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Studies in amine oxide rearrangement: Meisenheimer rearrangement of *m*-substituted tertiary amine oxides

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A number of N-substituted but-2-ynyl, allyl and 4-aryloxy-2-butynyl-N-methyl anilines **2a-c**, **3a-h** and **5d-f** have been synthesized in excellent yield. The *m*-substituted allylalkylaryl amines have been then treated with one equivalent of *m*-chloroperoxybenzoic acid (*m*-CPBA) to give products **9a-h** in 80-95% yield. The 4-aryloxy-2-butynyl-N-methyl anilines **5d-f** on treatment with *m*-CPBA proceed through the allene intermediate **7**.

Keywords: Meisenheimer rearrangement, *m*-substituted allylalkylaryl amines, *m*-CPBA, allene intermediate, amine oxide rearrangement

IPC: **Int.Cl.[7] C 07 D**

The construction of a five-membered pyrrole ring in 2,3-disubstituted indoles through rearrangement of aryl propargyl amine oxides was developed[1-6]. It was proposed that a [2,3] sigmatropic shift is followed by a unique Claisen rearrangement in which a [3,3] shift took place through two heteroatoms to give indoles in almost quantitative yield. The formation of indoles occur rapidly in one step by simply stirring a solution of aryl propargyl amine with one equivalent of *m*-chloroperoxybenzoic acid (*m*-CPBA) at rt without isolation of the labile amine oxide. The initial step in the reorganization of the aryl propargyl amine oxide is also the same [2,3] shift as in the case of the Meisenheimer rearrangement of allyl aryl amine oxides[7,8]. Extensive studies on the Meisenheimer rearrangement have been made and the accumulated knowledge[2] suggests that the formation of tertiary amine oxides of N-allyl tertiary amines prevails qualitatively in competition with the epoxidation. However, epoxidation occurred with *m*-CPBA in non-allylic systems[9]. We have recently observed that the presence of *m*-CPBA in the reaction mixture does not interfere with the Meisenheimer rearrangement. It has also been reported[10] that the amine oxide rearrangement of N,N-bis(4-aryloxy-2-butynyl)anilines with one equivalent of *m*-CPBA furnishes only one product, N-(4′-aryloxy-2′-butynyl)-2-(aryloxymethyl)-3-(*m*-chlorobenzoyloxymethyl) indoles, in high yield. This observation indicates that the [2,3] shift is very specific towards one reacting propargyl moiety and the other reacting propargyl moiety is completely unaffected and is appended on the indole nitrogen. A competitive study[11] of the Claisen rearrangement of substrates containing an allyl ether and a propargyl ether moieties in the same molecule was made earlier. Recently, a competitive study of an amine oxide rearrangement in a substrate tertiary amine with allylic and propargylic moieties, *e.g*. N-allyl, N-propargyl anilines was also reported[12]. It was reported[13] that the formation of O-[2-(2-methylbut-3-enyl)]-N-methyl-N-phenylhydroxylamine occurs readily in one step by stirring a solution of N-methyl-N-phenyl-N-[1-(3-methylbut-2-enyl)]amine with one equivalent of *m*-CPBA at rt without isolation of the labile amine oxide. This provided the motivation for a study of the amine oxide rearrangement in a substrate differently substituted N-methyl anilines with appropriate allylic, but-2-ynylic and 4-aryloxy-but-2-ynyl moieties, *e.g*. N-allyl, N-but-2-ynyl and N-(4′-aryloxy-2′-butynyl) anilines. However, so far no example on the amine oxide rearrangement of *m*-substituted anilines is available in literature. This led to the present study on the amine oxide rearrangement of *m*-substituted amine oxide derivatives. Herein is reported the results of the investigation.

