A novel synthesis of imidazoles *via* the cycloaddition of nitrile ylides to their imidoyl chloride precursors

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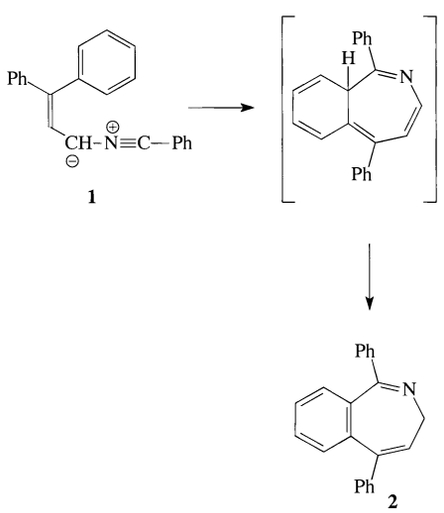
Received (in Cambridge, UK) 4th May 2001, Accepted 11th September 2001
First published as an Advance Article on the web 5th October 2001

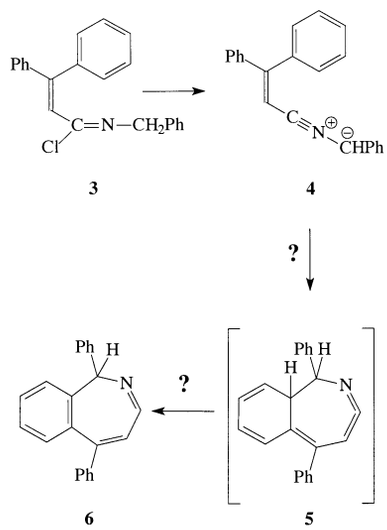
Generation of nitrile ylides, **4** and **22**, *via* the base-catalysed 1,3-dehydrochlorination of imidoyl chlorides, **3** and **21**, gives the imidazoles, **13**, **23** and **24**. These imidazoles are formed by the cycloaddition of the nitrile ylides, **4** and **22**, to their precursor imidoyl chlorides, **3** and **21**, and the observed regiochemistry of this cycloaddition has been rationalised by energy calculations on the frontier molecular orbitals of these reactants using semi-empirical (MOPAC PM3) methods.

The 1,7-electrocyclisation of α,β:γ,δ-unsaturated 1,3-dipoles is a useful route to seven-membered heterocycles.[1] Using this methodology, benzazepines **2** have been obtained as the sole products of the 1,7-electrocyclisation of diene-conjugated nitrile ylides **1**, followed by a [1,5]-H shift (Scheme 1).[2,3]



Scheme 1

The aim of this present work was to investigate the effect on the periselectivity of such nitrile ylide cyclisations of the inversion of the dipole moiety in such diene-conjugated nitrile ylides. The corresponding nitrile ylides **4** could, theoretically, also undergo a 1,7-electrocyclisation to a benzazepine **6** but only *via* a cumulene intermediate **5** (Scheme 2). We wish to report here that this inversion of the dipole group precludes the 1,7-electrocyclisation and the only products obtained from these nitrile ylide intermediates **4** are the formal products of a cycloaddition of the nitrile ylides to their imidoyl chloride precursors **3**.[4]



Scheme 2

Results and discussion

The nitrile ylides were prepared by the well established 1,3-dehydrochlorination of imidoyl chlorides,[5] which are themselves readily prepared from the corresponding amides. The synthesis of *N*-benzyl-3,3-diphenylpropenamide **10a** was achieved *via* ethyl 3-hydroxy-3,3-diphenylpropanoate **8**, which is readily available from the Reformatsky reaction of benzophenone **7** and ethyl bromoacetate[6] (Scheme 3). Condensation of the hydroxyester **8** with benzylamine gave the hydroxyamide **9**, which was dehydrated to the requisite amide **10a** using a mixture of acetic and concentrated sulfuric acids.

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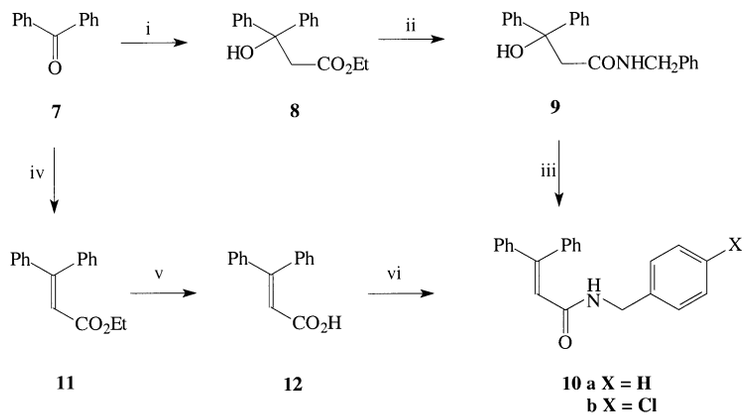
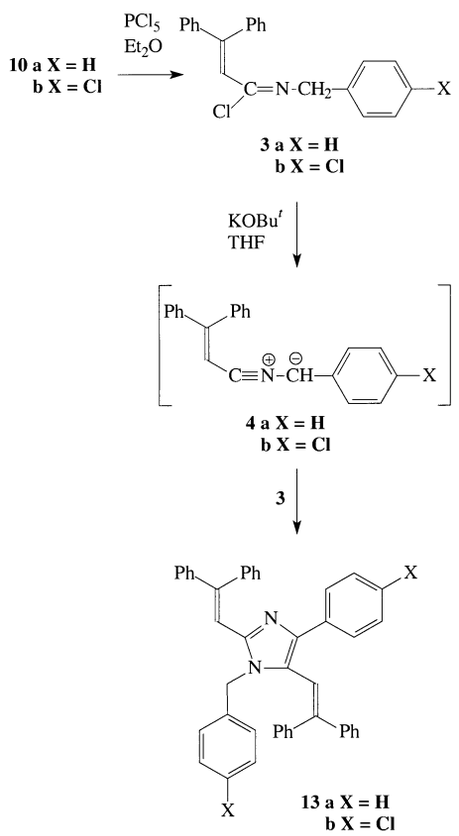
DOI: 10.1039/b104130b



Scheme 3 *Reagents and conditions*: i, $BrCH_2CO_2Et$, Zn, $PhCH_3$, Et_2O, reflux, 4 h, 90% or $[(CH_3)_2CH]_2NLi$, EtOAc, rt, 4 h, 95%; ii, $PhCH_2NH_2$, NH_4Cl, reflux, 16 h, 32% or $PhCH_2NH_2$, Et_2O, reflux, 16 h, 76%; iii, conc. H_2SO_4, AcOH, rt, 1 h, 77%; iv, $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, reflux, 12 h, 92%; v, KOH, EtOH, rt, 15 h, 94%; vi, 4-$ClC_6H_4CH_2NH_2$, Et_3N, DIPCDI, HOBt, rt, 20 h, 91%.

