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Lithiomethyl Ethyl Ether from Chloromethyl Ethyl Ether *via* a DTBB-Catalysed Lithiation

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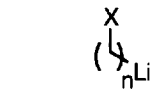
Abstract: The reaction of equimolecular amounts of chloromethyl ethyl ether (1) and a carbonyl compound [Bu^nCHO, Bu^tCHO, PhCHO, Pri_2CO, $Bu^t{}_2CO$, $(CH_2)_4CO$, 2-cyclohexenone, PhCOMe] with an excess of lithium powder (1:7 molar ratio) and a catalytic amount of DTBB (5 mol %) in THF at 0°C (Method A) leads, after hydrolysis, to the corresponding hydroxyethers **2**. The reaction can be also carried out in a two-step process: tandem lithiation at -90°C and reaction with the electrophile [Bu^nCHO, $(CH_2)_4CO$, PhCOMe, $PhMe_2SiCl$, CO_2, PhCN, $PhCONMe_2$, CyNCO, PhN=CHPh] at -90 to -60°C (Method B).

INTRODUCTION

Among functionalised organolithium compounds[1] of the type **I**[2], the coresponding α-substituted derivatives (**I**, n = 1), also called 'carbenoids', are interesting intermediates in synthetic organic chemistry because in the reaction with electrophilic reagents they are able to introduce a functional group at the α-position with respect to the electrophilic fragment. The preparation of these type of d[1]-reagents[3] has been achieved at low temperature by three different procedures depending on the starting material: (a) tin-lithium transmetallation from α-alkoxystannanes **II** with *n*-butyllithium[4]; (b) sulphur-lithium exchange from phenylthioketals of the type **III** by reductive cleavage with a lithium arene[5]; (c) deprotonation of some ethers (*t*-butyl[6a] or benzyl[6b] derivatives) or esters[6c,d] and related compounds[6e,g] **IV** with strong bases (usually *s*-butyllithium and a co-reagent such as tetramethylethylenediamine or potassium *t*-butoxide). However, to the best of our knowledge, a direct[7] route, which implies a chlorine-lithium exchange from chloromethyl ethers **V**, has not been used yet for the preparation of intermediates of the type **I** with X = OR and n = 1. As a general consideration, non-stabilised α-lithioethers are unstable species, even at low temperature, due to their tendency to undergo α-elimination [8a] or Wittig rearrangement[8] processes. On the other hand, we discovered recently[9] that the use of an arene catalyst [naphthalene or 4,4'-di-*tert*-butylbiphenyl (DTBB)][10] in lithiation reactions[11] allows not only the new routes for simple organolithium compounds starting from non-halogenated materials[12], but also the preparation of very reactive functionalised organolithium intermediates[13] or polylithium synthons[14] under very mild reaction conditions starting from commercially available chlorinated materials. In the present paper we describe the

preparation of an α-lithioether ot the type **I** with X = OEt and n = 1 from the corresponding α-chloroether of the type **V** by a DTBB-catalysed lithiation, and their reaction with different electrophiles either in a two-step or in a Barbier-type process[15].



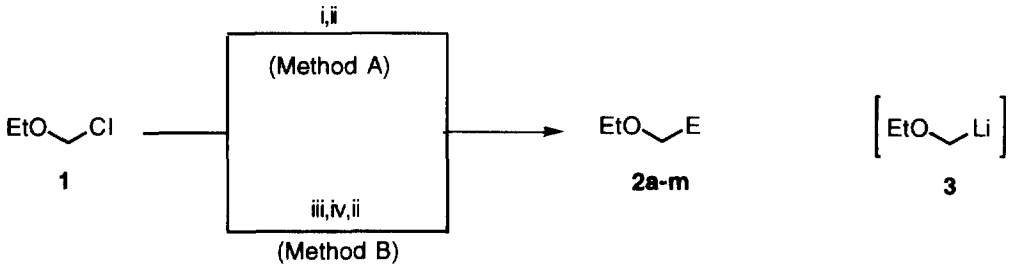
I

X = OR, NR_2, SR, SeR
n = 1,2,3, ...

