Pergamon

Tetrahedron, Vol. 53, No. 3, pp. 1111-1122, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01034-4

Condensation Reactions of 4,5-Dihydroimidazoles: Preparation and Conjugate Additions of 2-Alkenyl-4,5-dihydroimidazoles

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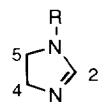
Abstract: Whereas 1-benzyl-2-lithiomethyl-4,5-dihydroimidazole undergoes reversible 1,2-addition to aldehydes and ketones, the derived phosphonate salt, 1-benzyl-2-lithio(diethylphosphono)methyl-4,5-dihydroimidazole, affords the condensation products, 2-(1-alkenyl)-4,5-dihydroimidazoles; these latter undergo conjugate addition with carbon nucleophiles. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Motivated both by the wish to use the heterocycle 4,5-dihydroimidazole (2-imidazoline; **1**) in the transfer of functionalised carbon atoms (as does Nature *via* the tetrahydrofolate coenzymes[1]), and by the biological activity demonstrated for many dihydromidazoles, we have previously reported the C-alkylation and C-acylation of 2-(α-lithioalkyl)-4,5-dihydroimidazoles **2**;[2] these studies led to a synthesis of carboxylic acids and ketones.[2,3] As part of a wider programme to explore the properties of 4,5-dihydroimidazoles with nucleophilic reactivity at the α-carbon atom, we wished to extend this work to condensation reactions of the lithio-derivatives **2** to produce 2-(1-alkenyl)-4,5-dihydroimidazoles **3**. Some 2-alkenyl-4,5-dihydroimidazoles have been reported to have biological activity, e.g. anthelmintic or hypoglycemic;[4] their potential as acceptors in conjugate additions[5,6] and as 1-azadienes in cycloaddition processes was also of interest.[7] We report herein details of the (reversible) reaction of organolithiums **2** with aldehydes and ketones, a protocol for the successful synthesis of the alkenyl dihydroimidazoles **3** *via* a phosphonylation-condensation sequence,[8] and some examples of alkenes **3** as acceptors in conjugate additions; we also present a brief examination of the cycloaddition situation. Some of this work has previously been reported in preliminary form.[9]



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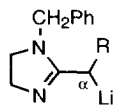

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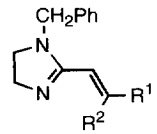
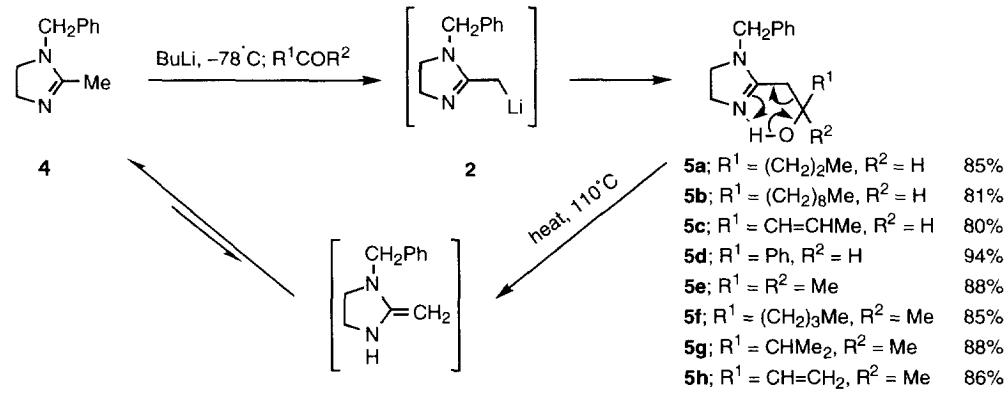


3

RESULTS AND DISCUSSION

The initial approach to alkenyl dihydroimidazoles **3** was based on addition of the nucleophile **2** (R = H) to aldehydes and ketones, followed by dehydration of the hydroxy-adducts formed. A limited number of adducts and condensation products have been reported between (mainly aromatic) aldehydes or ketones and 2-substituted 4,5-dihydroimidazoles without addition of extra base,[10] and *C*-hydroxyalkylation and condensation of the dianion formed from 2-methylbenzimidazole has been observed.[11]

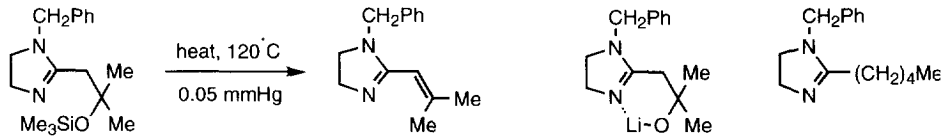
Metallation of 1-benzyl-2-methyl-4,5-dihydroimidazole **4** in the usual way (BuLi, THF, –78°C)[2] was followed by addition of a range of aldehydes (butanal, decanal, *E*-2-butenal and benzaldehyde) or of ketones (propanone, 2-hexanone, 3-methyl-2-butanone, 3-buten-2-one) to afford, after warming to 25°C and aqueous work-up, the 2-(2-hydroxyalkyl)-4,5-dihydroimidazoles **5** in good crude yield (Scheme 1). Reaction with the α,β-unsaturated carbonyl compounds afforded exclusively 1,2-addition. The adducts could not be fully characterized, however, as on standing an increasing contamination with the 2-methyl compound **4** was observed, monitored by the signal for the methyl group at δ 8.0 in the ^{1}H NMR spectrum. Attempted purification of adducts **5** by distillation at reduced pressure, led to good recoveries of starting materials **4**. This 'retro-aldol' reaction was also observed on heating the adducts in toluene (reflux, 2 h), and the facile reaction in non-polar media leads us to suggest tentatively the 'retro-ene' pathway drawn in Scheme 1 for this fragmentation. All attempts to induce elimination from the hydroxyalkyl adducts **5** by classical acid-mediated protocols were unsuccessful, with the retro-aldol reaction predominating. Reagents examined included hydrogen chloride in methanol or 2-propanol; toluene-*p*-sulfonic acid in chloroform with molecular sieves; acetic anhydride; glacial acetic acid with conc. hydrochloric acid; and trifluoroacetic acid.[12]



5a; $R^1 = (CH_2)_2Me$, $R^2 = H$ 85%
5b; $R^1 = (CH_2)_8Me$, $R^2 = H$ 81%
5c; $R^1 = CH{=}CHMe$, $R^2 = H$ 80%
5d; $R^1 = Ph$, $R^2 = H$ 94%
5e; $R^1 = R^2 = Me$ 88%
5f; $R^1 = (CH_2)_3Me$, $R^2 = Me$ 85%
5g; $R^1 = CHMe_2$, $R^2 = Me$ 88%
5h; $R^1 = CH{=}CH_2$, $R^2 = Me$ 86%