Results and Discussion

The amine oxide rearrangement of *ortho* and *para* substituted tertiaryaryl amine oxides has been amply exemplified[14-17]. The following substrate tertiaryaryl

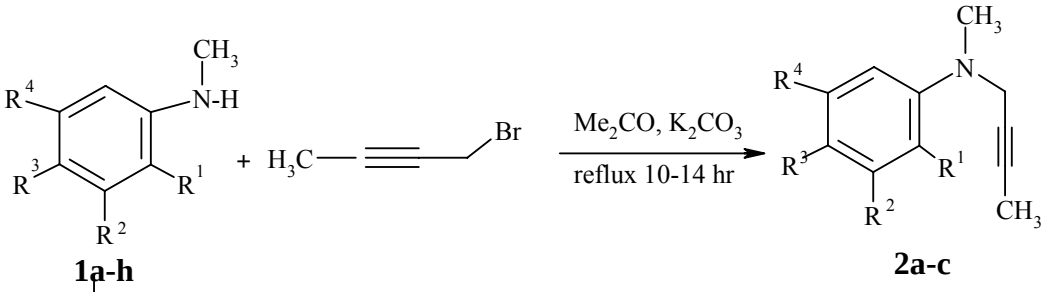
amines with *m*-substitution in the arylamine moiety have been prepared in 60-95% yield by the reaction of different N-alkyl anilines **1a-h** with but-2-ynylic or allylic bromides in refluxing acetone in the presence of anhydrous potassium carbonate for 10-25 hr (**Scheme I**).

Amine oxide rearrangement of *ortho* and *para* substituted N-alkyl, N-but-2-ynyl anilines has been extensively investigated[10]. The indole derivatives have been obtained in almost quantitative yield. Compound **2a** was subjected to the condition of amine oxide rearrangement by using one equivalent of *m*-CPBA in chloroform at 0-5°C. Highly polar amine oxide formation was indicated (TLC monitoring) within 20-25 min. The reaction mixture was stirred for an additional period of 12 hr at rt. No definite spot was detectable on TLC but only tailing was observed. So, no traceable product could be isolated. Similar observations were also made in case of compounds **2b** and **2c**. Attention was then concentrated on N-4-aryloxy-2-butynyl-*N*-methyl anilines **5d-f** (**Scheme II**). The substrate **5d** was subjected to the condition of amine oxide rearrangement by treating with one equivalent of *m*-CPBA in chloroform at 0-5°C. Here also highly polar amine oxide formation was completed within 25-30 min as indicated by TLC monitoring. The reaction mixture was then stirred for 10-12 hr at rt. Here too no definite spot was observed on TLC and work-up did not afford any traceable product. The same stirring was continued at 0-5°C instead of rt, but no expected cyclized product was obtained. Other substrates **5e, f** also did not afford any expected product of amine oxide rearrangement. [3,3] Sigmatropic rearrangement of *m*-substituted substrates has been studied by Bruce *e. al*.[18] So at this point it was thought that if an *ortho* or a *para* substituent was placed along with a *m*-substituent, the reaction might take the normal course. The other substrates **5e,f** were therefore subjected to the condition of amine oxide rearrangement. Here too no expected product was obtained. It was apparent that the substrates decomposed or polymerized under the condition of the rearrangement.

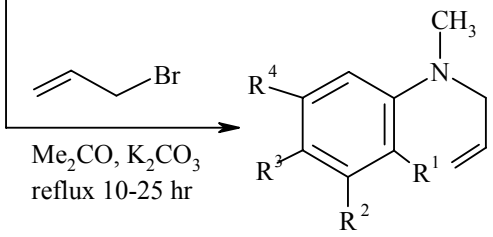
The study of the reaction of compound **5e** in a NMR tube at different time intervals was then attempted. The high field (300 MHz) ^{1}H NMR spectrum of the product **5e** showed two singlets each at δ 2.47 and 2.51 due to two C-CH_3 protons. The N-CH_3 protons appeared as a singlet at δ 2.91. The two singlets at δ 3.89 and 4.83 are due to the N-CH_2- and O-CH_2- protons, respectively.

