Tetrahedron Letters,Vol.23,No.32,pp 3257-3260,1982 0040-4039/82/323257-04$03.00/0
Printed in Great Britain

N,N-bis(silyl)enamines as protected primary vinylamines. Nucleophilic activation of the silicon-nitrogen bond.

Robert J.P. CORRIU, Vilam HUYNH, Joël J.E. MOREAU and Magali PATAUD-SAT

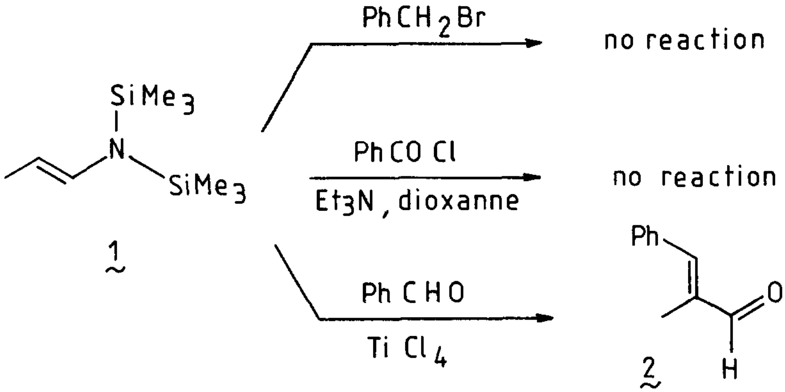
Laboratoire des Organométalliques - Equipe de Recherche associée au C.N.R.S. N° 554
Université des Sciences et Techniques du Languedoc - Place E. Bataillon 34060 Montpellier-cedex (France)

Summary :

N,N-bis(silyl)enamines react with electrophiles in the presence of catalytic amounts of nucleophile. The reaction of carbonyl compounds catalyzed by fluoride ion provides an interesting route to 2-aza-1,3-dienes. The methoxide ion catalyzed reaction of N,N-dimethylformamide gives rise to enamidines.

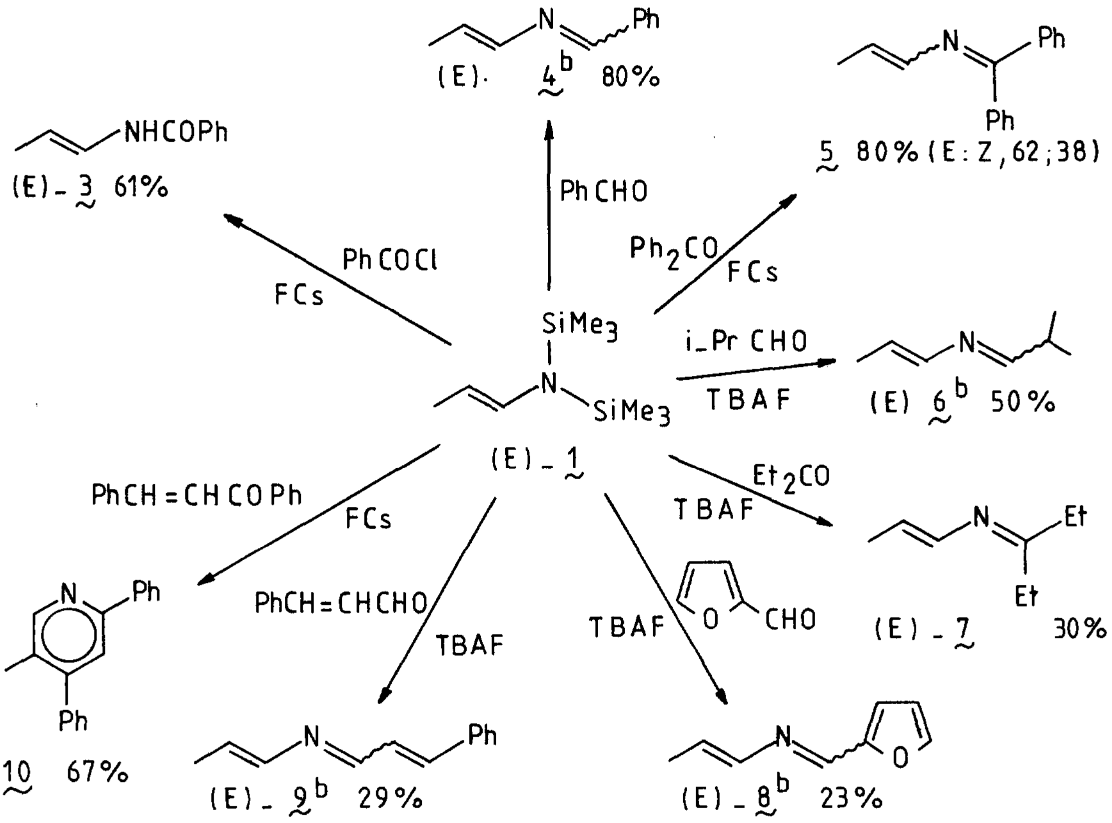
The increasing interest in the use of organosilicon compounds in organic synthesis led us to investigate the reactivity of N,N-bis(silyl)enamines. We recently reported easy routes to these compounds[1] which enable their use as reagents.

