The preparation of some 1,7b-disubstituted cyclopropa[*c*]isoquinolines *via* nitrile ylide cyclisations and their rearrangement to 2-benzazepines and 4-alkenyl-1,4-dihydroisoquinolines

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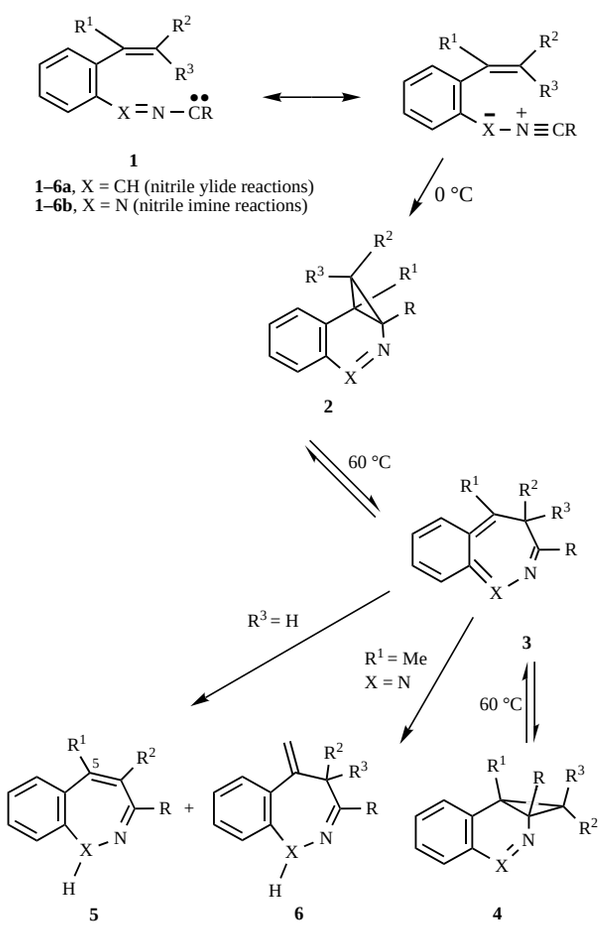
Diene-conjugated nitrile ylides of the type 1a, having substituents other than hydrogen in the R^1 position, cyclise normally to give the C-7b substituted cyclopropa[*c*]isoquinolines 2a. In cases where R^2 or R^3 = H the latter undergo the usual thermal rearrangement to give 5-substituted 2-benzazepines 5a. However, when R^2 and $R^3 \neq$ H and either is a CH_3 group, then the presence of the C-7b substituent in 2a diverts the thermal rearrangement into a new reaction path leading to the formation of 1,4-dihydro-4-alkenylisoquinolines 14 in high yield.

Introduction

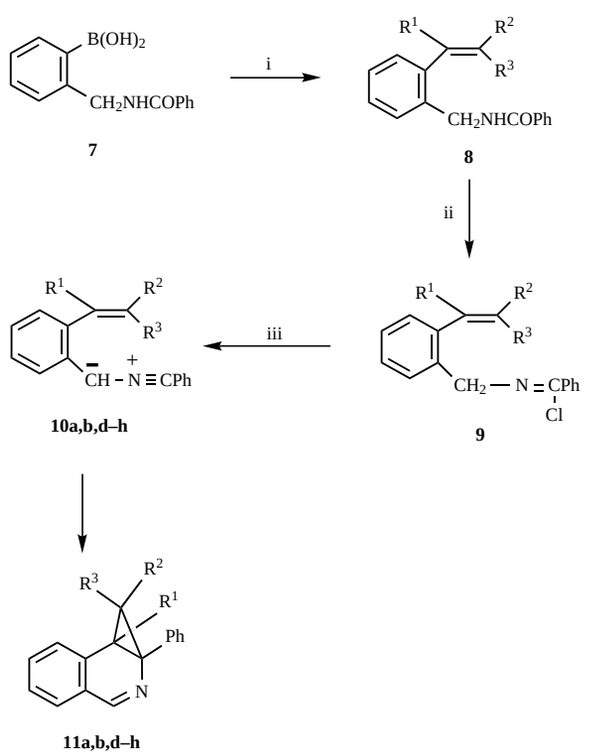
It has been shown in earlier work [1] that nitrile ylides of the type **1a** (Scheme 1, X = CH), when generated at room temperature



Scheme 1

or below, react to give cyclopropa[*c*]isoquinolines **2a**. The reaction is formally a 1,1-cycloaddition and is stereospecific in that R^2 and R^3 are in the *exo* and *endo* positions, respectively, in the primary products. The latter, on heating, undergo an equilibration with their isomers **4a** *via* ring expansion to **3a**. In cases where either R^2 or R^3 is a hydrogen atom this equilibration between **2a** and **4a** is accompanied by a slower [1,5] sigmatropic hydrogen shift which leads irreversibly to the 2-benzazepine **5a** in high yield. The reaction thus provides a useful synthetic route to the latter. Work in other groups [2,3] has shown that the analogous nitrile imines **1b** (Scheme 1, X = N) undergo an almost exactly parallel series of reactions giving the cyclopropa[*c*]cinnolines **2b** as the primary products and, similarly, providing a good route to the 1,2-benzodiazepines **5b**. However, an additional product **6b** was also isolated [2] in two cases where R^1 was a methyl group, possibly formed by a prototropic rearrangement in the intermediate **3b** or in the final product **5b**. In the earlier work [1] on the nitrile ylides **1a**, no reactants with a methyl group in the R^1 position had been studied and thus formation of products such as **6a** was not possible.