Compound **5e** was then treated with *m*-CPBA in chloroform in a NMR tube and the ^{1}H NMR spectrum of the reaction mixture was recorded after 15 min. Among other signals two signals appeared as singlets each at δ 2.26 and 2.33 due to two C-CH_3 protons. The singlet at δ 2.85 is due to the N-CH_3 protons. The two singlets at δ 3.99 and 4.63 are due to the N-oxide-methylene and O-CH_2- protons, respectively. The ^{1}H NMR spectrum was also recorded after 1 hr 30 min, 6 hr, 12 hr and 24 hr. From the comparison of ^{1}H NMR spectrum at different time intervals it was found that there was a gradual disappearance of the N-CH_2- peak and the appearance of two new signals, one at δ 5.26 (d, J = 12.0 Hz) and the other at δ 5.53 (d, J = 12.0 Hz) characteristic of allene[19,20]. The N-CH_3 protons appeared as a singlet at δ 2.84. The two signals at δ 2.26 and 2.34 are due to the two C-CH_3 protons. The two protons due to O-CH_2- appeared as a singlet at δ 4.58. The ^{1}H NMR spectra at different time intervals *e.g*. 1.5 hr and 6 hr showed the signal for allene intermediate. The ^{1}H NMR spectra at 12 hr interval showed negligible proton signal characteristic of allene intermediate. The ^{1}H NMR spectra at 24 hr interval did not show any traceable proton signal and it was assumed that this is due to the decomposition / polymerization of the material.

From the recording of the ^{1}H NMR at different time intervals it became apparent that the first [2,3] sigmatropic rearrangement might be occurring in *m*-substituted substrate amine oxides. The [2,3] rearrangement step *i.e.* Meisenheimer rearrangement of a number of allylalkylaryl amines with *m*-substituent in the aryl moiety was then studied. The amine oxide **8a** was prepared by slow addition of one equivalent of *m*-CPBA in chloroform to a solution of **3a** in the same solvent at 0-5°C during 25 min. The formation of a highly polar amine oxide was indicated by thin layer chromatography (TLC). A new product (a viscous oil) was obtained in 82% yield when the reaction mixture was kept at rt for 10 hr. The high field (300 MHz) ^{1}H NMR spectrum of the product showed a two proton multiplet at δ 5.16-5.30 and a one proton multiplet at δ 5.90-5.99 due to the presence of a terminal olefin CH_2=CH function. The IR spectrum clearly indicated the absence of any carbonyl group. No change was observed when this product was refluxed in dry methanol. This product was characterized as **9a** from its elemental analysis and spectroscopic data. The procedure was repeated with each of the substrates **3b-h** using one equivalent



1a-h **2a-c**

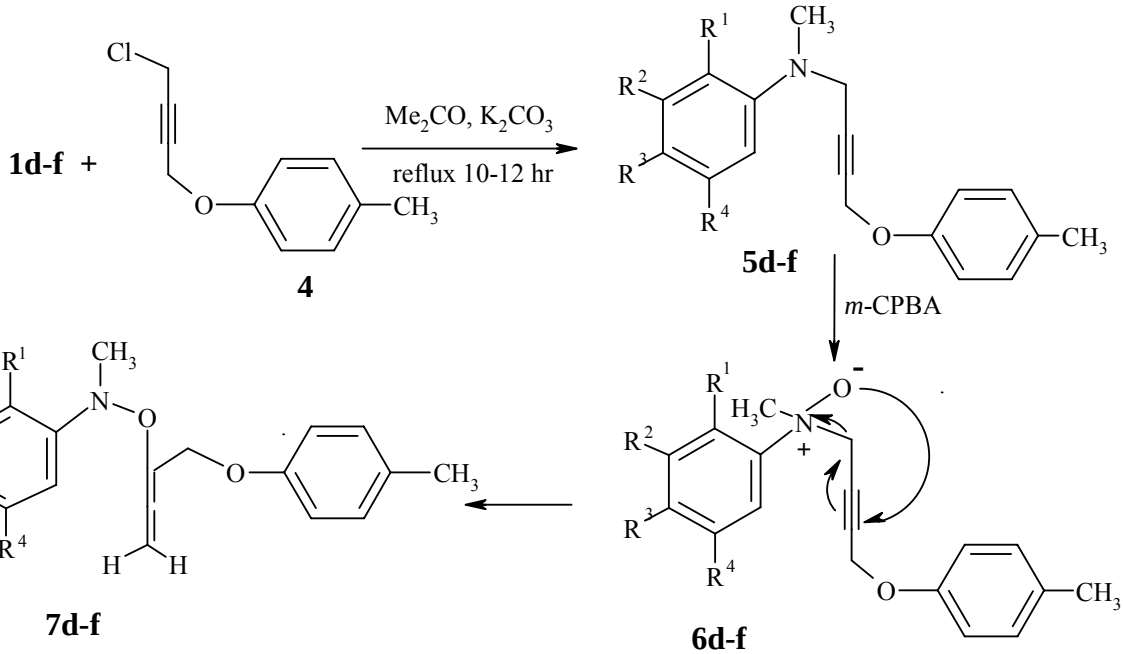


3a-h

a: $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
b: $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$
c: $R^1 = R^3 = R^4 = H$, $R^2 = NO_2$