Scheme 1

Trapping of the 2-(2-hydroxyalkyl)-4,5-dihydroimidazoles **5** was attempted with a variety of electrophilic reagents. Thus the solution of the lithio-salt obtained by the addition of propanone to the metallated dihydroimidazole **2**, was cooled to –78°C before addition of chlorotrimethylsilane. Removal of the solvent afforded the crude silylated adduct **6** as evidenced by the ^{1}H NMR spectrum, but aqueous work-up led to partial hydrolysis and reappearance of the starting dihydroimidazole **4** by retro-aldol reaction. Use of *tert*-butyldimethylsilyl chloride, to give a potentially less labile derivative, gave incomplete silylation.[13] Direct distillation of the crude trimethylsilyl ether **6** (Kugelrohr, 120°C, 0.05 mmHg) did not lead to purification but



6 **3g** **7** **8**

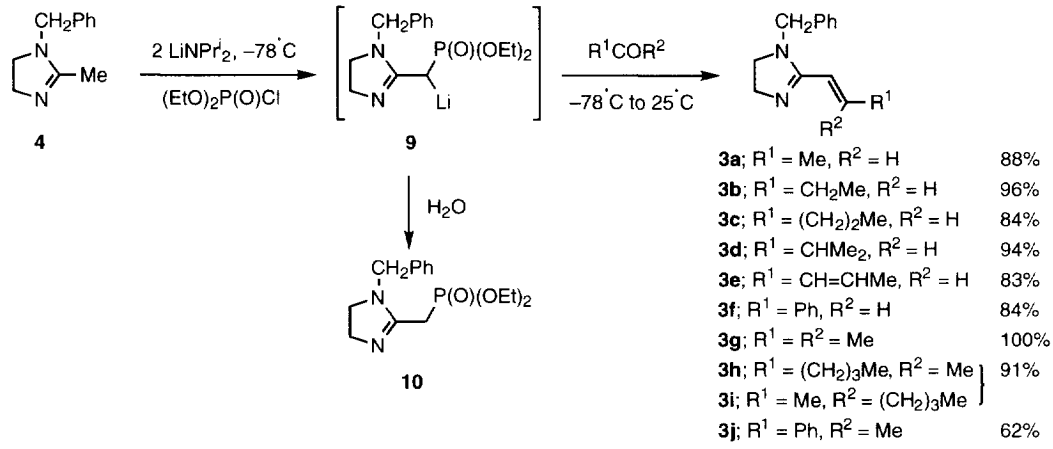
rather to thermolysis, affording the 2-(2-methyl-1-propenyl)-4,5-dihydroimidazole **3g**. This encouraging result could not however be extended to other examples.

When butanal was the carbonyl component, incomplete silylation was observed with chlorotrimethylsilane and also with the methyl trimethylsilyl ketene acetal formed from methyl propanoate.[14] Reactions with (2-methoxy)ethoxymethyl chloride–diisopropylethylamine, and with iodomethane were unsuccessful. This lack of reactivity is possibly attributable to lithium cation chelation in the salts of adducts **5**, as shown in **7** and related to the retro-aldol proposal of Scheme 1.

We next turned to the incorporation at the α-carbon atom of a heteroatom that could promote the desired elimination. Our first approach was based on the Peterson reaction.[15] Thus standard metallation of dihydroimidazole **4** was followed by successive additions of chlorotrimethylsilane, further butyl-lithium, and benzaldehyde. However, after work-up and thermolysis of the crude product, only starting material **4** was recovered with no indications of any alkene material. Attempts were next made to introduce a sulphur or selenium substituent at the α-carbon, for eventual oxidative elimination. Reaction of the lithio-derivative of **4** by either normal or inverse addition with 1-chloro-1-phenylthiobutane merely promoted elimination from the chlorosulphide.[16] Metallation of 1-benzyl-2-pentyl-4,5-dihydroimidazole **8** (BuLi, –78°C) and treatment with phenylselenenyl chloride followed by hydrogen peroxide, again afforded no alkene product.[17]

The strategy that did finally lead to success was based on the Wadsworth-Emmons reaction.[18,5a] Thus treatment of dihydroimidazole **4** with lithium diisopropylamide (2 equiv., THF, -78°C) followed by addition of diethyl chlorophosphate (1 equiv.) afforded the phosphonate salt **9**, which was quenched at –78°C with a variety of carbonyl compounds, both aldehydes (ethanal, propanal, butanal, 2-methylpropanal, 2-butenal and benzaldehyde) and ketones (propanone, 2-hexanone and acetophenone) to give, after 16 h at 25°C and chromatography on alumina (substantial decomposition occurred on silica) good yields of the 2-(1-alkenyl)-4,5-dihydroimidazoles **3** (Scheme 2). No reaction was observed with 3-methyl-2-butanone, presumably due to steric hindrance. The unsaturated dihydroimidazoles **3** were characterized, after chromatography, as their crystalline oxalate salts. Condensations with aldehydes afforded exclusively the *E*-alkenes (by ^{1}H NMR spectroscopy, $^3J_{CH=CH}$ ~17 Hz) whereas unsymmetrical ketones gave a mixture of geometric isomers with *E* predominating, e.g. 2-hexanone affording **3h**:**3i** (*E*:*Z*) 2:1. Interestingly, the crude product from acetophenone indicated an *E*:*Z* ratio of 8:1 but acid-base extraction gave pure *E* isomer **3j** directly (the ^{1}H NMR spectrum showed n.O.e. enhancements of the benzylic-CH_2 and aromatic signals, but not of the alkenyl-CH_3, on irradiation of the alkenyl-H).

The above one-pot formation of 2-alkenyl-4,5-dihydroimidazoles **3** from the 2-methyl compound **4** was found to be preferable to attempts to isolate and purify the 2-diethylphosphonomethyl-4,5-dihydroimidazole **10** before Wadsworth-Emmons condensation. Thus quenching with water of the reaction mixture after the addition of diethyl chlorophosphate did afford crude phosphonate **10** but attempted purification by chromatography or distillation did not improve the quality of the material. Other approaches to the synthesis of phosphonate **10**, by reaction of *N*-benzyl-1,2-diaminoethane with triethylphosphonoacetate, or with the

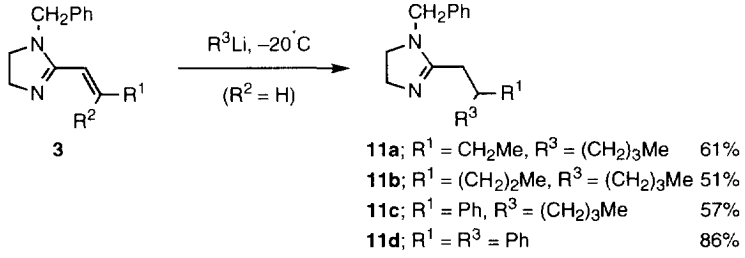


Scheme 2

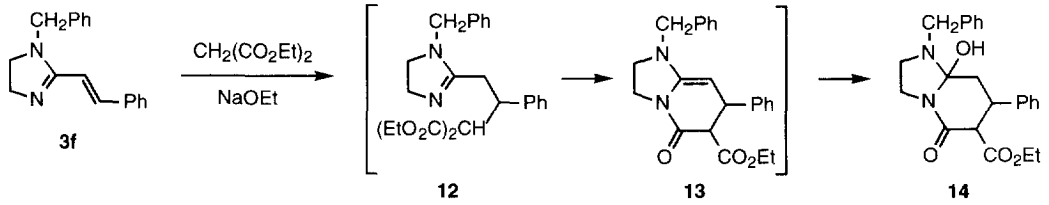
imidate obtained by Pinner reaction (ethanol–hydrogen chloride) of diethylphosphonoacetonitrile, were unsuccessful. Diisopropyl chlorophosphate could be substituted for the diethyl derivative in the one-pot protocol, e.g. to produce **3b** from 2-methyl compound **4**, but offered no advantage.[5a]

