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Preliminary communication

SYNTHESES OF *N*-SILYLFORMAMIDINES BY THE HYDROSILYLATION OF CARBODIIMIDES

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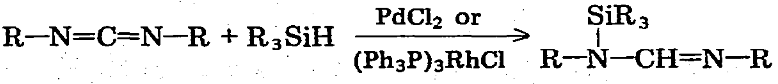
Summary

The hydrosilylation of carbodiimides was found to proceed at higher temperatures in the presence of catalytic amounts of palladium chloride or tris(triphenylphosphine)chlororhodium to afford *N*-silylformamidines in high yield. These were found to be good precursors to formamidines and *N*-acetylformamidines.

Organotin hydrides are known to add to isocyanates [1] and carbodiimides [2]. However, the corresponding reaction of organosilicon hydrides or organogermanium hydrides has not been reported, except for our recent work on the hydrosilylation of isocyanates catalyzed by palladium [3]. Now, we wish to report that the hydrosilylation of carbodiimides is catalyzed by palladium chloride or tris(triphenylphosphine)chlororhodium.



$$R{-}N{=}C{=}N{-}R + R_3SiH \xrightarrow[(Ph_3P)_3RhCl]{PdCl_2\ \text{or}} R{-}\overset{\overset{\displaystyle SiR_3}{|}}{N}{-}CH{=}N{-}R$$

R = isopropyl, cyclohexyl (I)

A typical procedure is as follows: a mixture of *N*,*N'*-diisopropylcarbodiimide (2.52 g, 20 mmol), triethylsilane (2.78 g, 24 mmol) and palladium chloride (35 mg, 0.2 mmol) was sealed in a pyrex tube and heated at 150° for 15 h. Distillation of the reaction mixture gave *N*,*N'*-diisopropyl-*N*-triethylsilylformamidine (3.95 g) in 82% yield. The yield of the product in the palladium chloride catalyzed reaction depends on the reaction conditions and good results were obtained at relatively high temperatures (~ 200°), although the reaction proceeds even at 120°. In the case of the rhodium catalyst, the most suitable temperature range is 130—150°. In the absence of these catalysts, the hydro-

TABLE 1

HYDROSILYLATION OF CARBODIIMIDES CATALYZED BY $\mathrm{PdCl_2}$ OR $\mathrm{(Ph_3P)_3RhCl}$

Carbodiimide	Hydrosilane [a]	Catalyst [b]	Conditions	Conversion [c] (%)	Yield (%)
i-Pr—N=C=N—Pr-i	$\mathrm{Et_3SiH}$	$\mathrm{PdCl_2}$	140°, 15 h	84	98
i-Pr—N=C=N—Pr-i	$\mathrm{EtMe_2SiH}$	$\mathrm{PdCl_2}$	140°, 15 h	75	93
i-Pr—N=C=N—Pr-i	$\mathrm{EtMe_2SiH}$	$\mathrm{PdCl_2}$	200°, 48 h	92	97
i-Pr—N=C=N—Pr-i	$\mathrm{PhMe_2SiH}$	$\mathrm{PdCl_2}$	200°, 48 h	100	83
i-Pr—N=C=N—Pr-i	$\mathrm{EtMe_2SiH}$	$\mathrm{(Ph_3P)_3RhCl}$	140°, 15 h	80	60
i-Pr—N=C=N—Pr-i	$\mathrm{PhMe_2SiH}$	$\mathrm{(Ph_3P)_3RhCl}$	150°, 36 h	100	80
$\mathrm{C_6H_{11}—N{=}C{=}N—C_5H_{11}}$ [e]	$\mathrm{Et_3SiH}$	$\mathrm{PdCl_2}$	200°, 48 h	96	96
$\mathrm{C_6H_{11}—N{=}C{=}N—C_6H_{11}}$	$\mathrm{EtMe_2SiH}$	$\mathrm{PdCl_2}$	200°, 48 h	64	95
$\mathrm{C_6H_{11}—N{=}C{=}N—C_6H_{11}}$	$\mathrm{Et_3SiH}$	$\mathrm{(Ph_3P)_3RhCl}$	140°, 15 h	60	75

[a] 10—50% excess hydrosilane was used. [b] 1 mol% of $\mathrm{PdCl_2}$ or 0.5 mol% of $\mathrm{(Ph_3P)_3RhCl}$ was used based on a carbodiimide. [c] Conversion based on a carbodiimide was determined by GLPC analysis. [d] Yield was determined by GLPC analysis based on carbodiimide consumed. [e] $\mathrm{C_6H_{11}}$ = cyclohexanyl.

silanes employed did not add at all to carbodiimides even at 200° (36 h reaction time). Results are summarized in Table 1.

