

FUNCTIONAL ALLYLSILANES: REACTIVITY OF PYRROLIDINOALLYLSILANES TOWARDS ELECTROPHILES

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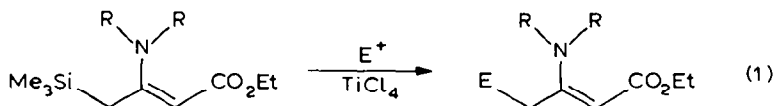
(Received June 20th, 1983)

Summary

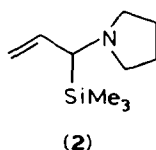
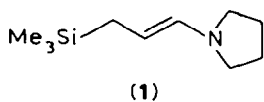
(3-Pyrrolidinoallyl)trimethylsilane (**1**) and (1-pyrrolidinoallyl)trimethylsilane (**2**) have been prepared from allylpyrrolidine. Compound **1** is both an allylsilane and an enamine. It exhibits enamine-type reactions with electrophiles leading to substituted β -trimethylsilyl aldehydes which are protected substituted acroleines. In contrast an allylsilane-type reaction occurs upon treatment with ketones in the presence of fluoride ion. Aminoallylsilane (**2**) is inert towards electrophiles activated by Lewis acids, but fluoride ion activation of **2** promotes reaction with carbonyl compounds to give a mixture of amino alcohols and amino furans.

Introduction

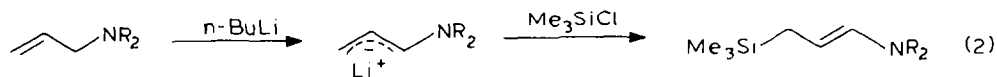
Allylsilanes were now extensively used in organic synthesis [1]. Our interest in the uses of functional allylsilanes [2] led us to investigate the reactivity of allylsilanes having a dialkylamino substituent. In a recent report Chan et al. showed that β -amino- γ -trimethylsilyl crotonate esters exhibited an unexpected regioselectivity in their reaction with electrophiles [3] (eq. 1).



We now report our results on the reactivity of allylsilanes **1** and **2**, which bear a γ and an α amino group, respectively.



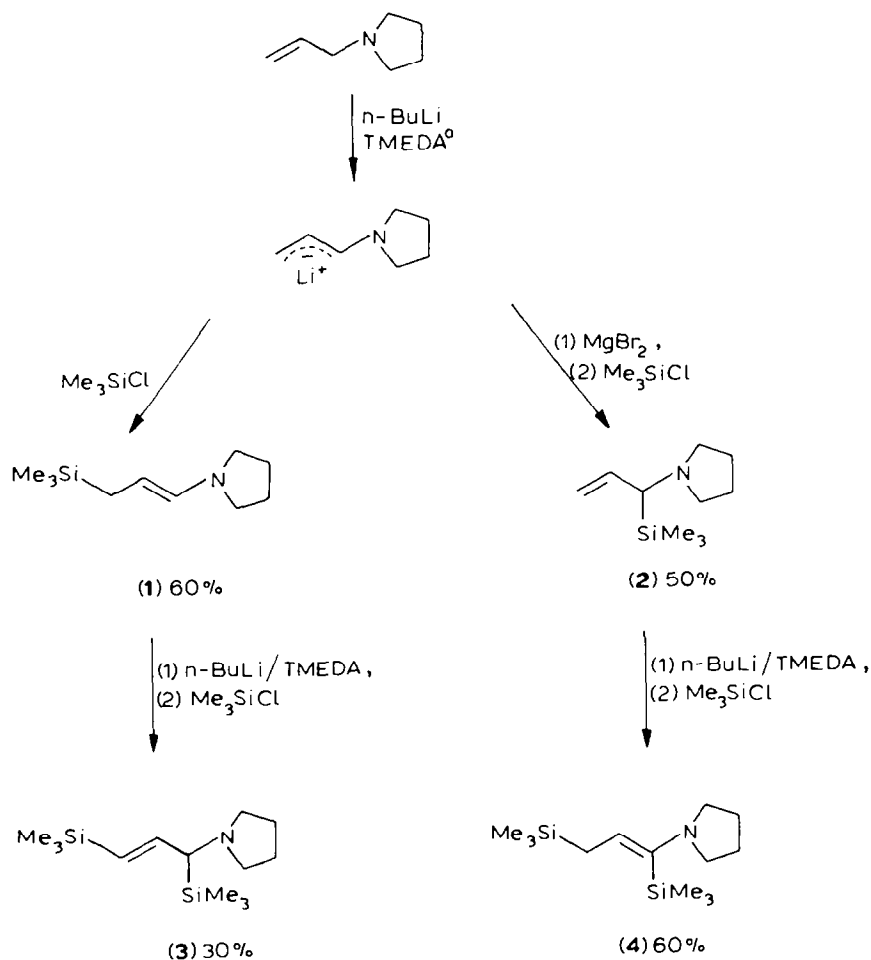
Trimethylsilyl enamines of type **1** have been obtained previously by several authors via the reaction of aminoallylic anions with trimethylchlorosilane [4–6] (eq. 2).



