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NEW PREPARATION OF *N,N*-BIS(TRIMETHYLSILYL)ENAMINES VIA IRON CARBONYL PHOTOCATALYSED ISOMERISATION OF UNSATURATED AMINES

R.J.P. CORRIU, V. HUYNH, J.J.E. MOREAU and M. PATAUD-SAT

Laboratoire des Organométalliques, Laboratoire associé au C.N.R.S. No. 349, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier-Cedex (France)

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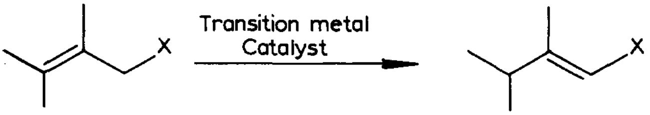
Summary

A new synthesis of *N,N*-bis(trimethylsilyl)enamines from straight chain olefinic amines has been devised which makes use of iron pentacarbonyl photocatalysed isomerisation. Complete conversion of the olefinic amines to the enamines was observed for substituted *N,N*-bis(trimethylsilyl)allylamines and non-allylic amines. The enamines obtained are potential sources of aldehydes and precursors of substituted aza-2-butadienes.

Introduction

We recently reported the preparation of *N,N*-disilylated enamines from nitriles using a disilylated iron carbonyl reagent [1] or rhodium catalysed hydrosilylation [2]. These enamines were shown to be very stable, and to have only a weak nucleophilic character, but fluoride ion was shown to activate the silicon–nitrogen bond and so provide an easy route to various 2-aza-1,3-dienes [3].

In order to provide a simpler route to these enamines we have studied their possible preparation from olefinic amines through carbon–carbon double bond isomerisation. Double bond migration in functional allylic compounds has been shown to provide an easy access to vinyl ethers [4,5] and enamides [6].



(X = OR , $OSiMe_3$, NHAc, $N(COR)_2$)

Little attention has been paid, however, to the transition metal catalysed isomerisation of allylamines ($X = NR_2$). Organic base catalysts were reported to be effective only for unsubstituted allylamines [7]. Recently cobalt and rhodium com-

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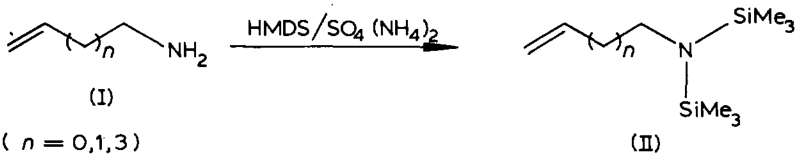
plexes were shown to catalyse the isomerisation of *N*,*N*-diethylnerylamine [8]. We therefore undertook a study of the isomerisation of unsaturated *N*,*N*-bis(trimethylsilyl)amines.

Results and discussion

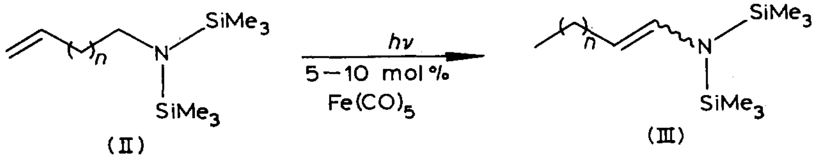
Unsaturated *N*,*N*-bis(trimethylsilyl)amines (II) were easily prepared by silylation of the corresponding primary amine (I) using hexamethyldisilazane (HMDS) in the presence of catalytic amounts of ammonium sulfate [9] (eq.1).



(n = 0,1,3)

(1)

Iron pentacarbonyl whose catalytic activity in double bond isomerisation is known [4b, 6a, 10] proved to be an efficient photocatalyst for the conversion of silylated amines II into *N*,*N*-bis(trimethylsilyl) enamines *. Exposure to UV light of hexane solution of amines II containing 5–10 mol% of iron-pentacarbonyl at room temperature, resulted in the formation of enamines (III) (eq. 2).



(n = 0,1,3)

(2)

As shown in Table 1, complete isomerisation took place and the enamines III were isolated in high yield. Various substituted allylamines (IIb–IIe) were converted to aldehyde-enamines (IIIb–IIIe). Substitution at the double bond did not affect the formation of the enamine. Isomerisation was observed for a trisubstituted double bond in IId and for vinylsilane IIe. The enamines III were obtained as a mixture of (*E*) and (*Z*) isomers. Some variations in the *Z*/*E* ratio were observed as a result of *cis-trans* isomerisation under the reaction conditions. The wide applicability of the procedure is illustrated by the isomerisation of but-3-enylamine IIf and hex-5-enylamine IIg for which double bond migration took place from the terminal position to the other end of the carbon chain. It is noteworthy that under the same conditions no isomerisation was observed in the case of allylpyrrolidine.