We have conducted preliminary studies on the conjugate addition properties of the 2-alkenyl-4,5-dihydroimidazoles **3** with carbon nucleophiles. In previous work we have shown that dihydroimidazoles are stable towards addition of organometallic reagents at C-2.[3] Likewise, no reaction was observed between the 2-(2-phenethenyl)-4,5-dihydroimidazole **3f** and the Grignard reagent, butylmagnesium bromide, over the temperature range –78°C to 20°C. In contrast, treatment of the 2-(1-butenyl), 2-(1-pentenyl) and 2-(2-phenylethenyl) compounds, **3b,c,f** respectively, with butyl- or phenyl-lithiums (THF; –20°C) gave the corresponding 1,4-adducts **11** in moderate yields (Scheme 3); there was no evidence of any 1,2-addition. The conjugate additions were less effective at –78°C; for example reaction of the 2-(2-phenylethenyl) compound **3f** with butyl-lithium afforded **11c** in only 28% yield. Taken together with our methods for cleavage of the dihydroimidazole moiety,[2,3] these additions constitute a route to β-substituted carboxylic acids and ketones.

Treatment of the 2-(2-phenethenyl) compound **3f** with diethyl malonate in ethanol in the presence of catalytic sodium ethoxide, afforded a crude product with ^{1}H NMR spectrum indicative of dihydroimidazole **12** formed by 1,4-addition of the malonate anion as a softer C-nucleophile, and from which the cyclol **14** was isolated after chromatography on silica. We presume cyclol **14** is formed by cyclisation of the adduct **12** to a hexahydroimidazo[1,2-*a*]pyridone **13** and subsequent hydration (Scheme 4); related examples of cyclol formation have been observed elsewhere in our work.[19]

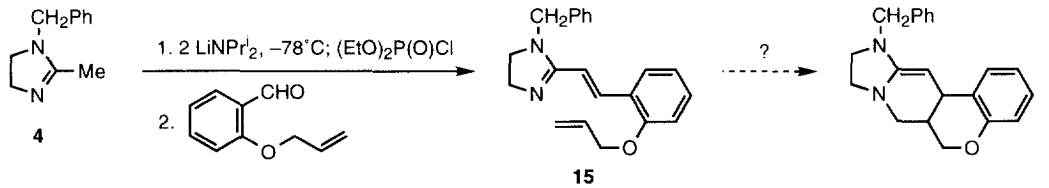


Scheme 3



Scheme 4

The cycloaddition properties of the 2-amino-1-azadienes **3** were briefly investigated. 1-Azadiene systems have received only limited attention,[20] and show diminished reactivity towards typical electrophilic dienophiles unless activated, e.g. in α,β-unsatured hydrazones.[21] Activation by *N*-acylation[22] or *N*-sulphonylation[23] can facilitate reaction with unactivated or electron-rich alkenes. We were unclear whether our heterodienes **3** might react as electron-rich dienes (from the 2-amino substituent[24]) or electron-poor dienes (by analogy with the reactions of 2-silyloxy-1-azadienes[25]), and stepwise processes could also be envisaged. In the event no cycloadduct could be isolated from reaction of either 2-(2-phenethenyl) compound **3f**, chosen to exclude imine-enamine tautomerism,[20a] or of 2-(1-propenyl)dihydroimidazole **3a** with either *N*-phenylmaleimide, butyl vinyl ether, methyl acrylate or acrylonitrile (with or without added zinc chloride as Lewis-acid) in benzene or dichloromethane at room temperature for extended periods, or in toluene at reflux. In the expectation that an intramolecular cycloaddition might be more favourable, the substrate **15** was prepared from salicylaldehyde by *O*-allylation[26] and condensation with the dihydroimidazole **4** *via* the phosphonylation and Wadsworth-Emmons reaction procedure (Scheme 5). Triene **15** was heated at reflux in benzene but starting material was recovered after 60 h. Addition of various Lewis-acids (tin(IV) chloride, titanium(IV) chloride, boron trifluoride etherate or zinc chloride) had no effect and attempted photolytic closure[27] was unsuccessful, whilst heating in xylene at reflux caused decomposition. We conclude that, if cycloaddition is to be observed with dienes **3**, different electronic combinations will be necessary, and studies in this direction are underway.



Scheme 5

EXPERIMENTAL

General: Melting points were measured on a capillary apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 710B spectrometer. ^{1}H NMR spectra were recorded, using tetramethylsilane as internal standard, at 100 or 90 MHz using JEOL MH-100 or Perkin-Elmer R32 spectrometers, respectively, unless otherwise stated; ^{1}H NMR spectra at 250 MHz and ^{13}C NMR spectra at 67.5 MHz were determined using a Bruker WM250 spectrometer. Mass spectra were obtained using an AEI MS902 spectrometer. Butyllithium solutions were standardised by the diphenylacetic acid method. Ether refers to diethyl ether. All solvents were dried and distilled before use.

1-Benzyl-2-(2-hydroxypentyl)-4,5-dihydroimidazole **5a**. To 1-benzyl-2-methyl-4,5-dihydroimidazole[2] **4** (1.4 g, 8.0 mmol) stirred in dry THF (25 cm^3) at –78°C under nitrogen was added butyl-lithium (7.7 cm^3 of a 1.24M solution in hexanes, 9.6 mmol) and the mixture stirred for 1 h. Butanal (0.64 g, 8.9 mmol) was added dropwise whilst the temperature was maintained at –78°C, and then the mixture was allowed to warm to 20°C over 1 h. After stirring for a further 16 h the solution was concentrated under reduced pressure and the residue partitioned between chloroform (50 cm^3) and iced water (50 cm^3). The organic extract was dried ($MgSO_4$) and concentrated under reduced pressure to give the crude dihydroimidazole **5a** (1.68 g, 85%) as a colourless oil; ν_{max} (film) 3300 (br), 2960, 2930, 2860, 1610, 1500, 745, 700 cm^{-1}; δ_H ($CDCl_3$) 7.1 (5H, br s, Ph), 5.2 (1H, br s, OH), 4.2 (2H, s, PhC*H*$_2$), 3.9 (1H, m, CH), 3.5-3.7, 3.0-3.2 (each 2H, t, NCH_2CH_2N), 2.3 (2H, br s, CH_2), 1.5 (4H, m, CH_2CH_2), 0.9 (3H, t, CH_3). N.B. Yields quoted for dihydroimidazoles **5a-h** are for crude material isolated directly from aqueous work-up as described, and containing 0-5% of dihydroimidazole **4** from retro-aldol reaction (*vide supra*), increasing on standing or on further purification.

