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DTBB-Catalysed Lithiation of 2,3-Dichloropropene and Related Chloroamines: Synthetic Applications

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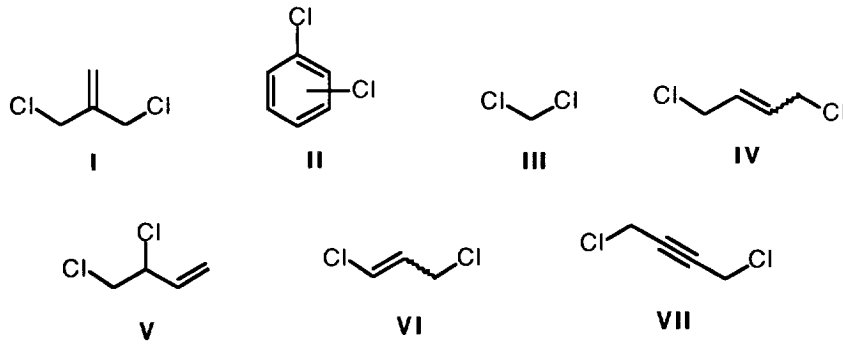
Abstract: The reaction of 2,3-dichloropropene (**1**) and different carbonyl compounds (**2**) with an excess of lithium powder (1:7 molar ratio) in the presence of a catalytic amount of DTBB (5 mol %) in THF at 0°C leads, after hydrolysis with water, to the corresponding methylenic 1,4-diols **3** in a Barbier-type process. The cyclisation of diols **3** under acidic conditions (hydrochloric or phosphoric acid) yields the corresponding substituted methylenic tetrahydrofurans **4**. Finally, 2,3-dichloropropene (**1**) is converted into the corresponding allylic chloroamines **5** and then submitted to the tandem naphthalene-catalysed lithiation-S_E reaction with different electrophiles affording the corresponding functionalised amines **7**. The last process fails for oxygen- or sulfur-containing chloroallylic materials **8**.

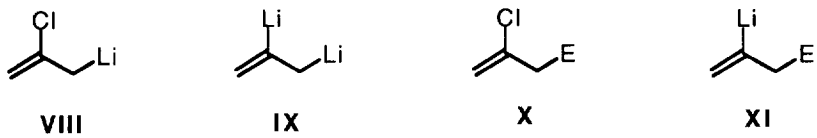
INTRODUCTION

An important problem to be solved concerning the preparation of very unstable organolithium compounds[1] is the lithiation process at low temperature. When the starting material is a halogen-, oxygen- or sulfur-containing compound, the corresponding heteroatom/lithium exchange can be performed, under very mild reaction conditions, using a solution of a lithium-arene, naphthalene, biphenyl or 4,4'-di-*tert*-butylbiphenyl (DTBB) being the most common arene used[2]. Recently, we have found that the activity of lithium metal in lithiation reactions can be increased very much using a catalytic amount of an arene instead of a stoichiometric amount of the aromatic component[3]. Taking advantage of this new methodology we have been able to lithiate, under very mild conditions, not only chlorinated precursors[4], but also sulfur-[5] (thioethers[3], sulfonates[5a], sulfates[5b,c] or sulfones[5d]) or phosphorous-containing[6] (phosphates) materials, carbonyl derivatives[7], oxygenated[8] or nitrogenated[9] saturated heterocycles and other systems[8c,10]. So, we could develop new methodologies for organolithium compounds bearing or not a functionality in the molecule[11]. Concerning chlorinated precursors, we think that dichlorinated species of the type **I**[4b,d], **II**[4c], **III**[4i], **IV/V**[4j], **VI**[4l] and **VII**[4l] are specially interesting both from a theoretical and a practical point of view due to the difficulty of stabilising the corresponding dianionic intermediate[12] and also because in the reaction with electrophiles are accessible directly polyfunctionalised organic molecules. In this paper we describe the arene-catalysed lithiation of 2,3-dichloropropene (**1**) followed by reaction with electrophilic reagents[13] as well as the same process applied to the corresponding 2-chloroallyl amines, easily prepared from **1** by a S_N-type reaction with secondary amines.

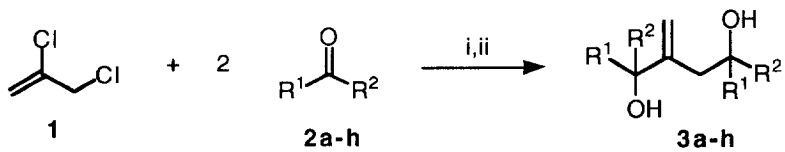


RESULTS AND DISCUSSION

The main problem inherent to the lithiation of 2,3-dichloropropene (**1**) is that after the first chlorine/ lithium exchange, giving probably the allylic derivative **VIII**, a very fast β-elimination takes place yielding allene; in fact, the reaction of this dichlorinated material with zero valent metals is a known procedure to obtain pure allene gas[14]. Thus, the very easy β-elimination prevents the second metallation to give the dilithiated species **IX**[15-18]. For the above mentioned reasons we had to perform the lithiation in the presence of the electrophile, that is under the so-called Barbier-type reaction conditions.



The reaction of 2,3-dichloropropene (**1**) and a carbonyl compound **2** (1:2 molar ratio) with an excess of lithium powder (1:7 molar ratio) in the presence of a catalytic amount of DTBB (5 mol %) in THF at 0°C led after hydrolysis with water, to the corresponding methylenic 1,4-diols **3** (Scheme 1 and Table 1). In the case of using aromatic carbonyl compounds such as benzaldehyde (**2c**) or propiophenone (**2h**) (Table 1, entries 3 and 8, respectively) the reaction had to be performed at -40°C in order to avoid undesirable by-processes. The use of naphthalene as the arene catalyst led to poorer results: the same reaction as above with pivalaldehyde (**2b**) or cyclohexanone (**2g**) as carbonyl compounds but using naphthalene instead of DTBB[19] afforded compounds **3b** and **3g** in 54 and 21% yields (GLC), respectively (Table 1, entries 2 and 7, and footnotes f and i, respectively).



Scheme 1. *Reagents and conditions*: i, Li excess (1:7 molar ratio), DTBB cat. (5 mol %), THF, 0°C; ii, H_2O.

Table 1. Preparation of 1,4-Diols **3**

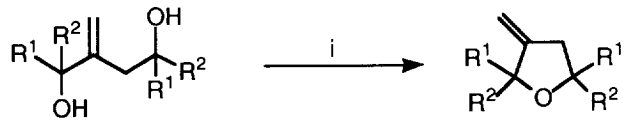
Entry	Carbonyl compound			Product[a]		
	No.	R^1	R^2	No.	Yield (%)[b]	R_f[c] [mp (°C)][d]
1	**2a**	Pr^i	H	**3a**	71 (1:1)	0.45 [e]
2	**2b**	Bu^t	H	**3b**	82[f] (8:7)	0.30, 0.32 [66-67, 81-82]
3[g]	**2c**	Ph	H	**3c**	73 (5:4)	0.38[h] [e]
4	**2d**	Pr^n	Me	**3d**	46 (2:1)	0.42 [e]
5	**2e**	Et	Et	**3e**	52	0.38 [50-51]
6	**2f**	$-(CH_2)_4-$		**3f**	70	0.41 [83-84]
7	**2g**	$-(CH_2)_5-$		**3g**	56[i]	0.38 [101-102]
8[g]	**2h**	Ph	Et	**3h**	30 (1:1)	0.45 [e]

[a] All products **3** were ≥95% pure (300 MHz ^1H NMR and GLC). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1**; in parenthesis the diastereoisomer ratio from ^1H (entries 1, 4 and 8) or ^{13}C NMR (entry 3) or after chromatographic separation (entry 2) is given. [c] Silica gel, hexane/ethyl acetate: 8/2. [d] From hexane/ethyl acetate. [e] Syrup. [f] A 54% yield (GLC) was obtained by using naphthalene instead of DTBB as catalyst, under the same reaction conditions. [g] The reaction was performed at -40°C. [h] Silica gel, hexane/ethyl acetate: 7/3. [i] A 21% yield (GLC) was obtained by using naphthalene instead of DTBB under the same reaction conditions.