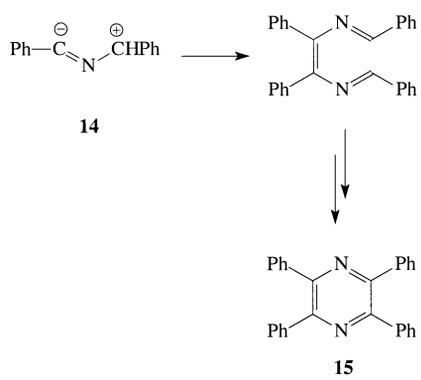
Attempts to prepare the *N*-(4-chlorobenzyl) analogue **10b** *via* this route proved unsuccessful and this derivative was eventually synthesized from 3,3-diphenylpropenoic acid **12** by standard amide bond formation using diisopropylcarbodiimide (DIPCDI) and 1-hydroxybenzotriazole. The acid **12** was prepared by hydrolysis of the corresponding ethyl ester **11**, which was readily obtained from the Wittig–Horner reaction of benzophenone **7** and ethyl diethoxyphosphorylacetate (Scheme 3).[7]

The chlorination of the amides **10a**,**b** with phosphorus pentachloride gave the imidoyl chlorides **3a**,**b**, which were treated with potassium *tert*-butoxide, at 0 °C in the dark, to give orange solids. Spectroscopic analysis of these solids indicated that they did not correspond to the products of a 1,7-electrocyclisation but appeared to be dimers of the nitrile ylides **4a**,**b** (Scheme 4).



Scheme 4

Dimerisation of nitrile ylides **14**, in the absence of dipolarophiles, is a well known reaction and results in the formation of pyrazines **15**,[8] *via* either a head-to-head or head-to-tail dimerisation (Scheme 5). The spectroscopic data for the products obtained from the reaction of these nitrile ylides **4a**,**b** did not correspond to that expected for a pyrazine and the products were eventually identified as imidazoles **13**. The structure of the imidazole **13a** was confirmed by NOE experiments; irradiation of the benzylic singlet at δ 4.58 resulted in enhancement of the alkene singlets at δ 6.52 (4.0%) and δ 6.57 (15.2%)—indicating the close proximity of the benzylic CH_2 to both alkene protons.

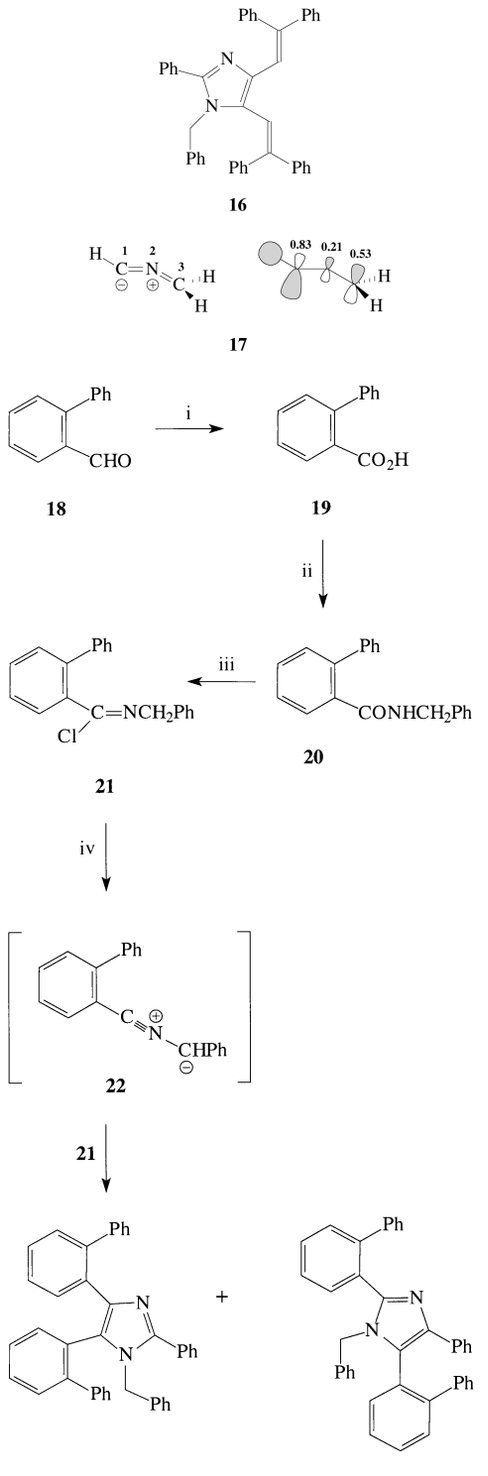


Scheme 5

An imidazole **16** could result from the cycloaddition of a nitrile ylide **4** to its precursor imidoyl chloride **3**, followed by dehydrochlorination, but the regioisomer obtained **13** is not that which is predicted by FMO theory. With all dipolarophiles, except the very electron rich, nitrile ylide cycloadditions are dipole HOMO controlled according to Sustmann's classification.[9] That is, the interaction of the dipole HOMO with the dipolarophile LUMO is the dominant frontier orbital interaction. Caramella and Houk[10] have optimised the geometry of the parent nitrile ylide, formonitrile methylide‡ **17**, by *ab initio* LCAO-MO-SCF calculations, and shown that this nitrile ylide prefers a 'bent' allenic geometry to a linear propargylic geometry by 46.4 kJ mol^{-1}. Caramella and Houk[10] also showed that the HOMO of this 'bent' nitrile ylide, is heavily localised on the methine (C-1) terminus and this is compatible with protonation at this carbon in simple substituted nitrile ylides and with the regioisomers obtained in bimolecular nitrile ylide cycloadditions.[11] The interaction of the 3-phenylcinnamonitrile arylmethyl ylide HOMO with the imidoyl chloride LUMO would thus be expected to produce the imidazole regioisomer **16**.