1-Benzyl-2-(2-hydroxyundecyl)-4,5-dihydroimidazole **5b**. Dihydroimidazole **5b** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.05 g, 6.1 mmol), butyl-lithium (4.6 cm^3 of a 1.45M solution in hexanes, 6.7 mmol) and decanal (1.04 g, 6.7 mmol) using the same method as for dihydroimidazole **5a** to give crude dihydroimidazole **5b** (1.61 g, 81%) as a colourless oil; ν_{max} (film) 3300 (br), 2920, 2850, 1605, 1495, 770, 700 cm^{-1}; δ_H ($CDCl_3$) 7.25 (5H, br s, Ph), 4.8 (1H, br s, OH), 4.25 (2H, s, PhC*H*$_2$), 3.9 (1H, m, CH), 3.5-3.8, 3.0-3.3 (each 2H, t, NCH_2CH_2N), 2.25 (2H, br s, CH_2), 2.2 (16H, br s, $(CH_2)_8$), 1.85 (3H, t, CH_3); *m/z* 330 (M^+), 203, 174, 173, 91 (100%).

1-Benzyl-2-(2-hydroxy-3-pentenyl)-4,5-dihydroimidazole **5c**. Dihydroimidazole **5c** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.43 g, 8.2 mmol), butyl-lithium (6.2 cm^3 of a 1.45M solution in hexanes, 9.0 mmol) and *E*-2-butenal (0.63 g, 9.0 mmol) using the same method as for dihydroimidazole **5a** to give crude dihydroimidazole **5c** (1.6 g, 80%) as a colourless oil; ν_{max} (film) 3300 (br), 2975, 2860, 1605, 1500, 760, 700 cm^{-1}; δ_H ($CDCl_3$) 7.1 (5H, br s, Ph), 5.4-5.6 (3H, m, CH=CH, OH), 4.3 (1H, m, C*H*OH), 4.2 (2H, s, PhC*H*$_2$), 3.5-3.7, 3.0-3.2 (each 2H, t, NCH_2CH_2N), 2.3 (2H, br s, CH_2), 1.6 (3H, d, CH_3).

1-Benzyl-2-(2-hydroxy-2-phenylethyl)-4,5-dihydroimidazole **5d**. Dihydroimidazole **5d** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.25 g, 7.18 mmol), butyl-lithium (5.4 cm^3 of a 1.45M solution in hexanes, 7.9 mmol) and benzaldehyde (0.84 g, 7.9 mmol) using the same method as for dihydroimidazole **5a** to give crude dihydroimidazole **5d** (1.9 g, 94%); ν_{max} (film) 3300 (br), 2950, 2850, 1650 (br), 1500, 1040, 760, 700 cm^{-1}; δ_H ($CDCl_3$) 7.4 (10H, m, Ph), 4.1 (2H, s, PhC*H*$_2$), 4.05 (1H, s, CH), 3.5 (br s, OH), 3.4-3.6, 2.9-3.2 (each 2H, t, NCH_2CH_2N), 2.5 (2H, br s, CH_2), 1.9 (3H, s, CH_3).

1-Benzyl-2-(2-hydroxy-2-methylpropyl)-4,5-dihydroimidazole **5e**. Dihydroimidazole **5e** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.5 g, 8.6 mmol), butyl-lithium (7.3 cm^3 of a 1.3M solution in hexanes, 9.5 mmol) and propanone (0.55 g, 9.5 mmol) using the same method as for dihydroimidazole **5a** to give crude dihydroimidazole **5e** (1.75 g, 88%) as a colourless oil; ν_{max} (film) 3300, 3000, 2900, 1602, 1500, 1030, 740, 700 cm^{-1}; δ_H ($CDCl_3$) 7.1 (5H, br s, Ph), 5.6 (1H, br s, OH), 4.2 (2H, s, PhC*H*$_2$), 3.0-3.2, 3.5-3.7 (each 2H, t, NCH_2CH_2N), 2.3 (2H, s, CH_2), 1.3 (6H, s, 2 x CH_3); *m/z* 232 (M^+), 174, 120, 92, 91 (100%), 65.

1-Benzyl-2-(2-hydroxy-2-methylhexyl)-4,5-dihydroimidazole **5f**. Dihydroimidazole **5f** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.27 g, 7.3 mmol), butyl-lithium (6.45 cm^3 of a 1.24M solution in hexanes, 8.0 mmol) and 2-hexanone (0.8 g, 8.0 mmol) using the same method as for dihydroimidazole **5a** to

give crude dihydroimidazole **5f** (1.7 g, 85%) as a colourless oil; ν_{max} (KBr) 3250, 2950, 2900, 2850, 1600, 1540, 1490, 1020, 760, 700 cm^{-1}; δ_H ($CDCl_3$) 7.1 (5H, br s, Ph), 5.6 (1H, br s, OH), 4.2 (2H, s, PhCH_2), 3.5-3.8, 3.0-3.3 (each 2H, t, NCH_2CH_2N), 2.3 (2H, s, CH_2), 1.5 (6H, m, $(CH_2)_3$), 1.2 (3H, s, CH_3), 0.9 (3H, t, CH_3).

1-Benzyl-2-(2-hydroxy-2,3-dimethylbutyl)-4,5-dihydroimidazole **5g**. Dihydroimidazole **5g** was prepared from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.34 g, 7.7 mmol), butyl-lithium (6.5 cm^3 of a 1.3M solution in hexanes, 8.45 mmol) and 3-methyl-2-butanone (1.3 g, 15 mmol) using the same method as for dihydro-imidazole **5a** to give crude dihydroimidazole **5g** (1.76 g, 88%) as a colourless oil; ν_{max} (film) 3300, 3000, 2800, 1602, 1500, 760, 700 cm^{-1}; δ_H ($CDCl_3$) 7.1 (5H, br s, Ph), 6.0 (1H, br s, OH), 4.2 (2H, s, PhCH_2), 3.5-3.7, 3.0-3.2 (each 2H, t, NCH_2CH_2N), 2.3 (2H, s, CH_2), 1.8 (1H, m, CH), 1.1 (3H, s, CH_3), 0.9 (6H, d, $(CH_3)_2$).

1-Benzyl-2-(2-hydroxy-2-methyl-3-butenyl)-4,5-dihydroimidazole **5 h** (with S. C. HIRST). Dihydro-imidazole **5h** was made from 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.0 g, 5.7 mmol), butyl-lithium (4.2 cm^3 of a 1.5M solution in hexanes, 6.3 mmol) and 3-buten-2-one (0.51 cm^3, 6.3 mmol) using the same method as for dihydro-imidazole **5a** to give crude dihydroimidazole **5h** (1.21 g, 86%) as a colourless oil; δ_H ($CDCl_3$) 7.3 (5H, br s, Ph), 6.0 (1H, dd, *J* 11, 17 Hz, C*H*=CH_2), 5.25 (1H, dd, *J* 2, 17 Hz, CH=C*H*H), 5.05 (1H, dd, *J* 2, 11 Hz, CH=CH*H*), 4.3 (2H, s, PhCH_2), 3.7 (1H, br s, OH), 3.6-3.8, 3.0-3.3 (each 2H, t, NCH_2CH_2N), 2.45 (2H, s, CH_2), 1.3 (3H, s, CH_3).

