Pergamon

Tetrahedron Vol. 50, No. 27, pp. 8185-8194, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00430-7

Photoinduced Electron Transfer (PET) Promoted Cyclisations of 1-[N-Alkyl-N-(Trimethylsilyl)methyl]amines Tethered to Proximate Olefin: Mechanistic and Synthetic Perspectives#

Ganesh Pandey*, G. Devi Reddy and G. Kumaraswamy

Division of Organic Chemistry (synthesis)
National Chemical Laboratory
Pune- 411008, INDIA
FAX: 91-212-330233

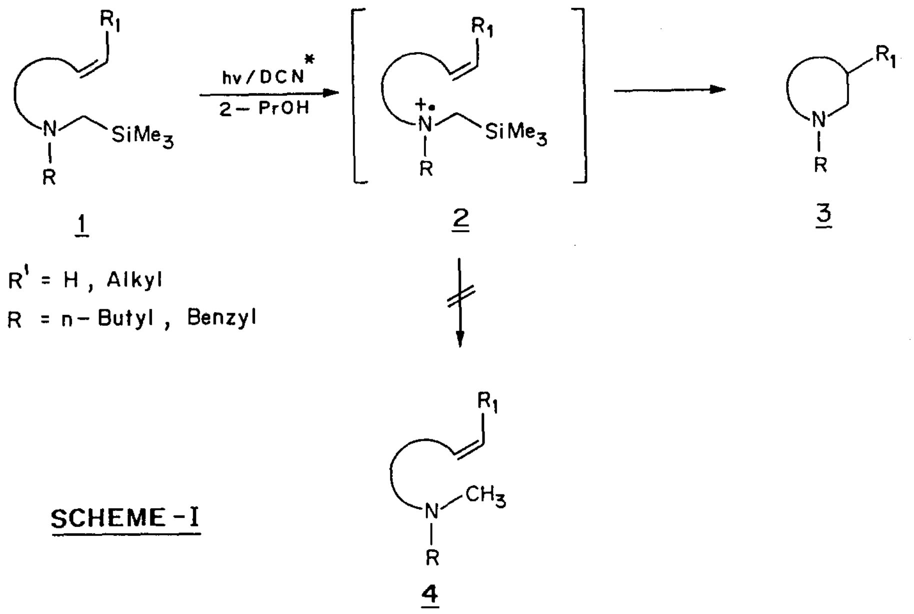
Abstract: *Upon PET reaction, amines of type* **1** *undergo efficient cyclisations to produce pyrrolidines and piperidines. Mechanistically, involvement of delocalised α-silylmethyl amine radical cation as reactive intermediate in such cyclisations are described.*

Radical ions are suggested to be critical intermediates in the development of recent organic reactivity concept[1] and the efficient fragmentation of these intermediates to charged and neutral radicals, simultaneously, have provided organic chemists with an unique opportunity of discovering new and synthetically useful chemical reactions. Photoinduced electron transfer (PET) reactions[2] have been recognised as an attractive strategy to generate radical ions and researches during the last decade have led to the development of interesting and useful chemical transformations from the fragmentation of cation radicals, in particular[3].

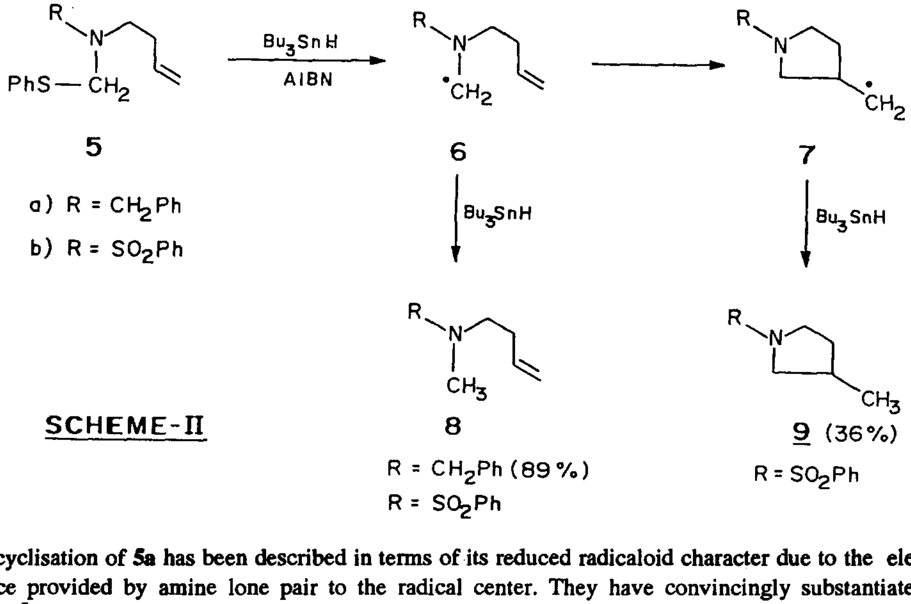
Cation radicals generated by PET processes from α-trialkyl substituted donors are reported[4] to undergo selective desilylation to produce neutral non-silicon containing radicals even when competitive deprotonation pathways are available. Mariano etal[5] have extended the same concept to α-silylmethylamine radical cations, generated by SET initiated photoreactions (direct as well as sensitized) and reported[5] the generation of free "nucleophilic" α-amino radicals which have been utilised for the conjugate addition to unsaturated esters and ketone groups. The arguments in favour of such radicals are based on the failure of their addition to olefins devoid of electron withdrawing substituents[5]. However, these results are in sharp contrast to our preliminary and independant observation[6] on a related study where PET reactions of α-silylated methylamines of type **1** gave