The isomerisation probably involves intermediate π-allyliron carbonyl complexes as proposed for the iron pentacarbonyl photocatalysed alkene isomerisation [10]. Stepwise migration of the double bond (eq. 3) is indicated by the observation of intermediate alkenylamines before completion of the isomerisation.

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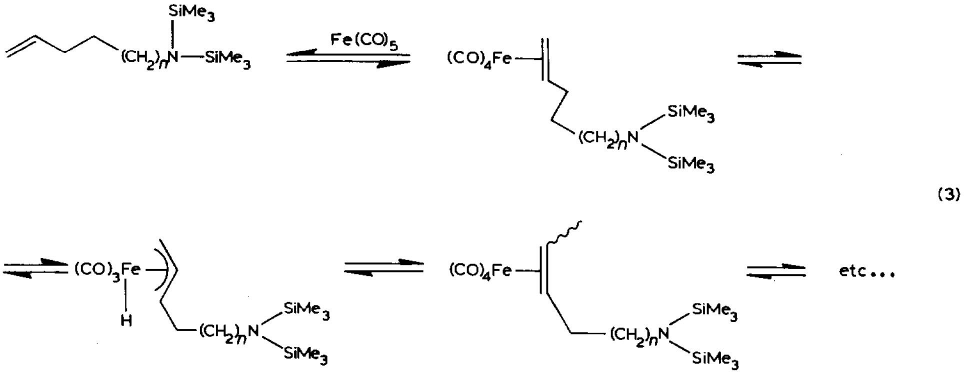
* *Editor's note.* We are aware that the iron pentacarbonyl cannot strictly be called a photocatalyst, but this usage has appeared previously (see, e.g. ref. 10), and we cannot think of a simple acceptable alternative.

TABLE 1

ISOMERISATION OF OLEFINIC *N,N*-BIS(TRIMETHYLSILYL)AMINES CATALYSED BY $Fe(CO)_5$ [a]

N,N-bis(trimethylsilyl)alkenyl amine		Reaction time (h)	*N,N*-bis(trimethylsilyl)-enamine		Isolated yield	*Z/E* [d]
$CH_2{=}CHCH_2N(SiMe_3)_2$	(IIa)	10	$CH_3CH{=}CHN(SiMe_3)_2$	(IIIa)	90	0/100
$CH_3CH{=}CHCH_2N(SiMe_3)_2$ [b]	(IIb)	15	$CH_3CH_2CH{=}CHN(SiMe_3)_2$	(IIIb)	84	70/ 30
$CH_2{=}C(CH_3)CH_2N(SiMe_3)_2$	(IIc)	30	$(CH_3)_2C{=}CHN(SiMe_3)_2$	(IIIc)	77	–
$(CH_3)_2C{=}CHCH_2N(SiMe_3)_2$	(IId)	48	$(CH_3)_2CHCH{=}CHN(SiMe_3)_2$	(IIId)	76	60/ 40
$Me_3SiCH{=}CHCH_2N(SiMe_3)_2$ [c]	(IIe)	96	$Me_3SiCH_2CH{=}CHN(SiMe_3)_2$	(IIIe)	70	70/ 30
$CH_2{=}CH(CH_2)_2N(SiMe_3)_2$	(IIf)	48	$CH_3CH_2CH{=}CHN(SiMe_3)_2$	(IIIf)	83	0/100
$CH_2{=}CH(CH_2)_4N(SiMe_3)_2$	(IIg)	96	$CH_3(CH_2)_3CH{=}CHN(SiMe_3)_2$	(IIIg)	75	35/ 65

[a] Catalyst: 10 mol%. [b] (*E*) isomer. [c] (*Z*) isomer. [d] Determined by ^1H NMR.

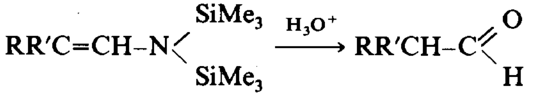


(3)

The stability of the *N,N*-bis(trimethylsilyl)enamine III leads to quantitative migration of the double bond.