Retro-aldol reaction of 1-benzyl-2-(2-hydroxypentyl)-4,5-dihydroimidazole **5a** *by distillation at reduced pressure*. 1-Benzyl-2-(2-hydroxypentyl)-4,5-dihydroimidazole **5a** (1.68 g, 6.8 mmol) was heated in a Kugelrohr distillation apparatus under reduced pressure (0.1 mmHg). Collection of the fraction distilling at 100-110°C (oven temp.) gave 1-benzyl-2-methyl-4,5-dihydroimidazoline **4** (1.0 g, 85%) identical with a sample prepared by reaction of *N*-benzyl-1,2-diaminoethane and ethyl acetimidate hydrochloride.

Distillation of 1-benzyl-2-(2-hydroxy-2-methylpropyl)-4,5-dihydroimidazole **5g** (1.95 g, 8.4 mmol) by the method described above for dihydroimidazole **5a** and collection of the fraction distilling at 95-100°C (oven temp.) gave 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.36 g, 93%) identical with a standard sample.

Retro-aldol reaction of 1-benzyl-2-(2-hydroxy-2-methylpropyl)-4,5-dihydroimidazole **5g** *by heating in toluene*. 1-Benzyl-2-(2-hydroxy-2-methylpropyl)-4,5-dihydroimidazole **5g** (0.25 g, 1.1 mmol) in toluene (10 cm^3) was heated at reflux for 2 h. After cooling the reaction mixture was concentrated under reduced pressure to give 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (0.13 g, 70%) identical with a standard sample .

1-Benzyl-2-(2-methyl-1-propenyl)-4,5-dihydroimidazole **3g** *by thermolysis of silyl ether* **6**. 1-Benzyl-2-methyl-4,5-dihydroimidazole **4** (1.15 g, 6.6 mmol) was treated with butyl-lithium (5.1 cm^3 of a 1.42M solution in hexanes, 7.2 mmol) and propanone (0.42 g, 7.2 mmol) using the same method as for preparation of dihydroimidazole **5a** except that after addition at –78°C was complete, the mixture was allowed to warm to 10°C over 4 h and then cooled to –78°C, and treated dropwise with chlorotrimethylsilane (0.78 g, 7.2 mmol) . After warming to 20°C and stirring for a further 3 h, the reaction mixture was concentrated under reduced pressure to give the crude *O*-silylated adduct **6** (1.88 g), containing LiCl. The residue was heated at 120°C (oven temp.) in a closed Kugelrohr apparatus (initial pressure 0.05 mmHg) for 2 h. Subsequent Kugelrohr distillation (oven temp. 85-90°C) at 0.1 mmHg gave alkenyl dihydroimidazole **3g** (1.19g, 60%) as a colourless oil, identical with a sample prepared by Wadsworth-Emmons condensation (*vide infra*).

1-Benzyl-2-(1-pentenyl)-4,5-dihydroimidazole **3c** *by Wadsworth-Emmons condensation*. To lithium diisopropylamide [18.43 mmol, from butyl-lithium (13.0 cm^3 of a 1.42M solution in hexanes) and diisopropylamine (1.86 g)], stirred in dry THF (15 cm^3) at –78°C under nitrogen was added 1-benzyl-2-methyl-4,5-dihydroimidazole **4** (1.53 g, 8.79 mmol) in dry THF (10 cm^3) and the mixture stirred for 1 h. Diethyl chlorophosphate (1.66 g, 9.62 mmol) was added dropwise, whilst maintaining the temperature at –78°C, and the solution stirred for a further 2 h. To this was added freshly distilled butanal (0.85 cm^3, 9.63 mmol), again maintaining the temperature at –78°C, and then the reaction mixture was allowed to warm to 20°C and stirred for a further 16 h. The solvent was removed under reduced pressure, and the residue partitioned between water and chloroform. The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to give the crude 1-benzyl-2-(2-alkenyl)-4,5-dihydroimidazole, which was purified by column chromatography on alumina (grade III), eluting with isopropylamine–chloroform (0.25:99.75 v/v), to afford alkenyl dihydroimidazole **3c** (1.69 g, 84%) as a yellow oil (Found: M^+ 228.1622. $C_{15}H_{20}N_2$ requires M 228.1626); ν_{max} (film) 2950, 2900, 2850, 1640, 1600, 1500, 1460, 750, 700 cm^{-1}; δ_H ($CDCl_3$) 7.35 (5H, br s, Ph), 6.6-7.0 (1H, dt, *J* 6, 18 Hz, CH=C*H*CH_2), 6.05 (1H, d, *J* 18 Hz, C*H*=CHCH_2), 4.4 (2H, s, PhCH_2), 3.65-3.9, 3.1-3.35 (each 2H, m, NCH_2CH_2N), 2.0-2.3 (2H, m, $CH_2CH_2CH_3$), 1.25-1.65 (2H, m, CH_2Me), 0.95 (3H, t, CH_3); *m/z* 228 (M^+). A portion of compound **3c** in dry ethanol was added dropwise to a saturated solution of oxalic acid in ether, the solid was collected and recrystallised from ethanol–ether to afford the oxalate salt, m.p. 113-114°C (Found: C, 64.1; H, 7.1; N, 9.1. $C_{17}H_{22}N_2O_4$ requires C, 64.13; H, 6.97; N, 8.80%). N.B. For many of the 4,5-dihydroimidazoles described below it did not prove possible (in part due to their hygroscopic nature) to obtain satisfactory combustion analyses. In addition to the reported spectroscopic data and accurate mass measurement, the purity of these materials was confirmed by t.l.c. examination; oxalate salts, *vide supra*, were prepared where possible.

1-Benzyl-2-(3-methyl-1-butenyl)-4,5-dihydroimidazole **3d**. Alkenyl dihydroimidazole **3d** was prepared from 2-methylpropanal (0.9 cm^3, 4.82 mmol) using the same method as for compound **3c**, but on half scale, to give alkenyl dihydroimidazole **3d** (0.94 g, 94 %) as a yellow oil (Found: M^+ 228.1616. $C_{15}H_{20}N_2$ requires *M* 228.1626); ν_{max} (film) 2840, 1650, 1595, 1450 cm^{-1}; δ_H ($CDCl_3$) 7.4 (5H, br s, Ph), 6.7-7.0 (1H, dd, *J* 6, 18 Hz, CH=C*H*CH), 6.05 (1H, d, *J* 18 Hz, C*H*=CHCH), 4.4 (2H, s, PhCH_2), 3.7-3.9, 3.1-3.4 (each 2H, m, NCH_2CH_2N), 2.35-2.6 (1H, m, C*H*$(CH_3)_2$), 1.12, 1.05 (each 3H, d, CH_3); *m/z* 228 (M^+). The oxalate salt had m.p. 122-124°C from ethanol–ether (Found: C, 64.3; H, 7.1: N, 9.0. $C_{17}H_{22}N_2O_4$ requires C, 64.13; H, 6.97; N, 8.80%).