N-Benzyl-2-phenylbenzamide **20** was prepared from 2-phenylbenzoic acid **19**, itself easily prepared by the oxidation of

‡ The IUPAC name for formonitrile methylide is (methylideneazoniumdiyl)methanide.



Scheme 6 *Reagents and conditions*: i, $K_2Cr_2O_7$, H_2SO_4, rt, 4 days, 52%; ii, 2-chloro-1-methylpyridinium iodide, $PhCH_2NH_2$, Bu_3N, DCM, rt, 16 h, 77%; iii, PCl_5, Et_2O, reflux; iv, KOBu^t, THF, 0 °C.

2-phenylbenzaldehyde **18** (Scheme 6). 2-Phenylbenzaldehyde was prepared by the method of Cullen and Sharp.[12]

Generation of *N*-benzyl-2-phenylbenzonitrile ylide **22**, by chlorination of the corresponding amide **20**, followed by 1,3-dehydrochlorination of the imidoyl chloride **21**, gave a mixture of the products **23** and **24** (Scheme 6). In this case, the ratio of isomers obtained was approximately 1 : 1 (actually 51 : 39), with the structure of the major isomer confirmed—by a single crystal X-ray structure (Fig. 1)—as the 'expected' product **23** of the cycloaddition, whilst the minor product **24** was the regioisomer which is not that which is predicted by FMO theory. An interesting feature of the ^{1}H NMR spectra of both regioisomers **23**

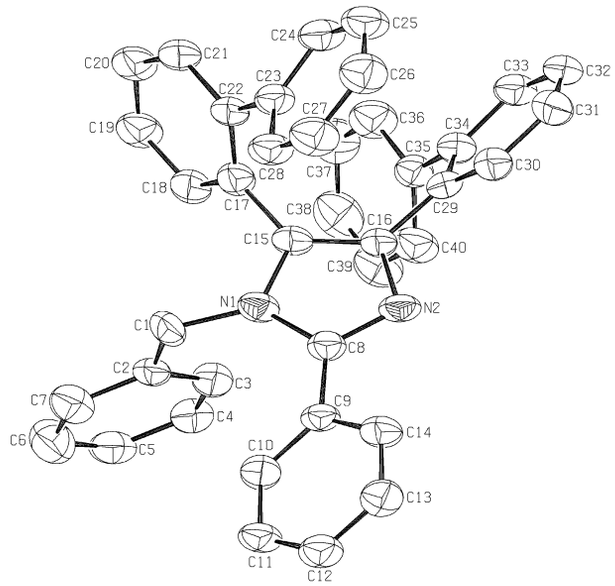
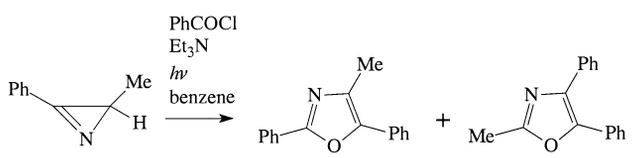


Fig. 1 Crystal structure of imidazole **23**.

and **24** is the non-equivalence of the methylene protons of the benzylic group, which, in both cases, appear as pairs of doublets, with a coupling constant of 16.5 Hz.

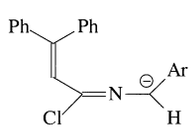
A number of other examples of nitrile ylides giving the 'wrong' regioisomer in [3 + 2] cycloadditions have been reported. For example, photolysis of azirine **25** in the presence of benzoyl chloride and triethylamine gave mostly oxazole **26** together with a small amount of the expected product **27** (Scheme 7).[13] It has been proposed that those processes that lead



25 **26** **27**

Scheme 7

to the formation of the 'wrong' regioisomer involve the trapping of a deprotonated imidoyl chloride, *e.g.* **28**, rather than a



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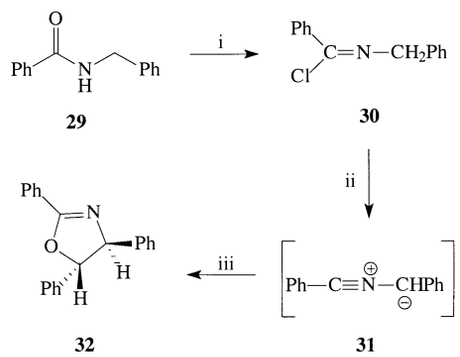
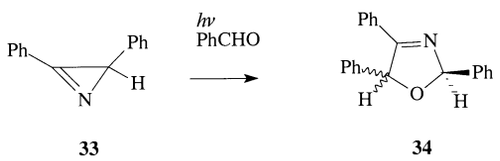
nitrile ylide cycloaddition reaction. To test this proposal for these systems, we have attempted to investigate the cycloaddition of a conjugated nitrile ylide with a hetero-dienophile. Our initial attempts at trapping the nitrile ylides, **4** or **22**, were unsuccessful, but a related nitrile ylide **31** (generated by the same 1,3-dehydrochlorination route from the amide **29** *via* the imidoyl chloride **30**) underwent a cycloaddition with benzaldehyde to give the oxazole **32** as the sole product (Scheme 8). Once again, this is the opposite regioisomer to that predicted by FMO theory. The opposite regioisomer **34** has previously been obtained by trapping the nitrile ylide, generated by photolysis of the azirine **33**, with benzaldehyde (Scheme 9).[14] In order to account for this discrepancy, we have performed energy calculations on the frontier molecular orbitals of the dipoles and dipolarophiles using semi-empirical (MOPAC PM3)[15] methods with Insight II (Release 2000)/MOPAC software