Concerning the possible mechanistic pathway, we think that after the first allylic lithiation the intermediate **VIII** is formed, which in the absence of the electrophile suffers β-elimination yielding allene. However, working in the presence of the electrophilic agent (Barbier-type reaction conditions) intermediate **VIII** reacts rapidily to give the corresponding compound **X**, which is lithiated also in a fast process leading to the functionalised organolithium derivative **XI**. This is the last species before the preparation of compound **3** by reaction of **XI** with a second molecule of electrophile. We find this mechanistic possibility more probable than the formation of the very unstable dilithiated species **IX**[16-18]. On the other hand, we could not isolate compounds of the type **X** even performing the reaction at -110°C: we always obtained products **3** contaminated with variable amounts of the product resulting from the abstraction by the intermediate **XI** of a proton from the reaction media[20]. In addition, the temperature plays an important role: at low temperature (<-78°C) the reaction works worse than at 0°C because the transformation **VIII**→**X** is then a slow process and the β-elimination competes advantageously giving allene as the main product.

Methylene 1,4-diols **3** can be easily transformed into the corresponding substituted tetrahydrofurans **4**[21]. Thus, treatment of diols **3** with 3N hydrochloric acid yielded the expected products **4** (Scheme 2 and Table 2). The reaction failed for diols **3a** and **3b**. In the case of diol **3h** it was necessary to use more concentrated acid (9

N) in order to achive the preparation of compound **4h** (Table 2, entry 6 and footnote i). Curiously, under these stronger conditions diol **3g** gave directly the endocyclic olefin **4'g** (82%; 20°C, 20h). Finally, the cyclisation of **3e** to **4e** needed the use of 85% phosphoric acid as condensation reagent (Table 2, entry 3).



3a-h **4c-h**

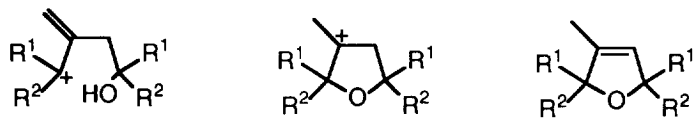
Scheme 2. *Reagent*: i, 3 N HCl, diethyl ether.

Table 2. Preparation of Methylenetetrahydrofurans **4**

Entry	Starting diol **3**	Reaction time (h)	Product[a] No.	R^1	R^2	Yield (%)[b]	R_f[c]
1	**3c**	20	**4c**	Ph	H	97 (1:1)	0.67[d,e]
2	**3d**	44	**4d**	Pr^n	Me	77 (1:1)	0.50[e,f]
3	**3e**	1[g]	**4e**	Et	Et	95[h]	0.72[f]
4	**3f**	1	**4f**	$-(CH_2)_4-$		90	0.59[d]
5	**3g**	5	**4g**	$-(CH_2)_5-$		83	0.48[f]
6	**3h**	15[i]	**4h**	Ph	Et	50 (1.7:1)	0.34[e,f]

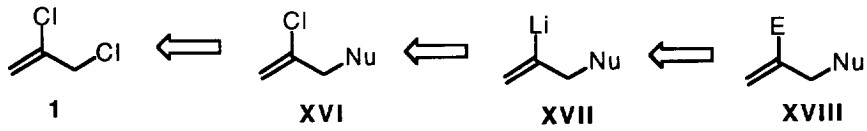
[a] All products **4** were ≥95% pure (300 MHz ^1H NMR and GLC). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting diol **3**; in parenthesis the corresponding diastereoisomers ratio (GLC) is given. [c] Silica gel. [d] Hexane/ethyl acetate: 9/1. [e] The same R_f value was obtained for the two diastereoisomers. [f] Hexane. [g] 85% H_3PO_4 was used instead of 3 N HCl. [h] 69% yield using 3 N HCl. [i] 9 N HCl was used instead of 3 N HCl.

Carbenium ions **XIV** and **XV** are probably involved in the cyclisation process **3**→**4** and in the isomerisation reaction **4g**→**4'g**, respectively.



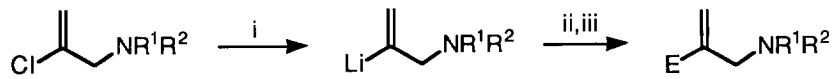
XIV **XV** **4'g**

In the last part of this study we considered the successive introduction of a nucleophile at the allylic position (**1**→**XVI**) followed by the condensation with an electrophile (**XVII**→**XVIII**) at the vinylic position after the corresponding lithiation (**XVI**→**XVII**) (Scheme 3).



Scheme 3.

We first prepared the corresponding derivatives from morpholine (**5a**) and *N*-methylbenzylamine (**5b**) by successive treatment of the corresponding secondary amine with sodium hydride and 2,3-dichloropropene (**1**) in THF at 65°C. Compounds **5a,b** were submitted to catalytic lithiation at -75°C using an excess of lithium powder (1:7 molar ratio) and naphthalene[22] as the catalyst (10 mol %). After *ca.* 2 h the starting material **5** disappeared and the corresponding electrophile was added (1:1.3 molar ratio) allowing the temperature to rise to -40°C, performing then the hydrolysis obtaining the expected functionalised amines **7** (Scheme 4 and Table 3).



5a: R^1-R^2=$(CH_2)_2O(CH_2)_2$ **6a,b** **7aa-bf**
5b: R^1=Me, R^2=$PhCH_2$

Scheme 4. *Reagents and conditions*: i, Li excess (1: 7 molar ratio), $C_{10}H_8$ cat. (10 mol %), THF, -78°C; ii, E⁺=Bu^tCHO, PhCHO, Me_2CO, $(c\text{-}C_3H_5)_2CO$, $(CH_2)_4CO$, Me_3SiCl, -78 to -40°C; iii, H_2O-HCl, -40 to 20°C.

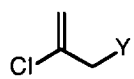
To our best knowledge there is only one intermediate of the type **6** described in the literature[23], derived from dimethyl allylamine, prepared by bromine/lithium exchange with n-butyllithium at low temperature[24].

However, when oxygen- or sulfur-containing chloroallyl derivatives of the type **8** [Y=O, S; prepared from 2,3-dichloropropene (**1**) following the same procedure as for compounds **5**] were submitted to the same tandem reaction shown in Scheme 4, only decomposition compounds were obtained, even working under Barbier-type reaction conditions. These results are in good agreement either with the decomposition of the corresponding intermediate of the type **VIII** or **XI** (with E=OR, SR) by a β-elimination giving allene due to the fact that the RO- and SR- groups are better leaving groups than the corresponding R_2N- one.