NCL Communication No. 5991.

almost quantitative yield of the cyclised product **3**, without the trace amount of any other observable product including α-amino radical reduction product **4** (**SCHEME I**).



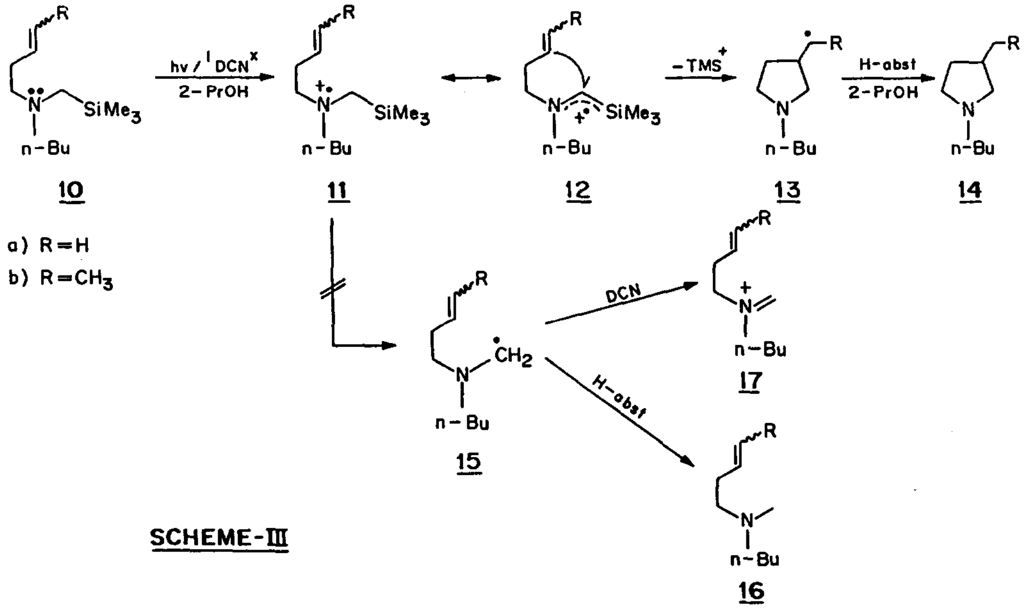
Further contrast to Mariano's[5] observation may be found from Padwa's group[7] where free α-aminoradicals, generated by the conventional reductive cleavage of -C-S- bond of N-alkenyl-N-(phenylthio)methylamine **5a** by Bu_3SnH, are found to be incapable of addition to π-bond. The



lack of cyclisation of **5a** has been described in terms of its reduced radicaloid character due to the electronic assistance provided by amine lone pair to the radical center. They have convincingly substantiated their arguments[7] by demonstrating the enhancement in the cyclisation of radical **6**, by placing an electron withdrawing sulphonyl group on nitrogen atom of amine (e.g **5b**) to retard the electronic assistance of amine to the radical species (**SCHEME II**). Indeed, understanding of these features have led to the generation and extensive utilisation of α-acylamino radicals for the synthesis of several biologically active nitrogen heterocycles[8-10]. Therefore, to settle the ambiguity of the mechanism involved in the cyclisations[6] of compounds of type **1**, we probed this aspect of the reaction with extensive experimentation and results suggest that the cyclisations involve delocalized α-silyl methylamine cation radical of **1** itself as reactive intermediate. The detailed experimental observations that serve the basis of our postulates and the synthetic perspective of these cyclisations for the construction of substituted pyrrolidines and piperidines have been discussed in this report.

RESULTS AND DISCUSSION

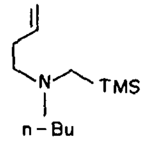
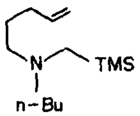
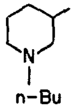
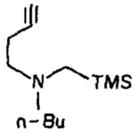
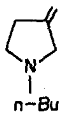
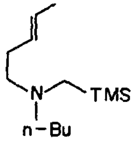
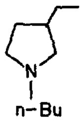
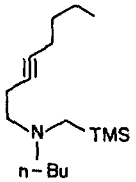
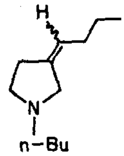
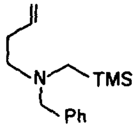
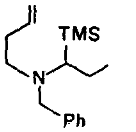
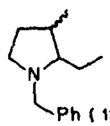
At the outset we selected α-silylmethylamine **10a** for studying PET reaction under our established experimental conditions[11]. **10a** was conveniently obtained (80 % yield) by refluxing together a mixture of N-butyl-N-[(trimethylsilyl)methyl] amine (itself prepared by heating n-butylamine and $TMSCH_2Cl$), and 1-bromobutene for 10-12 h in dry CH_3CN in the presence of K_2CO_3. PET reaction performed by irradiating a mixture of **10a** (15 mmol) and 1,4- dicyanonaphthalene (DCN, 4.5 mmol) in 2-propanol through a Pyrex filter light (>280 nm, 450-W Hanovia medium pressure lamp, all light absorbed by DCN) without removing