Table 1 Energies and frontier orbital coefficients for nitrile ylides **4**, **22**, and **31**

Dipole	**31**	**4**	**22**
HOMO/eV	−7.55	−7.49	−7.51
C1	−0.46	+0.38	+0.46
N2	+0.05	−0.03	−0.05
C3	+0.61	−0.50	−0.60
LUMO/eV	−0.45	−0.84	−0.50
C1	+0.22	−0.19	+0.19
N2	−0.40	+0.36	−0.37
C3	+0.24	−0.15	+0.23



Scheme 8 *Reagents and conditions*: i, PCl_5, Et_2O, reflux, 16 h; ii, KOBu^t, THF, rt, 16 h; iii, PhCHO, THF, 38%.



Scheme 9

(MSI/Biosymm, CA, U.S.A) on a Silicon Graphics Indigo II workstation.

These semi-empirical calculations predict a linear geometry for the simplest nitrile ylide, formonitrile methylide **17**, in contrast to previous work by Caramella and Houk.[10] It has previously been shown that the optimised geometry and the MO energies and coefficients of the nitrilium betaines are dependent upon the theoretical method used, with the 'bent' allenic structure being the only stable minimum at higher levels of theory.[16] The incorporation of substituents with extended conjugation at both termini of the nitrile ylide system would, however, be expected to result in the linearisation of the dipole through an increase in the delocalisation, and this is, in fact, substantiated by the MOPAC PM3 calculations. Optimisation of the geometry of all three dipoles, **4**, **22**, and **31**, results in linear nitrile ylides, and the calculated energies and coefficients of the orbitals on the methine (C1) and methylene (C3) carbon atoms for both the HOMO and LUMO are given in Table 1. The HOMO and LUMO energies and coefficients for the precursor imidoyl chlorides, **3** and **21**, and for benzaldehyde, are given in Table 2. As expected, the dipole HOMO–dipolarophile LUMO is the dominant interaction. Close inspection of the HOMO for each of these dipoles shows that, in each case, the coefficient on the methylene (C3) carbon is greater than that on the methine (C1). The methylene carbon atom would therefore be expected to react with the carbon atom of the double bond (C=O or C=N) of the dipolarophile, which has the larger coefficient in the LUMO. In the case of 2-phenylbenzonitrile benzyl ylide **22** the ratio of isomers obtained was approx. 1 : 1 and this may be due to steric factors due to the presence of the sterically demanding biphenyl group. These results are, therefore, in agreement with the experimental findings and the one anomaly

Table 2 Energies and frontier orbital coefficients for dipolarophiles PhCHO, **3** and **21**

Dipolarophile	PhCHO	**3**	**21**
HOMO/eV	−10.05	−9.19	−9.52
C	−0.01	−0.05	−0.03
X	−0.15	+0.06	+0.14
LUMO/eV	−0.48	−0.44	−0.11
C	−0.36	−0.14	−0.14
X	+0.33	+0.03	0.00

is the regioisomer **34** which was previously obtained by trapping the nitrile ylide, generated by photolysis of the azirine **33**, with benzaldehyde. In this case, the photochemical generation of the nitrile ylide may lead to an excited state and the observed regioisomer may be explained by the overlap of this new, excited state, HOMO with the benzaldehyde LUMO.

In conclusion, we have discovered a new cycloaddition of nitrile ylides, to their imidoyl chloride precursors to give imidazoles, the regiochemistry of which can be predicted by MOPAC PM3 calculations. These semi-empirical calculations predict a linear dipole, with the HOMO localised on the methylene carbon atom. Although calculations at higher levels predict 'bent' allenic geometries for simpler nitrilium betaines, these semi-empirical results are useful for the prediction of the regiochemistry of the cycloaddition of these more complex and highly conjugated dipoles.

Experimental

Mps were determined on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C or Carlo Erba 1106 Elemental Analyser. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR or Unicam research series FTIR spectrophotometer using sodium chloride plates. ^{1}H NMR spectra were acquired on a JEOL GSX 270 FT NMR at 270 MHz, Bruker WM360 spectrometer at 360 MHz, or Bruker AVANCE 300 at 300 MHz. Coupling constants are given in Hz and all chemical shifts are relative to an internal standard of tetramethylsilane. ^{13}C NMR spectra were obtained on the JEOL GFX 270 FT NMR (68 MHz) spectrometer, Bruker WM360 (90 MHz), and Bruker AVANCE 300 (75 MHz). Low resolution electron impact mass spectra were obtained on a Trio 2000 VG or Fisons Platform II. High resolution spectra were obtained on a VG ZAB-E spectrometer (EPSRC Mass Spectrometry Service Centre, Swansea) or Bruker APEX II FT mass spectrometer. Thin layer chromatography was performed on Merck silica gel $60F_{254}$. All solvents were purified according to standard procedures. Diethyl ether and tetrahydrofuran were freshly distilled over sodium wire with a trace of benzophenone. Toluene was distilled from, and stored over, sodium wire. Fisons silica gel 60 (35–70 micron) was used for wet flash chromatography. The samples were applied in liquid form or were pre-adsorbed onto silica 60 (35–70 micron) from dichloromethane solutions. 2-Phenylbenzaldehyde **18** was prepared by the method of Cullen and Sharp.[12] *N*-Benzylbenzamide **29** was prepared by the method of Erdik and Daskapan.[17] Ethyl 3,3-diphenylprop-2-enoate **11** was prepared by the method of Wang and Shi[7] and 3,3-diphenylprop-2-enoic acid **12** by the method of Collomb, Cantegrel, and Deshayas.[18]