N,N-dialkyl enamines are nucleophilic reagents and react with a large variety of electrophiles with carbon-carbon bond formation[2]. In contrast, N,N-bis(silyl)enamines appeared to be weak nucleophiles. We did not observe any reaction of propenylamine 1 with benzylbromide or benzoylchloride. Only a poor yield of α-methylcinnamaldehyde 2 was obtained upon reaction with benzaldehyde.



However, we found that catalytic amounts of fluoride ion, known to activate Si-H[3], Si-O[4,5] and Si-C[6] bonds, allowed an enhanced reactivity towards electrophiles. The reactions of enamine 1 catalyzed by CsF or tetrabutylammonium fluoride (TBAF) are presented in Scheme 1. Whereas fluoride ion activated silyl enol ether[4,5] or allylsilane[6] react with electrophiles leading to the formation of carbon-carbon bonds, N,N-bis(silyl)enamines result in

Scheme 1 : Fluoride-ion catalyzed reaction of (E)-$CH_3CH=CHN(SiMe_3)_2$ with electrophiles [a]



a) Reactions were carried out using 5 % CsF in DMF (N,N-dimethylformamide) at 80°C or 5 % TBAF in THF at room temperature. The reaction with benzaldehyde illustrates the standard procedure : To a mixture of 6 g (3×10^{-2} mol.) of (E)-$CH_3CH=CHN(SiMe_3)_2$ and 0.22 g (5 %) of CsF in 10 ml of dry degassed DMF, is added 3.1 g (3×10^{-2} mol.) of benzaldehyde. The well stirred mixture is heated at 80°C for 2 hours and then poured into 50 ml of water. After extraction with ether and drying, the 2-aza-1,3 diene 4 (3.5g, 80 %) is isolated by distillation (Eb : 128 °C/20 mm)

b) The syn-anti stereochemistry of the carbon-nitrogen double bond has not been determined. The ^1H NMR spectra at 100 MHz show a singlet for the C$\underline{H}$=N proton.

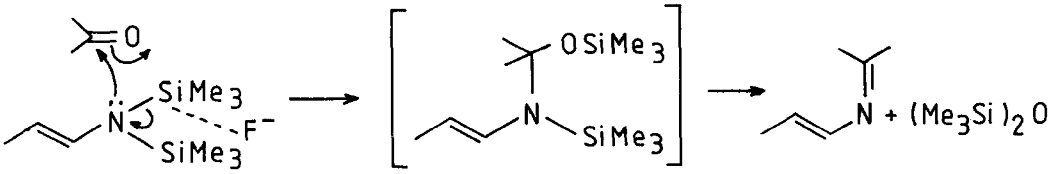
carbon-nitrogen bond formation.

Reaction of benzoylchloride gave the enamide 3. Interestingly, the reaction of carbonyl compounds gave rise to the 2-aza-1,3-dienes 4-8. Good yields were obtained with benzaldehyde and benzophenone. However, enolisable carbonyl compounds gave lower yields owing to a competitive crotonisation reaction. Similarly, cinnamaldehyde gave rise to the azatriene 9.

In these reactions, with the exception of benzophenone, the configuration of the carbon-carbon bond is retained.

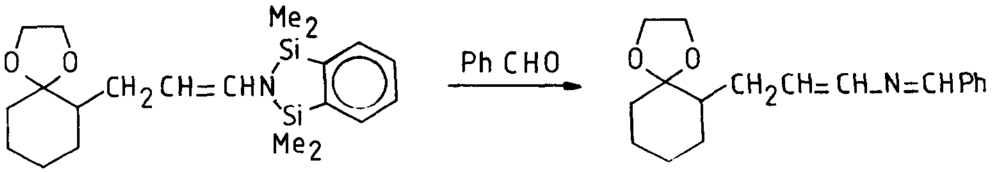
Reaction of carbonyl compounds provides a simple route to 2-aza-1,3-dienes[7] which are synthons of 6-membered N-heterocycles[8]. Interestingly, the reaction of 1 with chalcone yielded the substituted pyridine 10 probably through cyclization of an intermediate azatriene.

The formation of these hetero-dienes can be explained *via* a nucleophilic attack of the nitrogen atom in 1 on the carbonyl group followed by a β-elimination of hexamethyldisiloxane, which was identified in the reaction mixture. As previously reported for nucleophilic substitution activated by nucleophiles [3,5,9] the role of the fluorine catalyst is to weaken the silicon-nitrogen bond through a nucleophilic activation at silicon.