1, 3 **a**: $R^1 = R^3 = R^4 = H$, $R^2 = Cl$
b: $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$
c: $R^1 = R^3 = R^4 = H$, $R^2 = NO_2$
d: $R^1 = R^3 = R^4 = H$, $R^2 = Br$
e: $R^1 = CH_3$, $R^2 = Cl$, $R^3 = R^4 = H$
f: $R^1 = R^4 = H$, $R^2 = Cl$, $R^3 = CH_3$
g: $R^1 = R^4 = H$, $R^2 = NO_2$, $R^3 = Cl$
h: $R^1 = CH_3$, $R^2 = R^3 = H$, $R^4 = Cl$

Scheme I



4 **5d-f** **6d-f** **7d-f**

d: $R^1 = R^3 = R^4 = H$, $R^2 = Br$
e: $R^1 = CH_3$, $R^2 = Cl$, $R^3 = R^4 = H$
f: $R^1 = R^4 = H$, $R^2 = Cl$, $R^3 = CH_3$

Scheme II

of *m*-CPBA and only the Meisenheimer products **9b-h** were obtained in 80-95% yield (**Scheme III**).

This result of the Meisenheimer rearrangement of **3a-h** to give products **9a-h** clearly shows that [2,3] sigmatropic rearrangement step in amine oxide rearrangement occurs even when a *m*-substituent is present in the aryl amine moiety of the substrate. However, the subsequent [3,3] sigmatropic rearrangement after the occurrence of [2,3] sigmatropic rearrangement in case of substrates **2a-c** and **5d-f** perhaps is not facile and destruction of the material occurred by decomposition/polymerization.

Experimental Section

Melting points were determined in a sulphuric acid bath and are uncorrected. UV-Vis absorption spectra were recorded in EtOH on a Shimadzu UV-2401 PC spectrophotometer and IR spectra in KBr discs on a Perkin-Elmer L 120-000A instrument. ^{1}H NMR spectra were run in $CDCl_3$ with TMS as an internal standard on a Bruker AC-250 (300 MHz) instrument at the Indian Institute of Chemical Biology, Kolkata (chemical shifts in δ, ppm). Elemental analyses and mass spectra were recorded at RSIC (CDRI), Lucknow on a JEOL D-300 (E1) instrument. Silica gel (60-120 mesh) was obtained from Spectrochem, India. Extracts were dried over anhydrous sodium sulphate. Petroleum ether refers to the fraction boiling between 60°C and 80°C.

General procedure for the synthesis of tertiary amines 2a-c, 3a-h and 5d-f

A mixture of substituted N-methyl aniline **1a-c** (1.5 mmole) and the propargylic bromide (0.198 g, 1.5 mmole) was refluxed in dry acetone (100 mL) in the presence of anhydrous potassium carbonate (3 g) for 10-14 hr. Progress of the reaction was monitored by TLC. The reaction mixture was cooled and filtered and the solvent was removed. The residual liquid was subjected to column chromatography using petroleum ether as eluent to give compounds **2a-c**.

Similarly, a mixture of substituted N-methyl anilines **1a-h** (1.5 mmole) and the allylic bromide (0.18 g, 1.5 mmole) or a mixture of substituted N-methyl anilines **1d-f** (1.5 mmole) and 1-aryloxy-4-chlorobut-2-yne **4** (0.291 g, 1.5 mmole) was refluxed in dry acetone (100 mL) in the presence of anhydrous potassium carbonate (3 g). Usual work-up and column chromatography furnished product **3a-h** or **5d-f** respectively.