Table 3. Preparation of Compounds **7**

Entry	Starting material **5**	Electrophile E+	Product[a] No.	R1	R2	E	Yield (%)[b]	R_f[c]
1	**5a**	Bu^tCHO	**7aa**	$-(CH_2)_2O(CH_2)_2-$		Bu^tCHOH	77	0.45[d]
2	**5a**	PhCHO	**7ab**	$-(CH_2)_2O(CH_2)_2-$		PhCHOH	35	0.48[d]
3	**5a**	Me_2CO	**7ac**	$-(CH_2)_2O(CH_2)_2-$		Me_2COH	25	0.29[e]
4	**5a**	$(c\text{-}C_3H_5)_2CO$	**7ad**	$-(CH_2)_2O(CH_2)_2-$		$(c\text{-}C_3H_5)_2COH$	44	0.63[e]
5	**5a**	Me_3SiCl	**7ae**	$-(CH_2)_2O(CH_2)_2-$		Me_3Si	20	0.65[f]
6	**5b**	Bu^tCHO	**7ba**	Me	Ph	Bu^tCHOH	75	0.61[e]
7	**5b**	PhCHO	**7bb**	Me	Ph	PhCHOH	54	0.59[e]
8	**5b**	Me_2CO	**7bc**	Me	Ph	Me_2COH	30	0.46[f]
9	**5b**	Et_2CO	**7bd**	Me	Ph	Et_2COH	62	0.46[f]
10	**5b**	$(c\text{-}C_3H_5)_2CO$	**7be**	Me	Ph	$(c\text{-}C_3H_5)_2COH$	68	0.81[e]
11	**5b**	$(CH_2)_4CO$	**7bf**	Me	Ph	$(CH_2)_4COH$	40	0.45[g]

[a] All products **7** were ≥95% pure (300 MHz ^1H NMR and GLC). [b] Isolated global yield after column chromatography (silica gel, hexane/ethyl acetate) based on 2,3-dichloropropene (**1**), precursor of the starting materials **5**. [c] Silica gel. [d] Hexane/ethyl acetate: 1/1. [e] Hexane/ethyl acetate: 7/3. [f] Hexane/ethyl acetate: 8/2. [g] Hexane.



8a : Y=OPh
8b : Y=OCH_2Ph
8c : Y=SBu^t
8d : Y=SPh
8e : Y=SCH_2Ph

From the results described in this paper we conclude that 2,3-dichloropropene (**1**) is a versatile starting material for the introduction of two electrophiles (to give compounds **3**) or for the successive introduction of a nitrogenated nucleophile at the allylic position and an electrophile at the vinylic one, involving in both cases an arene-catalysed lithiation process.

EXPERIMENTAL PART

General.- M.p.s are uncorrected and were measured on a Reichert thermovar apparatus. IR spectra were determined with a Pye Unicam SP3-200 spectrometer. ^1H and ^{13}C NMR spectra were recorded in a Bruker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (*J*) are measured in Hz. ^{13}C NMR assignements were made on the basis of DEPT experiments. MS (EI) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of

volatile distilled products and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 12 m HP-1 capillary column (0.2 mm diam, 0.33 μm film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=275°C, T_{column}=60°C (3 min) and 60-270°C (15°C/min). Thin layer chromatography (TLC) was carried out on Scheleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Microanalyses were performed by the Microanalyses Service of the University of Alicante. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Solvents were dried by standard procedures[25]. Lithium powder (Strem), starting chlorinated material **1** as well as DTBB and the electrophiles used were commercially available (Aldrich, Fluka), the last ones being dried by conventional methods[25].

Preparation of Compounds **3**. *General Procedure*.- 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) was added a solution of 2,3-dichloropropene (**1**; 2 mmol) and the corresponding carbonyl compound (**2**; 4 mmol, 1:2 molar ratio) in THF (5 ml) for *ca.* 2h at 0°C (-40°C for benzaldehyde and propiophenone). The resulting mixture was then hydrolysed with water (10 ml) and neutralised with 3 N hydrochloric acid and extracted with diethyl ether (3x10 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 **3**. Yields and R_f values are included in Table 1; spectroscopic and analytical data follow.

2,7-Dimethyl-4-methylene-3,6-octanediol (**3a**): ν (film) 3350 (OH), 3075, 1640 (C=CH), 1125 and 1030 cm^{-1} (C-O); δ_H 0.80 (3H, d, *J*=6.7, C*H*$_3$CH), 0.84 (3H, d, *J*=6.7, C*H*$_3$CH), 0.90-1.10 (18H, m, 6xC*H*$_3$CH), 1.60-1.90 [4H, m, 4xC*H*(CH$_3$)$_2$], 2.05-2.15 (2H, m, 2xC=CC*H*H), 2.22 (1H, d, *J*=13.8, C=CCH*H*), 2.37 (1H, dd, *J*=14.4, 2.3, C=CCH*H*), 2.35, 3.05 (4H, 2br s, 4xOH), 3.41-3.51 (1H, m, CH$_2$C*H*OH), 3.51-3.62 (1H, m, CH$_2$C*H*OH), 3.68 (1H, d, *J*=8.4, CH$_2$=CC*H*O), 3.71 (1H, d, *J*=8.1, CH$_2$=CC*H*O), 4.98 (1H, s, C=CH*H*), 5.00 (1H, s, C=CH*H*), 5.05 (1H, s, C=CH*H*) and 5.11 (1H, s, C=C*H*H) ; δ_C 17.45, 17.7, 18.0, 18.35, 18.4, 18.65, 19.1, 19.35 [4x(*C*H$_3$)$_2$CH], 31.1, 31.85, 33.3, 33.9 [4x(CH$_3$)$_2$*C*H], 35.7, 37.25 (2xC=*C*CH$_2$), 75.0, 77.45, 81.5, 81.8 (4xCO), 114.9, 114.95 (2xC=*C*H$_2$), 147.5 and 148.5 (2x*C*=CH$_2$); *m/z* 125 [M+-H$_2$O-(CH$_3$)$_2$CH, 3%], 81 (16), 55 (31), 45 (11), 43 (100) and 41 (99).

4-Methylene-2,2,7,7-tetramethyl-3,6-octanediol (**3b**): major diastereoisomer: mp 66-67°C; ν (film) 3410 (OH), 3075, 1640 (C=CH), 1060, and 1010 cm^{-1} (C-O); δ_H 0.90 [9H, s, (CH$_3$)$_3$C], 0.92 [9H, s, (CH$_3$)$_3$C], 1.91 (1H, dd, *J*=14.2, 10.6, H$_2$C=CC*H*H), 2.1 (2H, br s, 2xOH), 2.42 (1H, dd, *J*=14.2, 2.2, H$_2$C=CCH*H*), 3.45 (1H, dd, *J*=10.6, 2.2, CH$_2$C*H*OH), 3.85 (1H, s, CH$_2$=CC*H*O), 5.05 (1H, s, C=CH*H*) and 5.10 (1H, s, C=C*H*H) ; δ_C 25.65, 26.35 [2x(*C*H$_3$)$_3$C], 34.8 (C=*C*CH$_2$), 35.4, 36.8 [2x(CH$_3$)$_3$*C*], 79.25, 83.7 (2xCO), 114.6 (C=*C*H$_2$) and 149.15 (*C*=CH$_2$); *m/z* 163 (M+-2H$_2$O-CH$_3$, 1%), 157 (11), 139 (12), 121 (47), 95 (53), 93 (16), 87 (14), 81 (18), 72 (52), 71 (24), 70 (18), 69 (34), 67 (12), 57 (96), 55 (27), 45 (11), 43 (72) and 41 (100) (Found: C, 71.9; H, 12.0. $C_{13}H_{26}O_2 \cdot 0.2H_2O$ requires C, 71.64; H, 12.21). Minor diastereoisomer: mp 81-82°C; ν (film) 3340 (OH), 3075, 1640 (C=CH), 1070 and 1010 cm^{-1} (C-O); δ_H 0.87 [9H, s, (CH$_3$)$_3$C], 0.89 [9H, s, (CH$_3$)$_3$C], 2.12 (1H, dd, *J*=13.5, 10.2, H$_2$C=CC*H*H), 2.20 (1H, dd, *J*=13.5, 2.7, H$_2$C=CCH*H*), 3.21 (1H, dd, *J*=10.1, 2.7, CH$_2$C*H*OH), 3.50 (2H, br s, 2xOH), 3.80 (1H, s, CH$_2$=CC*H*O), 4.96 (1H, s, C=CH*H*) and 4.99 (1H, s, C=C*H*H) ; δ_C 25.7, 26.35 [2x(*C*H$_3$)$_3$C], 33.95, 34.9 [2x(CH$_3$)$_3$*C*], 34.45 (C=*C*CH$_2$), 82.1, 82.35 (2xCO), 115.15 (C=*C*H$_2$) and 148.7 (*C*=CH$_2$); *m/z* 214 (M+, 0.4%), 157 (36), 139 (36), 122 (13), 121 (98), 111 (11), 110 (10), 97 (10), 95 (100), 93 (21), 87 (23), 83 (10), 81 (27), 79