Crystal data for 1-benzyl-4,5-bis(biphenyl-2-yl)-2-phenylimidazole 23

$C_{40}H_{30}N_2$, M = 538.66. Monoclinic, a = 10.257(2), b = 28.375(5), c = 10.590(2) Å, β = 112.21(3)°, V = 2853.5(9) Å^3, T = 150 K, colourless crystal (0.30 × 0.25 × 0.25 mm), space group $P2(1)/n$, Z = 4, μ = 0.073 mm^{-1}, 8026 reflections measured, 3913

independent reflections, $R_{int} = 0.0627$, wR_2 and $R_1 = 0.1374$ and 0.0626 ($I > 2\sigma(I)$) and 0.1863 and 0.1598 (all data). The structure was solved *via* direct methods (SHELXS-97)[19] and refined on F_o^2 by full-matrix least-squares (SHELXL-97).[20] Non-hydrogen atoms were refined as anisotropic; hydrogens were in idealised positions with U_{iso}s tied to the U_{eq}s of the parent atom. Full parameters of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Centre. CCDC reference number 163765. See http://www.rsc.org/suppdata/p1/b1/b104130b/ for crystallographic files in .cif or other electronic format.

Ethyl 3-hydroxy-3,3-diphenylpropanoate 8

Method 1. In a flame-dried 3-necked flask, ethyl bromoacetate (51.8 g, 34.4 cm^3, 0.31 mol) and benzophenone **7** (27 g, 0.15 mmol) in dry toluene (40 cm^3) and dry ether (110 cm^3) were added to activated powdered zinc (20 g) under N_2. A few crystals of iodine were added and the mixture heated, using a heat gun, to initiate the reaction. After mechanically stirring overnight, the mixture was allowed to warm in an ultra-sound bath, followed by refluxing for 4 h. On cooling to room temperature, the reaction mixture was poured into cold H_2SO_4 (100 cm^3, 10% w/v). The organic phase was separated and washed with cold H_2SO_4 (2 × 50 cm^3, 5% w/v). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give *ethyl 3-hydroxy-3,3-diphenylpropanoate* **8** as a pale orange solid, which was recrystallised from petroleum ether 60–80 °C (36.4 g, 90%), mp 77–81 °C (lit.[6] mp 87 °C) (Found: C, 75.3; H, 6.9. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%); ν_{max} (liquid film)/cm^{-1} 3508 (OH), 1698 (C=O); δ_H (360 MHz, $CDCl_3$) 1.20 (3H, t, *J* 6.9 Hz, CH_3), 3.30 (2H, s, CH_2), 4.12 (2H, q, *J* 6.9 Hz, CH_2), 4.80 (1H, s, OH), 7.1–7.4 (10H, m, Ar-H); δ_C (90MHz, $CDCl_3$) 13.9 (CH_3), 45.9 (CH_2), 60.9 (CH_2), 125.7 (4 × CH), 127.3 (4 × CH), 128.2 (2 × CH), 145.9 (2 × quat.), 172.7 (quat., C=O); *m*/*z* 270 (M$^+$, 68%), and 183 (100).

Method 2. *n*-Butyllithium (50 cm^3, 1.6 M solution in hexanes, 0.08 mol) was added dropwise to diisopropylamine (8.09 g, 11.2 cm^3, 0.08 mol) at −78 °C and the mixture was stirred at −78 °C for 30 minutes. Ethyl acetate (50 cm^3, 0.51 mol) was added and after a further 30 minutes at −78 °C, a solution of benzophenone **7** (14.0 g, 0.077 mol) in dry ethyl acetate (50 cm^3) was added dropwise. The mixture was allowed to warm to room temperature over 4 hours, then quenched with water (100 cm^3) and extracted with ethyl acetate (2 × 100 cm^3). The combined, dried organic phases were evaporated to give the ester **8** (19.8 g, 95%), which had identical analytical and spectroscopic data to that prepared previously.

N-Benzyl-3-hydroxy-3,3-diphenylpropanamide 9

Method 1. A mixture of ethyl 3-hydroxy-3,3-diphenylpropanoate **8** (10 g, 0.037 mol), benzylamine (14.7 g, 15 cm^3, 0.14 mol) and powdered ammonium chloride (1 g) was refluxed overnight, under N_2. After cooling, water (10 cm^3) and ether (30 cm^3) were added. The aqueous phase was separated and extracted with ether (2 × 50 cm^3). The combined organic layers were dried ($MgSO_4$), and the solvent evaporated under reduced pressure to give a pale brown oil. After refrigeration for 36 h, the precipitated solid was filtered to give *N-benzyl-3-hydroxy-3,3-diphenylpropanamide* **9** as off-white crystals. Recrystallisation from ethanol, followed by washing with cold petroleum 40–60 °C gave white crystals (3.95 g, 32%), mp 163–165 °C (Found: C, 79.4; H, 6.5; N, 4.1. $C_{22}H_{21}NO_2$ requires C, 79.8; H, 6.3; N, 4.2%); ν_{max} (liquid film)/cm^{-1} 3313 (NH), 1639 (C=O), 1599 (C=C); δ_H (360 MHz, $CDCl_3$) 3.10 (2H, s, CH_2), 4.3 (2H, s, CH_2), 6.1 (1H, s, OH), 6.3 (1H, s, NH), 6.81–6.89 (2H, m, Ar-H), 7.2–7.45 (13H, m, Ar-H); δ_C (90 MHz, $CDCl_3$) 43.0 (CH_2), 46.4 (CH_2), 125.9 (CH), 126.7 (CH), 127.1 (CH), 128.3 (CH), 128.6 (CH), 137.5 (quat.), 145.9 (2 × quat.), 171.9 (quat., C=O); *m*/*z* 331 (M$^+$, 17%), 314 (100), 254 (25), and 183 (25).

Method 2. The hydroxyester **8** (5 g, 0.0185 mol) was dissolved in dry ether (50 cm^3) and cooled to 5 °C. Benzylamine (2.0 g, 0.018 mol) was then added dropwise to the cold solution and the reaction mixture was allowed to warm to room temperature. The solution was then refluxed for 16 h, cooled, and quenched with ice–water (50 cm^3). The organic phase was washed with 2 M aq. hydrochloric acid (50 cm^3), 2 M aq. sodium hydroxide (50 cm^3), then water (50 cm^3) before drying ($MgSO_4$). Evaporation under reduced pressure, followed by chromatography on silica, eluting with petroleum ether 40–60 °C–ethyl acetate (100 : 0 to 80 : 20) gave the hydroxyamide **9** (4.43 g, 76%), mp 165 °C. The spectroscopic data were identical to those obtained for the previous sample.