This paper reports the generation and reactions of the range of nitrile ylides **10a**,**b**,**d**–**h**, (Scheme 2) all of which have R^1 =Me



Scheme 2 *Reagents*: i, $R^2R^3C{=}C(R^1)Br$, Pd(0); ii, PCl_5 or $SOCl_2$–$HCONMe_2$; iii, KOBu^t or $LiN(SiMe_3)_2$ at 0 °C

Table 1 Identification of substituents

Compounds	Substituents
8–16	
a	R^1 = Me; R^2 = H; R^3 = H
b	R^1 = Me; R^2 = H; R^3 = Ph
c	R^1 = Me; R^2 = Ph; R^3 = H
d	R^1 = Me; R^2 = Me; R^3 = Me
e	R^1 = Me; R^2 = Me; R^3 = Ph
f	R^1 = Me; R^2 = Ph; R^3 = Me
g	R^1 = Et; R^2 = Me; R^3 = Me
h	R^1 = Me; R^2 = Ph; R^3 = Ph

or Et (the substituents are identified in Table 1). The work had two initial objectives. Firstly, it was of interest to find out whether the presence of groups larger than hydrogen in the R^1 position would impede the cyclisation reaction, *i.e.* whether it would be possible to use this route to prepare 2-benzazepines such as **5a** with a substituent on C-5. This was in question because it had been shown earlier[4] that 1.7 electrocyclisation reactions in analogous biaryl systems are inhibited by steric factors which prevent the reactant adopting the helical transition state required for cyclisation. It was thought possible that the interaction between the R^1 group in **10** and the adjacent aromatic hydrogen atom could have a similar effect. Secondly, if the cyclisation should take place, the main interest was to find out whether it would lead to compounds of the type **6a**, analogues of the nitrile imine products **6b**. Such products could arise *via* a base-induced hydrogen shift in intermediates of the type **3a** (R^1 = Me, Et) and, if formed, would be of use in the further chemical elaboration of the 2-benzazepine system.

Results and discussion

Preparation of precursors 8a–h and generation of the nitrile ylides 10a,b,d–h

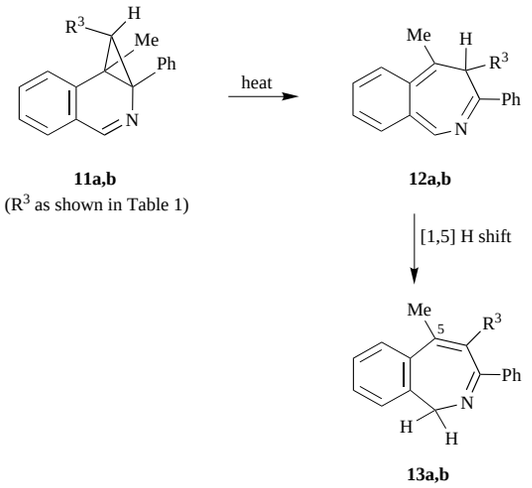
The nitrile ylides were generated from the amides **8** (Scheme 2) by the method used in earlier work,[1,4] *i.e.* conversion into the imidoyl chlorides **9** followed by 1,3-dehydrochlorination of the latter in THF at 0 °C using a strong non-nucleophilic base.

Preparation of precursors 8a–h. The amides **8** were easily prepared in high yields by the Suzuki coupling of the boronic acid **7**[5] with a set of bromoalkenes whose substituents are shown in Table 1. Interestingly, in most of these compounds, the polysubstituted alkenyl groups were sufficiently bulky to be inhibited from free rotation on the NMR timescale at room temperature and hence to give ^{1}H NMR spectra in which the benzylic methylene protons were diastereotopic (*J ca.* 14.5 Hz).

The cyclisation reactions. In the event it proved that the presence of non-hydrogen substituents (methyl or ethyl) in the R^1 position of **10** did not in any way impede the cyclisation reaction and in all cases the reactions gave the cyclopropa[*c*]isoquinolines **11** (Scheme 2) in yields (66–80%) not inferior to those obtained in the earlier work. The products were identified by comparison of their ^{1}H and ^{13}C NMR spectra with those obtained previously.[1]

Thermal isomerisation of the cyclopropa[*c*]isoquinolines 11a,b,d–h

Cyclopropa[*c*]isoquinolines with R^2 or R^3 = H. The first two examples studied **11a**,**b** (Scheme 3) (R^3 = H, Ph, respectively) both isomerised, as expected, *via* the general route determined earlier (Scheme 1) to give the 2-benzazepines **13a**,**b** in yields of 100 and 75%, respectively. The products were identified by comparison of their ^{1}H and ^{13}C NMR spectra with similar compounds prepared in the earlier work.[1] These conversions show that the general route can be used for the synthesis of these 5-substituted derivatives even in the case **13b** (R^3 = Ph) where there are three adjacent substituents. There was however a marked difference in the rate of the isomerisation reactions.

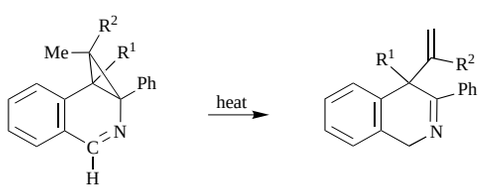


11a,b (R^3 as shown in Table 1) **12a,b** **13a,b**

Scheme 3

The compound **11a** (R^3 = H) isomerised easily and quantitatively in refluxing benzene (12 h) and even converted slowly at room temperature, whereas **11b** (R^3 = Ph) required 24 h at the higher temperature of refluxing toluene. It is difficult to see how the presence of the phenyl group in the latter could disfavour the first step (**11b**→**12b**) and it therefore seems likely that the observed effect is due to the combined effect of the three substituents on the shape of **12b** which, probably by flattening the ring, makes the ring inversion or the transition state for the sigmatropic hydrogen migration less accessible.

Cyclopropa[*c*]isoquinolines with R^2 and $R^3 \neq$ H. All the other examples in the series **11d**–**h** were of this type and hence were unable to follow the general reaction path (Scheme 1) leading to **5a**. The alternative path for nitrile imines (Scheme 1) which gave compounds of the type **6b** was reported to occur for the cyclisation of **1b** ($R^1 = R^2 = R^3$ = Me). In the reaction of the analogous nitrile ylide **10d** it was found that the cyclopropa[*c*]isoquinoline **11d** was the only product even though the reaction was carried out in the presence of excess base. The thermal isomerisation of **11d** required 24 h at reflux in *p*-xylene and gave, not **6a** (R = Ph, $R^2 = R^3$ = Me), but 1,4-dihydro-4-isopropenyl-4-methyl-3-phenylisoquinoline **14d** ($R^1 = R^2$ = Me) (Scheme 4)



11d–g (R^1, R^2 as shown in Table 1) **14d,f,g**

Scheme 4

in quantitative yield. It seems likely that the product is formed *via* a homo [1,5] sigmatropic hydrogen shift which, although it is a well known reaction for appropriately substituted cyclopropanes,[6] is a new mode of rearrangement for this system. The structure of the product was confirmed by X-ray crystallography (Fig. 1).