SCHEME-III

dissolved oxygen from the solution indicated (monitored by GC) the complete transformation of **10a** to a single product within 3h. Usual work up and purification furnished cyclised product **14a** in almost quantitative yield with no other observable product and with complete recovery of DCN (98%)[11]. Similarly, PET reaction of **10b** which has got relatively electron- rich olefin also underwent smooth cyclisation to give corresponding pyrrolidine **14b**.

TABLE - 1 **PET Promoted cyclisations of α-methyl silylated amines (10a-b and 18-22).**

Precursor	Irradiation time (h)	Product [a]	Yield [c]
 10a	3·5	 14a	84
 18	4·0	 23	80
 19	4·0	 24	80
 10b	3	 14b	84
 20	4	 25 (1:1 Mixture)[b]	80
 21	3	 26	85
 22	3	 (1:1 Mixture)[b] 27	80

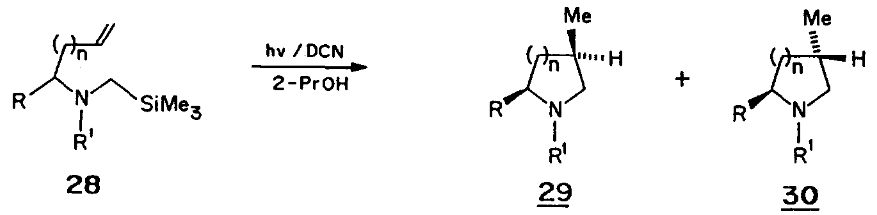
a) *Characterised by IR, ^1H NMR and Mass spectrometry*; b) *Diastereomeric ratio determined by GC (Methylsilicone, fused silica, 50 mts)*; c) *Yields calculated based on the % disappearance of starting amines, isolated but not optimized.*

It may be pertinent to mention that if free α-amino radical **15** was the reactive intermediate in these photocyclisations, the formation of trace amount of reduction product **16** was very much likely as noted by Padwa etal[7]. The generation of **15** is further questionable based on the well established fact from our group[11] as well as from others[12] that if such radical species were formed it would have efficiently undergone further one electron oxidation, due to the high ground state reduction potential of DCN (-1.28 ev)[13] and low oxidation potential[14] of **15**, to generate iminium cation species **17** and thereby terminating or reducing the cyclisation yield. It is very unlikely that the cyclisation rate of **15** will completely dominate over the formation of **17**. Absence of either **16** or product arising out of the iminium cation intermediate (likely demethylation product) coupled with the high yield of cyclisation product **14** strongly rules out the possibility of free α-amino radical intermediacy in these reactions.

Thus effective cyclisation of **10** to **14**, though appears to involve some sort of radical pathways, may not albeit be through a free α-amino radical intermediate. To rationalise our results, we postulate α-silylmethyl radical cation of **12** itself as reactive species participating in the cyclisation[15] where radical cationic moiety is delocalised between the nitrogen and silicon atom due to the vertical overlap of filled -C-Si- orbital and half vacant nitrogen orbital (β-silicon effect)[16] as shown in **Scheme III**. Subsequent addition of π-electron of the olefin to the electron deficient species **12** followed by TMS^+ group elimination and usual sequence of termination step of **13** by H-abstraction from 2-propanol leads to the formation of **14**. Therefore, it is probable that the addition of olefin to **12** and desilylation step is simultaneous and assisted.

To probe further the generality of this transformation and to utilise the cyclisation strategy for the construction of pyrrolidine and piperidine ring systems, fundamental heterocyclic units in various biologically important alkaloids[17], series of silylated amines were subjected to PET cyclisation and the results are given in **Table I**.