(12), 72 (74), 71 (38), 70 (24), 69 (42), 67 (12), 57 (97), 55 (27), 45 (10), 43 (49) and 41 (80) (Found: C, 71.3; H, 11.9. $C_{13}H_{26}O_2 \cdot 0.2H_2O$ requires C, 71.64; H, 12.21).

1,4-Diphenyl-2-methylene-1,4-butanediol (**3c**): ν (film) 3310 (OH), 1640, 1605, 760, 700 (C=CH), 1080 and 1040 cm^{-1} (C-O) ; δ_H 2.25-2.55 (4H, m, 2xCH_2CO), 3.0 (4H, br s, 4xOH), 4.70, 4.81 (2H, 2m, 2xCH_2CHO), 4.96 (1H, s, CH_2=CCHO), 5.14, 5.18, 5.19, 5.24 (4H, 4s, 4xC=CH_2) 5.36 (1H, s, CH_2=CCHO) and 7.20-7.40 (20H, m, 4xPh); δ_C 41.55, 42.4 (2xC=CCH_2), 73.1, 74.55, 77.1, 77.2 (4xCO), 115.75, 115.9 (2xC=CH_2), 125.65, 125.75, 126.1, 126.5, 127.05, 127.4, 127.45, 127.6, 128.2, 128.3, 128.35, 128.4, 141.95, 142.1, 143.9, 144.0, 147.1 and 147.95 (4xPh, 2xH_2C=*C*); *m/z* 236 (M^+-H_2O, 5%), 131 (12), 130 (92), 129 (60), 128 (10), 115 (27), 108 (39), 107 (75), 105 (26), 104 (11), 91 (11), 79 (100), 78 (14), 77 (86) and 51 (18).

4,7-Dimethyl-5-methylene-4,7-decanediol (**3d**): ν (film) 3240 (OH), 3070, 1625 (C=CH), 1160 and 1010 cm^{-1} (C-O); δ_H 0.85-0.96 (12H, m, 4xCH_3 CH_2), 1.21, 1.25, 1.31, 1.35 (12H, 4s, 4x$COCH_3$), 1.17-1.70 (16H, m, 4xCH_2CH_2), 2.17 (1H, d, *J*=14, C=CC*H*H), 2.32 (1H, d, *J*=13, C=CC*H*H), 2.44 (1H, d, *J*=13, C=CC*H*H), 2.53 (1H, d, *J*=14, C=CC*H*H), 3.30 (4H, br s, 4xOH), 4.85 (2H, s, 2xC=C*H*H), 5.03 (2H, s, 2xC=C*H*H); δ_C 14.5, 14.55, 14.55, 14.6 (4xCH_3CH_2), 17.35, 17.4, 17.45, 17.45 (4xCH_2CH_3), 26.7, 27.55, 29.25, 29.7 (4xCH_3CO), 43.85, 43.95 (2xC=CCH_2), 44.75, 45.2, 45.75, 46.25 (4x$CH_2CH_2CH_3$), 72.45, 72.75 (2xCH_2COCH_2), 74.7, 74.75 (2xCH_2COC=C), 114.1, 114.3 (2xC=CH_2) and 151.55, 151.6 (2x*C*=CH_2); *m/z* 199 (M^+-CH_3, 0.4%), 153 (28), 110 (22), 95 (61), 87 (41), 81 (31), 71 (19), 69 (27), 68 (17), 67 (14), 57 (17), 55 (16), 45 (63), 43 (100) and 41 (68).

3,6-Diethyl-4-methylene-3,6-octanediol (**3e**): mp 50-51°C; ν (film) 3270 (OH), 3075, 1625 (C=CH), 1140 and 1020 cm^{-1} (C-O); δ_H 0.84 (6H, t, *J*=7.7, 2xCH_2CH_3), 0.87 (6H, t, *J*=8.0, 2xCH_2CH_3), 1.57 (8H, m, 4xCH_2CH_3), 2.32 (2H, s, C=CCH_2), 2.95, 4.20 (2H, 2br s, 2xOH), 4.92 (1H, s, C=C*H*H) and 4.93 (1H, s, C=CH*H*); δ_C 8.05 (2C), 8.10 (2C) (4xCH_3) 30.8 (2C), 33.15 (2C) (4xCH_2CH_3), 40.8 (C=CCH_2), 74.95, 77.35 (2xCO), 114.35 (C=CH_2), 149.5 (*C*=CH_2); *m/z* 186 (M^+-CH_2=CH_2, 1%), 167 (41), 110 (13), 95 (38), 87 (36), 81 (20), 69 (17), 67 (10), 57 (100), 55 (11), 45 (19), 43 (19) and 41 (17) (Found: C, 72.9; H, 12.5. $C_{13}H_{26}O_2$ requires C, 72.85; H, 12.23).

2,3-Bis-(1-hydroxycyclopentyl)propene (**3f**): mp 83-84°C; ν (film) 3240 (OH), 3080, 1625 (C=CH), 1190 and 1010 cm^{-1} (C-O); δ_H 1.50-1.20 (16H, m, 8xring CH_2), 2.47 (2H, s, C=CCH_2), 3.70 (2H, br s, 2xOH), 4.84 (1H, s, C=CH*H*) and 5.10 (1H, s, C=C*H*H); δ_C 23.15 (2C), 23.4 (2C), 39.3 (2C), 39.8 (2C) (8xring CH_2), 45.5 (C=CCH_2), 82.0, 83.7 (2xCO), 113.45 (C=CH_2) and 150.75 (*C*=CH_2); *m/z* 193 (M^+-OH, 1%), 192 (M^+-H_2O, 3%), 108 (16), 93 (38), 91 (18), 85 (19), 80 (10), 79 (28), 77 (22), 67 (56), 65 (14), 57 (18), 55 (55), 53 (18), 43 (36), 42 (48) and 41 (100) (Found: C, 74.0; H, 10.9. $C_{13}H_{22}O_2$ requires C, 74.24; H, 10.54).

