

A NOVEL ROUTE TO FORMAMIDES AND THEIR DERIVATIVES.

REDUCTION OF ISOCYANATES VIA HYDROSILYLATION CATALYZED BY PALLADIUM

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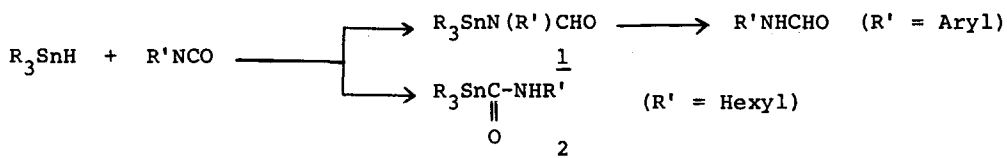
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(Received in Japan 31 August 1973; received in UK for publication 25 September 1973)

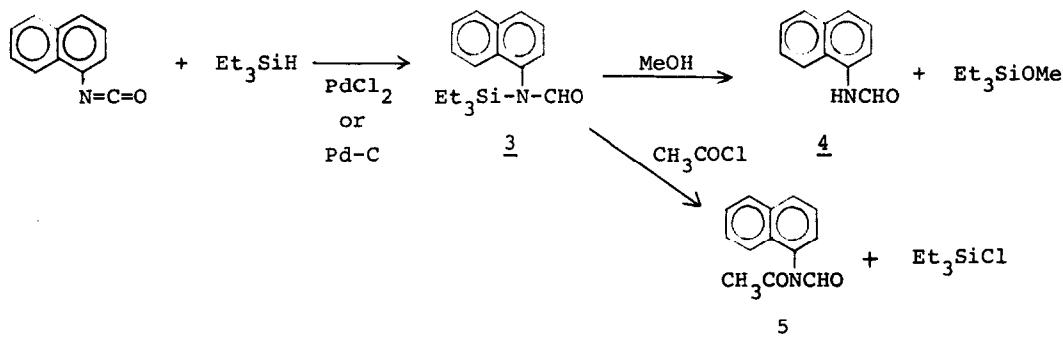
Among the hydrides of the group IV elements, organotin hydrides are known to react with isocyanates across the carbon-nitrogen double bond to afford a triorgano(N-arylformamido)tin 1 or a triorgano(N-alkylcarbamoyl)tin 2.^{1,2} The former can be further converted to N-arylformamide with triorganotin hydride.¹ This is distinctly different from the reaction of isocyanates with LiAlH₄, which produces N-methylamines.³ The corresponding reactions of silicon hydrides and germanium hydrides have not been reported and in fact they lack reactivity toward isocyanates without a proper catalyst.



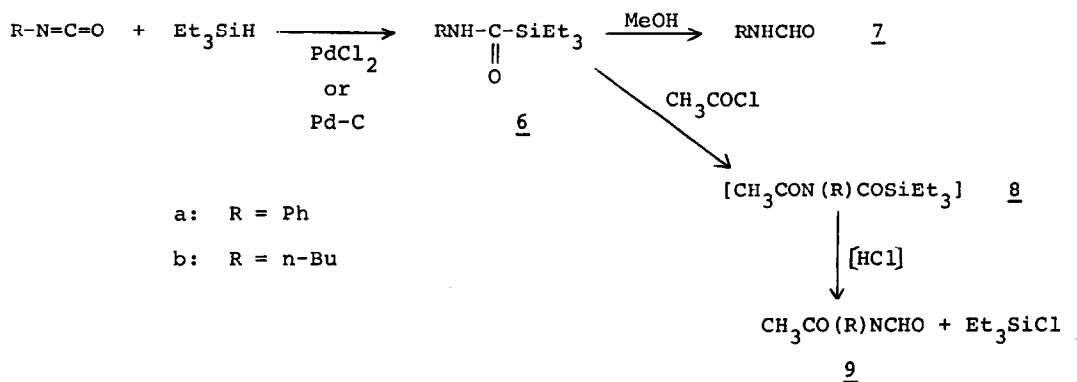
We found, however, that a hydrosilylation of isocyanates does really occur in the presence of PdCl₂ or Pd-C, and that the orientation of the reaction depends on the structure of isocyanates. Now, we wish to report novel catalytic reactions of triethylsilane with isocyanates, which furnishes a novel route to formamides and their derivatives.