Results and discussion

Synthesis of (pyrrolidino-allyl)silanes

As depicted in Scheme 1, (3-pyrrolidinoallyl)- and (1-pyrrolidinoallyl)-trimethylsilanes (**1** and **2**) were made from the pyrrolidinoallyl anion [6]. Allylpyrrolidine was metallated by *n*-BuLi/TMEDA as described by Martin and Du Priest [6].



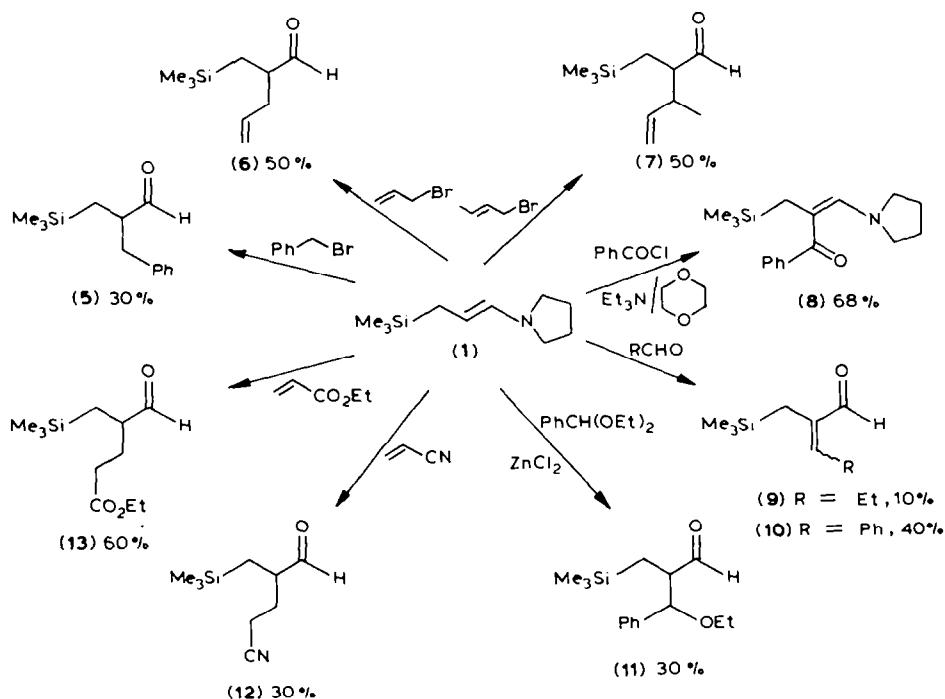
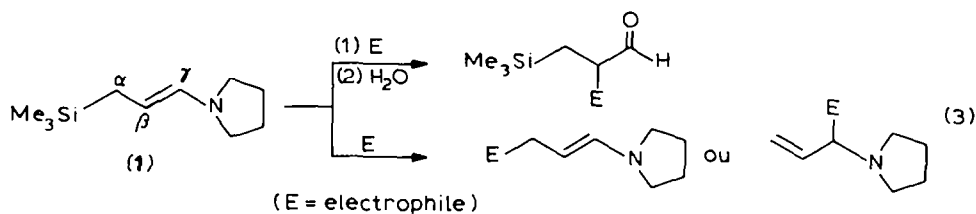
SCHEME 1. Trimethylsilylation of allylpyrrolidine. (^a Compound **1** has been obtained in 70% yield using metallation with *s*-butyllithium in THF [6].)

Treatment of the allyl anion with trimethylchlorosilane gave the known (3-pyrrolidinoallyl)trimethylsilane (**1**) [6] in 60% yield. As previously observed in related cases, the regioselectivity of the silylation reaction can be reversed by changing the counterion of the allyl anion [6–8]. Thus treatment of the lithium anion with magnesium bromide and then trimethylchlorosilane gave (1-pyrrolidinoallyl)trimethylsilane (**2**) in 50% yield.

Compounds **1** and **2** can in turn both be metallated by *n*-butyllithium, and quenching with trimethylchlorosilane gives the two isomeric bis-silylated compounds **3** and **4**.