2,3-Bis-(1-hydroxycyclohexyl)propene (**3g**): mp 101-102°C; ν (film) 3360 (OH), 3075, 1620 (C=CH), 1140 and 1030 cm^{-1} (C-O); δ_H 1.15-1.82 (20H, m, 10xring CH_2), 2.38 (2H, s, C=CCH_2), 3.37 (2H, br s, 2xOH), 4.85 (1H, s, C=CH*H*) and 5.09 (1H, s, C=C*H*H); δ_C 22.15 (2C), 22.4 (2C), 25.7, 25.75, 37.75 (2C), 38.05 (2C) (10xring CH_2), 44.3 (C=CCH_2), 71.15, 72.85 (2xCO), 114.1 (C=CH_2) and 151.85 (*C*=CH_2); *m/z* 220 (M^+-H_2O, 6%), 177 (14), 163 (12), 122 (100), 117 (11), 107 (49), 99 (94), 97 (10), 95 (18), 94 (19), 93 (41), 91 (17), 81 (79), 80 (26), 79 (47), 78 (10), 77 (17), 69 (23), 68 (11), 67 (40), 57 (14), 56 (12), 55 (87), 53

(20), 43 (43) and 41 (63) (Found: C, 75.5; H, 11.3. $C_{15}H_{26}O_2$ requires C, 75.63; H, 10.92).

3,6-Diphenyl-4-methylene-3,6-octanediol (**3h**): ν (film) 3390 (OH), 1670, 1635, 1600, 760, 700 (C=CH), 1130 and 1065 cm^{-1} (C-O) ; δ_H 0.68, 0.69, 0.75, 0.80 (12H, 4t, *J*=7.4, 7.4, 7.3, 7.3, 4xCH_2CH_3), 1.55 (4H, br s, 4xOH), 1.50-2.20 (8H, m, 4xCH_2CH_3), 2.41 (1H, d, *J*=14.4, $CHHC=CH_2$), 2.45 (2H, s, $CH_2C=C$), 2.55 (1H, d, *J*=14.4, $CHHC=CH_2$), 4.30 (1H, s, C=CH*H*), 4.98 (1H, s, C=CH*H*), 5.03 (1H, s, C=CH*H*) , 5.26 (1H, s, C=CH*H*) and 7.10-7.30 (20H, m, 4xPh) ; δ_C 7.65, 7.8, 8.1, 8.2 (4xCH_3), 33.7, 33.75, 33.75, 36.1 (4xCH_2CH_3), 45.5, 46.5 (2x$CH_2C=C$), 77.2, 77.65, 78.8, 82.0 (4xCO), 116.0, 116.8 (2xC=CH_2), 125.3, 125.65, 125.85, 125.9, 126.2, 126.3, 126.35, 126.35, 127.8, 127.85, 127.95, 128.25, 145.4, 145.45, 145.55, 146.3, 147.3 and 148.65 (4xPh, 2x$H_2C=C$); *m/z* 281 (M^+-CH_2CH_3, 1%), 263 (15), 158 (28), 143 (12), 135 (60), 129 (100), 115 (14), 105 (70), 91 (22), 77 (48), 57 (74) and 43 (11).

Preparation of Compounds **4**. *General procedure.*- A mixture of the corresponding diol **3** (1 mmol) and 3 N hydrochloric acid (10 ml) in diethyl ether (10 ml) was stirred at room temperature until the disappearance of the starting material (GLC; see Table 2). The resulting mixture was extracted with diethyl ether (3x10 ml) and the organic layer was dried over Na_2SO_4 and evaporated to yield a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) affording the pure title compounds **4**. In the case of compounds **4e** and **4h** 85% phosphoric acid in hexane and 9 N hydrochloric acid were respectively used instead of 3 N hydrochloric acid. On the other hand, compound **4'g** was obtained working with 9 N hydrochloric acid. Reaction times, yields and R_f values are included in Table 2; spectroscopic and analytical data follow.

2,5-Diphenyl-3-methylenetetrahydrofuran (**4c**): ν (film) 1700, 1650, 1580 (C=CH) and 1010 cm^{-1} (C-O); δ_H 2.67-2.75 (2H, m, 2xCH*H*CHO), 3.00-3.10 (2H, m, 2xCH*H*CHO), 4.66 (1H, m, C=CH*H*), 4.74 (1H, q, *J*=2.1, C=CH*H*), 4.95 (1H, m, CH_2CHO), 4.99 (1H, m, C=C*H*H), 5.04 (1H, q, *J*=2.1, C=C*H*H), 5.22 (1H, t, *J*=7.0, CH_2CHO), 5.28 (1H, m, CH_2CHO), 5.48 (1H, br s, CH_2CHO) and 7.22-7.38 (20H, m, 4xPh); δ_C 41.0, 41.0, 41.9, 41.9 (4xCH_2CO), 79.6, 80.1, 82.8, 83.9 (4xCO), 106.9, 107.7 (2xC=CH_2), 125.8, 126.1, 126.8, 127.2, 127.5, 127.7, 127.8, 128.4, 128.4, 128.4, 141.4, 141.4, 141.7, 142.5 (4xPh), 150.7 and 151.9 (2x$C=CH_2$); *m/z* 237 (M^++1, 3%), 236 (M^+, 17), 131 (13), 130 (100), 129 (88), 128 (29), 127 (12), 116 (11), 115 (43), 105 (72), 104 (37), 91 (20), 78 (11), 77 (34) and 51 (13).

2,5-Dimethyl-3-methylene-2,5-dipropyltetrahydrofuran (**4d**): ν (film) 3030, 1640 (C=CH), 1110 and 1140 cm^{-1} (C-O); δ_H 0.86-0.97 (12H, m, 4xCH_2CH_3), 1.16 (3H, s, CCH_3), 1.22 (3H, s, CCH_3), 1.27 (3H, s, CCH_3), 1.30 (3H, s, CCH_3), 1.15-1.60 (16H, m, 4xCH_2CH_2), 2.31-2.51 (4H, m, 2xC=CCH_2), 4.75 (2H, br s, 2xC=CH*H*) and 4.90 (2H, br s, 2xC=CH*H*); δ_C 14.5, 14.5, 14.6, 14.65 (4xCH_2CH_3), 17.6, 17.6, 17.7, 18.0 (4xCH_2), 26.5, 26.8, 28.2, 28.3 (4xCCH_3), 44.2, 44.4, 44.9, 45.3, 45.4, 45.5 (6xCH_2), 80.2, 80.3, 83.5, 83.8 (4xCO), 104.4, 104.5 (2xC=CH_2) and 156.2 (2x$C=CH_2$); *m/z* 196 (M^+, 0.3%), 153 (31), 95 (12), 43 (100) and 41 (48).

2,2,5,5-Tetraethyl-3-methylenetetrahydrofuran (**4e**): ν (film) 3080, 1640 (C=CH) and 985 cm^{-1} (C-O); δ_H 0.83 (6H, t, *J*=7.3, 2xCH_3CH_2), 0.85 (6H, t, *J*=7.2, 2xCH_3CH_2), 1.35-1.70 (8H, m, 4xCH_3CH_2), 2.40 (2H, s, $CH_2C=C$), 4.67 (1H, s, C=CH*H*) and 4.92 (1H, s, C=CH*H*); δ_C 8.5 (2C), 8.55 (2C), (4xCH_3), 30.4 (2C), 31.9 (2C) (4xCH_3CH_2), 43.9 ($CH_2C=C$), 82.8, 86.3 (2xCO), 104.85 (C=CH_2) and 154.4 ($C=CH_2$); *m/z* 196 (M^+, 0.3%), 167 (44), 95 (16), 67 (11), 57 (100), 55 (18), 53(12), 43 (20) and 41 (33).

