



The possibility of carbenic character for **2** is presaged by the known (high-temperature) isomerization of acylsilanes into silyloxycarbenes,^{10,11} and it has long been suggested that, for acylsilanes, a significant contributor to the resonance hybrid is a structure without a silicon–acyl bond.¹² In the present instance, however, no evidence of carbene formation (e.g. alkenic dimer) was observed upon heating **2** in the absence of electrophilic co-reactants.^{13,14} It therefore appears that the carbenic behavior of **2** must be polarization induced. Previous examples of insertions by *preformed* nucleophilic carbenes into the C–H bonds of terminal acetylenes¹⁵ and β -diketones^{5c} have been rationalized by a proton abstraction–recombination mechanism. However, for the present transformations, we favor a process which is initiated by electron transfer from electron-rich carbamoylsilane to electrophilic co-reactant. Confirmation of this process awaits further experimentation.

References

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- From deprotonation of oxazolinium salts: (a) Wanzlick, H. W.; Steinmaus, H. *Chem. Ber.* **1968**, *101*, 244. (b) Haake, P.; Bausher, L. P.; Miller, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 35.
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- Except for the reaction of Eq. (1), where chloroform was used as solvent, substrate and **2** (10% molar excess) in dry benzene were treated as indicated under an argon atmosphere. Products were obtained by kugelrohr distillation except in the case of Eq. (2), where aqueous acid hydrolysis afforded the substituted benzaldehyde, mp 102.5–103.0°C (cyclohexane–benzene). All products gave satisfactory IR, ¹H and ¹³C NMR spectra and elemental analyses.
- The product shown (Eq. (4)) consists of a ca. 1:10 isomeric mixture.
- The first Ni- or Rh-catalyzed carbamoylstannylation has recently been reported: (a) Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 10221; (b) Hua, R.; Ozonawa, S.; Tanaka, M. *Organometallics* **2000**, *19*, 3269.
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- While this work was in progress, a comment appeared concerning the possibility of rearranging a (generic) carbamoylsilane into a siloxyaminocarbene: Pezacki, J. P.; Loncke, P. G.; Ross, J. P.; Warkentin, J.; Gadosy, T. A. *Org. Lett.* **2000**, *2*, 2733. It is as yet unclear whether the specific nitrogen substitution found in **2** contributes to the facile carbene-like behavior of this compound.
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- No change in the NMR spectrum of **2** (in toluene-*d*₈) was observed when the sample was slowly heated to 90°C and then returned to ambient. Also, **2** may be cleanly trisilylated at 145°C (Ref. 6).
- Less electrophilic species, viz., trimethoxymethane or phenylacetylene, did not undergo reaction under similar conditions.
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