The generality of the reaction was explored by studying three other examples **11e**–**g** (substituents identified in Table 1). The isomeric pair of compounds **11e** and **11f** reacted more slowly but both gave **14f** in high yield. The isomer **11e** has its methyl group in the *exo* position and obviously cannot directly undergo a homo [1,5] sigmatropic hydrogen shift and must therefore react *via* isomerisation to give **11f** before the hydrogen migration. These clean conversions of compounds **11e** and **11f** into **14f** contrast strongly with the previously studied[1] thermolysis of compound **11** (R^1 = H, R^2 = Ph, R^3 = Me) (Scheme 5) (and its isomer with the groups on C-1 transposed) which gave the

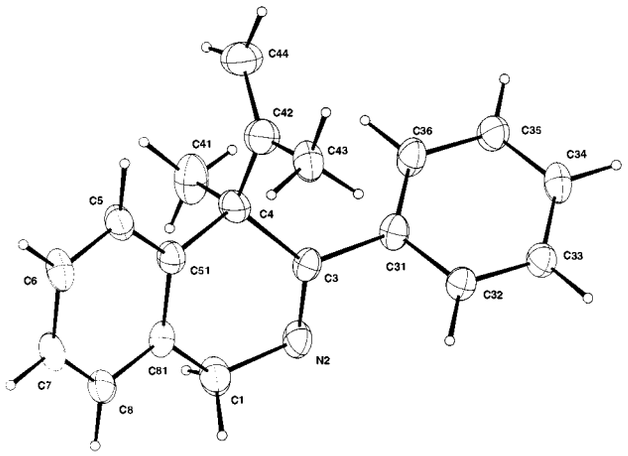
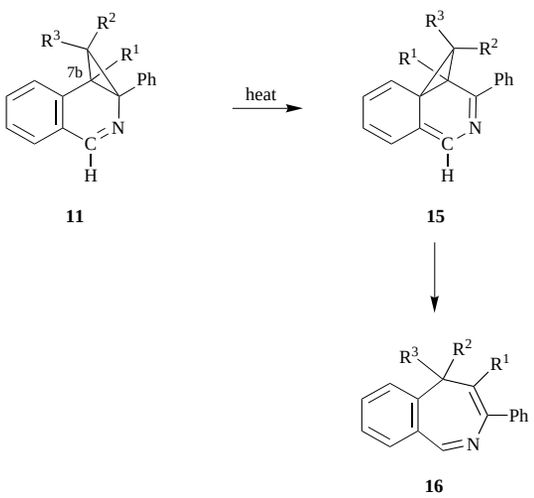


Fig. 1 Crystal structure of compound **14d**



Scheme 5

5*H*-2-benzazepine **16** (R^1 = H, R^2 = Ph, R^3 = Me) (structure confirmed by X-ray crystallography). Compound **11f** differs from this reactant only in the presence of the methyl group (R^1) at C-7b but this clearly serves to divert completely the reaction into the new path. The cause of this effect is not understood at present. The next reactant in the series, **11g** (R^1 = Et, Scheme 4), also followed the same path to give **14g** in 90% yield, so the ethyl group can be seen to have a similar effect.

The final reactant **11h** by the nature of its substituents (R^1 = Me; R^2 = R^3 = Ph) was unable to follow either of the reaction paths in Schemes 3 or 4 and was studied to find out whether the presence of the C-7b methyl group would completely inhibit the path in Scheme 5. In the event the reactant isomerised very slowly (40% after 6 days at reflux in *p*-xylene) to give a product whose mass and ^{1}H NMR spectra were consistent with structure **16h** (R^1 = Me; R^2 = R^3 = Ph) but which proved to be too unstable to characterise fully. The C-7b methyl group in the reactant therefore does not fully suppress this reaction path but does slow it down.

In none of these cases was any product of the type **6a** formed either in the initial nitrile ylide cyclisations, or in the subsequent thermal rearrangements of the cycloprop[*c*]isoquinolines, or when the latter were heated in the presence of lithium bis(trimethylsilylamide).

This work has therefore shown that for diene-conjugated nitrile ylides of the type **1a**, the presence of substituents Me or Et in the R^1 position does not impede the cyclisation to give **2a**, and that (i) if R^2 or R^3 = H then the latter undergo the normal thermal rearrangement to give 5-substituted 2-benzazepines **5a**; (ii) where R^2 and $R^3 \neq$ H and either is a CH_3 group then the presence of the non-hydrogen R^1 substituent in the C-7b position in **2a** completely diverts the thermal rearrangement into a new path (Scheme 4) leading to the formation of 1,4-dihydro-4-alkenylisoquinolines **14** in high yield; and (iii) 5-alkylidene-2-benzazepines **6a** analogous to the products obtained from similar nitrile imines are not formed in these reactions.

Experimental

NMR spectra were run as solutions in deuteriochloroform unless otherwise stated. Chemical shifts are recorded as δ values. *J* Values are given in Hz. In the ^{13}C NMR spectra carbon multiplicity was established by single frequency off resonance decoupling or by DEPT. Mass spectra were obtained using electron ionisation at 70 eV unless otherwise stated. Preparative chromatography was carried out by the 'dry-column flash' technique[7] using silica gel (15 μm, Fluka Kieselgel GF_{254}) or the 'medium pressure' (MPLC) technique[8] using 100 × 2.5 cm columns packed with Merck Kieselgel 60 (230–240 mesh), and eluting solvents based on hexane admixed with ether or ethyl acetate. Ether refers to diethyl ether. 'Evaporation' of solvents indicates evaporation under reduced pressure using a rotary evaporator. All drying of solutions was done with anhydrous magnesium sulfate.

Solvents, reactants and starting materials

Tetrahydrofuran (THF) was distilled from sodium and benzophenone as required. Cyclohexane, hexane and *N*,*N*-dimethylformamide (DMF) were distilled from calcium hydride as required. 1,2-Dimethoxyethane (DME) was passed through a column of activated alumina and stored over 4 Å molecular sieves. The following materials were obtained from the suppliers indicated or were prepared by literature routes: 2-bromopropene (Avocado Research Chemicals Ltd.), (*Z*)- and (*E*)-2-bromo-1-phenylpropene[9,10] as a mixture, 2-bromo-3-methylbut-2-ene (Avocado Research Chemicals Ltd.), (*Z*)- and (*E*)-2-bromo-3-phenylbut-2-ene[11] (separated by dry-column flash chromatography), 3-bromo-2-methylpent-2-ene,[12] 2-bromo-1,1-diphenylpropene[13] and 2-(benzoylaminomethylphenyl)boronic acid[5] **7**.