13-Methylene-6-oxadispiro[4.1.4.2]tridecane (**4f**): ν (film) 3050, 1670 (C=CH), 1070 and 1110 cm^{-1} (C-O); δ_H 1.46-1.81 (16H, m, 8xring CH_2), 2.49 (2H, m, CH_2C=C), 4.72 (1H, m, C=CH*H*) and 4.79 (1H, m, C=CH*H*); δ_C 23.5 (2C), 24.9 (2C), 38.3 (2C), 41.9 (2C) (8xring CH_2) 45.2 (*C*H_2C=C), 88.5, 91.4 (2xCO), 102.9 (*C*H_2=C) and 157.6 (CH_2=*C*); *m/z* 194 (M^{+}+2, 1%), 193 (M^{+}+1,12), 192 (M^{+}, 100), 181 (10), 164 (16), 163 (66), 151 (32), 150 (14), 149 (87), 138 (11), 135 (26), 131 (13), 121 (25), 111 (54), 109 (14), 108 (41), 107 (20), 105 (10), 98 (21), 97 (11), 95 (23), 93 (78), 91 (46), 79 (67), 77 (41), 67 (57), 55 (47) and 41 (37) (Found: M^{+}, 192.1522. $C_{15}H_{24}O$ requires M, 192.1514).

14-Methylene-7-oxadispiro[5.1.5.2]pentadecane (**4g**): ν (film) 3040, 2890, 1430 (C=CH) and 1130 cm^{-1} (C-O); δ_H 1.16-1.74 (20H, m, 10xring CH_2), 2.46 (2H, m, CH_2C=C), 4.77 (1H, m, C=CH*H*) and 4.85 (1H, m, C=CH*H*); δ_C 12.15 (CH_3), 22.7 (2C), 23.7 (2C), 25.6, 25.7, 38.7 (2C), 39.0 (2C) (10xring CH_2), 43.8 (*C*H_2C=C), 79.6, 81.6 (2xCO), 103.6 (*C*H_2=C) and 157.6 (CH_2=*C*); *m/z* 221 (M^{+}+1, 8%), 220 (M^{+}, 50), 192 (11), 178 (16), 177 (62), 165 (16), 164 (15), 163 (30), 149 (12), 122 (23), 121 (32), 109 (17), 108 (11), 107 (37), 105 (12), 95 (26), 94 (15), 93 (25), 91 (28), 81 (28), 79 (59), 77 (42), 69 (20), 67 (37), 55 (70), 53 (28), 43 (30), 42 (26) and 41 (100) (Found: M^{+}, 220.1829. $C_{15}H_{24}O$ requires M, 220.1827).

14-Methyl-7-oxadispiro[5.1.5.2]pentadec-14-ene (**4'g**): ν (film) 2910, 2840, 1445 (C=CH) and 1080 cm^{-1} (C-O); δ_H 1.76-1.39 (23H, m, 10xring CH_2, C=CCH_3) and 5.44 (1H, br s, C=CH); δ_C 22.2 (2C), 23.6 (2C), 25.4, 25.7, 36.6 (2C), 39.7 (2C) (10xring CH_2), 86.0, 87.7 (2xCO), 141.7 (CH_3*C*=C) and 126.5 (C=*C*H); *m/z* 221 (M^{+}+1, 2%), 220 (M^{+}, 17), 178 (14), 177 (100), 149 (24), 135 (11), 120 (65), 108 (18), 107 (11), 93 (12), 91 (17), 79 (23), 76 (22), 67 (11), 55 (21), 53 (10), 43 (10) and 41 (33) (Found: M^{+}, 220.1825. $C_{15}H_{24}O$ requires M, 220.1827).

2,5-Diethyl-2,5-diphenyl-3-methylenetetrahydrofuran (**4h**): ν (film) 1660, 1590, 760, 700 (C=CH), 1120 and 985 cm^{-1} (C-O); δ_H 0.74, 0.74, 0.81, 0.92 (12H, 4t, *J*=7.4, 7.4, 7.3, 7.3, 4xCH_2CH_3), 1.66, 1.85, 1.87, 2.13 (8H, 4m, 4xCH_2CH_3), 2.76 (1H, ddd, *J*=14.8, 1.5, 1.2, C*H*HC=C), 2.79 (2H, s, CH_2C=C), 3.00 (1H, d, *J*=14.8, CH*H*C=C), 4.95, 4.97 (2H, 2dd, *J*=2.4, 1.2, 2.4, 1.5, C=CH_2), 5.13, 5.14 (2H, 2d, *J*=2.0, 2.0, C=CH_2), 7.07-7.26, 7.27-7.37, 7.39-7.47 and 7.55-7.60 (20H, 4m, 4xPh); δ_C 8.15, 8.65, 8.8, 8.9 (4xCH_3), 34.25, 34.5, 35.85, 36.7 (4x*C*H_2CH_3), 44.6, 45.3 (2x*C*H_2C=C), 84.25, 85.05 (2x*C*OCH_2C=C), 87.6, 87.6 (2x*C*OC=C), 106.1, 106.35 (2x*C*H_2=C), 125.4, 125.5, 125.8, 125.8, 126.15, 126.2, 126.3, 126.45, 127.6, 127.65, 127.7, 127.75, 145.4, 145.55, 146.05, 146.4 (24C, 4xPh), 153.45 and 153.75 (2x*C*=CH_2); *m/z* 263 (M^{+}-Et, 42%), 129 (13), 128 (11), 115 (10), 105 (100), 91 (14) and 77 (40).

Preparation of Chloroallyl Amines **5**. *General Procedure*.- To a suspension of sodium hydride (0.26 g, 11 mmol) in THf (15 ml) was added the corresponding amine (morpholine or *N*-methylbenzylamine; 10 mmol) and the mixture was refluxed for 1 h. To the cooled resulting mixture was added 2,3-dichloropropene (**1**; 1.1 g, 10 mmol) and it was refluxed again for 1 additional h. After cooling to room temperature the mixture was hydrolysed with water (15 ml), neutralised with 3 N hydrochloric acid and extracted with diethyl ether (3x10 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) to give the pure title compounds **5**.

2-Chloro-3-morpholinopropene (**5a**): 70% yield; R_f 0.42 (hexane/ethyl acetate: 7/3); ν (film) 3080, 1620 (C=CH), 1100 (C-O) and 720 cm^{-1} (C-Cl); δ_H 2.49 (4H, m, CH_2NCH_2), 3.13 (2H, s, C=CCH_2), 3.72 (4H, CH_2O), 5.35 and 5.41 (2H, 2s, C=CH_2); δ_C 51.8 (C=C*C*H_2), 53.0 (2C, 2xCH_2N), 66.7 (2C, 2xCH_2O),

114.65 (C=CH_2) and 138.2 (C=CH_2); *m/z* 161 (M^+, 21%), 126 (32), 100 (16), 96 (100), 86 (21), 77 (19), 75 (73), 68 (51), 56 (18), 55 (10), 49 (10), 12 (31) and 11 (29).

*3-(*N*-Benzyl-*N*-methyl)amino-2-chloro-1-propene* (**5b**): 55% yield; R_f 0.60 (hexane/ethyl acetate: 9/1); ν (film) 3040, 1620 (C=CH), 1250, 1020 (C-N) and 730 cm^{-1} (C-Cl); δ_H 2.26 (3H, s, CH_3), 3.17 (2H, s, C=CCH_2), 3.57 (2H, s, PhCH_2), 5.34, 5.44 (2H, 2s, C=CH_2) and 7.32 (5H, m, Ph); δ_C 41.85 (CH_3), 61.3 (C=CCH_2), 63.4 (PhCH_2), 114.2 (C=CH_2), 127.05, 128.25, 128.85, 134.55 and 139.85 (Ph, C=CH_2); *m/z* 197 (M^++2, 2%), 196 (M^++1, 1), 195 (M^+, 6), 134 (36), 118 (12), 91 (100), 65 (20), 51 (10) and 42 (32).