In order to gain further insight into our proposed mechanism, the stereochemical aspect of such cyclisations were probed by taking **28a** as an example. The identical PET reaction of **28a**, as reported for **10**, gave

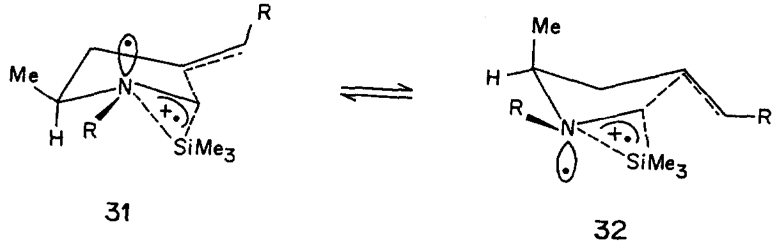


	29/30	YIELD %
a) $R = CH_3$, $R^1 = n\text{-}C_4H_9$, n=1	50 : 50	80
b) $R = CH_3$, $R^1 = -CH_2Ph$, n=1	50 : 50	85
c) R = Ph, $R^1 = -CH_2Ph$, n=1	60 : 40	85
d) R = Ph, $R^1 = CH_2Ph$, n=2	56 44	82

SCHEME-IV

diastereomeric mixture of pyrrolidine derivatives **29a** and **30a** in 1:1 ratio which was determined by capillary GC (methylsilicone, fused silica, 50 mts) analysis (**SCHEME IV**).

The absence of diastereoselectivity in the cyclisation of **28** in comparison to analogous 3-substituted-5-hexenyl radical carbocyclisation stereochemistry[18], further supports that free radicals are not involved in such photocyclisations. A plausible explanation to this observed non-stereoselectivity can be forwarded by considering the low energy barrier (0.5 Kcal/mole) for the interconversion of the two possible transition states **31** and **32** due to the flipping of the electrons in empty *p*-orbital of nitrogen and thereby making



SCHEME-V

non-distinguishable position (axial or equatorial) for the substituent for a particular defined state (**SCHEME V**). Further study with compounds **28b-d** indicates that the diastereoselectivity is independant of the size of substituent either at α-position of amine nitrogen or on the nitrogen atom of the amine.

Based on the above observations, it may be concluded that PET cyclisations of amines **1** do not involve free α-aminoradical, instead, initially produced α-silylmethyl amino radical cation delocalised between nitrogen and silicon atom due to vertical overlap of the filled -C-Si- orbital and half-filled nitrogen orbital serves as reactive intermediate. Finally, it may also be suggested that such type of cyclisations have considerable potential for the synthesis of pyrrolidines and piperidines.

Acknowledgements: One of us (GDR) is thankful to CSIR, New Delhi, for the award of senior research fellowship.

EXPERIMENTAL

The chemicals and reagents used in this study were commercial grade pure and some of them were used after further purification. Dicyanonaphthalene (DCN) was prepared by following standard procedure[19]. The chromatography was performed using silicagel (Acme India, finer than 200 mesh). The solvents used during experiments were purified, unless otherwise stated, by standard literature procedure.

All the compounds were characterised by IR, ^1H and ^{13}C NMR, Mass spectroscopy. Nuclear Magnetic Resonance spectra obtained for ^1H and ^{13}C were recorded on BRUKER 200 MHz, VARIAN GEMINI 200MHz and FT 80MHz, in $CDCl_3$, using tetramethyl silane as internal reference. Chemical shifts are given on (ppm) scale, the coupling constants (J values) are reported in Hertz. Infrared spectra were recorded on Perkin-Elmer model 283B, and values are reported in cm^{-1}. Mass spectra were recorded on VG-MICRO MASS 7070 model, and GC analysis were performed by using OV-17 (10%, 10'+1/8") and methyl silicone (fused silica, 25mts) capillary columns. Equipments used for photolysis were 450-W Hanovia medium pressure mercury lamp, Pyrex filtered immersion well and reaction vessels were from ACE glass USA.

General method for the synthesis of α-methyl silylated amines (10a-b and 18-21).

The syntheses were accomplished in two steps.

15.13g (0.1253mol) of $TMSCH_2Cl$ and 27.12g (0.371mol) butyl amine were refluxed with stirring for 2.5h. The reaction was cooled to room temperature and 0.1N NaOH solution was added in order to hydrolyse the organic salt which had formed. The aqueous layer was extracted with ether, dried over anhydrous Na_2SO_4, concentrated and distilled under reduced pressure (at 5mm, 80-82° c) to get N-butyl-N-[(trimethylsilyl) methyl] amine (86%) as a colourless liquid. Corresponding N-benzyl derivative which is precursor for amines **21,22,28b,c** and **d** was prepared in the same manner.

32.5mmol of corresponding bromoalkyne or alkene, was added dropwise with stirring to a refluxing solution of N-butyl-N-[(trimethylsilyl) methyl] amine (5.16g, 32.5 mmol) in dry acetonitrile containing (6.62g, 48.75 mmol) of anhydrous K_2CO_3. After 10-12h of reflux, the reaction mixture was allowed to cool to room temperature and solid material was filtered off, washed with ethyl acetate, combined filtrates were concentrated and purified by column chromatography to give corresponding tertiary amines as liquids (75-82%). The detailed spectral characteristics of these amines are as follows.

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-3-butene (10a).

Yield 80%.; ^{1}H NMR (200 MHz): 0.095(s, 9H), 0.92(t, J=7, 3H), 1.26-1.39(m, 4H), 1.93(s, 2H), 2.16-2.54(m, 6H), 4.98-5.15(m, 2H), 5.2-5.5(m, 1H).; IR (Neat): 2910, 1620, 1440, 1235 and 840; Mass: (m/z:213).