Synthesis of the *N*-(2-alkenylbenzyl)benzamides 8a–h

These compounds were synthesised by the general method described in detail for the first example, in all cases the reaction time was 20 h.

***N*-(2-Isopropenylbenzyl)benzamide 8a.** 2-Bromopropene (1.52 g, 12.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.66 g, 0.58 mmol, 4.8 mol% catalyst) were stirred in 1,2-dimethoxyethane (50 cm^3) under dry nitrogen for 20 min. 2-(Benzoylaminomethylphenyl)boronic acid **7** (3.38 g, 13.2 mmol) and sodium carbonate (3.42 g, 12.0 mmol) in water (16.5 cm^3) were added and the mixture heated at reflux for 20 h. The reaction mixture was allowed to cool to room temperature and passed through a pad of alumina. The DME was removed *in vacuo* and dichloromethane (100 cm^3) was added. The organic layer was separated, dried and the solvent removed *in vacuo* to give a brown oil. Dry-column flash chromatography (silica, hexane–ethyl acetate, 9:1) gave *N*-(2-isopropenylbenzyl)-benzamide **8a** as a white solid (1.96 g, 65%), mp 92–93 °C from ethanol [Found: C, 81.1; H, 6.8; N, 5.5%; $(M + 1)^+$, 252.1391. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%; $(M + 1)^+$, 252.1388]; δ_H(200 MHz, $CDCl_3$) 2.07 (3 H, m, CH_3), 4.64 (2 H, d, *J* 5.5, CH_2), 4.90 (1 H, m, CH), 5.24 (1 H, m, CH), 6.57 (1 H, br, NH), 7.14–7.51 (7 H, m, Ar-H), 7.72–7.79 (2 H, m, Ar-H); δ_C(50 MHz, $CDCl_3$) 24.8 (CH_3), 41.8 (CH_2), 115.5 (CH_2), 126.7 (CH), 127.2 (CH), 127.3 (CH), 128.2 (CH), 128.4 (CH), 128.7 (CH), 131.2 (CH), 134.3 (quat.), 143.5 (quat.), 144.8 (quat.), 167.0 (quat.); ν_{max}(Nujol)/cm^{-1} 1636 (C=O), 3331 (NH).

(*Z*)- and (*E*)-*N*-[2-(1-Methyl-2-phenylethenyl)benzyl]benzamide 8b and 8c. The usual work-up gave a brown oil which on dry-flash column chromatography (silica, hexane–ethyl acetate,

9 : 1) followed by MPLC (silica, hexane–ethyl acetate, 9 : 1) gave (a) (*Z*)-*N*-[2-(1-methyl-2-phenylethenyl)benzyl]benzamide **8b** as a white solid (21%), mp 147–148 °C from hexane–ethanol [Found: C, 84.4; H, 6.5; N, 4.3%; $(M + 1)^+$, 328.1701. $C_{23}H_{21}NO$ requires C, 84.4; H, 6.5; N, 4.3%; $(M + 1)^+$, 328.1701]; δ_H(250 MHz, $CDCl_3$) 2.22 (3 H, m, CH_3), 4.12 (1 H, dd, *J* 14.2 and 3.5, CH_2), 4.77 (1 H, dd, *J* 14.2 and 7.6, CH_2), 5.74 (1 H, br, NH), 6.57 (1 H, m, CH; 12% NOE enhancement on irradiation at δ 2.22), 6.83–7.46 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 28.1 (CH_3), 41.5 (CH_2), 126.6 (CH), 126.7 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 130.3 (CH), 131.0 (CH), 133.9 (quat.), 134.0 (quat.), 136.9 (quat.), 137.7 (quat.), 141.8 (quat.), 166.6 (quat.); ν_{max}(Nujol)/cm^{-1} 1632 (C=O), 3317 (NH); (b) (*E*)-*N*-[2-(1-methyl-2-phenylethenyl)benzyl]benzamide **8c** as a white solid (10%), mp 112–113 °C from hexane–ethanol [Found: C, 84.4; H, 6.5; N, 4.3%; $(M + 1)^+$, 328.1701. $C_{23}H_{21}NO$ requires C, 84.4; H, 6.5; N, 4.3%; $(M + 1)^+$, 328.1701]; δ_H(250 MHz, $CDCl_3$) 2.24 (3 H, d, *J* 1.5, CH_3), 4.73 (2 H, d, *J* 5.5, CH_2), 6.45 (1 H, m, CH; no NOE enhancement on irradiation at δ 2.24), 6.57 (1 H, br, NH), 7.24–7.77 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 20.2 (CH_3), 41.9 (CH_2), 126.6 (CH), 126.7 (CH), 127.3 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.9 (CH), 134.2 (quat.), 134.5 (quat.), 137.2 (quat.), 137.8 (quat.), 145.3 (quat.), 167.1 (quat.); ν_{max}(Nujol)/cm^{-1} 1632 (C=O), 3317 (NH); and (c) *N*-(2-phenylbenzyl)benzamide as a white solid (40%), mp 95–96 °C from hexane–ethanol (lit.,[4] 94.5–95.5 °C).

***N*-[2-(1,2-Dimethylprop-1-enyl)benzyl]benzamide 8d.** White solid (70%), mp 105 °C from hexane–ethanol [Found: C, 81.4; H, 8.0; N, 4.7%; $(M + 1)^+$, 280.169 98. $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%; $(M + 1)^+$, 280.170 14]; δ_H(250 MHz, $CDCl_3$) 1.42 (3 H, m, CH_3), 1.80 (3 H, m, CH_3), 1.90 (3 H, m, CH_3), 4.47 (1 H, dd, *J* 14.7 and 5.5, CH_2), 4.56 (1 H, dd, *J* 14.7 and 5.6, CH_2), 6.45 (1 H, br, NH), 7.01–7.77 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 19.7 (CH_3), 20.6 (CH_3), 21.8 (CH_3), 41.6 (CH_2), 126.5 (CH), 126.7 (2 × CH), 127.5 (CH), 128.2 (CH), 128.2 (CH), 128.4 (2 × CH), 128.9 (CH), 131.2 (CH), 134.3 (quat.), 134.7 (2 × quat.), 144.5 (quat.), 167.0 (quat.); ν_{max}(Nujol)/cm^{-1} 1637 (C=O), 3327 (NH).