Preparation of Compounds **7**. *General Procedure.*- To a green suspension of lithium powder (50 mg, 7 mmol; 1:7 molar ratio) and naphthalene (12 mg, 0.1 mmol; 10 mol %) in THF (10 ml) was added the corresponding chloroamine **5** (1 mmol) in THF (5 ml) at -78°C and it was stirred for 2 h at the same temperature. Then the corresponding electrophile (1.3 mmol) was added and stirring was continued allowing the temperature to rise to -40°C during *ca.* 2h. The resulting mixture was hydrolysed with water (10 ml), neutralised with 3 N hydrochloric acid and extracted with diethyl ether (3x10 ml). The organic layer was dried over Na_2SO_4 and evaporated (15 Torr) giving a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the pure title compounds **7**. Yields and R_f values are included in Table 3; spectroscopic and analytical data follow.

4,4-Dimethyl-2-morpholinomethyl-1-penten-3-ol (**7aa**): ν (film) 3380 (OH), 3040 and 1620 cm^{-1} (C=CH); δ_H 0.94 [9H, s, C(CH_3)$_3$], 2.37-2.66 (4H, m, CH_2NCH_2), 2.77 (1H, d, J=12.4, CCHHN), 3.52 (1H, d, J=12.4, CCHHN), 3.69-3.72 (4H, m, CH_2OCH_2), 3.94 (1H, s, CHOH) and 5.02 (2H, s, H_2C=C); δ_C 26.3 [C(CH_3)$_3$], 36.0 [C(CH_3)$_3$], 53.0 (CCH_2N), 64.2 (2C), 66.8 (2C) {4C, O[(CH_2)$_2$}$_2$N, 84.3 (CO), 119.1 (H_2C=C) and 141.9 (H_2C=C); *m/z* 213 (M^+, 4%), 156 (100), 126 (12), 100 (95), 96 (10), 88 (35), 87 (54), 86 (38), 83 (16), 70 (20), 69 (13), 57 (59), 56 (27), 55 (17), 44 (10), 43 (21), 42 (22) and 41 (60) (Found: M^+, 213.1732. $C_{12}H_{23}NO_2$ requires M, 213.1729).

1-Phenyl-2-morpholinomethyl-2-propen-1-ol (**7ab**): ν (film) 3380 (OH), 3040 and 1690 cm^{-1} (C=CH); δ_H 2.44 (4H, m, CH_2NCH_2), 2.80 (1H, d, J=12.4, CCHHN), 3.07 (1H, d, J=12.4, CCHHN), 3.72 (4H, m, CH_2OCH_2), 5.00 (1H, s, CHOH), 5.18 (1H, s, HHC=C), 5.34 (1H, s, HHC=C) and 7.32 (5H, m, Ph); δ_C 53.2 (2C, CH_2NCH_2), 62.2 (CCH_2N), 66.8 (2C, CH_2OCH_2), 78.6 (CO), 117.4 (H_2C=C), 125.6, 127.0, 128.1, 143.3 and 144.4 (Ph, H_2C=C); *m/z* 233 (M^+, 10%), 146 (28), 145 (46), 131 (22), 129 (14), 128 (13), 115 (16), 104 (15), 100 (100), 96 (19), 91 (13), 88 (36), 87 (47), 86 (16), 79 (17), 77 (33), 56 (19), 42 (12) and 41 (10) (Found: M^+, 233.1404. $C_{14}H_{19}NO_2$ requires M, 233.1416).

2-Methyl-3-morpholinomethyl-3-buten-2-ol (**7ac**): ν (film) 3500-3100 (OH), 3040, 1620 (C=CH), 1100 and 1000 cm^{-1} (C-O); δ_H 1.37 (6H, s, 2xCH_3), 2.52 (4H, m, CH_2NCH_2), 3.19 (2H, s, CCH_2N), 3.70 (4H, t, J=4.6, CH_2OCH_2), 4.90 (1H, d, J=0.9, HHC=C) and 5.09 (1H, d, J=0.9, HHC=C); δ_C 30.2 (2C, 2xCH_3), 53.1 (2C, CH_2NCH_2), 63.4 (CCH_2N), 66.8 (2C, CH_2OCH_2), 72.95 (CO), 113.9 (H_2C=C) and 149.0 (H_2C=C); *m/z* 186 (M^++1, 1%), 185 (M^+, 12), 152 (27), 140 (13), 100 (100), 96 (34), 86 (26), 70 (15), 69 (20), 68 (11), 67 (11), 59 (28), 57 (17), 56 (49), 55 (22), 54 (13), 44 (12), 43 (97), 42 (47) and 41 (52) (Found: M^+, 185.1413. $C_{10}H_{19}NO_2$ requires M, 185.1416).

1,1-Dicyclopropyl-2-morpholinomethyl-2-propen-1-ol (**7ad**): ν (film) 3360-3200 (OH), 3060 and 1625 cm^{-1} (C=CH); δ_H 0.34-0.98 [10H, m, 2x(*c*C_3H_5)], 2.48 (4H,br s, CH_2NCH_2), 3.24 (2H, s, CCH_2N), 3.67 (4H, m, CH_2OCH_2), 4.96 (1H, s, *H*HC=C) and 5.40 (1H, s, *H*HC=C); δ_C -0.3 (4C), 20.2 (2C) [6C, 2x(*c*C_3H_5)], 52.9 (C*C*H_2N), 64.0 (2C, CH_2NCH_2), 66.8 (2C, CH_2OCH_2), 72.9 (CO), 115.15 (H_2C=C) and 149.0 (H_2C=*C*); *m/z* 237 (M+-1, 1%), 196 (66), 128 (20), 127 (10), 100 (100), 96 (15), 87 (22), 86 (29), 79 (10), 70 (10), 69 (38), 57 (21), 56 (29), 55 (22), 53 (10), 43 (12), 42 (28) and 41 (59) (Found: M+, 237.1718. $C_{14}H_{23}NO_2$ requires M, 237.1718).

2-Trimethylsilyl-3-morpholino-1-propeno (**7ae**): ν (film) 3040 (C=CH), 1120, 1010 (C-O), 1240 and 840 cm^{-1} [$Si(CH_3)_3$]; δ_H 0.11 (9H, s, 3xCH_3), 2.36 (4H, m, CH_2NCH_2), 3.03 (2H, m, CCH_2N), 3.68 (4H, m, CH_2OCH_2), 5.41 (1H, m, *H*HC=C) and 5.68 (1H, m, *H*HC=C); δ_C -1.4 (3C, 3xCH_3), 53.6 (2C, CH_2NCH_2), 66.4 (C*C*H_2N), 67.1 (2C, CH_2OCH_2), 126.5 (H_2C=C) and 149.5 (H_2C=*C*); *m/z* 200 (M+-1, 1%), 199 (M+, 5), 100 (100), 73 (27), 59(12), 56 (12), 45 (15), 43 (15) and 42 (14) (Found: M+, 199.1398. $C_{10}H_{21}NOSi$ requires M, 199.1392).