Reactions of compound **1** with electrophiles

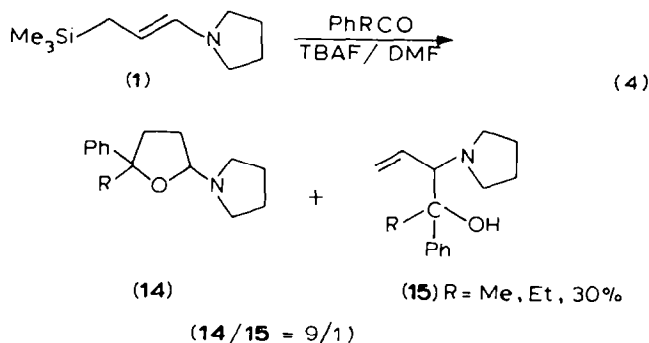
Compound **1** is both an enamine and an allylsilane. The reactions with electrophiles might therefore occur at the central β -carbon atom or at one of the terminal α - or γ -carbon atoms (eq. 3).



SCHEME 2. Reactivity of compound **1** with various electrophiles.

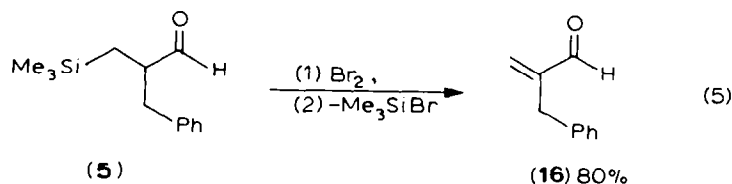
As shown in Scheme 2, compound **1** exhibited the usual nucleophilic character of an enamine function [9]. Benzyl and allyl bromide gave the α -alkylated aldehydes **5** and **6** in 30 and 50% yields. Crotyl bromide gave the α -(1-methylallyl) aldehyde **7**, as expected for nitrogen alkylation in a first step followed by an intramolecular rearrangement [9]. Reaction with benzoyl chloride in the presence of triethylamine gave the keto enamine **8** in 68% yield. Reactions with propionaldehyde and benzaldehyde gave poor yields of the corresponding α - β unsaturated aldehydes **9**, **10**. Reaction with benzaldehyde diethyl acetal in the presence of zinc chloride did not give better yields of compound **11**. The reaction with the activated olefins acrylonitrile and ethyl acrylate gave the expected Michael adducts **12** and **13**.

In all cases the β -carbon atom in compound **1** appeared to be the most nucleophilic centre. The nucleophilicity of the enamine function is greater than that of the allylsilane. However a different type of reaction was observed in the reactions of electrophiles in the presence of a nucleophilic catalyst. Thus reversed regioselectivity was obtained in the reaction of ketones with compound **1** in the presence of tetrabutylammonium fluoride (TBAF) (eq. 4).



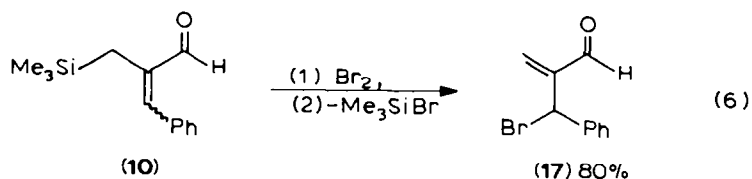
Fluoride ion activation [10–12] of compound **1** generated the allyl anion equivalent, which yielded predominantly the aminofuran **14**.

The reactions of γ -trimethylsilyl enamine **1** with electrophiles gave β -trimethylsilyl aldehydes in moderate yield, although not much lower than those obtained in electrophilic substitutions or additions to aldehydic enamines [9]. The compounds obtained are protected α - β unsaturated aldehydes which can be regenerated by bromination followed by debromosilylation [13]. To illustrate this possibility, the aldehyde **5** was converted into α -benzylacrolein (**16**) according to eq. 5

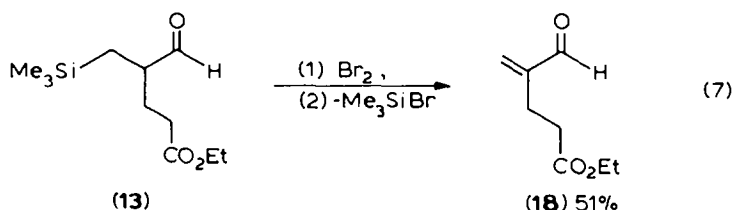


Similarly the α - β unsaturated aldehyde **10** was converted into the α -(1-bromoben-

zyl)acroleine (17) in 80% yield (eq. 6).

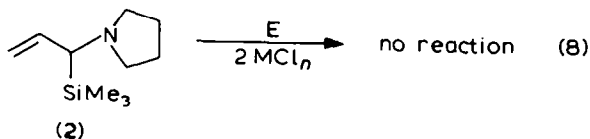


In the case of the aldehyde ester 13, the yield was lower because of a competing bromination at the α -carbon atom of the ester group (eq. 7).