N-Benzyl-3,3-diphenylprop-2-enamide 10a

N-Benzyl-3-hydroxy-3,3-diphenylpropanamide **9** (2 g, 6.04 mmol) was added to a cooled solution of concentrated sulfuric acid (4 cm^3) and glacial acetic acid (16 cm^3). The mixture was stirred for 1 h, under N_2. The reaction was quenched with water (100 cm^3), followed by the addition of ethyl acetate (100 cm^3). The organic phase was separated, washed with $NaHCO_3$ (20 cm^3, 10% w/v), water (3 × 100 cm^3), dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give *N-benzyl-3,3-diphenylprop-2-enamide* **10a** as a pale yellow solid. Recrystallisation from ethanol gave an off-white solid (1.46 g, 77%), mp 185–187 °C (Found: C, 84.3; H, 6.3; N, 4.3. $C_{22}H_{19}NO$ requires C, 84.3; H, 6.1; N, 4.4%); ν_{max} (liquid film)/cm^{-1} 3303 (NH), 1633 (C=O), 1602 (C=C); δ_H (360 MHz, $CDCl_3$) 4.3 (2H, s, CH_2), 5.5 (1H, s, NH), 6.4 (1H, s, C=CH), 6.94–6.96 (2H, m, Ar-H), 7.21–7.39 (13H, m, Ar-H); δ_C (90 MHz, $CDCl_3$) 43.6 (CH_2), 122.4 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.3 (CH), 137.6 (quat.), 138.4 (quat.), 140.6 (quat.), 149.6 (quat.) 166.5 (quat., C=O); *m*/*z* 313 (M$^+$, 100%), 207 (94), and 179 (98).

N-(*p*-Chlorobenzyl)-3,3-diphenylprop-2-enamide 10b

To an ice-cooled solution of 3,3-diphenylpropenoic acid (12.0 mmol), 4-chlorobenzylamine (1.70 g, 12.0 mmol), triethylamine (2.0 cm^3) and 1-hydroxybenzotriazole (2.0 g) in dichloromethane (70 cm^3) was added diisopropylcarbodiimide (1.90 cm^3, 12.0 mmol), dropwise. with stirring. After 0.5 hours, the ice bath was removed, and stirring was continued for 20 h at room temperature. The solution was washed with 2 M aq. HCl solution (20 cm^3), 2 M aq. NaOH solution (20 cm^3), water (20 cm^3) and brine (20 cm^3), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography on silica eluting with hexane–diethyl ether (1 : 1) to give *N-(p-chlorobenzyl)-3,3-diphenylprop-2-enamide* **10b** as a white solid. Recrystallisation from hexane–ether gave a white solid (3.81 g, 92%), mp 153–155 °C (Found: C, 75.9; H, 5.4; N, 4.0. $C_{22}H_{18}NOCl$ requires C, 76.0; H, 5.2; N, 4.0%); ν_{max} (liquid film)/cm^{-1} 3268 (NH), 1637 (C=O), and 1599 (C=C); δ_H (270 MHz, $CDCl_3$) 4.22 (2H, d, *J* 5.6 Hz, CH_2), 5.60 (1H, br s, NH), 6.41 (1H, s, C=CH), 6.85 (2H, d, *J* 8.6 Hz, Ar-H), 7.15–7.35 (12H, m, Ar-H); δ_C (68 MHz, $CDCl_3$) 42.7 (CH_2), 122.2 (CH), 127.9 (2 × CH), 128.4 (2 × CH), 128.45 (CH), 128.5 (2 × CH), 128.7 (2 × CH), 129.0 (3 × CH), 129.2 (2 × CH), 133.0 (quat.), 136.3 (quat.), 138.4 (quat.), 140.5 (quat.), 149.75 (quat.), 166.5 (quat.); *m*/*z* 349 (M$^+$, 16%), 347 (M$^+$, 48), 208 (38), 207 (100), and 178 (45).

Generation and reaction of 3,3-diphenylpropenylidyneammonio-(phenyl)methanide 4a

N-Benzyl-3,3-diphenylprop-2-enamide **10a** (0.5 g, 1.59 mmol)

was dissolved in dry ether (20 cm^3). Phosphorus pentachloride (0.5 g, 2.43 mmol) was added and the mixture refluxed overnight, with stirring, under N_2. After cooling, the solvent was removed under reduced pressure, followed by removal of the phosphorus oxychloride under high vacuum for 4 h. The resulting orange gum was dissolved in dry THF (20 cm^3) and the reaction mixture protected from the light and cooled to 0–5 °C in ice–water. Potassium *tert*-butoxide (0.9 g, 8.02 mmol) was then added in one portion and the solution was allowed to warm to room temperature, with stirring, overnight. The mixture was poured into aq. NH_4Cl solution (20 cm^3, 10% w/v) and extracted with ethyl acetate (3 × 10 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give a yellow oil (0.59 g, 63%), which was purified by column chromatography on silica, eluting with petroleum ether 40–60 °C–ethyl acetate (100 : 0 to 70 : 30), to give *1-benzyl-2,5-bis(2′,2′-diphenylethenyl)-4-phenylimidazole* **13a** as a yellow solid (0.42 g, 89%), mp 162–164 °C (Found: C, 89.3; H, 5.8; N, 4.5. $C_{44}H_{34}N_2$ requires C, 89.5; H, 5.8; N, 4.7%); δ_H (360 MHz, $CDCl_3$) 4.57 (2H, s, CH_2), 6.50 (1H, s, C=CH), 6.56 (1H, s, C=CH), 6.88–7.52 (30H, m, Ar-H); δ_C (90 MHz, $CDCl_3$) 47.3 (CH_2), 115.1 (CH), 116.6 (CH), 126.3 (CH), 126.4 (CH), 127.4 (CH), 127.6 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.9 (CH), 129.9 (CH), 130.1 (CH), 130.3 (CH), 135.9 (CH), 126.4 (quat.), 135.1 (quat.), 137.3 (quat.), 139.4 (quat.), 139.6 (quat.), 139.8 (quat.), 142.3 (quat.), 142.4 (quat.), 144.8 (quat.), 147.5 (quat.), 148.1 (quat.); *m/z* 590 (M^+, 100%), 499 (23), and 422 (6).