II : Y = $SnBu^n_3$
III : Y = SPh
IV : Y = H
V : Y = Cl

RESULTS AND DISCUSSION

The reaction of a mixture of equimolecular amounts of commercially available chloromethyl ethyl ether (**1**) and a carbonyl compound [Bu^nCHO, Bu^tCHO, PhCHO, Pri_2CO, Bu^t_2CO, $(CH_2)_4CO$, 2-cyclohexenone, PhCOMe] with an excess of lithium powder (1:7 molar ratio) and a catalytic amount of DTBB (5 mol %) in THF at 0°C (slow addition: *ca.* 45 min) gave, after hydrolysis with water, the corresponding ethoxy alcohols **2a-h** (Scheme 1, Method A and Table 1, entries 1, 3-7, 9 and 10). Some remarks about this reaction are: (a) when naphthalene was used as catalyst instead of DTBB the yields are, in general lower (see, for instance, Table 1, entry 10 and footnote f); (b) the reaction works nicely with different carbonyl compounds, even with very hindered ketones, such as diisopropyl or di-*tert*-butyl ketone (Table 1, entries 5 and 6, respectively); (c) in some cases the yields are better by adding the reagents **1** and **2** at once onto the activated lithium suspension (not slowly; see above).



Scheme 1. *Reagents and conditions*: i, E+ = Bu^nCHO, Bu^tCHO, PhCHO, Pri_2CO, Bu^t_2CO, $(CH_2)_4CO$, 2-cyclohexenone, PhCOMe, Li powder, DTBB cat. (5 mol %), THF, 0°C; ii, H_2O; iii, Li powder, DTBB cat. (5 mol %), THF, -90°C; iv, E+ = Bu^nCHO, $(CH_2)_4CO$, PhCOMe, $PhMe_2SiCl$, CO_2, PhCN, $PhCONMe_2$, CyNCO, PhN=CHPh, -90 or -90 to -60°C (see text).

Alternatively, the transformation **1**→**2** can be carried out in a two-step process, the corresponding intermediate of the type **3** being generated before the addition of the electrophilic reagent (Scheme 1, Method B). The two more important differences compared to the reaction performed under Barbier-type reaction conditions (Method A) are: (a) the reaction temperature has to be kept around -90°C in order to avoid decomposition of ethoxymethyllithium (**3**) and (b) not only carbonyl compounds [Bu^nCHO, $(CH_2)_4CO$, PhCOMe; Scheme 1 and Table 1, entries 2, 8 and 11] can be used as electrophiles, but also other type of reagents [$PhMe_2SiCl$, CO_2, PhCN, $PhCONMe_2$, CyNCO, PhN=CHPh; Scheme 1 and Table 1, entries 12-17]. In all cases the hydrolysis temperature was between -90 and -80°C except in the case of the reaction with carbonyl derivatives (Table 1, entries 2, 8, 11 and 17] or carbon dioxide (Table 1, entry 13) in which the best results were obtained allowing the temperature to rise to -60 or 0°C, respectively.

Table 1. Preparation of Compounds **2**

Entry	Method	Electrophile E+	Product **2**[a]			
			No.	E	Yield (%)[b]	R_f[c]
1	A	Bu^nCHO	**2a**	Bu^nCHOH	87	0.25
2	B	Bu^nCHO	**2a**	Bu^nCHOH	82	0.25
3	A	Bu^tCHO	**2b**	Bu^tCHOH	81	0.31
4	A	PhCHO	**2c**	PhCHOH	84[d]	0.18
5	A	Pr^i_2CO	**2d**	Pr^i_2COH	75[d]	0.63
6	A	Bu^t_2CO	**2e**	Bu^t_2COH	70[d]	0.75
7	A	$(CH_2)_4CO$	**2f**	$(CH_2)_4COH$	94	0.29
8	B	$(CH_2)_4CO$	**2f**	$(CH_2)_4COH$	90	0.29
9	A	-[e]	**2g**	$(CH_2)_4CH=CHC(OH)$	98	0.20
10	A	PhCOMe	**2h**	PhC(OH)Me	94 (57)[f]	0.33
11	B	PhCOMe	**2h**	PhC(OH)Me	91	0.33
12	B	$PhMe_2SiCl$	**2i**	$PhMe_2Si$	86	0.70[g]
13	B	CO_2	**2j**	CO_2H	88	0.12[g]
14	B	PhCN	**2k**	PhCO	75	0.44[g]
15	B	$PhCONMe_2$	**2k**	PhCO	80	0.44[g]
16	B	CyNCO[h]	**2l**	CyNHCO[h]	81	0.27[g]
17	B	PhCH=NPh	**2m**	PhCH(NHPh)	85	0.53[g]