Reactivity of compound 2 with electrophiles

We also studied the reactivity towards electrophiles of (1-pyrrolidinoallyl)trimethylsilane (2) in which both the amino and trimethylsilyl group are in an allylic position. Surprisingly, compound 2 did not react with electrophiles in the presence of Lewis acids. No reaction was observed with acid chlorides, benzaldehyde, or benzaldehyde diethyl acetal, even in the presence of two molar equivalents of TiCl_4 or AlCl_3 (eq. 8).



(E = CH_3COCl , PhCOCl , PhCHO , $\text{PhCH}(\text{OEt})_2$;
 $\text{MCl}_n = \text{TiCl}_4$, AlCl_3)

The presence of the pyrrolidino substituent in compound 2 inhibits the reaction of Lewis acid activated electrophiles. Such a deactivation was not observed in the case of β -amino- γ -trimethylsilyl crotonate esters [3]. The formation of a stable amine-Lewis acid complex in this case may account for the lack of reaction of compound 2. Activation of compound 2 by CsF or TBAF promoted the reaction with carbonyl compounds (eq. 9).

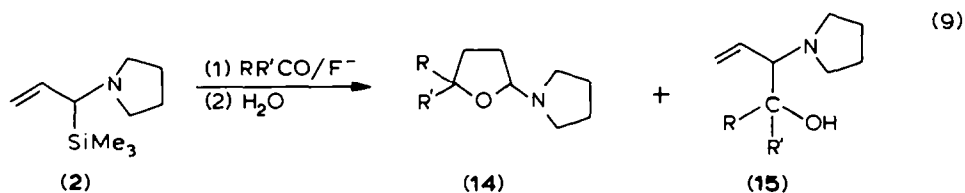


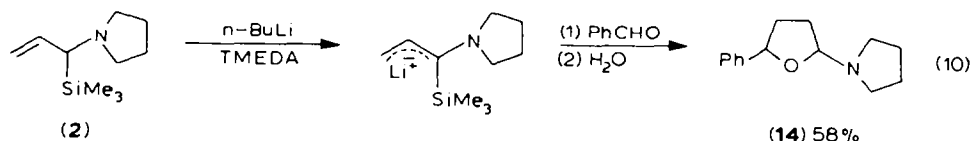
TABLE 1

REACTIONS OF COMPOUND **2** WITH CARBONYL COMPOUNDS^a CATALYSED BY FLUORIDE ION (eq. 9)

Carbonyl compounds	Catalyst ^b	Solvent	React time (h)	Yield (14 + 15) (%)	Ratio 14 / 15
PhCHO	FCs	DMF	30	55	2/3
PhCHO	TBAF	THF ^c	72	53	1/1
(CH ₃) ₂ CHCHO	FCs	DMF	30	30	2/3
(CH ₃) ₂ CO	FCs	DMF	30	40	3/2
PhCH ₂ CO	FCs	DMF	30	40	3/2
Ph(CH ₂) ₂ CO	TBAF	DMF	24	40	1/1

^a All reactions were carried out at room temperature. ^b Catalyst concentration: CsF 10 mol. %, TBAF 10 mol. %. ^c Refluxing THF.

Aldehydes and ketones gave mixtures of amino alcohols and aminofurans, corresponding to the reaction of the allylsilane with or without rearrangement. The results are summarized in Table 1. No regioselectivity was observed in the reactions of compound **2** in contrast with the more regioselective reactions of compound **1** (eq. 3). Our results confirm the tendency of fluoride ion-activated allylsilanes to react without allylic rearrangement [11]. A more hindered reactant (ketone rather than aldehyde) favored the formation of furan **14**. Regiospecific formation of compound **14** can be achieved via the allyl anion derived from compound **2** (eq. 10).



Experimental

All experiments were done under nitrogen. Solvents were dried and deoxygenated before use. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer in the form indicated. The ¹H NMR spectra were recorded on a Varian EM 360. Chemical shifts, δ , are relative to Me₄Si. The mass spectra were obtained on a JEOL JMS DI00 apparatus.