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-4-pentene (18).

Yield 82%.; ^{1}H NMR (200 MHz): 0.12(s, 9H), 0.93(t, J=7.2, 3H), 1.29-1.49(m,6H), 1.90(s,2H), 2.04-2.20(m, 4H), 2.38-2.42(m, 2H), 5.02-5.15(m, 2H), 5.86-5.93(m, 1H).; IR (Neat): 2900,2800, 1450, 1255 and 830; Mass: (m/z:227).

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-3-butyne (19).

Yield 79%.; ^{1}H NMR (200 MHz): 0. 15(s, 9H), 0.90(t, J=7.2, 3H), 1.25-1.40(m, 4H), 1.95(s,3H), 2.26-2.34(m,2H), 2.37(t, J=7.4, 2H), 2.65(t, J=7.4, 2H).; IR (Neat): 3310,2900, 2800, 1255 and 850; Mass: (m/z: 211).

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-3-pentene (10b).

Yield 77%.; ^{1}H NMR (200 MHz): 0.098(s, 9H), 0.90(t, J=7.3, 3H), 1.25-1.73(m, 7H), 2.0 (s, 2H), 2.30-2.81(m,6H), 5.55-5.68(m, 2H).; IR (Neat): 2900, 2800, 1540, 1235 and 840; Mass: (m/z: 227).

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-3-octyne (20).

Yield 75%.; ^{1}H NMR (200 MHz): 0.15(s, 9H), 0.75-0.85(m, 6H), 1.22-1.28(m, 8H), 2.10(s, 2H), 2.46-2.70(m, 8H).; IR (Neat): 2900, 2100, 1255 and 850; Mass: (m/z: 267).

1-[N-Benzyl-N-[(trimethylsilyl)methyl]amino]-3-butene (21).

Yield 80%.; ^{1}H NMR (200 MHz): 0.120(s, 9H), 1.95-2.03(m, 2H), 2.15(s, 2H), 2.52(t, J=7.0, 2H), 3.56(s, 2H), 4.95-5,05(m, 2H), 5.82-5.93(m, 1H), 7.21-735(m, 5H).; IR (Neat): 2900, 2800, 1540, 1500, 1460, 1235 and 840; Mass: (m/z: 247).

Synthesis of 1-[N-Benzyl-N-[(1-trimethylsilyl)propyl]amino]-3-butene (22).

The synthesis was accomplished in three steps

1-Bromo 3-butene (4.35g, 32.5 mmol) and N-benzyl-N-cyanomethyl amine (4.74g, 32.5 mmol) (itself prepared by refluxing benzylamine and chloroacetonitrile in the presence of anhydrous K_2CO_3 in acetonitrile) were refluxed in dry acetonitrile containing anhydrous K_2CO_3 (6.5g, 48.2 mmol). Usual workup as described above followed by column chromatography [silicagel 60-120 mesh, hexane:ethyl acetate (9:1)] gave 5.8g (90%) of N-(3-butenyl)-N-(cyanomethyl) benzylamine as a liquid.

n-BuLi (15.50 ml, 1.8M, 28.03 mmol) was added dropwise to a stirred solution of diisopropylamine (2.83g, 28.03 mmol) in THF at -78° c. After 30 min, the resulting LDA solution was transferred by cannula to the suspension of the silyl ammonium salt derived from N-(3-butenyl)-N-(cyano methyl) benzylamine (3.72g, 18.6 mmol) and TMSCl (3.02g, 28.03 mmol) in THF at -78°c. The mixture was stirred at the same temperature for 3h, then allowed to come to room temperature. The contents were poured into saturated solution of NH_4Cl and extracted with ether. Organic extract was washed with water, dried over anhydrous Na_2SO_4 and concentrated to offer 6.09g (80%) of required product which was used without further purification.

Grignard reagent, prepared from ethyl bromide (1.69g, 15.7 mmol) and Mg turnings (0.44g, 18.3 mmol) was added to a solution of 1-[N-Benzyl-N-[(trimethylsilyl) acetonitrile]amino]-3-butene (3g, 11.0 mmol) in dry ether. The mixture was stirred at room temperature for 1h, then quenched with 10% HCl. 100 ml of ether was added to the mixture and the organic layer was extracted with 10% HCl. The HCl extract was made alkaline with conc. NH_4OH and extracted with ether, washed with water, brine and dried over anhydrous Na_2SO_4. Concentration followed by column chromatography of the crude product using hexane:ethylacetate (9:1) as eluent gave 2.26g (75%) of 1[N-Benzyl-N-[(1-trimethylsilyl) propyl]amino]-3-butene.