α-Naphthyl isocyanate was allowed to react with triethylsilane in the presence of 0.1 Mol% of PdCl₂ or 10 % Pd-C at 80° for 2-3 hr. Distillation of the

reaction mixture under reduced pressure gave *N*- α -naphthyl-*N*-triethylsilylformamide (3) in nearly quantitative yield. The silylformamide 3, thus obtained, was smoothly solvolysed to *N*- α -naphthylformamide (4) by methanol in quantitative yield. The silylformamide 3 was also converted to *N*- α -naphthyl-*N*-acetylformamide (5) quantitatively by the reaction with an equimolar acetyl chloride.



Phenyl isocyanate and *n*-butyl isocyanate were hydrosilylated in different fashion by triethylsilane in the presence of PdCl_2 or 10 % Pd-C . Thus, the addition of triethylsilane was observed across the carbon-nitrogen double bond of these isocyanates in the opposite orientation, and hitherto unknown carbamoyl silanes, 6a ($\text{R} = \text{Ph}$, 95 %) and 6b ($\text{R} = n\text{Bu}$, 46 %), were obtained. The reaction of the carbamoyl silane 6 with acetyl chloride afforded *N*-acetylformamide 9 in excellent yield, which might be formed through *N*-acetylcarbamoyl silane 8 with cleaving carbon-silicon bond.



The nmr spectrum of the carbamoyl silane 6a suggests the existence of a tautomerism between the structures 6A and 6B.⁴ A similar phenomenon was also observed in the case of 7a, i.e., the nmr spectrum of 7a displays four signals in the region δ 8.30-9.40. After D₂O treatment, two broad singlets disappeared while two singlets remained, which are reasonably assigned to C-H protons of the structures, 7A and 7B. The situation is similar in the case of 6b and 7b. Spectral data for these formamides and their derivatives are listed in the Table.

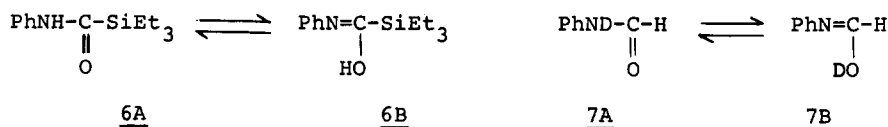


Table 1: 1:1 Adducts of Triethylsilane with Isocyanates and Their Derivatives⁵

Compound	IR (cm ⁻¹)		NMR (δ)			Bp (°C/mm) or Mp (°C)
	ν_{NH}	$\nu_{\text{C=O}}$	NH or OH	-CH=O	-COCH ₃	
<u>3</u>	---	1670sh 1630	---	7.05		140/0.12
<u>4</u>	3200	1655	8.63	8.63		141-142 (lit., ⁶ 137.5)
<u>5</u>	---	1650	---	10.60	1.94	79-81
<u>6a</u>	3270	1675	7.64 8.27			90/0.45
<u>7a</u>	3240	1670	8.61 9.00	8.35 8.79		45-46 (lit., ⁷ 47.5)
<u>9a</u>	---	1720 1685	---	9.40	2.05	55-57 (lit., ⁸ 56-57)
<u>6b</u>	3300	1670	8.12 8.17			82/1.0
<u>7b</u>	3260	1660	7.00-7.44	7.83 8.03		130/20 (lit., ⁹ 123/16)
<u>9b</u>	---	1725 1670	---	9.17	2.41	135/15

Consequently, the hydrosilylation of isocyanates catalyzed by palladium may open a novel device for the preparation of formamides and also for the synthesis of a new type of silicon compounds, carbamoyl silanes, and the intermediately formed silylated formamides and carbamoyl silanes have been found to serve a good precursor of N-acetyl formamides.

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4. D₂O treatment of the carbamoyl silane resulted in the formation of the corresponding formamide 7a.
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