Preparation of pyrrolidino allylsilanes

(3-Pyrrolidinoallyl)trimethylsilane (1). This compound was prepared using a slight modification of the reported procedure [6]. To a mixture of 20 g (0.18 mol) of allylpyrrolidine (prepared according to ref. 14), and 22 g (0.19 mol) of tetramethylethylene diamine (TMEDA) in 200 ml of anhydrous diethyl ether, at -10°C, was added dropwise 0.19 mol of n-butyllithium in 260 ml of diethyl ether. The mixture

was stirred for 48 h at room temperature to give a yellow suspension, then 22 g (0.2 mol) of trimethylchlorosilane in 150 ml of ether was added dropwise at room temperature and the mixture was stirred for an additional 24 h, then filtered. The solvent was removed under vacuum. Addition of 200 ml of n-pentane to the residue precipitated lithium salts, which were removed by filtration. After removal of pentane, the oily residue was distilled to give 20 g (yield 60%) of (3-pyrrolidinoallyl)trimethylsilane [6]. B.p. 98–100°C/20 mmHg, IR (CCl₄, cm⁻¹): $\nu(\text{C}=\text{C})$ 1640. NMR (CCl₄) (δ , ppm): 0.01 (9H, s); 1.3 (2H, d); 1.8 (4H, m); 2.9 (4H, m); 3.9 (1H, td, J_E 14 Hz); 5.9 (1H, td).

(1-Pyrrolidinoallyl)trimethylsilane (2). The allylpyrrolidine anion was prepared as above from 85 g (0.77 mol) of allylpyrrolidine, 94 g (0.8 mol) of TMEDA, and 800 ml (0.8 mol) of a 1 M solution of n-butyllithium in ether. After 48 h the mixture was slowly added to a freshly prepared solution of magnesium bromide (obtained from 22 g of magnesium and 152 g of dibromoethane) in 500 ml of a 3/1 mixture of diethyl ether and benzene. After 6 h stirring, at room temperature, 88 g (0.8 mol) of trimethylchlorosilane in 200 ml of ether were added dropwise and the mixture was stirred for 20 h at room temperature and refluxed for 2 h. After filtration the crude solution was treated with 500 ml of a 4 N HCl solution. The aqueous layer was then washed with ether, neutralised with a 10% NaOH solution, and extracted with ether, and the extracts were dried over sodium sulfate. After removal of the solvent, (1-pyrrolidinoallyl)trimethylsilane (**2**, 70 g, yield 50%) was isolated by distillation. B.p. 98–99°C/20 mmHg. IR (CCl₄, cm⁻¹): $\nu(\text{C}=\text{C})$ 1625. NMR (CCl₄) (δ , ppm): 0.02 (9H, s); 1.6 (4H, m); 2.2 (1H, m); 2.5 (4H, m); 4.8 (2H, m); 5.6 (1H, m). Mass spectrum: M^+ 183.

3-Pyrrolidino-1,3-bis(trimethylsilyl)-1-propene (3). To a mixture containing 3.7 g (2×10^{-2} mol) of compound **1** and 2.3 g (2×10^{-2} mol) of TMEDA in 50 ml of anhydrous diethyl ether at -20°C, was treated dropwise with 20 ml of a 1 M solution of n-butyllithium in ether. The mixture was allowed to warm to room temperature and stirred for 40 h. After cooling to -70°C, 2.2 g (2×10^{-2} mol) of trimethylchlorosilane in 20 ml of ether were added. The mixture was then stirred at room temperature for 0.5 h and poured on a mixture of ice and 2 N HCl. The aqueous layer was washed with ether and neutralised with 10% aqueous NaOH solution. After extraction with ether the ether extracts were dried over sodium sulfate, and compound **3** (1.5 g, yield 30%) was isolated by distillation. B.p. 135°C/20 mmHg, IR (CCl₄, cm⁻¹): $\nu(\text{C}=\text{C})$ 1605. NMR (CCl₄) (δ , ppm): 0.0 (18H, s); 1.7 (4H, m); 2.6 (5H, m); 5.6 (1H, d, J_E 18 Hz); 6.05 (1H, td). Mass spectrum: M^+ 255. Analysis: Found: C, 61.36; H, 11.47; N, 5.18. C₁₃H₂₉NSi₂ calcd.: C, 61.10; H, 11.67; N, 5.48%.

1-Pyrrolidino-1,3-bis(trimethylsilyl)-1-propene (4). A mixture containing 3.7 g (2×10^{-2} mol) of compound **2** and 2.3 g (2×10^{-2} mol) of TMEDA in 50 ml of anhydrous diethyl ether at -30°C was treated dropwise with 20 ml of a 1 M solution of n-butyllithium in ether. The mixture was then warmed to room temperature and stirred for 5 h. After cooling to -78°C, 2.2 g (2×10^{-2} mol) of trimethylchlorosilane in 20 ml of ether were added. The mixture was stirred for 0.5 h at room temperature and the solvents were removed under vacuum. Extraction of the residue with pentane and distillation gave compound **4** (3 g, yield 60%). B.p. 75–80°C/2 mmHg. NMR (CCl₄) (δ , ppm): 0.0 (9H, s), 0.13 (9H, s); 1.6 (2H, d); 1.8 (4H, m), 3.05 (4H, m); 5.0 (1H, t). Mass spectrum: M^+ 255.