2a: Yield 80%; viscous liquid; UV-Vis (EtOH): nm 220, 245, 283; IR (KBr): 2910, 1590, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.76 (t, 3H, *J* = 2.40 Hz, ≡C-CH_3), 2.92 (s, 3H, N-CH_3), 3.82-4.10 (m, 2H, N-CH_2-), 6.62-6.80 (m, 3H, ArH), 7.04-7.41 (m, 1H, ArH); MS: m/z 193, 195 (M^+). Anal. Found: C, 68.32; H, 6.07; N, 7.32. $C_{11}H_{12}NCl$ requires C, 68.22; H, 6.20; N, 7.24%.

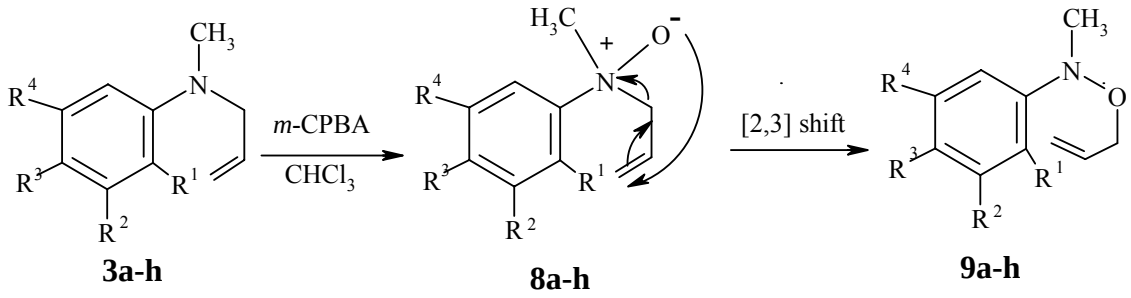
2b: Yield 78%; viscous liquid; UV-Vis (EtOH): nm 217, 242, 290; IR (KBr): 2910, 1600, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.77 (t, 3H, *J* = 2.40 Hz, ≡C-CH_3), 2.31 (s, 3H, C-CH_3), 2.91 (s, 3H, N-CH_3), 3.80-4.15 (m, 2H, N-CH_2-), 6.60-6.75 (m, 3H, ArH), 7.05-7.35 (m, 1H, ArH); MS: m/z 173 (M^+). Anal. Found: C, 83.37; H, 8.76; N, 7.99. $C_{12}H_{15}N$ requires C, 83.24; H, 8.67; N, 8.09%.

2c: Yield 85%; viscous liquid; UV-Vis (EtOH): nm 220, 251, 285; IR (KBr): 2920, 1605, 1500 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.79 (t, 3H, *J* = 2.40 Hz, ≡C-CH_3), 3.04 (s, 3H, N-CH_3), 4.04-4.12 (m, 2H, N-CH_2-), 7.15-7.40 (m, 2H, ArH), 7.51-7.71 (m, 2H, ArH); MS: m/z 204 (M^+). Anal. Found: C, 64.60; H, 5.94; N, 13.82. $C_{11}H_{12}N_2O_2$ requires C, 64.71; H, 5.88; N, 13.73%.

3a: Yield 95%; viscous liquid; UV-Vis (EtOH): nm 218, 255, 304; IR (KBr): 3050, 2900, 1620, 1560, 1490 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.06 (s, 3H, N-CH_3), 4.02-4.10 (m, 2H, N-CH_2-), 5.29-5.30 (m, 2H, =CH_2), 5.90-5.99 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.68-6.72 (m, 1H, ArH), 6.77-6.79 (m, 2H, ArH), 7.21-7.24 (m, 1H, ArH); MS: m/z 181, 183 (M^+). Anal. Found: C, 66.01; H, 6.53; N, 7.84. $C_{10}H_{12}NCl$ requires C, 66.12; H, 6.61; N, 7.71%.

3b: Yield 70%; viscous liquid; UV-Vis (EtOH): nm 216, 255, 300; IR (KBr): 3040, 2920, 1605, 1580, 1500 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.22 (s, 3H, C-CH_3), 2.92 (s, 3H, N-CH_3), 3.86-3.88 (m, 2H, N-CH_2-), 5.11-5.20 (m, 2H, =CH_2), 5.79-5.91 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.48-6.58 (m, 2H, ArH), 6.73-6.76 (m, 1H, ArH), 6.99 (m, 1H, ArH); MS: m/z 161 (M^+). Anal. Found: C, 81.90; H, 9.20; N, 8.77. $C_{11}H_{15}N$ requires C, 81.99; H, 9.32; N, 8.70%.