Generation and reaction of 3,3-diphenylpropenylidyneammonio-(*p*-chlorobenzyl)methanide 4b

N-(*p*-Chlorobenzyl)-3,3-diphenylprop-2-enamide **10b** (0.52 g, 1.5 mmol) was dissolved in dry ether (20 cm^3), phosphorus pentachloride (0.63 g, 3.0 mmol) was added and the mixture refluxed overnight, with stirring, under nitrogen. After cooling, the solvent was removed under reduced pressure, followed by high vacuum for 4 h. The resulting gum was dissolved in dry THF (20 cm^3), protected from light, cooled to 0–5 °C in an ice–water bath, and potassium *tert*-butoxide (1.12 g, 10 mmol) was added in one portion. The solution was allowed to warm to room temperature, with stirring, overnight. The mixture was poured into sat. aq. ammonium chloride solution (20 cm^3) and extracted with ether (2 × 20 cm^3). The combined organic layers were dried over magnesium sulfate and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica eluting with hexane–ether (70 : 30) to give a white solid, which was recrystallised from hexane–ether to give *1-(4-chlorobenzyl)-2,5-bis(2,2-diphenylethenyl)-4-(4′-chlorophenyl)imidazole* **13b** as white needles (0.72 g, 73%), mp 183–185 °C (Found: C, 79.7; H, 4.4; N, 3.8. $C_{44}H_{32}N_2Cl_2$ requires C, 80.1; H, 4.9; N, 4.2%) (Found: MH^+, 659.202. Calc. for $C_{44}H_{33}{}^{35}Cl_2N_2$: *MH*, 659.2015); ν_{max} (liquid film)/cm^{-1} 1600 (C=C); δ_H (270 MHz, $CDCl_3$) 4.59 (2H, s, CH_2), 6.46 (1H, s, C=CH), 6.52 (1H, s, C=CH), 6.80 (2H, m, Ar-H), 6.89 (2H, d, Ar-H), 7.10–7.42 (24H, m, Ar-H); δ_C (68 MHz, $CDCl_3$) 46.6 (CH_2), 114.5 (CH), 115.6 (CH), 125.6 (CH), 127.55 (2 × CH), 127.61 (2 × CH), 127.8 (2 × CH), 128.05 (3 × CH), 128.1 (4 × CH), 128.2 (2 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 128.4 (CH), 128.9 (2 × CH), 129.7 (2 × CH), 130.1 (CH), 132.0 (quat.), 133.25 (quat.), 133.35 (quat.), 135.55 (quat.), 138.6 (quat.), 139.1 (quat.), 139.2 (quat.), 141.95 (quat.), 142.2 (quat.), 144.8 (quat.), 148.2 (quat.), and 148.51 (quat.).

2-Phenylbenzoic acid 19

2-Phenylbenzaldehyde (3.6 g, 19.8 mmol) was suspended in a solution of acidified sodium dichromate [prepared from sodium dichromate (0.43 g, 35 mmol) dissolved in water (60 cm^3) and conc. sulfuric acid (8 cm^3)] and the reaction mixture was stirred at room temperature for 4 days. The reaction mixture was then basified by the careful addition of 30% aq. sodium hydroxide solution and extracted with ether (50 cm^3). The aqueous phase was acidified to pH 1 by the addition of conc. sulfuric acid and extracted with dichloromethane (2 × 50 cm^3). The combined dichloromethane extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give *2-phenylbenzoic acid* **19** as a white solid (2.04 g, 52%), mp 112–114 °C (lit.[21] mp 112–114 °C) (Found: MH^+, 199.0755. Calc. for $C_{13}H_{11}O_2$: *MH*, 199.075); ν_{max} (KBr)/cm^{-1} 3015 (OH), 1685 (C=O); δ_H (270 MHz, $CDCl_3$) 7.28–7.38 (7H, m), 7.48–7.54 (1H, m), 7.90–7.94 (1H, m), 11.92 (1H, br s, OH); δ_C (75 MHz, $CDCl_3$) 127.1 (CH), 127.3 (CH), 128.0 (2 × CH), 128.4 (2 × CH), 129.3 (quat.), 130.7 (CH), 131.2 (CH), 132.1 (CH), 141.0 (quat.), 143.4 (quat.), 174.05 (quat.).

N-Benzyl-2-phenylbenzamide 20

2-Phenylbenzoic acid (0.606 g, 3.03 mmol), 2-chloro-1-methylpyridinium iodide (0.852 g, 3.33 mmol), tributylamine (2.89 cm^3, 2.25 g, 12.12 mmol) and benzylamine (0.328 g, 3.06 mmol) were dissolved in dichloromethane (12 cm^3). After stirring for 16 hours, the reaction mixture was washed with water (10 cm^3), 1 M aq. hydrochloric acid (10 cm^3), then water (10 cm^3), and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure, followed by column chromatography on silica, eluting with petroleum ether 40–60 °C–ethyl acetate (80 : 20) gave *N-benzyl-2-phenylbenzamide* **20** as a white solid (0.665 g, 77%), mp 97–99 °C (Found: C, 83.7; H, 6.0; N, 4.9. $C_{20}H_{17}NO$ requires C, 83.6; H, 5.9; N, 4.9%) (Found: MH^+, 288.138. Calc. for $C_{20}H_{18}NO$: *MH*, 288.138); ν_{max} (KBr)/cm^{-1} 3251 (NH), 1654 (C=O); δ_H (270 MHz, $CDCl_3$) 4.27 (2H, d, *J* 5.2 Hz, CH_2Ph), 5.71 (1H, br s, NH), 6.82–6.85 (2H, m), 7.12–7.17 (3H, m), 7.30–7.45 (8H, m), 7.63 (1H, d, *J* 6.6 Hz); δ_C (75 MHz, $CDCl_3$) 43.9 (CH_2), 127.1 (CH), 127.4 (CH), 127.5 (CH), 127.55 (2 × CH), 128.3 (2 × CH), 128.5 (2 × CH), 128.6 (3 × CH), 129.9 (CH), 130.05 (CH), 135.5 (quat.), 137.35 (quat.), 139.35 (quat.), 140.0 (quat.), 169.3 (quat.).