[a] All compounds **2** were ≥95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield of pure compounds **2** after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting chloroether **1**. [c] Hexane/ethyl acetate: 9/1. [d] Isolated yield corresponding to the reaction carried out by adding the reactants at once (not slowly; see text) to the activated lithium suspension. [e] 2-Cyclohexenone was used as electrophile. [f] Naphthalene was used instead of DTBB as the arene catalyst. [g] Hexane/ethyl acetate: 7/3. [h] Cy = cyclohexyl.

From the results described in this paper we conclude that this methodology (DTBB-catalysed lithiation of chloromethyl ethyl ether followed by *in situ* reaction with electrophiles) represents a new and simple procedure to prepare lithiomethyl ethers, which are adequate intermediates for the synthesis of functionalised ethers.

EXPERIMENTAL PART

General.- For general information see reference 13.

Preparation of Compound **2** . *General Method A.* To a blue suspension of lithium powder (100 mg, 14 mmol; 1:7 molar ratio) and DTBB (26 mg, 0.1 mmol; 5 mol %) in THF (5 ml) at 0°C, a mixture of the starting chloromethyl ether (**1**, 2 mmol) [**CAUTION**: chloromethyl ethers are harmful chemicals and should be handled with special precautions] and the corresponding carbonyl compound (2 mmol) in THF (5 ml) was added during *ca.* 45 min. Then, the resulting mixture was hydrolysed with water (10 ml) and extracted with diethyl ether (2x10 ml) and ethyl acetate (2x10 ml). The organic layer was dried over Na_2SO_4 and evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding the pure title compounds **2**.

General. Method B. To a blue suspension of lithium powder (100 mg, 14 mmol; 1:7 molar ratio) and DTBB (26 mg, 0.1 mmol; 5 mol%) in THF (5 ml) at -90°C was added a solution of the corresponding starting chloromethyl ether (**1**, 2 mmol) [**CAUTION**: see above] in THF (0.5 ml; 5 min). Once the blue colour is recovered (5-10 min) the corresponding electrophile (2 mmol) in THF (1 ml) was added at the same temperature and stirring was continued for 4 additional h allowing the temperature to rise to -60°C[16]. The resulting mixture was then hydrolysed with water (10 ml) and extracted with diethyl ether (2x10 ml) and ethyl acetate (2x10 ml). The organic layer was dried over Na_2SO_4 and evaporated (15 Torr) to give a residue, wich was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding the pure title compounds **2**. When benzonitrile, N,N-dimethylbenzamide or cyclohexyl isocyanate was used as electofiles, after the lithiation step dry pentane (15 ml) was added *via cannula* at -90°C. Then the corresponding electrophile (2 mmol) in pentane (1 ml) was added to the resulting mixture at the same temperature and the reaction mixture was stirred for a period of *ca.* 2h[17a]. Then the resulting mixture was hydrolysed[17b] and worked up as above. In the case of using carbon dioxide as electrophile a balloon containing CO_2 was conected to the reaction flask maintaining vigorous stirring and the temperature was allowed to raise to 0°C for *ca.* 5h. The resulting mixture was hydrolysed with water (10 ml) and extracted with hexane (10 ml). The aqueous layer was acidified with conc. H_2SO_4 and extracted with ethyl acetate (5x10 ml). After drying the organic layer with Na_2SO_4 it was evaporated (60 Torr) and the resulting residue purified by flash chromatography (silica gel, pentane/ether) yielding the pure acid **2j**. Yields, R_f and specific rotations for compounds **2** are included in Table 1. Analytical and spectroscopic data for compounds **2** follow.