3c: Yield 70%; viscous liquid; UV-Vis (EtOH): nm 217, 251, 308; IR (KBr): 3090, 2905, 1580, 1530, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.11 (s, 3H, N-CH_3), 3.91-4.12 (m, 2H, N-CH_2-), 4.95-5.30 (m, 2H, =CH_2), 5.55-6.10 (m, 1H, -CH=), 6.81-7.50 (m, 4H, ArH); MS: m/z 192 (M^+). Anal. Found: C, 62.58; H, 6.11; N, 14.66. $C_{10}H_{12}N_2O_2$ requires C, 62.50; H, 6.25; N, 14.58%.



3a-h **8a-h** **9a-h**

Scheme III

3d: Yield 80%; viscous liquid; UV-Vis (EtOH): nm 217, 257, 307; IR (KBr): 3060, 2900, 1575, 1550, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.93 (s, 3H, N-CH_3), 3.89-3.91 (m, 2H, N-CH_2-), 5.11-5.17 (m, 2H, =CH_2), 5.75-5.87 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.59-6.63 (m, 1H, ArH), 6.78-6.81(m, 2H, ArH), 7.02-7.08 (t, 1H, *J* = 8.0 Hz, ArH); MS: m/z 225, 227 (M^+). Anal. Found: C, 53.20; H, 5.21; N, 6.33. $C_{10}H_{12}NBr$ requires C, 53.10; H, 5.31; N, 6.19%.

3e: Yield 68%; viscous liquid; UV-Vis (EtOH): nm 217, 254, 300; IR (KBr): 3060, 2910, 1610, 1560, 1470 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.36 (s, 3H, C-CH_3), 2.64 (s, 3H, N-CH_3), 3.44-3.46 (d, 2H, *J* = 6.0 Hz, N-CH_2-), 5.16-5.28 (m, 2H, =CH_2), 5.82-5.93 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.91-6.96 (m, 1H, ArH), 7.02-7.07 (m, 2H, ArH); MS: m/z 195, 197 (M^+). Anal. Found: C, 67.65; H, 7.29; N, 7.04. $C_{11}H_{14}NCl$ requires C, 67.52; H, 7.16; N, 7.16%.

3f: Yield 65%; viscous liquid; UV-Vis (EtOH): nm 216, 257, 311; IR (KBr): 3060, 2900, 1605, 1510, 1450 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.78 (s, 3H, C-CH_3), 3.42 (s, 3H, N-CH_3), 4.38-4.40 (m, 2H, N-CH_2-), 5.64-5.69 (m, 2H, =CH_2), 6.29-6.34 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 7.05-7.08 (m, 1H, ArH), 7.18-7.24 (m, 1H, ArH), 7.52-7.57 (m, 1H, ArH); MS: m/z 195, 197 (M^+). Anal. Found: C, 67.58; H, 7.24; N, 7.01. $C_{11}H_{14}NCl$ requires C, 67.52; H, 7.16; N, 7.16%.

3g: Yield 60%; viscous liquid; UV-Vis (EtOH): nm 219, 257, 302; IR (KBr): 3070, 2900, 1600, 1550, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.98 (s, 3H, N-CH_3), 3.91-3.93 (m, 2H, N-CH_2-), 5.06-5.18 (m, 2H, =CH_2), 5.72-5.78 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.73-6.77 (m, 1H, ArH), 7.06-7.08 (m, 1H, ArH), 7.24-7.27 (m, 1H, ArH); MS: m/z 226, 228 (M^+). Anal. Found: C, 53.10; H, 4.71; N, 12.22. $C_{10}H_{11}N_2O_2Cl$ requires C, 52.98; H, 4.86; N, 12.36%.

3h: Yield 70%; viscous liquid; UV-Vis (EtOH): nm 217, 253, 298; IR (KBr): 3040, 2900, 1605, 1570, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H, C-CH_3), 2.65 (s, 3H, N-CH_3), 3.44-3.46 (d, 2H, *J* = 6.0 Hz, N-CH_2-), 5.16-5.29 (m, 2H, =CH_2), 5.79-5.92 (ddd, 1H, *J* = 21.0, 10.2, 5.1 Hz, -CH=), 6.89-6.97 (m, 2H, ArH), 7.05-7.08 (m, 1H, ArH); MS: m/z 195, 197 (M^+). Anal. Found: C, 67.46; H, 7.10; N, 7.28. $C_{11}H_{14}NCl$ requires C, 67.52; H, 7.16; N, 7.16%.