Reactions of compound 1 with electrophiles

With benzyl bromide. Enamine **1** (9.2 g, 5×10^{-2} mol) was added dropwise to 8.6 g (5×10^{-2} mol) of benzyl bromide in 20 ml of acetonitrile and the mixture was refluxed for 10 h, the mixture was then hydrolysed with 2 N HCl. Extraction with ether was followed by washing of the ethereal layer with water and drying over sodium sulfate. After removal of the solvents, distillation of the residue afforded 2 g (yield 30%) of 2-benzyl-3-trimethylsilylpropanal (**5**). B.p. $80^{\circ}\text{C}/0.06$ mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1730. NMR (CCl_4) (δ , ppm): 0.0 (9H,s); 0.6 (2H,m); 2.7 (3H,m); 7.3 (5H,m); 9.65 (1H,d). Mass spectrum: M^+ 220. Aldehyde **5** was characterised as its 2,4-DNP(dinitrophenyl): M.p. $153-155^{\circ}\text{C}$. Mass spectrum: M^+ 400. Analysis: found: C, 57.10; H, 5.88; N, 14.18. $\text{C}_{19}\text{H}_{24}\text{N}_4\text{O}_4\text{Si}$ calcd.: C, 56.98; H, 6.03; N, 13.99%.

With allyl bromide. Using the procedure described above, the reaction of 2.6 g (1.4×10^{-2} mol) of enamine **1** with 1.8 g (1.5×10^{-2} mol) of allyl bromide after 1 h reflux gave 1.2 g (yield 50%) of 2-trimethylsilyl-4-pentalal (**6**). B.p. $100^{\circ}\text{C}/20$ mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1720; $\nu(\text{C}=\text{C})$ 1640. NMR (CCl_4) (δ , ppm): 0.02 (9H, s); 0.8 (2H, m); 2.3 (3H, m); 4.9 (2H, m); 5.4 (1H, m); 9.6 (1H, d). 2,4-DNP: M.p. 145°C ; mass spectrum: M^+ 350. Analysis: Found: C, 50.92; H, 6.32; N, 15.71. $\text{C}_{15}\text{H}_{22}\text{N}_4\text{O}_4\text{Si}$ calcd.: C, 50.62; H, 6.28; N, 15.92%.

With crotyl bromide. A similar procedure using 3.7 g (2×10^{-2} mol) of enamine **1** and 2.7 g (2×10^{-2} mol) of crotyl bromide 1.8 g (yield 50%) of 3-methyl-2-trimethylsilyl-4-pentalal (**7**). B.p. $110^{\circ}\text{C}/20$ mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1720; $\nu(\text{C}=\text{C})$ 1640. NMR (CCl_4) (δ , ppm): 0.02 (9H, s); 0.7 (2H, d); 1.0 (3H, d); 2.2 (2H, m); 5.1 (2H, m); 5.6 (1H, m); 9.6 (1H, d). 2,4-DNP: M.p. 116°C ; Mass spectrum: M^+ 364. Analysis: Found: C, 52.76; H, 6.88; N, 15.28. $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_4\text{Si}$ calcd.: C, 52.75; H, 6.59; N, 15.38%.

With benzoyl chloride. To a solution containing 2 g (1.1×10^{-2} mol) of enamine **1** and 1.2 g (1.2×10^{-2} mol) of triethylamine in 10 ml of dioxane at 0°C was added dropwise 1.6 g (1.15×10^{-2} mol) of benzoyl chloride in 5 ml of dioxane. The mixture was stirred for 10 h at room temperature. After filtration and removal of the solvent, distillation of the residue afforded 2.0 g (yield 68%) of 2-benzoyl-1-pyrrolidino-3-trimethylsilyl-1-propene (**8**). B.p. $175^{\circ}\text{C}/0.1$ mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1690, $\nu(\text{C}=\text{C})$ 1645, 1635. NMR (CCl_4) (δ , ppm): 0.0 (9H, s); 1.9 (6H, m); 3.3 (4H, m); 6.75 (1H, s); 7.25 (5H, m). Mass spectrum: M^+ 287. Analysis: Found: C, 70.91; H, 8.68; N, 4.87. $\text{C}_{17}\text{H}_{25}\text{NOSi}$ calcd.: C, 71.08; H, 8.71; N, 4.88%.

