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SYNTHESIS AND PROPERTIES OF SOME β-TRIORGANOSILYLENAMINES

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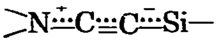
Summary

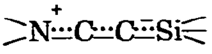
Ten β-triorganosilyl-substituted enamines were synthesized by the silylation of β-lithioenamines. They are thermally stable oils but are easily desilylated with protic compounds to give the parent enamines.

Introduction

Unstable aminoacetylenes are stabilized by β-silyl substitution via π-bonding as shown in A [1,2]. No report has appeared concerning β-silylenamines which may be expected to be similarly stabilized as shown in B. We have prepared some β-triorganosilyl-substituted enamines (IV) in order to examine the effect of silyl substitution.



(A)



(B)

Results and discussion

Synthesis of β-triorganosilylenamines (IV) was achieved by the silylation of β-lithioenamines (III), which were prepared by Duhamel's method [3] from the parent enamines (I) via β-bromoenamines (II). The results are summarized in Tables 1 and 2.

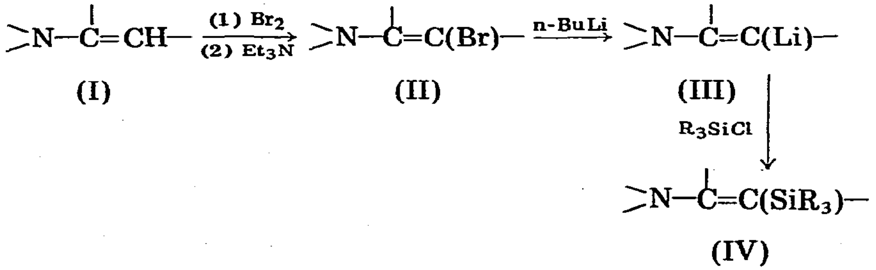


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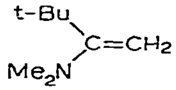
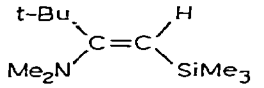
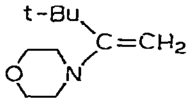
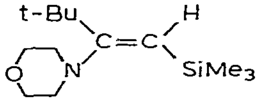
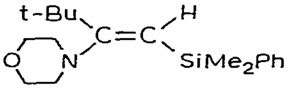
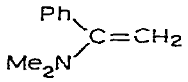
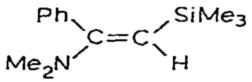
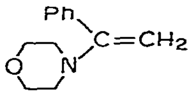
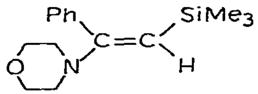
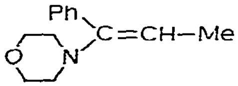
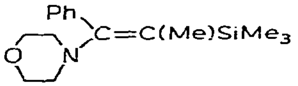
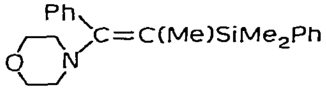
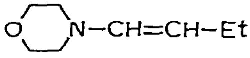
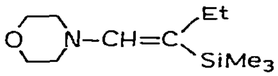
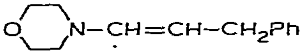
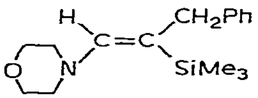
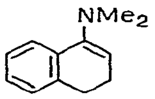
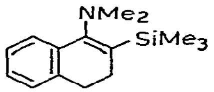
TABLE 1

β-TRIORGANOSILYLENAMINES

	Starting enamines (I)	β-Triorganosilylenamines (IV)		
		Structures	Yield (%) [a]	Ratio of $Z:E$ [b]
a			40	10:0
b			41	10:0
c			27	10:0
d			46	0:10
e			54	0:10
f			89	4:1
g			60	10:3
h			32	5:1
i			29	10:0
j			35	

[a] Yields are based on the parent enamines (I). [b] Ratios were established by NMR.

The IR and NMR spectra, and elemental analyses showed good agreement with the structures shown in Table 1.

β-Unsubstituted enamines (Ia, Ib, Id, and Ie) gave a single product, IVa—IVe, respectively. The configurations of these products were estimated by the

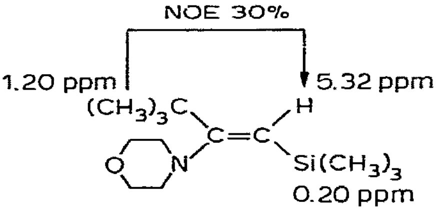
TABLE 2

CHARACTERIC DATA OF β-TRIORGANOSILYLENAMINES (IV)