*2-(*N*-Benzyl-*N*-methyl)aminomethyl-4,4-dimethyl-1-penten-3-ol* (**7ba**): ν (film) 3220 (OH), 3050, 3010, 1630, 1490 and 1450 cm^{-1} (C=CH); δ_H 0.90 [9H, s, $C(CH_3)_3$], 2.15 (3H, s, NCH_3), 2.74 (1H, d, *J*=12.6, CCH*H*N), 3.24 (1H, d, *J*=12.6, CCH*H*N), 3.66 (1H, d, *J*=12.5, NCH*H*Ph), 3.77 (1H, d, *J*=12.5, NCH*H*Ph), 3.99 (1H, s, C*H*OH), 5.02 (1H, s, *H*HC=C), 5.04 (1H, s, *H*HC=C) and 7.28 (5H, m, Ph); δ_C 26.3 [$C(CH_3)_3$], 35.9 [*C*$(CH_3)_3$], 41.25 (NCH_3), 61.6, 63.5 (2C, 2xCH_2), 84.5 (CO), 118.6 (H_2C=C), 127.3, 128.4, 129.2, 137.7 and 143.4 (Ph, H_2C=*C*); *m/z* 248 (M+, 1%), 190 (25), 134 (29), 122 (13), 121 (17), 120 (27), 92 (10), 91 (100), 57 (13) and 41 (20) (Found: M+, 247.1925. $C_{16}H_{25}NO$ requires M, 247.1925).

*1-Phenyl-2-(*N*-benzyl-*N*-methyl)aminomethyl-2-propen-1-ol* (**7bb**): ν (film) 3400-3100 (OH), 3020 and 1625 cm^{-1} (C=CH); δ_H 2.21 (3H, s, CH_3), 2.79 (1H, d, *J*=12.4, CCH*H*N), 3.20 (1H, d, *J*=12.4, CCH*H*N), 3.35 (1H, d, *J*=12.7, NCH*H*Ph), 3.65 (1H, d, *J*=12.7, NCH*H*Ph), 5.00 (1H, s, *H*HC=C), 5.16 (1H, s, *H*HC=C), 5.36 (1H, s, C*H*OH) and 7.34-7.20 (10H, m, 2xPh); δ_C 41.6 (CH_3), 62.1, 61.1 (2C, 2xCH_2), 78.9 (CO), 116.95 (H_2C=C), 125.7, 126.8, 127.4, 128.0, 128.5, 129.4, 137.5, 143.5 and 145.7 (2xPh, H_2C=*C*); *m/z* 268 (M+-1, 3%), 267 (12), 146 (16), 145 (23), 134 (21), 131 (13), 122 (20), 121 (16), 120 (33), 92 (12), 91 (100), 79 (13), 77 (25), 65 (14), 51 (10) and 42 (12) (Found: M+, 267.1615. $C_{18}H_{21}NO$ requires M, 267.1615).

*4-(*N*-Benzyl-*N*-methyl)amino-2-methyl-3-methylene-2-butanol* (**7bc**): ν (film) 3360 (OH), 3040 and 1640 cm^{-1} (C=CH); δ_H 1.25 (6H, s, 2xCH_3), 2.10 (3H, s, NCH_3), 3.15 (2H, d, *J*=1.1, CCH_2N), 3.45 (2H, s, CH_2Ph), 4.83 (1H, q, *J*=1.1, H*H*C=C), 4.99 (1H, d, *J*=1.1, H*H*C=C) and 7.22 (5H, m, Ph); δ_C 30.2 (2C, 2xCH_3), 41.2 (NCH_3), 61.9, 62.5 (2C, 2xCH_2), 73.0 (CO), 113.3 (H_2C=C), 127.3, 128.4, 129.15, 137.6 and 150.4 (Ph, H_2C=*C*); *m/z* 219(M+, 3%), 204 (10), 186 (11), 134 (41), 120 (17), 91 (100), 65 (15), 43 (14) and 42 (13) (Found: M+, 219.1621. $C_{14}H_{21}NO$ requires M, 219.1621).

*1-(*N*-Benzyl-*N*-methyl)amino-3-ethyl-2-methylene-3-pentanol* (**7bd**): ν (film) 3220 (OH), 3020, 3040, 1620, 1480 and 1440 cm^{-1} (C=CH); δ_H 0.77 (6H, t, *J*=7.4, 2xCH_3CH_2), 1.45-1.60 (4H, m, 2xCH_3CH_2), 2.06 (3H, s, NCH_3), 3.07, 3.45 (4H, 2s, 2xCH_2), 4.85 (1H, s, *H*HC=C), 4.97 (1H, s, *H*HC=C) and 7.18-7.26 (5H, m, Ph); δ_C 8.1 (2C, 2xCH_3CH_2), 32.8 (2C, 2xCH_3CH_2), 41.1 (NCH_3), 61.8, 63.5 (2C, 2xCH_2), 78.25 (CO), 115.0 (H_2C=C), 127.3, 128.4, 129.1, 137.8 and 147.4 (Ph, H_2C=*C*); *m/z* 247 (M+, 3%), 218 (39),

134 (71), 121 (13), 120 (27) and 91 (100) (Found: M+, 247.1938. $C_{16}H_{25}NO$ requires M, 247.1936).

3-(N-Benzyl-N-methyl)amino-1,1-dicyclopropyl-2-methylene-1-propanol (**7be**): ν (film) 3115 (OH), 3060, 1630, 1485 and 1445 cm^{-1} (C=CH); δ_H 0.24-0.98 [10H, m, 2x(cC_3H_5)], 2.08 (3H, s, NCH_3), 3.30 (2H, s, CCH_2N), 3.47 (2H, s, NCH_2Ph), 4.97 (1H, d, *J*=1.5, H*H*C=C), 5.40 (1H, d, *J*=1.5, H*H*C=C) and 7.22-7.32 (5H, m, Ph); δ_C -0.1, 0.1 (4C, 4xring CH_2), 20.2 (2C, 2xCH), 40.9 (NCH_3), 61.7, 63.25 (2C, 2xCH_2), 73.0 (CO), 114.6 (H_2C=C), 127.3, 128.3, 129.2, 137.5 and 150.3 (Ph, H_2C=*C*); *m/z* 272 (M++1, 1%), 271 (M+, 2), 230 (40), 134 (47), 120 (25), 92 (10), 91 (100), 69 (12), 65 (14), 44 (12), 42 (13) and 41 (18) (Found: M+, 271.1924. $C_{18}H_{25}NO$ requires M, 271.1936).

1-(1-Methylene-2-(N-benzyl-N-methyl)ethylamino-1-cyclopentanol (**7bf**): ν (film) 3500-3100 cm^{-1} (OH); δ_H 1.64-1.88 (8H, m, cC_5H_8), 2.18 (3H, s, NCH_3), 3.20 (2H, s, CCH_2N), 3.53 (2H, s, NCH_2Ph), 4.90 (1H, d, *J*=1.2, H*H*C=C), 5.08 (1H, d, *J*=1.2, H*H*C=C) and 7.32-7.25 (5H, m, Ph); δ_C 23.25 (2C), 39.8 (2C) (4C, 4xring CH_2), 41.4 (CH_3), 62.05, 63.6 (2C, 2xCH_2), 84.3 (CO), 112.7 (H_2C=C), 127.35, 128.4, 129.2, 137.7 and 148.5 (Ph, H_2C=*C*); *m/z* 245 (M+, 2%), 227 (13), 134 (34), 120 (49), 91 (100), 65 (14), 44 (12) and 41 (11) (Found: M+-H_2O, 227.1672. $C_{16}H_{21}N$ requires M, 227.1674).

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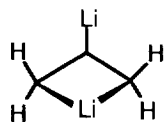
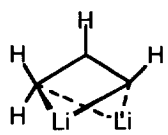


XII



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