With propanal. To a suspension of 6.7 g (5×10^{-2} mol) of aluminium trichloride in 50 ml of dichloromethane were added dropwise 2.9 g (5×10^{-2} mol) of propanal in 10 ml of dichloromethane and then 9.2 g (5×10^{-2} mol) of enamine **1** in 20 ml of dichloromethane. The mixture was stirred for 3 h at room temperature and then hydrolysed with saturated aqueous ammonium chloride. After extraction with ether, and removal of the solvent, the residue was distilled to give 0.9 g (yield 10%) of 2-(trimethylsilyl)methyl-2-pentalal (**9**). B.p. $98^{\circ}\text{C}/20$ mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1690; $\nu(\text{C}=\text{C})$ 1640. NMR (CCl_4) (δ , ppm): 0.0 (9H, s); 1.1 (3H, t); 1.7 (2H, s); 2.3 (2H, m); 6.3 (1H, m); 9.4 (1H, m). Mass spectrum: M^+ 170. 2,4-DNP: M.p. $120-122^{\circ}\text{C}$; mass spectrum: M^+ 350.

With benzaldehyde. A similar procedure but without added aluminium trichloride, involving 3.7 g (2×10^{-2} mol) of enamine **1** and 2.0 g (2×10^{-2} mol) of benzaldehyde, gave 1.8 g (yield 40%) of 2-(trimethylsilyl)methylcinnamaldehyde (**10**).

B.p. 75°C/0.03 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C=O})$ 1675; $\nu(\text{C=C})$ 1610. NMR (CCl_4) (δ , ppm): 0.0 (9H, s); 2.2 (2H, s); 7.2 (1H, s); 7.55 (5H, m); 9.7 (1H, s). Mass spectrum: M^+ 218. 2,4-DNP: M.p. 153°C; mass spectrum: M^+ 398. Analysis: Found: C, 57.3; H, 5.30; N, 13.4. $\text{C}_{19}\text{H}_{22}\text{N}_4\text{O}_4\text{Si}$ calcd.: C, 57.28; H, 5.55; N, 14.06.

With benzaldehyde diethylacetal. The same method, but using 3.7 g (2×10^{-2} mol) of enamine **1**, 3.6 g (2×10^{-2} mol) of benzaldehyde diethylacetal and 5.5 g (4×10^{-2} mol) of zinc chloride, gave 1.8 g (yield 30%) of 3-ethoxy-3-phenyl-2-(trimethylsilyl)methylpropanal (**11**) as a 1/1 mixture of the two diastereomers. B.p. 96°C/0.07 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C=O})$ 1725; $\nu(\text{C=C})$ 1610. NMR (CCl_4) (δ , ppm): 0.0 (9H, s); 0.55 (2H, m); 1.1, 1.3 (3H, t); 2.5 (1H, m); 2.15, 2.25 (2H, q); 4.2; 4.35 (1H, d); 7.3 (5H, m); 9.5, 9.65 (1H, d). Mass spectrum: M^+ 264.

With acrylonitrile. To a solution of 3.6 g (2×10^{-2} mol) of enamine **1** in 30 ml of acetonitrile at 5°C, was added 1.1 g (2×10^{-2} mol) of acrylonitrile. The mixture was stirred for 2 h at room temperature and refluxed for 1 h. After cooling, 5 ml of acetic acid in 20 ml of water were added and the mixture was refluxed for 2 h. After removal of the acetonitrile under vacuum, the residue was extracted with ether. 1.1 g (yield 30%) of 4-cyano-2-(trimethylsilyl)methyl butanal were isolated by distillation of the organic layer. B.p. 160–165°C/20 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2260; $\nu(\text{C=O})$ 1730. NMR (CCl_4) (δ , ppm): 0.1 (9H, s); 0.7 (2H, m); 1.8 (2H, m); 2.3 (2H, m); 2.8 (1H, m); 9.4 (1H, d). Mass spectrum: M^+ 183. 2,4-DNP; M.p. 114–115°C, mass spectrum; M^+ 363.

With ethyl acrylate. A similar procedure using 4.6 g (2.5×10^{-2} mol) of enamine **1** and 2.5 g (2.5×10^{-2} mol) of ethyl acrylate gave 3.5 g (yield 60%) of 4-ethoxycarbonyl-2-(trimethylsilyl)methylbutanal (**13**). B.p. 149–150°C/20 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C=O})$ 1740, 1730. NMR (CCl_4) (δ , ppm): 0.1 (9H, s); 0.8 (2H, m); 1.3 (3H, t); 1.9 (2H, m); 2.3 (3H, m); 4.1 (2H, q); 9.6 (1H, d). Mass spectrum M^+ 230. Analysis: Found: C, 57.20; H, 9.70. $\text{C}_{11}\text{H}_{22}\text{O}_3\text{Si}$ calcd.: C, 57.36; H, 9.62. 2,4-DNP: M.p. 74–75°C.