1-Ethoxy-2-hexanol (**2a**): ν (film) 3420 (OH) and 1115 cm^{-1} (C-O); δ_H 0.90 (3H, t, J=6.6, $CH_3CH_2CH_2$), 1.21 (3H, t, J=7.0, CH_3CH_2O), 1.24-1.48 (6H, m, $CH_2CH_2CH_2$), 2.54 (1H, s, OH) 3.25 (1H, dd, J=9.4,

8.0, OCH*H*CO), 3.40-3.65 (3H, m, C*H*$_2$OC*H*HCO) and 3.76 (1H, m, CH$_2$C*H*OCH$_2$); δ_C 13.9 (*C*H$_3$CH$_2$CH$_2$), 15.05 (*C*H$_3$CH$_2$O), 22.65 (CH$_3$*C*H$_2$CH$_2$), 27.65 (CH$_3$CH$_2$*C*H$_2$), 32.8 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 66.55 (CH$_3$*C*H$_2$O), 70.25 (CH$_2$*C*OCH$_2$) and 74.9 (O*C*H$_2$CO); *m/z* 146 (M+, 0.1%), 87 (28), 86 (20), 69 (100), 61 (31), 59 (46), 57 (13), 45 (13), 43 (15) and 41 (23).

1-Ethoxy-3,3-dimethyl-2-butanol (**2b**): ν (film) 3460 (OH) 1110 and 1090 cm^{-1} (C-O); δ_H 0.92 [9H, s, (CH$_3$)$_3$C], 1.21 (3H, t, *J*=7.0, C*H*$_3$CH$_2$O), 2.56 (1H, s, OH) 3.28 (1H, t, *J*=9.2, OCH*H*CO) and 3.42-3.61 (4H, m, OCH*H*CO, CH$_3$C*H*$_2$, OCH$_2$C*H*OH); δ_C 15.1 (*C*H$_3$CH$_2$), 25.9 [3C, (*C*H$_3$)$_3$C], 33.2 [(CH$_3$)$_3$*C*], 66.5 (CH$_3$*C*H$_2$O), 71.45 (O*C*H$_2$CO) and 77.2 (OCH$_2$*C*HOH); *m/z* 131 (M+-CH$_3$, 0.3%), 89 (45), 88 (12), 87 (100), 69 (48), 61 (90), 59 (35), 57 (44), 45 (25), 43 (21) and 41 (31).

2-Ethoxy-1-phenylethanol (**2c**): ν (film) 3400 (OH), 1600 (ArC=C), 1110, 1060 (C-O), 755 and 700 cm^{-1} (ArC-H); δ_H 1.24 (3H, t, *J*=7.0, C*H*$_3$CH$_2$O), 2.87 (1H, d, *J*=2.0, OH), 3.43 (1H, dd, *J*=9.7, 9.1, OCH*H*CO), 3.51-3.65 (3H, 2m, OCH*H*CO, CH$_3$C*H*$_2$O), 4.88 (1H, ddd, *J*=9.1, 2.4, 2.0, PhC*H*O), 7.25-7.41 (5H, m, ArH); δ_C 15.05 (*C*H$_3$CH$_2$), 66.65 (CH$_3$*C*H$_2$O), 72.65 (ArCO), 76.1 (O*C*H$_2$CO), 126.05 (2C, ArCH), 127.7 (ArCH), 128.25 (2C, ArCH) and 140.3 (ArC); *m/z* 167 (M++1, 1%), 166 (M+, 7%), 107 (100), 79 (33) and 77 (15).