From a synthetic point of view, this method offers a useful transformation of unsaturated primary amines into *N,N*-bis(trimethylsilyl)enamines, which are potential aldehyde equivalents [1] and precursors of substituted 2-aza-1,3-dienes [3].

Hydrolysis of enamines III by dilute HCl gave the corresponding aldehydes (eq. 4), which were characterized as their 2,4-dinitrophenylhydrazone derivatives.

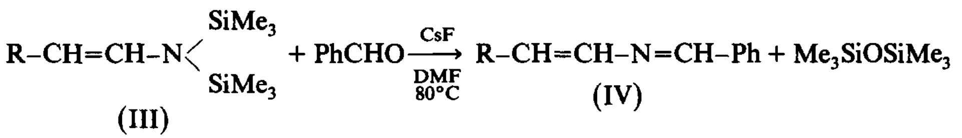


$$\mathrm{RR'C{=}CH{-}N}\begin{matrix}\mathrm{SiMe_3}\\ \mathrm{SiMe_3}\end{matrix} \xrightarrow{H_3O^+} \mathrm{RR'CH{-}C}\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix} \qquad (4)$$

(III)

(R = H, R′ = Me, Et, i-Pr, n-Bu, Me_3SiCH_2; R = R′ = Me)

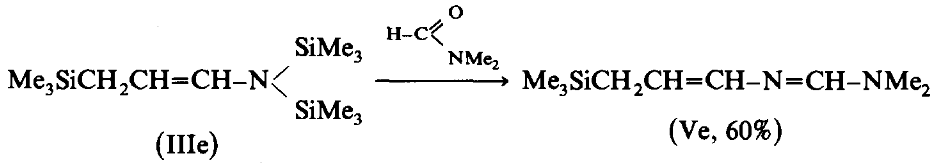
The synthetic utility of the enamines III is illustrated by the preparation of the 2-aza-1,3-dienes (IV) and the enamidine (V) by nucleophilic activation of the silicon-nitrogen bond [3]. Reaction of benzaldehyde in the presence of fluoride ion led to the expected azadienes IVb and IVd (eq. 5) in good yield.



$$\underset{\text{(III)}}{R{-}CH{=}CH{-}N\langle^{SiMe_3}_{SiMe_3}} + PhCHO \xrightarrow[\substack{\text{DMF}\\ 80^\circ\text{C}}]{\text{CsF}} \underset{\text{(IV)}}{R{-}CH{=}CH{-}N{=}CH{-}Ph} + Me_3SiOSiMe_3 \qquad (5)$$

(R = Et, IIIb; R = i-Pr, IIId) (IVb, 71%; IVd, 65%)

The reaction of dimethyl formamide with enamine IIIe in the presence of sodium methoxide gave the trimethylsilylenamidine Ve (eq. 6).



$$\underset{\text{(IIIe)}}{Me_3SiCH_2CH{=}CH{-}N\langle^{SiMe_3}_{SiMe_3}} \xrightarrow{H{-}C\langle^{O}_{NMe_2}} \underset{\text{(Ve, 60\%)}}{Me_3SiCH_2CH{=}CH{-}N{=}CH{-}NMe_2} \qquad (6)$$

Experimental

All experiments were carried out under nitrogen. Solvents were dried and deoxygenated before use. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. The ^1H NMR spectra were measured on a Varian EM 360; chemical shifts (δ) are relative to Me_4Si. The mass spectra were obtained with a Jeol JMS D100 spectrometer. All photochemical reactions were performed at room temperature in a quartz reaction vessel using an immersed Hanovia 450 W high pressure mercury lamp.

The *N,N*-bis(trimethylsilyl) olefinic amines IIa–IId, IIf, IIg were preparated by silylation of the corresponding primary amines with hexamethyldisilazane [9]. The tris(trimethylsilyl)allylamine IIe was available in our laboratory [11].

Isomerisation reactions

General procedure. A solution containing 2×10^{-2} mol of unsaturated amine IIa–IIg and 0.39 g (2×10^{-3} mol) of iron pentacarbonyl in 200 ml of dry degassed hexane was irradiated with an immersed 450 W high pressure mercury lamp for several hours at room temperature. (When times longer than 48 h were needed, the irradiation was stopped after 48 h and the walls of the vessel were cleaned to remove a brown deposit.) The solvent was then removed under reduced pressure, and distillation of the oily residue gave the *N,N*-bis(trimethylsilyl)enamines IIIa–IIIg.