Yield 75%.; ^{1}H NMR (200 MHz): 0.095(s, 9H), 0.95(t, J=7.0, 3H), 1.22-1.35(m, 2H), 1.95-2.23(m, 3H), 2.56(t, J=7.2, 2H), 3.65(s, 2H), 5.02-5.15(m, 2H), 5.75-5.91(m, 1H), 7.21-7.33(m, 5H).; IR (Neat): 2900, 1540, 1480, 1460, 1230 and 840; Mass: (m/z; 275).

General method for synthesis of α-methyl silyl amines (28a-d).

The syntheses were accomplished in three steps.

Corresponding aldehyde (22.4 mmol) was added dropwise at 0° C to the Grignard reagent prepared from appropriate alkenyl bromide (26.8 mmol) and Mg turnings (0.618g, 26.8 mmol) in dry ether. After 3h of reflux, contents were poured into 100 ml ice-water and quenched with dil H_2SO_4. Organic layer was separated, washed with water, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography to give corresponding alcohols as liquids (85-90%).

PBr_3 (33.0 mmol) was added dropwise at 0° C to the above alcohol (20 mmol) in dry ether while stirring. After additional 90 min of stirring it was diluted with ether and finally quenched with saturated NH_4Cl. The organic layer was separated and successively washed with water, saturated $NaHCO_3$ and brine. Removal of the solvent gave corresponding alkenyl bromides (85-90%) which were used for further reaction without purification.

22.5 mmol of corresponding alkenyl bromide and 22.5 mmol of N-alkyl-N-[(trimethyl silyl) methyl] amine were refluxed in dry acetonitrile containing 33.75 mmol of anhydrous K_2CO_3 in a similar manner as described for compound **10** gave α-methyl silyl amines (**28a-d**) as liquids (70-78%).

1-[N-Butyl-N-[(trimethylsilyl)methyl]amino]-1-methyl-3-butene (28a).

Yield 75%.; ^{1}H NMR (200 MHz): 0.11(s, 9H), 0.71-0.96(m, 6H), 1.17-1.39(m, 4H), 1.79(s, 2H), 2.17-2.32(m, 4H), 2.48-2.75(m, 1H), 4.65-5.02(m, 2H), 5.78-6.05(m, 1H).; IR (Neat): 2910, 1620, 1440, 1235 and 840; Mass: (m/z: 227).

1-[N-Benzyl-N-[(trimethylsilyl)methyl]amino]-1-methyl-3-butene (28b).

Yield 78%.; ^{1}H NMR (200 MHz): 0.12(s, 9H), 0.95(d, J=7.5, 3H), 1.95(s, 2H), 2.12-2.25(m, 2H), 2.58-2.75(m, 1H), 3.72(s, 2H), 4.75-5.05(m, 2H), 5.65-5.98(m, 1H), 7.21-7.35(m, 5H).; IR (Neat): 2910, 1540, 1480, 1235 and 840; Mass: (m/z: 261).

1-[N-Benzyl-N-[(trimethylsilyl)methyl]amino]-1-phenyl-3-butene (28c).

Yield 70%.; ^{1}H NMR (200 MHz): 0.12(s, 9H), 2.12(d, J= 13.2, 2H), 2.50-2.59(m, 1H), 2.65-2.82(m, 1H), 3.25(d, J=13.2, 1H), 3.70-3.78(m, 2H), 4.90-5.05(m, 2H), 5.70-5.85(m, 1H), 7.25-7.51(m, 10H).; IR (Neat): 2900, 2800, 1540, 1500, 1460, 1235 and 840; Mass: (m/z: 323).

1-[N-Benzyl-N-[(trimethylsilyl)methyl]amino]-1-phenyl-3-pentene (28d).

Yield 70%.; ^{1}H NMR (200 MHz): 0.15(s, 9H), 1.70(d, J=13.0, 1H), 1.85-1.95(m, 1H), 2.05-2.25(m, 4H), 3.20(d, J=13.1, 1H), 3.65(t, J=7.3, 1H), 3.73(d, J=13.1, 1H), 4.95-5.07(m, 2H), 5,75-5.92(m, 1H), 7.20-7.52(m, 10H).; IR (Neat): 2900, 2750, 1540, 1500, 1480, 1460 and 840; Mass: (m/z: 337).

General method of irradiation.

A mixture containing 15mmol of α-silylated methylamines (**10a-b,18-22** and **28a-d**) and DCN (0.08g, 4.5 mmol) in 2-propanol was irradiated in 500 ml irradiation vessel using 450-W Hanovia medium pressure lamp at ambient temperature for 2-4h without removing dissolved air from the reaction mixture. The lamp was housed into a Pyrex water jacketed immersion well which allowed only >280 nm light to pass through. The reaction progress was monitored by TLC and GC. When almost 90% of the starting materials were consumed, the photolysis was discontinued. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography to get corresponding cyclised products in high yields (80-85%) along with quantitative recovery of DCN. The cyclised products were characterised by ^{1}H NMR, IR and mass spectral data.

14a). Yield 84%.; ^{1}H NMR (200 MHz): 0.91(t, J=7.3, 3H), 1.03(d, J=6.7, 3H), 1.33-1.48(m, 7H), 2.20-2.37(m, 2H), 2.57-2.75(m, 4H).; IR (Neat): 2957, 2928 and 1458; Mass: (m/z: 141).