(*Z*)-*N*-[2-(1-Methyl-2-phenylprop-1-enyl)benzyl]benzamide 8e. White solid (63%), mp 141–143 °C from hexane–ethyl acetate [Found: C, 84.8; H, 7.1; N, 4.0%; $(M + 1)^+$, 342.1844. $C_{24}H_{23}NO$ requires C, 84.4; H, 6.8; N, 4.1%; $(M + 1)^+$, 342.1858]; δ_H(200 MHz, $CDCl_3$) 2.06 (3 H, s, CH_3), 2.13 (3 H, s, CH_3), 3.96 (1 H, dd, *J* 14.3 and 3.7, CH_2), 4.61 (1 H, dd, *J* 14.3 and 7.5, CH_2), 5.36 (1 H, br, NH), 7.06–7.54 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 20.5 (CH_3), 22.5 (CH_3), 41.1 (CH_2), 125.9 (CH), 126.8 (CH), 126.9 (2 × CH), 127.1 (CH), 127.5 (2 × CH), 128.2 (2 × CH), 128.6 (2 × CH), 128.7 (CH), 129.8 (CH), 131.2 (CH), 131.4 (quat.), 133.0 (quat.), 134.3 (quat.), 134.4 (quat.), 143.6 (quat.), 143.8 (quat.), 167.1 (quat.); ν_{max}(Nujol)/cm^{-1} 1635 (C=O), 3301 (NH).

(*E*)-*N*-[2-(1-Methyl-2-phenylprop-1-enyl)benzyl]benzamide 8f. White solid (78%), mp 125–127 °C from hexane–ethyl acetate [Found: C, 84.6; H, 7.0; N, 4.1%; $(M + 1)^+$, 342.1855. $C_{24}H_{23}NO$ requires C, 84.4; H, 6.8; N, 4.1%; $(M + 1)^+$, 342.1858]; δ_H(200 MHz, $CDCl_3$) 1.67 (3 H, CH_3), 1.78 (3 H, s, CH_3), 4.61 (2 H, br m, CH_2), 6.32 (1 H, br, NH), 6.91–7.72 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 22.2 (CH_3), 22.4 (CH_3), 41.6 (CH_2), 126.3 (CH), 126.7 (2 × CH), 127.0 (CH), 127.8 (CH), 128.0 (2 × CH), 128.1 (2 × CH), 128.4 (CH), 128.5 (2 × CH), 128.7 (CH), 131.3 (CH), 134.3 (quat.), 134.4 (quat.), 134.6 (quat.), 143.2 (quat.), 143.6 (quat.), 167.1 (quat.); ν_{max}(Nujol)/cm^{-1} 1636 (C=O), 3344 (NH).

***N*-[2-(1-Ethyl-2-methylprop-1-enyl)benzyl]benzamide 8g.** White solid (41%), mp 105 °C from hexane–ethyl acetate (Found: C, 81.8; H, 8.2; N, 4.5. $C_{20}H_{23}NO$ requires C, 81.9; H, 7.9; N, 4.8%); δ_H(200 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.5, CH_3), 1.42 (3 H, s, CH_3), 1.82 (3 H, s, CH_3), 2.14 (1 H, m, CH_3CH_2), 2.49 (1 H, m, CH_3CH_2), 4.54 (2 H, m, CH_2NH), 6.25 (1 H, br, NH), 7.00–7.80 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 12.6 (CH_3), 19.3 (CH_3), 22.1 (CH_3), 27.1 (CH_2), 41.7 (CH_2), 126.7 (2 × CH), 127.2 (CH), 128.1 (CH), 128.5 (2 × CH), 129.8 (CH), 131.3 (CH), 134.4 (quat.), 134.6 (quat.), 135.2 (quat.), 143.0 (quat.), 167.0 (quat.); ν_{max}(Nujol)/cm^{-1} 1636 (C=O), 3340 (NH).

***N*-[2-(1-Methyl-2,2-diphenylethenyl)benzyl]benzamide 8h.** White solid (0.56 g, 54%), mp 144–146 °C from hexane–ethanol [Found: C, 86.4; H, 6.4; N, 3.3%; $(M + 1)^+$, 404.2001. $C_{29}H_{25}NO$ requires C, 86.3; H, 6.3; N, 3.5%; $(M + 1)^+$, 404.2014]; δ_H(250 MHz, $CDCl_3$) 2.11 (3 H, s, CH_3), 4.18 (1 H, dd, *J* 14.4 and 3.6, CH_2), 4.88 (1 H, dd, *J* 14.4 and 7.7, CH_2), 5.54 (1 H, br, NH), 6.89–7.59 (19 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 24.6 (CH_3), 40.8 (CH_2), 126.1 (CH), 126.7 (CH), 126.9 (2 × CH), 127.2 (CH), 127.3 (CH), 127.4 (2 × CH), 128.1 (2 × CH), 128.2 (2 × CH), 129.1 (CH), 129.7 (CH), 129.8 (2 × CH), 130.2 (2 × CH), 131.2 (CH), 133.9 (quat.), 134.2 (quat.), 134.5 (quat.), 139.6 (quat.), 141.9 (quat.), 142.4 (quat.), 142.9 (quat.), 167.1 (quat.); ν_{max}(Nujol)/cm^{-1} 1640 (C=O), 3291 (NH).

Generation of the nitrile ylides 10a,b,d–h derived from the amides 8a,b,d–h and their cyclisation to give the 1a,7b-dihydro-1a-phenyl-1*H*-cyclopropa[*c*]isoquinolines 11a,b,d–h

The amides were converted into the imidoyl chlorides **9a**,**b**,**d**–**h** by reaction with phosphorus pentachloride or (chloromethylidene)(dimethyl)iminium chloride (prepared *in situ* by reaction of thionyl chloride with the reaction solvent DMF). This is described in detail for the preparation of **11a** and **11g** respectively. The imidoyl chlorides (not isolated or purified) were converted into the nitrile ylides (**10**) by reaction, as solutions in THF at 0 °C, with lithium bis(trimethylsilyl)amide (1.0 M in THF) or solid potassium *tert*-butoxide as described in detail for the preparation of **11a** and **11f**, respectively. The reactions were all worked-up as described for **11a**.