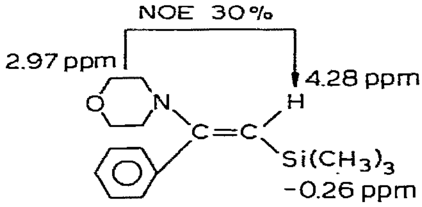
	Formula	B.p. (°C) (mmHg)	IR (cm^{-1}) ν(C=C)	NMR (CDCl$_3$) δ (ppm) Si(CH$_3$)$_3$		Analysis (%) Found (calcd.)		
				Z	E	C	H	N
a	$C_{11}H_{25}NSi$	81–90(21)	1590	0.00		[a]		
b	$C_{13}H_{27}NOSi$	80–81(0.3)	1585	0.20		64.73 (64.67)	11.20 (11.27)	5.81 (5.80)
c	$C_{18}H_{29}NOSi$	110–123(0.03)	1580	0.48		71.15 (71.23)	9.77 (9.63)	4.31 (4.61)
d	$C_{13}H_{21}NSi$	60–70(0.4)	1565		−0.24	71.07 (71.17)	9.71 (9.65)	6.47 (6.38)
e	$C_{15}H_{23}NOSi$	99–106(2)	1565 1590		−0.26	69.11 (68.91)	8.98 (8.87)	5.05 (5.36)
f	$C_{16}H_{25}NOSi$	99–105(0.01)	1590 1620	0.16	−0.32	69.95 (69.76)	9.16 (9.15)	5.21 (5.08)
g	$C_{21}H_{27}NOSi$	135–137(0.05)	1595 1620	0.49	−0.08	74.71 (74.73)	8.04 (8.06)	4.16 (4.15)
h	$C_{11}H_{23}NOSi$	62–63(0.5)	1660	0.14	0.05	62.04 (61.91)	11.17 (10.86)	6.73 (6.56)
i	$C_{16}H_{25}NOSi$	96–106(0.06)	1600 1620	−0.04		70.14 (69.76)	9.30 (9.15)	4.99 (5.08)
j	$C_{15}H_{23}NSi$	105–107(3)	1560 1590	0.24		73.28 (73.40)	9.46 (9.45)	6.26 (5.71)

[a] Unstable compound.

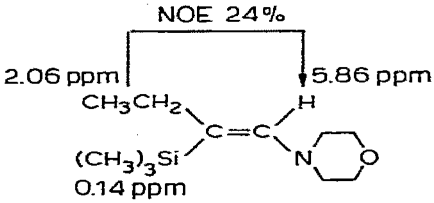
nuclear Overhauser effect (NOE). Irradiation of the tert-butyl signal of IVb or the 3,5-position signals of morpholino group of IVe resulted in 30% enhancement of the integrated intensity of each vinyl proton. Thus, IVb and analogs, IVa and IVc, were assigned as *Z* isomers, and IVe and IVd as *E* isomers.



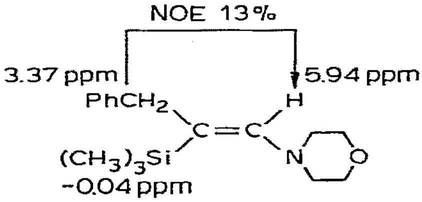
(IVb)



(IVe)



(*Z*-IVh)



(IVi)

The NMR spectra of IVd and IVe exhibited abnormal upfield shifts for the trimethylsilyl groups (δ —0.24 and —0.26 ppm), which may be attributed to the diamagnetic anisotropy effect of the *cis*-phenyl groups on the silyl groups.

The reaction of If with trimethylchlorosilane or dimethylphenylchlorosilane gave a mixture of *cis* and *trans* isomers. The NMR spectra of the mixtures were characterized by two methyl signals, showing the presence of two types of silyl groups. Isomers having the silyl groups in a normal region (δ 0.16 and 0.49 ppm) were assigned as *Z*, and the others, whose Me_3Si resonances appeared in an upfield region (δ —0.32 and —0.08 ppm), as *E* isomers. The geometrical configurations of IVh and IVi also were determined by the NOE method.

These β-silylenamines are thermally stable and could be distilled without detectable decomposition. (Distillation of the parent enamines causes partial polymerization.) However, they were easily desilylated with protic compounds and were sensitive to atmospheric moisture, giving the parent enamines. As a result of this sensitivity, IV were less useful than the parent enamines for routine preparative purposes.

Experimental

NMR spectra were recorded on a JEOL Model MH-100 spectrometer employing Me_4Si and/or CH_2Cl_2 as internal standard. NOE were measured using a JEOL Model FX-100 spectrometer. IR spectra were taken on a JASCO Model IRA-2 spectrometer. All boiling and melting points are uncorrected. All reaction were carried out under a nitrogen atmosphere.

Preparation of β-triorganosilylenamines (IV): general procedure

To a solution of the enamine (I, 20 mmol) in diethyl ether (200 ml) was added Br_2 (3.52 g, 22 mmol) in diethyl ether (20 ml) at —50°C. After stirring for 2—4 h, a solution of triethylamine (2.00 g, 20 mmol) in ether (50 ml) was added. The reaction mixture was allowed to warm to room temperature, and stirring was continued overnight. Precipitated triethylamine hydrobromide was filtered and the ether was evaporated under reduced pressure to give the crude β-bromoenamine (II).

n-Butyllithium (15% in hexane, 14 ml, 23 mmol) was added dropwise to a solution of II in THF (40 ml) at —70°C. After 1—3 h of stirring, a solution of the triorganochlorosilane (25 mmol) in THF (10 ml) was added at —65 to —70°C. The reaction mixture was filtered and the precipitate was washed with n-hexane. The filtrate and washings were combined, concentrated, and distilled to give IV. The results are shown in Tables 1 and 2.

Reaction of Z-1-morpholino-2-trimethylsilyl-3-phenylpropene (IVi) with benzyl alcohol

A solution of IVi (1.04 g, 3.8 mmol) and benzyl alcohol (1.36 g, 12.6 mmol) in ether (2 ml) was stirred for 4 h at room temperature. It was then distilled to give 1-morpholino-3-phenylpropene (Ii, 0.76 g, 87%) and benzyloxytrimethylsilane [4] (0.38 g, 55%), which were identified by comparison with authentic samples.

Reaction of E-1-morpholino-1-phenyl-2-trimethylsilylethene (IVe) with morpholine

A solution of IVe (0.80 g, 2.7 mmol) in morpholine (10 ml) was stirred for 19 h at room temperature, and then was distilled to give 1-morpholino-1-phenylethene (Ie, 0.21 g, 41%) and 4-trimethylsilylmorpholine [5] (0.123 g, 25%), which were identified by comparison with authentic samples.

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