1-Benzyl-2-(1,3-pentadienyl)-4,5-dihydroimidazole **3e**. Alkenyl dihydroimidazole **3e** was prepared from 2-butenal (0.80 cm^3, 9.7 mmol) using the same method as for compound **3c** to give alkenyl dihydroimidazole **3e** (1.65 g, 83%) as an oil (Found: M^+ 226.1459. $C_{15}H_{18}N_2$ requires *M* 226.1469); ν_{max} (film) 2940, 2860, 1645, 1620, 1580, 1495, 1440, 1410, 750, 700 cm^{-1}; δ_H ($CDCl_3$) 7.15-7.45 (6H, m, C*H*=CH, Ph), 5.75-6.35 (3H, m, 3 x C*H*=CH), 4.3 (2H, s, PhCH_2), 3.6-3.9, 3.1-3.3 (each 2H, m, NCH_2CH_2N), 1.8 (3H, d, CH_3); *m/z* 226 (M^+). The oxalate salt had m.p. 141-143°C from ethanol–ether (Found: C, 64.4; H, 6.5; N, 9.0. $C_{17}H_{20}N_2O_4$ requires C, 64.54; H, 6.37; N, 8.85%).

1-Benzyl-2-(2-phenylethenyl)-4,5-dihydroimidazole **3f**. Alkenyl dihydroimidazole **3f** was prepared from benzaldehyde (1 cm^3, 9.84 mmol) using the same method as for compound **3c** to give alkenyl dihydroimidazole **3f** (1.93 g, 84%) as a yellow semi-solid(Found: M^+ 262.1448. $C_{18}H_{18}N_2$ requires *M* 262.1469); ν_{max} (film) 3030, 2930, 2860, 1640, 1580, 1495, 1450 cm^{-1}; δ_H ($CDCl_3$) 7.7 (1H, d, *J* 17 Hz, PhC*H*=CH),

7.35 (5H, br s, Ph), 6.65 (1H, d, *J* 17 Hz, PhCH=C*H*), 4.4 (2H, s, PhCH_2), 3.7-3.95, 3.15-3.4 (each 2H, m, NCH_2CH_2N); *m/z* 262 (M^+). The oxalate salt had m.p. 128-130°C (Found: C, 67.45; H, 5.7; N, 7.8. $C_{20}H_{20}N_2O_4.0.25H_2O$ requires C, 67.31; H, 5.79; N, 7.85%); **3f** recovered from the salt had m.p. 80-82°C.

1-Benzyl-2-(2-methyl-1-propenyl)-4,5-dihydroimidazole **3g**. Alkenyl dihydroimidazole **3g** was prepared from propanone (0.7 cm^3, 9.7 mmol) using the same method as for compound **3c** to give alkenyl dihydroimidazole **3g** (1.94 g, 100%) as a yellow oil (Found: M^+ 214.1478. $C_{14}H_{18}N_2$ requires M, 214.1470); ν_{max} (film) 3050, 2950, 2850, 1650, 1600 (br), 1495, 740, 700 cm^{-1}, δ_H ($CDCl_3$) 7.2-7.4 (5H, br s, Ph), 5.75 (1H, s, CH=C), 4.25 (2H, s, PhCH_2), 3.6-3.9, 3.0-3.3 (each 2H, t, NCH_2CH_2N), 2.05, 1.85 (each 3H, d, CH_3); m/z 214 (M^+), 199, 174, 91 (100%). The oxalate salt had m.p. 80-82°C from ethanol–ether (Found: C, 63.4; H, 6.7; N, 9.2. $C_{16}H_{20}N_2O_4$ requires C, 63.14; H, 6.62; N, 9.20%).

1-Benzyl-2-(2-methyl-1-hexenyl)-4,5-dihydroimidazole **3h,i**. Alkenyl dihydroimidazoles *E*-**3h** and *Z*-**3i** were prepared from 2-hexanone (1.2 cm^3, 9.7 mmol) using the same method as for compound **3c** to give alkenyl dihydroimidazoles **3h,i** (2.15 g, 91%) as an oil (Found: M^+ 270.2099. $C_{18}H_{26}N_2$ requires *M* 270.2096). The ^1H NMR spectrum indicated a mixture of geometric isomers, 2:1 *E*-**3h**:*Z*-**3i**; δ_H ($CDCl_3$) 7.2-7.5 (5H, m, Ph), 5.75 (1H, m, CH=C), 4.3 (2H, s, PhCH_2), 3.7-3.95, 3.1-3.3 (each 2H, m, NCH_2CH_2N), 2.5 (0.66H, t, CH_2C=C, *Z*-isomer), 2.0-2.3 (3.33H, m, CH_2C=C, CH_3C=C, *E*-isomer), 1.85 (1H, d, CH_3C=C, *Z*-isomer), 1.1-1.7 (4H, m, (CH_2)$_2$$CH_3$), 0.9 (3H, m, CH_2CH_3); *m/z* 270 (M^+). The oxalate salt had m.p. 108-109°C from ethanol–ether (Found: C, 66.2; H, 8.0; N, 7.7. $C_{20}H_{28}N_2O_4$ requires, C, 66.64; H, 7.83; N, 7.77%).

1-Benzyl-2-(2-methyl-2-phenylethenyl)-4,5-dihydroimidazole **3j**. Alkenyl dihydroimidazole **3j** was made from acetophenone (1.2 cm^3, 9.63 mmol) using the same method as for compound **3c** to give, before chromatography, the crude reaction product. The ^1H NMR spectrum indicated some unreacted acetophenone, and a geometric isomer mixture of the alkenyl dihydroimidazole, 8:1 *E*:*Z*; δ_H ($CDCl_3$) 6.3 (0.89H, s, CH=C, *E*-isomer), 6.05 (0.11H, s, CH=C, *Z*-isomer), 2.45 (2.67H, d, CH_3, *E*-isomer), 2.2 (0.33H, d, CH_3, *Z*-isomer). Repeated column chromatography over alumina gave poor separation of starting material from products. The mixture in 2M hydrochloric acid was washed with ether, the aqueous layer basified with solid sodium hydrogencarbonate and extracted with ether to give alkenyl dihydroimidazole **3j** (1.5 g, 62%) as pure *E*-isomer (Found: M^+ 276.1673. $C_{19}H_{20}N_2$ requires M, 276.1626); ν_{max} (film) 3040, 2940, 2860, 1645, 1600, 1500, 1460, 1415, 1365, 1320, 1280, 1220, 1010, 750, 695 cm^{-1}; δ_H ($CDCl_3$) 7.2-7.6 (10H, m, Ph), 6.3 (1H, s, CH=C), 4.3 (2H, s, PhCH_2), 3.6-4.0, 3.1-3.4 (each 2H, m, NCH_2CH_2N), 2.45 (3H, s, Me); *m/z* 276 (M^+).