1a,7b-Dihydro-7b-methyl-1a-phenyl-1*H*-cyclopropa[*c*]isoquinoline 11a. *N*-(2-Isopropenylbenzyl)benzamide **8a** (0.5 g, 1.99 mmol), dry ether (40 cm^3) and phosphorus pentachloride (0.54 g, 2.2 mmol) were heated at reflux under dry nitrogen for 24 h. The solvent was removed *in vacuo* and the residue dried under high vacuum at 30–40 °C for 2–3 h. Dry THF (30 cm^3) was added and the solution cooled to 0 °C. Lithium bis(trimethylsilyl)amide (2.99 cm^3, 2.99 mmol) was added dropwise with rapid stirring under dry nitrogen. The mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature. Ammonium chloride (25% w/v, 30 cm^3) was added and the mixture stirred for 10 min. The organic layer was separated and the aqueous layer extracted with dichloromethane (DCM) (2 × 30 cm^3). The combined organic layers were dried and the solvent removed *in vacuo*. Dry-column flash chromatography (silica, hexane–ethyl acetate, 9 : 1) gave **11a** as a yellow oil (0.35 g, 75%) [Found: $(M + 1)^+$, 234.1279. $C_{17}H_{15}N$ requires $(M + 1)^+$, 234.1283]; δ_H(250 MHz, $CDCl_3$) 0.18 (1 H, d, *J* 5.1, CH_2), 1.29 (3 H, s, CH_3), 2.51 (1 H, d, *J* 5.1, CH_2), 7.25–7.63 (9 H, m, Ar-H), 8.29 (1 H, s, CH); δ_C(63 MHz, $CDCl_3$) 19.0 (CH_3), 24.6 (CH_2), 31.0 (quat.), 57.4 (quat.), 123.5 (quat.), 124.7 (CH), 125.5 (CH), 127.0 (CH), 128.1 (2 × CH), 129.1 (2 × CH), 129.5 (CH), 131.2 (CH), 140.2 (quat.), 140.6 (quat.), 153.8 (CH); ν_{max}(Nujol)/cm^{-1} 1615 (C=N).

1a,7b-Dihydro-7b-methyl-1-*endo*,1a-diphenyl-1*H*-cyclopropa[*c*]isoquinoline 11b. Similarly the reaction of (*Z*)-*N*-[2-(1-methyl-2-phenylethenyl)benzyl]benzamide **8b** (0.24 g, 0.31 mmol) with phosphorus pentachloride (0.20 g, 0.34 mmol) for 24 h followed by lithium bis(trimethylsilyl)amide (1.10 cm^3, 1.10 mmol) gave **11b** as a white crystalline solid (0.15 g, 66%), mp 156–158 °C from pentane–DCM [Found: C, 89.4; H, 6.2; N, 4.2%; $(M + 1)^+$, 310.1591. $C_{23}H_{19}N$ requires C, 89.3; H, 6.2; N, 4.5%; $(M + 1)^+$, 310.1596]; δ_H(250 MHz, $CDCl_3$) 1.54 (3 H, s, CH_3), 3.30 (1 H, s, CH), 6.76–7.76 (14 H, m, Ar-H), 8.07 (1 H, d, *J* 0.7, HC=N); δ_C(63 MHz, $CDCl_3$) 21.1 (CH_3), 30.3 (C1),

34.6 (quat., C-7b), 61.2 (quat., C-1a), 125.6 (CH), 125.7 (CH), 125.9 (CH), 127.2 (CH), 128.2 (CH), 129.2 (CH), 131.2 (CH), 132.0 (CH), 132.8 (quat.), 136.9 (quat.), 141.8 (quat.), 155.2 (HC=N); ν_{max}(Nujol)/cm^{-1} 1600 (C=N).

1a,7b-Dihydro-1,1,7b-trimethyl-1a-phenyl-1*H*-cyclopropa-[*c*]isoquinoline 11d. Similarly the reaction of *N*-[2-(1,2-dimethylprop-1-enyl)benzyl]benzamide **8d** (0.75 g, 2.68 mmol) and phosphorus pentachloride (0.75 g, 3.59 mmol) for 60 h followed by lithium bis(trimethylsilyl)amide (4.04 cm^3, 4.04 mmol) gave **11d** as a white crystalline solid (0.53 g, 75%), mp 143–144 °C from hexane–ethanol (Found: C, 87.5; H, 7.5; N, 5.1%; M$^+$, 261.1515. $C_{19}H_{19}N$ requires C, 87.3; H, 7.3; N, 5.4%; M^+, 261.1518); δ_H(250 MHz, $CDCl_3$) 0.69 (3 H, s, CH_3), 1.35 (3 H, s, CH_3), 1.49 (3 H, s, CH_3), 7.25–7.55 (9 H, m, Ar-H), 8.30 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 15.7 (CH_3), 18.8 (CH_3), 18.9 (quat.), 20.1 (CH_3), 31.9 (quat.), 62.4 (quat.), 125.5 (CH), 125.6 (CH), 126.1 (CH), 126.8 (CH), 128.1 (CH), 128.3 (2 × CH), 130.8 (2 × CH), 131.2 (CH), 139.1 (quat.), 140.6 (quat.), 154.5 (quat.); *m*/*z* (EI) (M$^+$, 261, 27%), 260 (100), 158 (33), 143 (80), 141 (12), 128 (34), 115 (20), 103 (11); ν_{max}(Nujol)/cm^{-1} 1618 (C=N).