With acetophenone. To a solution containing 3.6 g (2×10^{-2} mol) of enamine **1** and 2.4 g (2×10^{-2} mol) of acetophenone in 20 ml of *N,N*-dimethyl formamide was added 1 ml of 1 *M* solution of tetrabutylammonium fluoride in THF. The mixture was heated to 80°C for 24 h. The reaction mixture was then washed with water and extracted with ether. The organic layer was washed with 2 *N* HCl, and the aqueous layer collected, neutralised with 10% aqueous potassium hydroxide, and extracted with ether. The ethereal solution was dried over sodium sulfate, the solvent was removed and the residue distilled to give 1.3 g (yield 30%) of a mixture of aminofuran **14** [6] and amino alcohol **15** [6]. B.p. 90°C/0.08 mmHg.

With propiophenone. The same technique using 3.6 g (2×10^{-2} mol) of enamine **1** and 2.7 g (2×10^{-2} mol) of propiophenone gave 1.4 g of a mixture of **14** and **15**.

Bromodesilylation reactions

α -Benzylacrolein. A slow stream of nitrogen was bubbled through a solution of 1.1 g (5×10^{-3} mol) of aldehyde **5** in 20 ml of dichloromethane at -20°C . A solution of 0.26 ml (5×10^{-3} mol) of bromine in 10 ml of dichloromethane was then added slowly, and the mixture was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue distilled to give 0.6 g (yield 80%) of α -benzylacroleine **16**, B.p. 110–120°C/20 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C=O})$ 1695;

$\nu(\text{C}=\text{C})$ 1630. NMR (CCl_4) (δ , ppm): 3.45 (2H, m); 5.9 (2H, m); 7.2 (5H, m); 9.5 (1H, s). Mass spectrum M^+ 146.

α -(α -Bromobenzyl)acrolein. The same procedure using 2.2 g (10^{-2} mol) of aldehyde **10** and 0.52 ml (10^{-2} mol) of bromine gave 1.8 g (yield 80%) of the desilylated aldehyde **17**. B.p. 130–140°C/0.1 mmHg. M.p. 73–74°C. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1685; $\nu(\text{C}=\text{C})$ 1625. NMR (CCl_4) (δ , ppm): 4.2 (2H, m); 7.3 (1H, m); 7.5 (5H, m); 7.5 (5H, m); 9.5 (1H, s). Mass spectrum M^+ 226.

α -(2-Ethoxycarbonyl)ethylacrolein. The reaction of 2.3 g (10^{-2} mol) of aldehyde **13** with 0.52 ml of bromine gave 0.8 g (yield 51%) of the desilylated aldehyde **18**. B.p. 70°C/0.07 mmHg. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1735, 1695; $\nu(\text{C}=\text{C})$ 1630. NMR (CCl_4) (δ , ppm): 1.2 (3H, t); 2.5 (4H, m); 4.05 (2H, q); 6.05 (2H, m); 9.55 (1H, s).

Reactions of compound 2 with carbonyl compounds

A mixture of 2×10^{-2} mol of compound **2**, 2×10^{-2} mol of carbonyl compound and 2×10^{-2} mol of cesium fluoride in 30 ml of *N,N*-dimethyl formamide (or 2×10^{-3} mol of tetrabutylammonium fluoride in 30 ml of THF) was stirred for several hours. The mixture was then washed with water and extracted with ether. The ether solution was then treated with 2*N* HCl and the acidic aqueous layer separated and neutralized with 10% aqueous KOH. After extraction with ether and removal of the solvent, the residue was distilled to give a mixture of the aminofuran **14** and the amino alcohol **15** [6], which was analysed by ^1H NMR. The reaction times, yields, and compositions of the mixtures obtained are given in Table 1.

Metalation of compound 2 and reaction with benzaldehyde

A 1.2 *M* solution (18 ml) of *n*-butyllithium in ether was added dropwise to a mixture of 3.6 g (2×10^{-2} mol) of compound **2** and 2.3 g (2×10^{-2} mol) of TMEDA in 30 ml of anhydrous diethyl ether at -78°C . The mixture was allowed to warm to room temperature and then stirred for 24 h. The yellow solution was then cooled to -78°C and 2.1 g (2×10^{-2} mol) of benzaldehyde in 10 ml of ether was added. After 0.5 h stirring at room temperature the mixture was hydrolyzed as previously. Distillation gave 2.0 g (yield 58%) of the aminofuran **14** [6]. B.p. $106^\circ\text{C}/0.08$ mmHg. NMR (CCl_4) (δ , ppm): 1.8 (8H, m); 2.8 (4H, m); 4.9 (2H, m); 7.2 (5H, m). Mass spectrum: M^+ 217.

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