1-Benzyl-2-(1-propenyl)-4,5-dihydroimidazole **3a**. Alkenyl dihydroimidazole **3a** was prepared by the same method as for compound **3c** from dihydroimidazole **4** (1.0 g, 5.8 mmol), lithium diisopropylamide [12.8 mmol, from butyl-lithium (8.1 cm^3 of a 1.58M solution in hexanes) and diisopropylamine (1.3 g)], diethyl chlorophosphate (1.1 g, 6.4 mmol) and ethanal (1.5 cm^3, 27 mmol) to give alkenyl dihydroimidazole **3a** (1.02 g, 88%); δ_H (250 MHz; $CDCl_3$) 7.2-7.4 (5H, m, Ph), 6.7-6.8 (1H, dq, *J* 7, 15.5 Hz, CH=C*H*CH_3), 6.02 (1H, d, *J* 15.5 Hz, C*H*=$CHCH_3$), 4.34 (2H, s, PhCH_2), 3.74, 3.26 (each 2H, t, *J* 10 Hz, NCH_2CH_2N), 1.86 (3H, d, *J* 7 Hz, CH_3); *m/z* 200 (M^+, 50%), 185 (27), 155 (31), 127 (24), 99 (38), 91 (100). This material was not further purified but used directly for attempts at cycloaddition reactions as a 2-azadiene (*vide supra*).

1-Benzyl-2-(1-butenyl)-4,5-dihydroimidazole **3b**. Alkenyl dihydroimidazole **3b** was made by the same method as for compound **3c** from dihydroimidazole **4** (1.63 g, 9.4 mmol), lithium diisopropylamide [19.64 mmol, from butyl-lithium (14.55 cm^3 of a 1.35M solution in hexanes) and diisopropylamine (1.99 g)], diethyl

chlorophosphate (1.77 g, 10.3 mmol) and propanal (0.6 g, 10.35 mmol) to give alkenyl dihydroimidazole **3b** (1.88 g, 96%) (Found: M^+ 214.1448. $C_{14}H_{18}N_2$ requires M 214.1460); ν_{max} (film) 3050, 2950, 2850, 1660, 1610 (br), 1500, 1460, 750, 710 cm^{-1}; δ_H 7.2-7.5 (5H, m, Ph), 6.7-7.05 (1H, dt, J 7, 16 Hz, CH=C*H*CH_2), 6.05 (1H, d, J 16 Hz, C*H*=CHCH_2), 4.4 (2H, s, PhCH_2), 3.1-4.0 (4H, 2 x t, NCH_2CH_2N), 2.0-2.5 (2H, m, CH=CHCH_2), 1.05 (3H, t, J 7 Hz, CH_3); *m/z* 214 (M^+).

1-Benzyl-2-(1-butenyl)-2-imidazoline **3b** was also prepared by the same method as above but using diisopropyl chlorophosphate, from dihydroimidazole **4** (0.81 g, 4.65 mmol), lithium diisopropylamide [9.3 mmol, from butyl-lithium (7.2 cm^3 of a 1.29M solution in hexanes) and diisopropyl-amine (0.945 g)], diisopropyl chlorophosphate (0.845 g, 4.2 mmol) and propanal (0.48 g, 8.27 mmol) to give alkenyl dihydroimidazole **3b** (0.98 g, 98%) as a colourless oil, identical to material prepared from diethyl chlorophosphate.

1-Benzyl-2-diethylphosphonomethyl-4,5-dihydroimidazole **10**. 1-Benzyl-2-methyl-4,5-dihydroimidazole **4** (2.8 g, 16.1 mmol) in dry THF (10 cm^3) was added dropwise to lithium diisopropylamide [28.96 mmol, from butyl-lithium (22.45 cm^3 of a 1.29M solution in hexanes) and diisopropylamine (2.93 g)] in THF (50 cm^3) and stirred at –78°C under nitrogen for 1 h. Diethyl chlorophosphate (2.5 g, 14.49 mmol) was added dropwise, maintaining the temperature at –78°C, and the solution was stirred for a further 3 h, when the cold reaction mixture was quenched with water (150 cm^3), allowed to warm to 25°C and extracted with ether (3 x 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give crude phosphonate **10** (4.43 g, 89%) as a colourless oil; ν_{max} (film) 3350, 3000, 1640, 1600, 1500, 1460 cm^{-1}; δ_H ($CDCl_3$) 7.3 (5H, br s, Ph), 4.35 (2H, s, PhCH_2), 2.6-4.3 (10H, complex m, NCH_2CH_2N, CH_2, 2 x CH_2O), 1.2 (6H, m, 2 x CH_3CH_2O). Attempted purification (chromatography, distillation) was unsuccessful.

1-Benzyl-2-(2-ethylhexyl)-4,5-dihydroimidazole **11a**. To 1-benzyl-2-(1-butenyl)-4,5-dihydroimidazole **3b** (0.10g, 0.47 mmol) stirred in dry THF (2 cm^3) at –50°C under nitrogen was added butyl-lithium (0.7 cm^3 of a 1.4M solution in hexanes, 0.98 mmol) dropwise over a period of 15 min. After a further 1 h at this temperature the reaction was quenched with water and the mixture allowed to warm to 20°C. The reaction mixture was partitioned between water and chloroform, and the aqueous layer extracted with chloroform. The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. to leave a residue that was purified by column chromatography over silica gel (Merck Kieselgel 60 Art. 7729) under medium pressure, eluting with isopropylamine–chloroform (1:99 v/v), to give the dihydroimidazole **11a** (0.78 g, 61%) as an oil (Found: M^+ 272.2248. $C_{18}H_{28}N_2$ requires M 272.2252); ν_{max} (film) 3930, 2940, 1620, 1500, 1460, 1420, 1360, 1000, 940, 750, 730, 690 cm^{-1}; δ_H ($CDCl_3$) 7.25-7.5 (5H, br s, Ph), 4.3 (2H, s, PhCH_2), 3.05-3.8 (4H, 2 x t, NCH_2CH_2N), 2.25 (2H, d, CH_2C=N), 1.05-2.0 (9H, m, 4 x CH_2, CH), 0.75-1.05 (6H, t, 2 x CH_3); *m/z* 272 (M^+).

1-Benzyl-2-(2-propylhexyl)-4,5-dihydromidazole **11b**. Dihydroimidazole **11b** was prepared from 1-benzyl-2-(1-pentenyl)-4,5-dihydroimidazole **3c** (0.10 g, 0.43 mmol) using the same method as for dihydroimidazole **11a**. Column chromatography on silica, eluting with isopropylamine–chloroform (0.5:99.5 v/v), gave the dihydroimidazole **11b** (0.64 g, 51%) as an oil (Found: M^+ 286.2405. $C_{19}H_{30}N_2$ requires M 286.2409); ν_{max} (film) 3100, 2900, 2820, 1620, 1500, 1460, 1420, 1370, 1180, 1000, 935, 730, 690 cm^{-1}; δ_H ($CDCl_3$) 7.2-7.5 (5H, br s, Ph), 4.3 (2H, s, PhCH_2), 3.05-3.8 (4H, 2 x t, NCH_2CH_2N), 2.24 (2H, d, CH_2C=N), 1.1-2.1 (11H, m, 5 x CH_2, CH), 0.9 (6H, m, 2 x CH_3); *m/z* 286 (M^+).