2,4-Dimethyl-3-ethoxymethyl-3-pentanol (**2d**): ν (film) 3460 (OH) and 1110 cm^{-1} (C-O); δ_H 0.91 (6H, d, *J*=6.9, 2xCH$_3$CHC*H*$_3$), 0.95 (6H, d, *J*=6.9, 2xC*H*$_3$CHCH$_3$), 1.19 (3H, t, *J*=7.0, C*H*$_3$CH$_2$), 1.95 (2H, septet, *J*=6.9, 2xCH$_3$C*H*CH$_3$), 2.22 (1H, s, OH), 3.35 (2H, s, OC*H*$_2$CO) and 3.47 (2H, q, *J*=7, CH$_3$C*H*$_2$O); δ_C 15.1 (*C*H$_3$CH$_2$O), 17.15 (2C, 2x*C*H$_3$CHCH$_3$), 17.3 (2C, 2xCH$_3$CH*C*H$_3$), 32.95 (2C, 2xCH$_3$*C*HCH$_3$), 66.6 (CH$_3$*C*H$_2$O, 71.25 (O*C*H$_2$CO) and 75.5 (OCH$_2$*C*O); *m/z* 131 (M+-CH$_3$CHCH$_3$, 84%), 115 (74), 113 (23), 87 (29), 85 (32), 73 (19), 71 (100), 59 (40), 55 (21), 45 (14), 43 (53) and 41 (24) (Found: M+-CH$_3$CH$_2$CH$_3$, 131.1074. C$_7$H$_{15}$O$_2$ requires M, 131.1072).

3-Ethoxymethyl-2,2,4,4-tetramethyl-3-pentanol (**2e**): ν (film) 3520 (OH) and 1110 cm^{-1} (C-O); δ_H 1.04 [18H, s, 2x(CH$_3$)$_3$C], 1.20 (3H, t, *J*=7.0, C*H*$_3$CH$_2$), 3.01 (1H, s, OH), 3.42 (2H, s, OC*H*$_2$CO) and 3.49 (2H, q, *J*=7, CH$_3$C*H*$_2$O); δ_C 15.2 (*C*H$_3$CH$_2$O), 28.55 [6C, 2x(*C*H$_3$)$_3$C], 40.95 [2C, 2x(CH$_3$)$_3$*C*], 66.25 (CH$_3$*C*H$_2$O), 70.35 (O*C*H$_2$CO) and 77.4 (OCH$_2$*C*O); *m/z* 145 [M+-(CH$_3$)$_3$C, 46%], 143 (15), 101 (16), 99 (87), 87 (70), 85 (29), 59 (30), 57 (100), 43 (47) and 41 (36) (Found: M+-(CH$_3$)$_3$C, 145.1231. C$_8$H$_{17}$O$_2$ requires M, 145.1228).

1-Ethoxymethyl-1-cyclopentanol (**2f**)[18]: ν (film) 3400 (OH) and 1110 cm^{-1} (C-O); δ_H 1.21 (3H, t, *J*=7.0, C*H*$_3$CH$_2$), 1.50-1.90 (8H, m, 4xringCH$_2$), 2.37 (1H, s, OH), 3.37 (2H, s, OC*H*$_2$CO) and 3.55 (2H, q, *J*=7.0, CH$_3$C*H*$_2$O); δ_C 15.1 (*C*H$_3$CH$_2$O), 24.2 (2C, 2xring CH$_2$), 37.25 (2C, 2xring CH$_2$), 66.9 (CH$_3$*C*H$_2$O), 77.45 (O*C*H$_2$CO) and 81.4 (OCH$_2$*C*O); *m/z* 144 (M+, 1%) 85 (100), 84 (27), 67 (41), 57 (11), 55 (10), 43

(10) and 41 (13).