23). Yield 80%.; ^{1}H NMR (200 MHz): 0.91(t, J=7.1, 3H), 1.04(d, J=6.2, 3H), 1.28-1.48(m, 9H), 2.21-2.42(m, 2H), 2.52-2.75(m, 4H).; IR (Neat): 2940, 2855, 1355 and 840; Mass: (m/z: 155).

24). Yield 80%.; ^{1}H NMR (200 MHz): 0.85(t, J=7.2, 3H), 1.19-1.40(m, 6H), 2.34-2.39(m, 4H), 2.54-2.57(m, 2H), 4.83(d, J=8.8, 2H).; IR (Neat): 2910, 2800, 1135 and 940; Mass: (m/z: 139).

14b). Yield 84%.; ^{1}H NMR (200 MHz): 0.85-1.05(m, 6H), 1.18-1.45(m, 9H), 2.00-2.32(m, 2H), 2.40-2.65(m, 4H).; IR (Neat): 2950, 2859, 1255 and 1015; Mass: (m/z: 155).

25). Yield 80%.; ^{1}H NMR (200 MHz): 0.95-1.00(m, 6H), 1.20-1.45(m, 8H), 1.92-2.00(m, 2H), 2.15-2.25(m, 2H), 2.30-2.49(m, 4H), 2.52-2.71(m, 2H), 5.39-6.35(m, 1H).; ^{13}C NMR (50.4 MHz): 138.3, 121.0 and 120.65(equal intensity) 59.71, 56.7, 54.4, 31.59, 29.31, 27.2, 22.3, 20.7, 18.4, 16.9, 14.0.; IR (Neat): 2900, 2800, 1535, 1430 and 1020; Mass: (m/z: 195).

26). Yield 85%.; ^{1}H NMR (200 MHZ): 1.02(d, J=6.9, 3H), 1.32-1.40(m, 3H), 2.57-2.75(m, 4H), 3.69(s, 2H), 7.29-7.32(m, 5H).; IR (Neat): 2900, 2800, 1510, 1445 and 1240; Mass: (m/z: 175).

27).Yield 80%.; ^{1}H NMR (200 MHZ): 0.92(t, J=7.0, 3H), 1.05(d, J=6.3, 3H), 1.22-1.53(m, 5H), 2.53-2.75(m, 3H), 3.65(s, 2H), 7.21-7.34(m, 5H).; IR (Neat): 2900, 2800, 1510, 1480, 1430 and 840; Mass: (m/z: 203).

29a). Yield 80%.; ^{1}H NMR (200 MHz): 0.89-0.95(m, 6H), 1.01(d, J=6.5, 3H), 1.21-1.56(m, 7H), 1.98-2.24(m, 4H), 2.73-2.81(m, 1H).; ^{13}C NMR (50.4 MHz): 62.04, 59.65, 52.21, 44.75, 42.60, 40.09, 28.91, 20.52, 19.59, 14.00,; IR (Neat): 2900, 2810, 1420, 1235 and 1030; Mass: (m/z: 155).

29b). Yield 85%.; ^{1}H NMR (200 MHz): 0.95(d, J=6.6, 3H), 1.10(d, J=6.5, 3H), 1.35-1.50(m, 3H), 2.53-2.62(m, 2H), 2.75-2.81(m, 1H), 3.7(s, 2H), 7.29-7.32(m, 5H).; ^{13}C NMR (50.4 MHz): 128.32, 127.82, 127.34, 126.95, 126.42, 63.02, 62.22, 55.65, 44.68, 30.35, 21.78, 14.82,; IR (Neat): 2900, 2820, 1510, 1480 and 1240; Mass: (m/z: 189).

29c) Yield 85%.; ^{1}H NMR (200 MHZ): 1.05(d, J=6.6, 3H), 1.25-1.48(m, 2H), 1.80-2.05(m,1H), 2.35-2.52(m, 2H), 3.10(d, J=11.0, 1H), 3.48-3.60(m, 1H), 3.90(d, J=11.0, 1H), 7.20-7.55(m, 10H).; ^{13}C NMR (50.4 MHz): 126.4-128.3(aromatic carbons), 70.38, 60.46, 57.82, 44.78, 30.4, 21.8.; IR (Neat): 2900, 2800, 1510, 1455 and 1240; Mass: (m/z: 251).

29d). Yield 82%.; ^{1}H NMR (200 MHz): 1.15(d, J=6.7, 3H), 1.29-1.51(m, 4H), 1.55-2.05(m, 1H), 2.30-2.50(m, 2H), 3.05(d, J=11.00, 1H), 3.45-3.55(m, 1H), 3.85(d, J=11.0, 1H), 7.15-7.60(m, 10H).; ^{13}C NMR (50.4 MHz): 126.42-128.40(aromatic carbons), 71.35, 60.1, 57.7, 44.7, 31.3, 29.5, 20.83,; IR (Neat): 2900, 2800, 1510, 1350,and 1250; Mass: (m/z: 265).

