphthyl)-N-acetylformamide, IVa, 0.71 g (95%).

The characterization data of the N-acetylformamides (IV) thus obtained are summarized in Table 4.

Hydrosilylation of carbodiimides

The hydrosilylation of N,N'-diisopropylcarbodiimide by triethylsilane is described. A mixture of N,N'-diisopropylcarbodiimide (2.52 g, 20 mmol), triethylsilane (2.78 g, 24 mmol) and palladium dichloride (35 mg, 1 mol%) was sealed in a pyrex tube and was heated at 150°C for 15 hr. Distillation of the reaction mixture gave N,N'-diisopropyl-N-triethylsilylformamidine (Va, 3.95 g) in 82% yield. The results are summarized in Table 5. The spectral and analytical data on the characterization of the N-silylformamidines (Va-e) are listed in Table 6.

Reaction of N-silylformamidines (V) with methanol

N-Silylformamidines (V) were allowed to react with methanol in a similar manner to that described for the reaction of N-silylformamides (I). Excess methanol and methoxytriethylsilane were evaporated under reduced pressure and the resulting colorless solid was purified by sublimation or recrystallization to give the pure formamidine (VI). N,N'-Diisopropylformamidine (VIa): Yield 98%. Colorless needles, m.p. 47-48°C. NMR(CCl₄): δ 1.10(d, J=6Hz, 12H, CH₃), 3.43(septet, J=6Hz, 2H, CH), 4.77(s, 1H, NH) and 7.30(s, 1H, -CH=N). IR(neat): 3250(ν_{NH}) and 1650 cm⁻¹($\nu_{\text{C=N}}$). (Found: C, 65.34; H, 12.35. C₇H₁₆N₂ Calcd.: C, 65.57; H, 12.58%.) N,N'-Dicyclohexylformamidine (VIb): Yield 97%. Colorless prisms from hexane, m.p. 101-102°C (lit. [17] 100-102°C). NMR(CDCl₃): δ 0.73-2.10(m, 20H, CH₂), 2.66-3.37(m, 2H, CH), 4.43(s, 1H, NH) and 7.22(s, 1H, -CH=N). IR

(neat): 3180, 3120, 3075 (ν_{NH}) and 1670 cm^{-1} ($\nu_{\text{C=N}}$).

Reaction of N-silylformamidines (V) with acetyl chloride

N-Triethylsilylformamidines (V) were allowed to react with acetyl chloride with stirring at ambient temperature for 1 hr in a manner similar to that described above. The reaction mixture either was distilled under reduced pressure or the crude product was recrystallized from hexane to give the N-acetylformamidines (VII). N,N'-Diisopropyl-N-acetylformamidine (VIIa): Yield 35%. B.p. 44°C/0.4 Torr. NMR(CCl_4): δ 1.13(d, J=6Hz, 6H, CH_3), 1.33(d, J=7Hz, 6H, CH_3), 2.17(s, 3H, CH_3CO), 3.30 (septet, J=6Hz, 1H, CH), 4.77(septet, J=7Hz, 1H, CH) and 8.05 (s, 1H, CH=N). IR(neat): 1690 ($\nu_{\text{C=O}}$) and 1640 cm^{-1} ($\nu_{\text{C=N}}$). (Found: C, 63.65; H, 10.80. $\text{C}_9\text{H}_{18}\text{N}_2\text{O}$ Calcd.: C, 63.49; H, 10.66%). N,N'-Dicyclohexyl-N-acetylformamidine (VIIb): Yield 95%. Colorless needles, m.p. 80-81°C. NMR(CDCl_3): δ 1.08-2.60 (m, 20H, CH_2), 2.33(s, 3H, CH_3CO), 3.19(m, 1H, CH), 4.43(triplet of triplet, J=3, 12Hz, 1H, CH) and 8.27(broad s, 1H, CH=N). IR(KBr disk): 1675 ($\nu_{\text{C=O}}$) and 1640 cm^{-1} ($\nu_{\text{C=N}}$). (Found: C, 71.65; H, 10.38. $\text{C}_{15}\text{H}_{26}\text{N}_2\text{O}$ Calcd.: C, 71.95; H, 10.47%.)

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