1-Ethoxymethyl-2-cyclohexen-1-ol (**2g**): ν (film) 3425 (OH), 1645 (C=C) and 1110 cm^{-1} (C-O); δ_H 1.21 (3H, t, *J*=7.0, CH_3CH_2), 1.55-1.83 (4H, m, $COCH_2CH_2CH_2$), 1.90-2.15 (2H, m, $OCH_2CH_2CH_2$), 2.56 (1H, s, OH), 3.29 (1H, d, *J*=9.1, OCHHCO), 3.36 (1H, d, *J*=9.1, OCHHCO), 3.55 (2H, q, *J*=7.0, CH_3CH_2O), 5.64 (1H, m, $HC=CHCH_2$) and 5.88 (1H, m, $HC=CHCH_2$); δ_C 15.0 (CH_3CH_2O), 18.85 (ring CH_2), 25.3 (ring CH_2), 32.9 (ring CH_2), 66.95 (CH_3CH_2O), 69.25 (OCH_2CO), 77.25 (OCH_2CO), 129.45 and 131.15 (C=C); *m/z* 138 (M^+-H_2O, 0.2%) and 97 (100) (Found: M^+-H_2O, 138.1047. $C_9H_{14}O$ requires M, 138.1045).

1-Ethoxy-2-phenyl-2-propanol (**2h**)[19]: ν (film) 3420 (OH), 1595 (ArC=C), 1105 (C-O), 760 and 695 cm^{-1} (ArC-H); δ_H 1.17 (3H, t, *J*=7.0, CH_3CH_2O), 1.52 (3H, s, CH_3CO), 2.95 (1H, s, OH), 3.50 (1H, d, *J*=9.3, OCHHCO), 3.48-3.56 (2H, m, CH_3CH_2O), 3.57 (1H, d, *J*=9.3, OCHHCO), 7.21-7.27 (1H, m, ArH), 7.30-7.37 (2H, m, ArH) and 7.44-7.49 (2H, m, ArH); δ_C 14.95 (CH_3CH_2), 26.7 (CH_3CO), 66.95 (CH_3CH_2O), 73.7 (PhCO), 78.4 (OCH_2CO), 124.95 (2C, ArCH), 126.8 (ArCH), 128.05 (2C, ArCH) and 144.55 (ArC); *m/z* 180 (M^+, 3%), 122 (10), 121 (100), 77 (10) and 43 (58).

Dimethyl(ethoxymethyl)phenylsilane (**2i**): ν (film) 1248 ($SiCH_3$), 1115, 1095 (C-O), 840, 814 ($SiCH_3$), 728 and 698 cm^{-1} (ArC-H); δ_H 0.32 [6H, s, $(CH_3)_2Si$], 1.16 (3H, t, *J*=7.0, CH_3CH_2), 3.31 (2H, s, OCH_2Si), 3.46 (2H, q, *J*=7.0, CH_3CH_2O), 7.31-7.38 (3H, m, ArH) and 7.52-7.58 (2H, m, ArH); δ_C 4.35 [2C, $(CH_3)_2Si$], 15.0 (CH_3CH_2O), 63.5 (OCH_2Si), 70.5 (CH_3CH_2O), 127.75 (ArC), 129.1 (2C, ArCH), 133.8 (2C, ArCH) and 137.85 (ArCH); *m/z* 179 (M^+-CH_3, 2%), 165 (36), 136 (25), 135 (100), 107 (10), 105 (15), 103 (24), 91 (13), 45 (12) and 43 (42) (Found: M^+-CH_3CH_2, 165.0727. $C_9H_{13}OSi$ requires M, 165.0736).

2-Ethoxyacetic acid (**2j**)[20]: ν (film) 3450 (OH), 1732, 1738 (C=O) and 1124 cm^{-1} (C-O); δ_H 1.26 (3H, t, *J*=7.0, CH_3CH_2), 3.63 (2H, q, *J*=7.0, CH_3CH_2O), 4.13 (2H, s, OCH_2CO) and 8.11 (1H, br s, OH); δ_C 14.8 (CH_3CH_2O), 67.3 (CH_3CH_2O), 67.4 (OCH_2CO) and 175.0 (C=O).