REFERENCES

1. a) Kochi, J.K. *Angew.Chem.Int.,Ed (Eng).* **1988**, *27*, 1227. (b) Pross, A. *Adv. Phys.Org.Chem.* **1985**, *21*, 99. (c) Pross, A.; Shaik, S.S. *Acc. Chem. Res.* **1983**, *16*, 363.

2. Fox, M.; Chanon, M."Photoinduced Electron Transfer Reactions" Part A-D, **1988**, Elsevier, Amsterdam.

3. a) Pandey, G. *Topics in Current Chemistry* **1993**, *168*, 175. (b) Mattay, J. *Synthesis*. **1989**, 233.

4. a) Ohga, K.; Mariano, P.S. *J.Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Yoon, U.C.; Mariano, P.S. *J.Org. Chem.* **1984**, *49*, 213. (c) Lan, A.J.Y.; Quillen, S.L.; Heuckeroth, R.O.; Mariano, P.S. *J. Am. Chem. Soc.* **1984**, *106*, 6439. (d) Borg, R.M.; Heuckeroth, R.O.; Lan, A.J.Y.; Quillen, S.L.; Mariano, P.S. *ibid* **1987**, *109*, 2728.

5. a) Jeon, Y.T.; Lee, C-P.; Mariano, P.S. *J. Am. Chem. Soc.* **1991**, *113*, 8847. (b) Xu, W.; Zhang, X-M.; Mariano, P.S. *J. Am. Chem. Soc.* **1991**, *113*, 8863. (c) Jung, Y.S.; Swartz, W.H.; Xu, W.; Mariano, P.S.; Grein, N.J.; Schultz, A.G. *J. Org. Chem.* **1992**, *57*, 6037.

6. Pandey, G.; Kumaraswamy, G.; Bhalerao, U.T. *Tetrahedron Lett.* **1989**, *30*, 6059.

7. Padwa, A.; Nimmesgern, H.; Wong, G.S.K. *J.Org.Chem.* **1985**, *50*, 5620.

8. Dener, J.M.; Hart, D.J. *Tetrahedron* **1988**, *44*, 7037 and references cited therein.

9. a) Esch, P.M.; Hiemstra, H.; Speckamp, N.M. *Tetrahedron* **1990**, *31*, 759. (b) Udding, J.H.; Tuijp, J.M.; Hiemstra, H.; Speckamp, W.N. *Tetrahedron* **1994**, *50*, 1907.

10. a) Ueno, Y.; Khare, R.K.; Okawana, M. *J. Chem. Soc. Perkin Trans I* **1983**, 2637. (b) Han, B.H.; Park, M.H.; Waha, S.T. *Tetrahedron Lett.* **1987**, *28*. 3957. (c) Danishefsky, S.J.; Panek, J.S. *J. Am. Chem. Soc.* **1987**, *109*, 917.

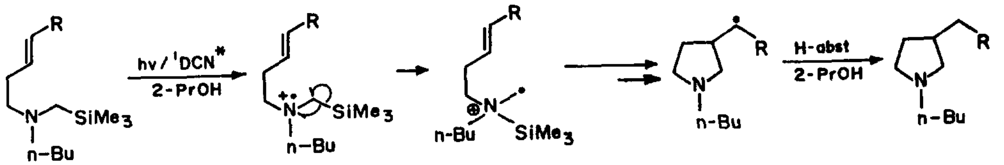
11. Pandey, G. *Synlett.* **1992**, 546.

12. a) Bartholomew, R,F.; Davidson, R.S.; Howell, M.J. *J. Chem. Soc. Chem Commun.* **1971**, **2804**. (b) Hall, L.R.; Iwamoto, R.T.; Hanzlik, R.P. *J.Org. Chem.* **1989**, *54*, 2446.

13. Arnold, D.R.; Wong, P.C.; Marouls, A.J.; Cameron, T.S. *Pure and Appl. Chem.* **1980**, *52*, 2609.

14. Griller, D.; Lossing, F.P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

15. A reviewer has suggested the possibility of an alternative mechanism by involving the rearrangement of **11** to produce α-amine radical salt as shown below.



However, we feel that desilylation of α-amino radical cation would be much faster process than rearrangment involving energetically unfavourable homolytic C-Si bond cleavage.

16. Yoshida, J-i; Maekawa, T.; Murata, T.; Matsunaga, S.I.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962.

17. Pyrrolidine, piperidine and pyridine Alkaloids in "The Alkaloids" specialist periodical Reports, The Chemical Society London **1971**, Vol 1 and **1983**, Vol 13.

18. Beckwith, A.L.J. *Tetrahedron* **1981**, *37*, 3073.

19. Krishna, A. Ph.D thesis, submitted to Osmania University Hyderabad, 1989.

(*Received in UK* 11 *April* 1994; *revised* 12 *May* 1994; *accepted* 13 *May* 1994)