5d: Yield 90%; viscous liquid; UV-Vis (EtOH): nm 217, 245, 289; IR (KBr): 3020, 2910, 1590, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, C-CH_3), 2.90 (s, 3H, N-CH_3), 4.03 (s, 2H, N-CH_2-), 4.61 (s, 2H, O-CH_2-), 6.68-6.71 (m, 1H, ArH), 6.78-6.81 (m, 2H, ArH), 6.89-6.91 (m, 2H, ArH), 7.03-7.10 (m, 3H, ArH); MS: m/z 343, 345 (M^+). Anal. Found: C, 62.88; H, 5.06; N, 4.14. $C_{18}H_{18}NOBr$ requires C, 62.79; H, 5.23; N, 4.07%.

5e: Yield 92%; viscous liquid; UV-Vis (EtOH): nm 217, 251, 300; IR (KBr): 3020, 2920, 1590, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.47 (s, 3H, C-CH_3), 2.51 (s, 3H, C-CH_3), 2.91 (s, 3H, N-CH_3), 3.89 (s, 2H, N-CH_2-), 4.83 (s, 2H, O-CH_2-), 7.00-7.15 (m, 2H, ArH), 7.20-7.27 (m, 5H, ArH); MS: m/z 313, 315 (M^+). Anal. Found: C, 72.79; H, 6.29; N, 4.56. $C_{19}H_{20}NOCl$ requires C, 72.73; H, 6.38; N, 4.47%.

5f: Yield 80%; viscous liquid; UV-Vis (EtOH): nm 216, 252, 303; IR (KBr): 3040, 2930, 1610, 1495cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.71 (s, 6H, 2 C-CH_3), 3.29 (s, 3H, N-CH_3), 4.44 (s, 2H, N-CH_2-), 5.03 (s, 2H, O-CH_2-), 7.03-7.07 (m, 1H, ArH), 7.21-7.24 (m, 3H, ArH), 7.45-7.49 (m, 3H, ArH); MS: m/z 313, 315 (M^+). Anal. Found: C, 72.82; H, 6.49; N, 4.58. $C_{19}H_{20}NOCl$ requires C, 72.73; H, 6.38; N, 4.47%.

General procedure for the oxidation and Meisenheimer rearrangement of tertiary amines 3a-h.

m-Chloroperoxybenzoic acid (*m*-CPBA) (0.010 mole, 3.44 g, 50%) in chloroform (50 mL) was added to a well stirred solution of the appropriate tertiary amine (0.010 mole) in chloroform (50 mL), at 0-5°C over a period of 20 min. The reaction mixture was

stirred for a further duration of 10 hr and then it was washed with an aqueous solution of 10% potassium carbonate (3×50 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave a crude mass that was purified by column chromatography over silica gel using petroleum ether as eluent to furnish compounds **9a-h**.

9a: Yield 82%; viscous liquid; UV-Vis (EtOH): nm 217, 245, 290; IR (KBr): 2910, 1590, 1460 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.00 (s, 3H, N-CH_3), 4.25-4.27 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.16-5.30 (m, 2H, =CH_2), 5.90-5.99 (m, 1H, -CH=), 6.77-6.86 (m, 2H, ArH), 6.96-6.98 (m, 1H, ArH), 7.01-7.18 (m, 1H, ArH); MS: m/z 197, 199 (M^+). Anal. Found: C, 60.88; H, 6.18; N, 7.01. $C_{10}H_{12}NOCl$ requires C, 60.76; H, 6.08; N, 7.09%.

9b: Yield 92%; viscous liquid; UV-Vis (EtOH): nm 216, 248, 284; IR (KBr): 2900, 1560, 1470 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.37 (s, 3H, C-CH_3) 3.04 (s, 3H, N-CH_3), 4.26-4.28 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.14-5.27 (m, 2H, =CH_2), 5.91-6.14 (m, 1H, -CH=), 6.80-6.87 (m, 1H, ArH), 7.22-7.29 (m, 3H, ArH); MS: m/z 177 (M^+). Anal. Found: C, 74.67; H, 8.51; N, 7.83. $C_{11}H_{15}NO$ requires C, 74.58; H, 8.47; N, 7.91%.