Ethoxymethylphenylketone (**2k**)[21]: ν (film) 1701 (C=O), 1598 (ArC=C), 1141 (C-O), 756 and 691 cm^{-1} (ArC-H); δ_H 1.29 (3H, t, *J*=7.0, CH_3CH_2), 3.65 (2H, q, *J*=7.0, CH_3CH_2O), 4.75 (2H, s, $COCH_2CO$), 7.43-7.51 (2H, m, ArH), 7.53-7.62 (1H, m, ArH) and 7.91-7.98 (2H, m, ArH); δ_C 15.0 (CH_3CH_2O), 67.15 (CH_3CH_2O), 73.5 ($COCH_2CO$), 127.8 (2C, ArCH), 128.6 (2C, ArCH), 133.4 (ArCH), 134.9 (ArC) and 196.45 (C=O); *m/z* 121 (M^+-CH_3CH_2OH, 74%), 106 (17), 105 (100), 91 (17), 78 (14), 77 (87), 65 (11), 59 (17), 51 (60), 50 (25) and 41 (10).

N-Cyclohexyl-2-ethoxyacetamide (**2l**)[22]: ν (film) 3413, 3306 (NH), 1667 (C=O), 1530 (N-H, C-N), and 1119 cm^{-1} (C-O); δ_H 1.10-1.28 (3H, m, ring CH_2), 1.24 (3H, t, *J*=7.0, CH_3CH_2), 1.30-1.49 (2H, m, ring CH_2), 1.57-1.78 (3H, m, ring CH_2), 1.85-1.97 (2H, m, ring CH_2), 3.56 (2H, q, *J*=7.0, CH_3CH_2O), 3.74-3.90 (1H,

m, NCH) 3.90 (2H, s, $COCH_2CO$) and 6.45 (1H, br s, NH); δ_C 14.95 (CH_3CH_2O), 24.75 (2C, ring CH_2), 25.4 (ring CH_2), 33.0 (2C, ring CH_2), 47.4 (NCH), 66.95 (CH_3CH_2O), 69.85 ($COCH_2CO$) and 168.7 (C=O); *m/z* 186 (M^++1, 1%), 142 (16), 141 (93), 104 (54), 84 (15), 83 (100), 82 (30), 81 (15), 70 (14), 68 (29), 67 (48), 61 (11), 60 (94), 59 (96), 58 (17), 56 (36), 55 (95), 54 (30), 53 (13), 44 (18), 43 (60), 42 (37) and 41 (94) (Found: M^+, 185.1426. $C_{10}H_{19}NO_2$ requires M, 185.1416).

N,1-Diphenyl-2-ethoxyethylamine (**2m**): ν (film) 3397 (NH), 1602, 1504 (ArC=C), 1110 (C-N), 750, 701 and 693 (ArC-H); δ_H 1.19 (3H, t, *J*=7.0, CH_3CH_2O), 3.40-3.61 (2H, m, CH_3CH_2O), 3.50 (1H, dd, *J*=10.1, 8.8, NCHCHHO), 3.65 (1H, dd, *J*=10.1, 4.3, NCHCHHO), 4.48 (1H, dd, *J*=8.8, 4.3, $NCHCH_2O$), 4.60 (1H, s, NH), 6.47-6.55 (2H, m, $2xH_o$ of ArN), 6.61-6.68 (1H, m, H_p of ArN), 7.01-7.10 (2H, m, $2xH_m$ of ArN), 7.15-7.35 (3H, 2m, $2xH_m$ and H_p of ArC) and 7.37-7.43 (2H, m, $2xH_o$ of ArC); δ_C 15.05 (CH_3CH_2O), 58.1 ($NCHCH_2$), 66.25 (CH_3CH_2O), 74.9 ($NCHCH_2$), 113.95 (2C, $2xC_o$ of ArN), 117.6 (C_p of ArN), 126.7 (2C, ArC), 127.3 (ArC), 128.55 (2C, ArC), 128.9 (ArC), 140.8 (C_i of ArN); *m/z* 242 (M^++1, 1%), 241 (M^+, 6%), 183 (20), 182 (100), 104 (26), 77 (50) and 51 (16) (Found: M^+-$CH_2OCH_2CH_3$, 182.0972. $C_{13}H_{12}N$ requires M, 182.0970).

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