Compound IIa. The above procedure applied to 4.0 g (2×10^{-2} mol) of amine IIa using 0.4 g (2×10^{-3} mol) of iron pentacarbonyl gave after distillation 3.6 g (yield 90%) of enamine IIIa ((*E*) isomer) [12,13]. B.p. 70°C (22 mmHg. NMR (CCl_4) (δ,ppm): 0.1 (18H, s); 1.6 (3H, dd); 4.9 (1H, dq, J_E 14 Hz); 5.8 (1H, m). IR (CCl_4, cm^{-1}): ν(C=C) 1640. Mass spectrum: $M^+ = 201$. This preparation was scaled up using 74 g (0.37 mol) of amine IIa and 2.15 g (1.1×10^{-2} mol) of iron pentacarbonyl in 600 ml of hexane. In this case 65 g (yield 88%) of enamine IIIa ((*E*) isomer) were obtained.

Addition of enamine IIIa to an acidic solution of 2,4-dinitrophenylhydrazine gave a precipitate of propanal 2,4-DNP, which was recrystallised from ethanol. M.p. 145–147°C (lit. 14 M.p. 148°C).

Compound IIb. Use of 4.3 g (2×10^{-2} mol) of amine IIb and 0.4 g of iron pentacarbonyl gave 3.6 g (yield 84%) of enamine IIIb [13] as a 70/30 mixture of (Z) and (E) isomers. B.p. 76–79°C/20 mmHg. NMR (CCl_4) (δ,ppm); (Z) isomer: 0.09 (18H, s); 0.95 (3H, t); 2.05 (2H, m); 5.1 (1H, td; J_Z 7 Hz); 5.75 (1H, td); (E) isomer: 0.12 (18H, s); 1.0 (3H, t); 2.0 (2H, m); 5.05 (1H, td, J_E 14 Hz); 5.85 (1H, td). IR (CCl_4, cm^{-1}); ν(C=C) 1640. Mass spectrum $M^+ = 215$. Enamine IIIb hydrolysed to butanal. Butanal 2,4-DNP, M.p. 119°C (lit. 14 M.p. 123°C).

Compound IIc. Using 4.3 g of amine IIc, gave 3.3 g (yield 77%) of enamine IIIc. B.p. 79–80°C/20 mmHg. NMR (CCl_4) (δ,ppm): 0.07 (18H, s); 1.55 (3H, m); 1.65 (3H, m); 5.5 (1H, m). IR (CCl_4, cm^{-1}): ν(C=C) 1640. Mass spectrum: M^+ 215. 2-Methylpropanal-2,4-DNP, M.p. 173°C (lit. 14 M.p. 182°C).

Compound IId. Isomerisation of 4.6 g of unsaturated amine IId gave 3.5 g (yield 76%) of enamine IIId as a 60/40 mixture of (Z) and (E) isomers. B.p. 95°C/20 mmHg. NMR (CCl_4) (δ,ppm): (Z) isomer: 0.09 (18H,s); 1.0 (6H,d); 2.1 (1H,m); 4.8 (1H, dd, J_Z 8 Hz); 5.55 (1H, dd). (E) isomer: 0.13 (18H, s); 1.05 (6H, d); 2.1 (1H, m); 4.75 (1H,dd, J_E 14 Hz); 5.75 (1H, dd). IR (CCl_4, cm^{-1}): ν(C=C) 1640. Mass spectrum: M^+ 229. 3-Methylbutanal-2,4-DNP, M.p. 110°C (lit. 14 M.p. 107°C).

Compound IIe. Irradiation of 27.3 g (10^{-1} mol) of silylamine IIe in the presence of 2.0 g (10^{-2} mol) of iron pentacarbonyl in 600 ml of hexane gave 19 g (yield 70%) of silylenamine IIIe as a 70/30 mixture of (Z) and (E) isomers. B.p. 120°C/20 mmHg. NMR (CCl_4) (δ,ppm): Z isomer: 0.02 (9H, s); 0.11 (18H, s); 1.4 (2H, dd); 4.95 (1H, td, J_Z 7.5 Hz); 5.55 (1H, td); (E) isomer: 0.0 (9H, s); 0.05 (18H, s); 1.3 (2H, dd) 4.85 (1H, td, J_E 13.5 Hz); 5.5 (1H, td). IR (cm^{-1}): ν(C=C) 1645. Mass spectrum M^+ 273. 3-Trimethylsilylpropanal-2,4-DNP, M.p. 123°C (lit. 15 M.p. 129–130°C).