The IR spectra of the adducts showed no absorption band due to NH stretching, and their NMR spectra displayed a singlet in the region δ 7.4—7.5 ppm which is assigned to a methine proton. Thus, the adducts are *N*-silylformamidines (I). Spectral data for these products are shown in Table 2.

TABLE 2

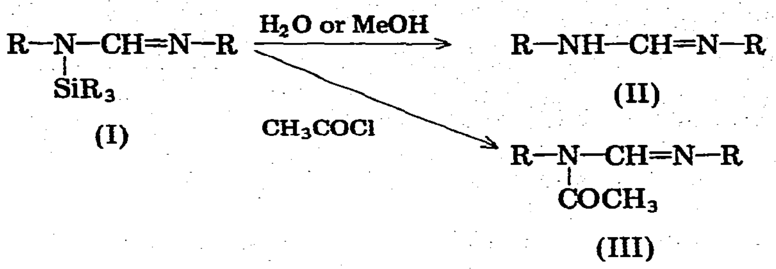
SPECTRAL DATA FOR THE OBTAINED *N*-SILYLFORMAMIDINES [a]

N-Silylformamidine	B.p. (°C/mmHg)	IR ($\mathrm{cm^{-1}}$)	NMR (δ, ppm)
		ν(C=N)	CH=N
$\mathrm{i\text{-}Pr(Et_3Si)N—CH{=}N—Pr\text{-}i}$	75/1.11	1630	7.43
$\mathrm{i\text{-}Pr(EtMe_2Si)N—CH{=}N—Pr\text{-}i}$	58/4	1640	7.49
$\mathrm{i\text{-}Pr(PhMe_2Si)N—CH{=}N—Pr\text{-}i}$	80/0.4	1635	[b]
$\mathrm{C_6H_{11}(Et_3Si)N—CH{=}N—C_6H_{11}}$ [c]	133/0.4	1630	7.53
$\mathrm{C_6H_{11}(EtMe_2Si)N—CH{=}N—C_6H_{11}}$	96/0.1	1640	7.50

[a] IR, NMR and elemental analyses for the new compounds are consistent with the assigned structures.
[b] A signal of the methine proton of this compound overlaps in phenyl protons. [c] $\mathrm{C_6H_{11}}$ = cyclohexanyl.

The *N*-silylformamidine (I) reacted exothermally with water or methanol to give a formamidine (II) [4] in quantitative yield. [*N,N'*-diisopropylformamidine, m.p. 47—48°, NMR ($\mathrm{CCl_4}$, TMS) δ 4.77 s (NH), 7.30 s (CH=N), IR (KBr disk) 3250 (ν(NH)) and 1650 $\mathrm{cm^{-1}}$ (ν(C=N)); *N,N'*-dicyclohexylformamidine, m.p. 101—102° (lit. [5] 100—102°)].

Treatment of *N*-silylformamidines (I) with an equimolar quantity of acetyl chloride at ambient temperature resulted in the production of *N*-acetylformamidines (II) in nearly quantitative yield, e.g., *N,N'*-diisopropyl-*N*-acetylformamidine [b.p. 44°/0.4 mmHg, NMR ($\mathrm{CCl_4}$, TMS) δ 2.17 s ($\mathrm{CH_3CO}$), 8.05 s (CH=N), IR (neat) 1690 (ν(C=O)) and 1640 $\mathrm{cm^{-1}}$ (ν(C=N))] and *N,N'*-dicyclohexyl-*N*-acetylformamidine [m.p. 80—81°, NMR ($\mathrm{CDCl_3}$, TMS) δ 2.33 s ($\mathrm{CH_3CO}$), 8.27 s (CH=N), IR (KBr disk) 1675 (ν(C=O)) and 1645 $\mathrm{cm^{-1}}$ (ν(C=N))].



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