1-Benzyl-2-(2-phenylhexyl)-4,5-dihydroimidazole **11c**. Dihydroimidazole **11c** was prepared from 1-benzyl-2-(2-phenylethenyl)-4,5-dihydroimidazole **3f** (0.25 g, 0.93 mmol) in dry THF (3.5 cm^3) and butyl-lithium (1.4 cm^3 of a 1.5M solution in hexanes, 2.1 mmol) using the same method as for dihydroimidazole **11a**. Column chromatography on silica, eluting with isopropylamine–chloroform (0.5:99.5 v/v), gave the dihydroimidazole **11c** (0.153 g, 57%) as an oil (Found: M^+ 320.2248. $C_{22}H_{28}N_2$ requires M 320.2252); ν_{max} (film) 3030, 2930, 2860, 1605, 1490, 1450, 760, 705 cm^{-1}; δ_H ($CDCl_3$) 7.1-7.5 (10H, m, 2 x Ph), 4.15 (2H, s, PhCH_2), 3.5-3.8 (2H, t, NC$H_2$$CH_2$N), 2.95-3.25 (3H, m, NCH_2CH_2N, PhCH), 2.55 (2H, 2 x d, CH_2C=N), 1.5-2.0 (2H, m, CH_2CH_2CH), 0.9-1.5 (4H, m, $CH_2CH_2CH_3$), 1.3 (3H, t, CH_3); *m/z* 320 (M^+).

1-Benzyl-2-(2,2-diphenylethyl)-4,5-dihydroimidazole **11d**. Dihydroimidazole **11d** was prepared from 1-benzyl-2-(2-phenylethenyl)-4,5-dihydroimidazole **3f** (0.23 g, 0.88 mmol) and phenyl-lithium (1.3 cm^3 of a 1.5M solution in cyclohexane, 1.95 mmol) using the same method as for dihydroimidazole **11a**. Column chromatography on silica, eluting with isopropylamine–chloroform (0.5:99.5 v/v), gave the dihydroimidazole **11d** (2.57 g, 86%) as an oil (Found: M^+ 340.1949. $C_{24}H_{24}N_2$ requires M 340.1939); ν_{max} (film) 3040, 3020, 2910, 2840, 1600, 1490, 1450, 740, 680 cm^{-1}; δ_H ($CDCl_3$) 7.1-7.5 (10H, m, Ph), 4.7 (1H, t, CH), 4.15 (2H, s, PhCH_2), 3.5-3.8 (2H, t, NC$H_2$$CH_2$N), 2.95-3.3 (4H, m, NCH_2CH_2N, CH_2C=N); *m/z* 340 (M^+).

1-Benzyl-6-ethoxycarbonyl-8a-hydroxy-7-phenyl-1,2,3,5,6,7,8,8a-octahydroimidazo[1,2-a]pyridin-5-one **14**. To diethyl malonate (0.38 g, 2.36 mmol) and sodium ethoxide (0.052 g, 0.77 mmol) in dry ethanol (3 cm^3) was added dropwise 1-benzyl-2-(2-phenylethenyl)-4,5-dihydroimidazole **3f** (0.25 g, 1.10 mmol) in dry ethanol (2 cm^3) and the solution heated at reflux for 2 h. On cooling, the solution was poured into 2M hydrochloric acid, washed with ether, the ether layer discarded and the aqueous layer basified with sodium hydroxide pellets and extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give an oil (0.314 g) that was purified by column chromatography over silica gel (Merck Kieselgel 60 Art. 7729) under medium pressure, eluting with triethyl-amine-chloroform (0.5:99.5 v/v), to afford the cyclol **14** (0.1745 g, 52%) as an oil; ν_{max} (film) 3350, 1740, 1680 cm^{-1}; δ_H ($CDCl_3$) 7.15-7.55 (10H, m, Ph), 3.95-4.25 (4H, m, OCH_2, CH_2NC=O), 3.65-3.95 (4H, m, PhCH_2, 2 x CH), 2.8-3.05 (4H, m, $PhCH_2NCH_2$, PhCHCH_2), 1.6 (1H, br s, OH), 1.1 (3H, t, CH_3); *m/z* 377 (M+H–H_2O, 7%), 376 (M–H_2O, 28), 304 (20), 303 (87), 91 (100).

1-Benzyl-2-{2-[2-(2-propenyl)oxyphenyl]ethenyl}-4,5-dihydroimidazole **15**. Alkenyl dihydroimidazole **15** was prepared by the same method as for compound **3c** from dihydroimidazole **4** (1.0 g, 5.8 mmol), lithium diisopropylamide [12.8 mmol, from butyl-lithium (8.1 cm^3 of a 1.58M solution in hexanes) and diisopropyl-amine (1.3 g)], diethyl chlorophosphate (1.1 g, 6.4 mmol) and 2-(2-propenyl)oxybenzaldehyde[27] (0.94 g, 5.8 mmol) to give alkenyl dihydroimidazole **15** (1.77 g, 96%) as a pale yellow oil (Found: M 318.1729. $C_{21}H_{22}N_2O$ requires M 318.1732); ν_{max} ($CDCl_3$) 3067, 3032, 2935, 1640, 1602, 1491, 1454 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.86 (1H, d, J 16 Hz, CH=CHAr), 7.2-7.4 (7H, m, Ar-H), 6.85-6.98 (3H, m, Ar-H, CHC=N), 5.90-6.05 (1H, m, CH_2=CH), 5.15-5.40 (2H, m, CH_2=CH), 4.58 (2H, dt, J 1.3, 4.6 Hz, OCH_2), 4.43 (2H, s, PhCH_2), 3.87, 3.36 (each 2H, t, J 10 Hz, NCH_2CH_2N); δ_C (67.5 MHz; $CDCl_3$) 163.8, 156.6, 137.7 (all C), 134.0, 132.7, 129.6, 128.6, 128.3, 128.0, 127.0 (all CH), 124.7 (C), 120.5 (CH), 117.5 (vinyl-CH_2), 116.1 & 112.0 (CH), 68.8, 52.3, 51.0, 50.5 (all CH_2); *m/z* 318 (M^+, 13%), 317 (25), 276 (11), 261 (26), 199 (11), 158 (20), 91 (100). This material was not further purified but used directly for attempts at cycloaddition reactions as a 2-azadiene (*vide supra*).

ACKNOWLEDGEMENTS

We thank Drs. J. Saunders and C. B. Chapleo for helpful discussions, Dr. S. C. Hirst for the preparation of **5c**, SERC and ICI Pharmaceuticals (M.W.A.) and Reckitt and Colman Pharmaceuticals (M.J.S.) for CASE studentships and financial support, and EPSRC for a postdoctoral fellowship (J.S.S.).

REFERENCES AND FOOTNOTES

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(*Received in UK* 18 *October* 1996; *accepted* 7 *November* 1996)