Compound IIf. Isomerisation of 1.1 g (5×10^{-3} mol) of amine IIf gave 0.9 g (yield 83%) of enamine IIIb ((E) isomer).

Compound IIg. Similarly 2.2 g (9×10^{-3} mol) of amine IIg isomerised to enamine IIIg as a 35/65 mixture of (Z) and (E) isomers (1.1 g, yield 75%). B.p. 115–120°C/20 mmHg. NMR (CCl_4) (δ,ppm): (Z) isomer: 0.09 (18H, s); 1.0 (3H, m); 1.4 (4H, m); 2.05 (2H, m): 5.0 (1H, td J_Z 8 Hz); 5.85 (1H, td); (E) isomer: 0.13 (18H, s); 1.0 (3H, m); 1.4 (4H, m); 2.05 (2H, m); 5.1 (1H, td, J_E 14 Hz); 5.9 (1H, td). IR (CCl_4, cm^{-1}): ν(C=C) 1640. Mass spectrum M^+ 243 hexanal-2,4-DNP, M.p. 102°C (lit. 14 M.p. 104°C).

Reactions of N,N-bis(trimethylsilyl)enamines with benzaldehyde

Enamine IIIb. A well stirred solution containing 2.2 g (10^{-2} mol) of enamine IIIb and 1.08 g (10^{-2} mol) of benzaldehyde in 10 ml of dry dimethyl formamide was heated at 80°C for 4 h in the presence of 0.15 g (10^{-3} mol) of cesium fluoride. The mixture was added to 40 ml of water. Extraction with 3 × 20 ml of diethyl ether was followed by washing of the organic layer with 3 × 10 ml of water and drying over sodium sulfate. After removal of the solvent the residue was distilled under reduced pressure to give 1.1 g (yield 71%) of 2-aza-1,3-diene IVb B.p. 142°C/20 mmHg. IR (CCl_4, cm^{-1}): ν(N=C) 1660; ν(C=C) 1610. NMR (CCl_4) (δ,ppm): (Z) isomer 70%: 1.15 (3H, t); 2.6 (2H, m); 5.35 (1H, td, J_Z 7 Hz); 6.65 (1H, td); 7.3 (3H, m); 7.7

(2H, m); 8.0 (1H, s); (E) isomer 30%: 1.15 (3H, t); 2.25 (2H, m); 6.1 (1H, td, J_E 14 Hz); 6.75 (1H, td); 7.3 (3H, m); 7.7 (2H; m); 8.0 (1H, s).

Enamine IIId. The same procedure applied to 2.3 g (10^{-2} mol) of enamine IIId gave 1.1 g (yield 65%) of 2-aza-1,3-butadiene IVd. B.p. 140°C/20 mmHg. IR (CCl_4, cm^{-1}): ν(N=C) 1655; ν(C=C) 1605. NMR (CCl_4) (δ,ppm): (Z) isomer, 60%: 1.0 (6H, d); 2.3 (1H, m); 5.05 (1H, dd, J_Z 8 Hz); 6.4 (1H, dd); 7.2 (3H, m); 7.6 (2H, m); 7.9 (1H, s); (E) isomer, 40%; 1.0 (6H, d); 2.3 (1H, m); 5.85 (1H, dd, J_E 14 Hz); 6.55 (1H, dd); 7.2 (3H, m); 7.6 (2H, m); 7.9 (1H, s).

Reaction of enamine IIIe with dimethyl formamide

A well stirred solution of 5.5 g (2×10^{-2} mol) of enamine IIIe in 10 ml of dimethyl formamide was heated to 100°C for 2 h in the presence of 0.3 g (5.5×10^{-3} mol) of sodium methoxide. The mixture was extracted with pentane (3 × 20 ml) and the pentane solution was washed with water (2 × 10 ml) and dried over sodium carbonate. After removal of the solvent the residue was distilled to give 2.2 g (yield 60%) of enamidine Ve. B.p. 95–100°C/20 mmHg. NMR (CCl_4) (δ, ppm): (Z) isomer 70%: 0.02 (9H, s); 1.6 (2H, d); 2.9 (6H, s); 4.6 (1H, td, J_Z 8 Hz); 5.8 (1H, td); 7.3 (1H, s); (E) isomer, 30%: 0.0 (9H, s); 1.6 (2H, d); 2.9 (6H, s); 5.3 (1H, td, J_E 13 Hz); 6.3 (1H, td) 7.2 (1H, s).

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