9c: Yield 95%; viscous liquid; UV-Vis (EtOH): nm 220, 245, 283; IR (KBr): 2900, 1605, 1460 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.20 (s, 3H, N-CH_3), 4.35-4.37 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.20-5.51 (m, 2H, =CH_2), 5.82-6.35 (m, 1H, -CH=), 7.35-7.90 (m, 4H, ArH); MS: m/z 208 (M^+). Anal. Found: C, 57.78; H, 5.80; N, 13.40. $C_{10}H_{12}N_2O_3$ requires C, 57.69; H, 5.77; N, 13.46%.

9d: Yield 80%; viscous liquid; UV-Vis (EtOH): nm 216, 246, 287; IR (KBr): 2920, 1580, 1450 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.07 (s, 3H, N-CH_3), 4.32-4.34 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.24-5.38 (m, 2H, =CH_2), 5.95-6.07 (m, 1H, -CH=), 6.91-6.94 (m, 1H, ArH), 7.06-7.21(m, 3H, ArH); MS: m/z 241, 243 (M^+). Anal. Found: C, 49.50; H, 5.08; N, 5.87. $C_{10}H_{12}NOBr$ requires C, 49.59; H, 4.96; N, 5.79%.

9e: Yield 85%; viscous liquid; UV-Vis (EtOH): nm 216, 244, 285; IR (KBr): 2910, 1570, 1440 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.31 (s, 3H, C-CH_3), 2.83 (s, 3H, N-CH_3), 4.15-4.17 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.15-5.28 (m, 2H, =CH_2), 5.86-5.99 (m, 1H, -CH=), 7.06-7.16 (m, 2H, ArH), 7.42-7.46 (m, 1H, ArH); MS: m/z 211, 213 (M^+). Anal. Found: C, 62.49; H, 6.74; N, 6.51. $C_{11}H_{14}NOCl$ requires C, 62.41; H, 6.62; N, 6.62%.

9f: Yield 84%; viscous liquid; UV-Vis (EtOH): nm 217, 245, 289; IR (KBr): 2920, 1610, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H, C-CH_3), 3.15 (s, 3H, N-CH_3), 4.42-4.44 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.34-5.48 (m, 2H, =CH_2), 6.09-6.18 (m, 1H, -CH=), 6.91-6.95 (m, 1H, ArH), 7.18-7.24 (m, 2H, ArH); MS: m/z 211, 213 (M^+). Anal. Found: C, 62.33; H, 6.50; N, 6.72. $C_{11}H_{14}NOCl$ requires C, 62.41; H, 6.62; N, 6.62%.

9g: Yield 80%; viscous liquid; UV-Vis (EtOH): nm 219, 246, 281; IR (KBr): 2900, 1610, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.99 (s, 3H, N-CH_3), 4.20-4.22 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.13-5.25 (m, 2H, =CH_2), 5.80-5.88 (m, 1H, -CH=), 6.94-6.98 (m, 1H, ArH), 7.24-7.36 (m, 2H, ArH); MS: m/z 242, 244 (M^+). Anal. Found: C, 49.41; H, 4.50; N, 11.42. $C_{10}H_{11}N_2O_3Cl$ requires C, 49.48; H, 4.54; N, 11.55%.

9h: Yield 88%; viscous liquid; UV-Vis (EtOH): nm 217, 242, 280; IR (KBr): 2910, 1600, 1480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.19 (s, 3H, C-CH_3), 2.82 (s, 3H, N-CH_3), 4.13-4.15 (d, 2H, *J* = 6.0 Hz, O-CH_2-), 5.13-5.26 (m, 2H, =CH_2), 5.87-5.96 (m, 1H, -CH=), 6.97-7.05 (m, 2H, ArH), 7.47 (s, 1H, ArH); MS: m/z 211, 213 (M^+). Anal. Found: C, 62.46; H, 6.47; N, 6.77. $C_{11}H_{14}NOCl$ requires C, 62.41; H, 6.62; N, 6.62%.

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