1a,7b-Dihydro-1,7b-dimethyl-1-*endo*,1a-diphenyl-1*H*-cyclopropa[*c*]isoquinoline 11e. A similar reaction of (*Z*)-*N*-[2-(1-methyl-2-phenylprop-1-enyl)benzyl]benzamide **8e** (0.20 g, 0.59 mmol) with phosphorus pentachloride (0.17 g, 1.37 mmol) for 60 h followed by lithium bis(trimethylsilyl)amide (2.36 cm^3, 2.36 mmol) gave **11e** as a white solid (0.13 g, 70%), mp 179–181 °C from pentane–DCM [Found: C, 88.9; H, 6.4; N, 4.0%; (M + 1)$^+$, 324.1752. $C_{24}H_{21}N$ requires C, 89.1; H, 6.55; N, 4.3%; (M + 1)$^+$, 324.1752]; δ_H(200 MHz, $CDCl_3$) 1.49 (3 H, s, CH_3), 1.68 (3 H, s, CH_3), 7.03–7.64 (14 H, m, Ar-H), 7.75 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 18.9 (CH_3), 23.4 (CH_3), 33.5 (quat.), 34.3 (quat.), 62.7 (quat.), 125.2 (CH), 125.4 (2 × CH), 127.0 (CH), 127.1 (2 × CH), 128.0 (CH), 128.4 (2 × CH), 131.0 (2 × CH), 131.2 (CH), 131.5 (quat.), 139.3 (quat.), 139.9 (quat.), 140.6 (quat.), 154.6 (HC=N); ν_{max}(Nujol)/cm^{-1} 1623 (C=N).

1a,7b-Dihydro-1,7b-dimethyl-1-*exo*,1a-diphenyl-1*H*-cyclopropa[*c*]isoquinoline 11f. A similar reaction of (*E*)-*N*-[2-(1-methyl-2-phenylprop-1-enyl)benzyl]benzamide **8f** (0.5 g, 1.50 mmol) with phosphorus pentachloride (0.43 g, 2.0 mmol) for 60 h followed by solid potassium *tert*-butoxide (0.34 g, 3.0 mmol) gave **11f** as a colourless oil (0.35 g, 72%) [Found: (M + 1)$^+$, 324.1763. $C_{24}H_{21}N$ requires (M + 1)$^+$, 324.1752]; δ_H(200 MHz, $CDCl_3$) 1.01 (3 H, s, CH_3), 1.58 (3 H, s, CH_3), 7.13–7.75 (14 H, m, Ar-H), 8.47 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 20.8 (CH_3), 22.6 (CH_3), 28.8 (quat.), 32.8 (quat.), 61.9 (quat.), 125.9 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 127.3 (quat.), 127.6 (2 × CH), 127.9 (2 × CH), 128.6 (CH), 130.5 (2 × CH), 131.0 (2 × CH), 132.0 (CH), 138.3 (quat.), 140.7 (quat.), 141.4 (quat.), 156.0 (HC=N); ν_{max}(Nujol)/cm^{-1} 1625 (C=N).

7b-Ethyl-1a,7b-dihydro-1,1-dimethyl-1a-phenyl-1*H*-cyclopropa[*c*]isoquinoline 11g. Thionyl chloride (0.06 cm^3, 0.81 mmol) was added to *N*-[2-(1-ethyl-2-methylprop-1-enyl)-benzyl]benzamide **8g** (0.2 g, 0.68 mmol) in dry DMF (0.8 g, 10.2 mmol) and stirred under a nitrogen atmosphere for 30 min. The solvent was removed *in vacuo* and the residue dried under high vacuum at 30–40 °C for 2–3 h. Dry THF (15 cm^3) was added and the solution cooled to 0 °C. Lithium bis(trimethylsilyl)-amide (2.72 cm^3, 2.72 mmol) was added dropwise with rapid stirring under dry nitrogen. The mixture was stirred at 0 °C for 1 h, then allowed to warm to room temperature. The usual work-up gave **11g** as a yellow oil (0.15 g, 80%) [Found: (M + 1)$^+$, 276.1761. $C_{20}H_{21}N$ requires (M + 1)$^+$, 276.1752]; δ_H(200 MHz, $CDCl_3$) 0.59 (3 H, s, CH_3), 1.00 (3 H, t, CH_3), 1.34 (3 H, s, CH_3), 1.44 (1 H, q, CH_2), 2.09 (1 H, q, CH_2), 7.18–7.41 (9 H, m, Ar-H), 8.21 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 12.4 (CH_3), 16.5 (CH_3), 19.1 (quat.), 20.3 (CH), 23.1 (CH_2), 37.1 (quat.), 62.6 (quat.), 125.6 (CH), 126.5 (quat.), 127.0 (CH), 127.4 (CH), 128.3 (2 × CH), 128.6 (CH), 130.7 (2 × CH), 130.9 (CH), 137.2 (quat.), 140.8 (quat.), 154.8 (HC=N); ν_{max}(Nujol)/cm^{-1} 1626 (C=N).

1a,7b-Dihydro-7b-methyl-1,1,1a-triphenyl-1*H*-cyclopropa-[*c*]isoquinoline 11h. *N*-[2-(1-methyl-2,2-diphenylethenyl)-benzyl]benzamide **8h** (0.15 g, 0.39 mmol) in dry DMF (0.46 g, 5.89 mmol) was reacted with thionyl chloride (0.034 cm^3, 0.46 mmol) as described for **11g**. Further reaction with potassium *tert*-butoxide (0.26 g, 2.34 mmol) gave **11h** as a yellow solid (0.10 g, 67%) [Found: C, 90.2; H, 6.2; N, 3.35%; (M + 1)$^+$, 386.1935. $C_{29}H_{23}N$ requires C, 90.4; H, 6.0; N, 3.6%; (M + 1)$^+$, 386.1909]; δ_H(200 MHz, $CDCl_3$) 1.76 (3 H, s, CH_3), 6.77–7.80 (19 H, m, Ar-H), 7.83 (1 H, s, HC=N); δ_C(63 MHz, $CDCl_3$) 22.3 (CH_3), 35.4 (quat.), 42.9 (quat.), 62.6 (quat.), 125.1 (CH), 125.7 (CH), 125.8 (CH), 125.9 (CH), 126.1 (CH), 126.6 (CH), 127.7 (2 × CH), 127.9 (2 × CH), 128.2 (CH), 128.3 (CH), 130.8 (2 × CH), 131.1 (2 × CH), 131.7 (CH), 138.4 (quat.), 140.0 (quat.), 140.1 (quat.), 140.4 (quat.), 155.8 (HC=N); ν_{max}(film)/cm^{-1} 1625 (C=N).

Thermal isomerisation products of the 1a,7b-dihydro-1a-phenyl-1*H*-cyclopropa[*c*]isoquinolines 11a,b,d–h

Compounds **11a**,**b**,**d**–**h** were heated under reflux under nitrogen in the solvent indicated and the reactions were worked up by the method given for the first example.