Generation and reaction of biphenyl-2-ylmethylidyneammonio-(phenyl)methanide 22

To a solution of *N*-benzyl-2-phenylbenzamide **20** (0.341 g, 1.19 mmol) in dry ether (10 cm^3) was added phosphorus pentachloride (0.372 g, 1.8 mmol) and the reaction mixture was refluxed for 16 hours. After cooling, the solvent was removed under high-vacuum. The yellow oily residue was dissolved in dry tetrahydrofuran (10 cm^3), cooled to 0 °C and protected from light. Potassium *tert*-butoxide (0.667 g, 5.95 mmol) was added in one portion and the reaction was allowed to warm to room temperature overnight. The resulting red solution was poured into saturated aq. ammonium chloride (20 cm^3) and extracted with ethyl acetate (3 × 25 cm^3). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to give an orange oil which was purified, by column chromatography on silica eluting with petroleum ether 40–60 °C–ethyl acetate (100 : 0 to 90 : 10) to give two fractions. The lower fraction was identified as *1-benzyl-4,5-bis(biphenyl-2-yl)-2-phenylimidazole* **23** (0.163 g, 51%) mp 174–176 °C (Found: C, 89.4; H, 5.6; N, 5.1. $C_{40}H_{30}N_2$ requires C, 89.2; H, 5.6; N, 5.2%) (Found: M^+, 538.239. Calc. for $C_{40}H_{30}N_2$: *M*, 538.241); ν_{max} (KBr)/cm^{-1} 1600 (C=C/C=N); δ_H (270 MHz, $CDCl_3$) 4.63 (1H, d, *J* 16.5, C*H*^{a}H), 4.87 (1H, d, *J* 16.5, CH^{b}H), 6.11 (1H, d, *J* 7.9), 6.55 (4H, m), 6.73–7.36 (23H, m); δ_C (75 MHz, $CDCl_3$) 48.3 (CH_2), 126.3 (CH), 126.6 (2 × CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 127.5 (CH), 127.6 (CH), 127.9 (quat.), 128.0 (CH), 128.2 (2 × CH), 128.6 (CH), 128.7 (3 × CH), 128.75 (3 × CH), 128.8 (CH), 128.9 (2 × CH), 129.3 (2 × CH), 129.9 (CH), 129.95 (CH), 130.2 (CH), 131.1 (quat.), 131.65 (CH), 132.1 (CH), 133.4 (quat.), 137.5 (quat.), 139.5 (quat.), 140.8 (quat.), 141.3 (quat.), 142.3 (quat.), 142.35 (quat.), 147.8 (quat.).

The higher running fraction was identified as *1-benzyl-2,5-bis(biphenyl-2-yl)-4-phenylimidazole* **24**, which was obtained as a yellow oil (0.125 g, 39%) (Found: M^+, 538.241. Calc. for $C_{40}H_{30}N_2$: *M*, 538.241); ν_{max} (KBr)/cm^{-1} 1603 (C=C/C=N); δ_H (270 MHz, $CDCl_3$) 4.30 (1H, d, *J* 16.5 Hz, C*H*^{a}H), 4.65 (1H, d, *J* 16.5 Hz, C*H*^{b}H), 6.50 (2H, m), 6.95–7.60 (26H, m).

Generation and trapping of benzylidyneammonio(phenyl)-methanide 31

N-Benzylbenzamide **29** (0.50 g, 2.37 mmol) was dissolved in dry THF (25 cm^3) and phosphorus pentachloride (0.49 g, 2.37 mmol) was added. The mixture was refluxed overnight under N_2 and, after cooling, the solvent was removed under reduced pressure at high vacuum. The residual orange gum was dissolved in dry THF (20 cm^3) and benzaldehyde (0.50 g, 4.72 mmol) was added. The reaction mixture was cooled to 0 °C and potassium *tert*-butoxide (0.53 g, 4.74 mmol) was added in one portion. The solution was stirred and allowed to warm to room temperature overnight. The reation mixture was quenched with saturated aqueous ammonium chloride solution (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic layers were dried and evaporated under reduced pressure to give a brown oil, which was purified by flash chromatography on silica, eluting with petroleum ether 40–60 °C–diethyl ether (90 : 10) to give *2,4,5-triphenyl-4,5-dihydrooxazole* **32** as white crystals, mp 93–95 °C (0.27 g, 38%) (lit.[22] mp 86–87.5 °C) (Found: C, 84.4; H, 5.8; N, 4.7. $C_{21}H_{17}NO$ requires C, 84.3; H, 5.7; N, 4.7%) (Found: MH^+, 300.138. Calc. for $C_{21}H_{17}NO$: *MH*, 300.138); ν_{max} (liquid film)/cm^{-1} 1648 (C=N), 1601 (C=C), 1580 (C=C); δ_H (270 MHz, $CDCl_3$) 5.22 (1H, d, *J* 7.2), 5.41 (1H, d, *J* 7.2), 7.23–7.50 (13H, m), 8.15 (2H, d, *J* 6.8); δ_C (68 MHz, $CDCl_3$) 79.4 (CH), 89.4 (CH), 126.1 (3 × CH), 127.15 (2 × CH), 128.15 (CH), 128.0 (2 × CH), 128.7 (2 × CH), 128.8 (2 × CH), 129.2 (2 × CH), 132.8 (CH), 140.9 (quat.), 142.4 (2 × quat.), 164.4 (quat.).

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