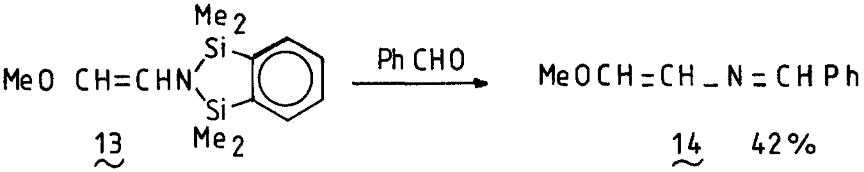
It is at first surprising to observe a nucleophilic attack by an anionic nitrogen. We assume that this reaction at carbonyl is controlled by the subsequent elimination of disiloxane. This contrasts sharply with the behaviour of silyl enol ether [4,5] and N,N-dialkyl-enamines[2] for which nucleophilic attack occurs at the β-carbon atom.

The synthetic possibilities are illustrated by the reactions of functional bis(silyl) enamines 11 and 13.



11

12 50%



We also observed a similar reaction with the carbonyl group of N,N-dimethylformamide catalyzed by sodium methoxide. This provides a direct route to the enamidines [8,10] 15-16 in good yields.

$$CH_3CH{=}CHN(SiMe_3)_2 \xrightarrow[MeONa]{HCONMe_2} CH_3CH{=}CH{-}N{=}CHNMe_2$$

15 82 %

$$Me_3SiCH_2CH{=}CHN(SiMe_3)_2 \xrightarrow[MeONa]{HCONMe_2} Me_3SiCH_2CH{=}CH{-}N{=}CHNMe_2$$

16 60 %

N,N-bis(silyl)enamines appear to react as protected primary vinylamines with carbonyl compounds providing easy access to a variety of hetero-dienes.

References

1 - R.J.P. CORRIU, J.J.E. MOREAU and M. PATAUD-SAT, J. Org. Chem., 46, 3372 (1981): id., J. Organometal. Chem., (1982) in press. R.J.P. CORRIU, V. HUYNH and J.J.E. MOREAU, to be published.

2 - A.G. COOK, "Enamines : synthesis, structure and reactions" Marcel Dekker Ed., New-York (1969).

3 - J. BOYER, R.J.P. CORRIU, R. PERZ and C. REYE, J. Organometal. Chem., 157, 153 (1978) ; id., ibid., 172, 143 (1979) ; id., Tetrahedron, 37, 2165 (1981) ; J. BOYER, R.J.P. CORRIU, R. PERZ, M. POIRIER and C. REYE, Synthesis, 558 (1981).

4 - R. NOYORI, K. YOKOYAMA, J. SAKATA, I. KUWAJIMA, E. NAKAMURA and M. SHIMIZU, J. Amer. Chem. Soc., 99, 1265 (1977) ; R. NOYORI, I. NISHIDA and J. SAKATA, J. Amer. Chem. Soc., 103, 2106 (1981).

5 - J. BOYER, R.J.P. CORRIU, R. PERZ and C. REYE, J. Organometal. Chem., 184, 157 (1980) ; id., J.C.S. Chem. Commun., 122 (1981).

6 - A. HOSOMI, A. SHIRAHATA and M. SAKURAI, Tetrahedron Lett., 3043 (1978).

7 - T. KAUFFMANN, E. KOPPELMANN and M. BERG, Angew. Chem. Int. Ed. Engl., 9, 163 (1970) ; J.P. SCHOENI and J.P. FLEURY, Tetrahedron, 31, 671 (1975) ; A. DEHNEL, J.P. FINET and G. LAVIELLE, Synthesis, 474 (1977) ; Yu. S. DOL'SKAYA, G. Ya. KONDRAT'EVA and N.I. GOLOVINA, Izv. Akad. Nauk. S.S.S.R., Ser. Khim., Engl. Transl., 550 (1978) ; S.D. WORLEY, K.G. TAYLOR, B. VENUGOPALAN and M.S. CLARK, Jr., Tetrahedron, 34, 833 (1978).

8 - A. DESMOULIN, H. GORISSEN, A.M. HESBAIN-FRISQUE and L. GHOSEZ, J. Amer. Chem. Soc., 97, 4409 (1975) ; R. GOMPPER and U. HEINEMANN, Angew. Chem. Int. Ed. Engl., 20, 196 (1981) and references therein ; F. SAINTE, B. SERCKX-PONCIN, A.M. HESBAIN-FRISQUE and L. GHOSEZ, J. Amer. Chem. Soc., 104, 1428 (1982).

9 - R.J.P. CORRIU, G. DABOSI and M. MARTINEAU, J. Organometal. Chem., 154, 33 (1978).

10 - L.S. COOK and B.J. WAKEFIELD, Tetrahedron Lett., 147 (1976) ; L.S. COOK and B.J. WAKEFIELD, J.C.S. Perkin I, 2392 (1980).

(Received in France 25 March 1982)