5-Methyl-3-phenyl-1*H*-2-benzazepine 13a. Compound **11a** (0.1 g, 0.43 mmol) in dry benzene (2 cm^3) was heated under reflux for 12 h. Evaporation of the solvent and dry-column flash chromatography of the residual brown oil (silica, hexane–ethyl acetate, 9 : 1) gave 5-methyl-3-phenyl-1*H*-2-benzazepine **13a** as a brown crystalline solid (0.1 g, 100%), mp 111–112 °C from pentane–dichloromethane [Found: C, 87.4; H, 6.8; N, 5.9%; (M + 1)$^+$, 234.1264. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5; N, 6.0%; (M + 1)$^+$, 234.1283]; δ_H(200 MHz, $CDCl_3$, 245 K) 2.49 (3 H, d, J 1.2, CH_3), 3.93 (1 H, d, J 10.5, CH_2), 5.00 (1 H, d, J 10.5, CH_2), 6.90 (1 H, br s, CH), 7.25–7.78 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 23.8 (CH_3), 56.3 (CH_2), 107.5 (CH), 124.2 (CH), 125.5 (CH), 126.0 (CH), 127.6 (2 × CH), 127.9 (CH), 128.0 (2 × CH), 129.3 (CH), 129.9 (CH), 137.6 (quat.), 137.8 (quat.), 138.7 (quat.), 147.4 (quat.), 165.1 (quat.); ν_{max}(Nujol)/cm^{-1} 1618 (C=N).

5-Methyl-3,4-diphenyl-1*H*-2-benzazepine 13b. Compound **11b** (0.1 g, 0.32 mmol) in toluene (5 cm^3) was heated under reflux for 24 h and gave 5-methyl-3,4-diphenyl-1*H*-2-benzazepine **13b** as a yellow glassy foam (0.07 g, 75%) [Found: (M + 1)$^+$, 310.1606. $C_{23}H_{19}N$ requires (M + 1)$^+$, 310.1596]; δ_H(200 MHz, $CDCl_3$) 2.35 (3 H, s, CH_3), 4.08 (1 H, d, J 9.9, CH_2), 4.91 (1 H, d, J 9.9, CH_2), 7.05–7.63 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 21.6 (CH_3), 55.8 (CH_2), 126.8 (CH), 126.9 (CH), 127.0 (CH), 127.1 (CH), 127.4 (2 × CH), 127.7 (2 × CH), 128.3 (CH), 128.4 (CH), 128.6 (2 × CH), 130.6 (2 × CH), 136.6 (quat.), 138.8 (quat.), 139.4 (quat.), 139.6 (quat.), 139.7 (quat.), 143.0 (quat.), 167.3 (C=N); ν_{max}(Nujol)/cm^{-1} 1606 (C=N).

1,4-Dihydro-4-isopropenyl-4-methyl-3-phenylisoquinoline 14d. Compound **11d** (0.1 g, 0.38 mmol) in *p*-xylene (5 cm^3) was heated under reflux for 24 h and gave 1,4-dihydro-4-isopropenyl-4-methyl-3-phenylisoquinoline **14d** as a white solid (0.1 g, 100 %), mp 68–69 °C from pentane [Found: C, 87.6; H, 7.6; N, 5.0%; (M + 1)$^+$, 262.1601. $C_{19}H_{19}N$ requires C, 87.3; H, 7.3; N, 5.4%; (M + 1)$^+$, 262.1596]; δ_H(200 MHz, $CDCl_3$) 1.49 (3 H, d, J 0.8, CH_3), 1.61 (3 H, s, CH_3), 5.02 (1 H, d, J 21, CH_2), 5.11 (1 H, m, C=CH_2), 5.12 (1 H, d, J 21, CH_2), 5.26 (1 H, br s, C=CH_2), 7.17–7.88 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 20.9 (CH_3), 25.1 (CH_3), 48.5 (quat.), 56.0 (CH_2), 112.8 (CH_2), 123.8 (CH), 124.8 (CH), 125.4 (CH), 126.4 (CH), 127.1 (CH), 127.5 (CH), 127.6 (CH), 128.4 (CH), 132.6 (quat.), 134.3 (quat.), 138.3 (quat.), 140.7 (quat.), 147.5 (quat.), 171.4 (quat.); ν_{max}(Nujol)/cm^{-1} 1628 (C=N).

1,4-Dihydro-4-methyl-3-phenyl-4-(1-phenylethenyl)iso-quinoline 14f. Compound **11e** (0.06 g, 0.18 mmol) in *p*-xylene (2 cm^3) was heated under reflux for 48 h and gave 1,4-dihydro-4-

methyl-3-phenyl-4-(1-phenylethenyl)isoquinoline **14f** as a colourless oil (0.05 g, 83%) [Found: $(M + 1)^+$, 324.1743. $C_{24}H_{21}N$ requires $(M + 1)^+$, 324.1752]; δ_H(200 MHz, $CDCl_3$) 1.71 (3 H, CH_3), 4.63 (1 H, d, *J* 21, CH_2), 4.88 (1 H, d, *J* 21, CH_2), 5.41 (1 H, br s, C=CH_2), 5.54 (1 H, br s, C=CH_2), 6.55–7.45 (14 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 26.1 (CH_3), 48.6 (quat.), 52.9 (CH_2), 115.3 (CH_2), 125.0 (CH), 125.5 (CH), 126.6 (CH), 126.7 (CH), 127.2 (CH), 127.3 (2 × CH), 127.4 (2 × CH), 127.5 (2 × CH), 127.8 (2 × CH), 128.2 (CH), 138.7 (quat.), 140.8 (quat.), 141.0 (quat.), 151.5 (quat.), 154.6 (quat.), 171.8 (quat.); ν_{max}(Nujol)/cm^{-1} 1638 (C=N).

Compound **11f** (0.15 g, 0.46 mmol) in *p*-xylene (5 cm^3) was heated under reflux for 48 h and gave 1,4-dihydro-4-methyl-3-phenyl-4-(1-phenylethenyl)isoquinoline **14f** as a colourless oil (0.1 g, 66%), identical with the sample obtained in the thermolysis of **11e**, and 1a,7b-dihydro-1,7b-dimethyl-1-*endo*-phenyl-1a-phenyl-1*H*-cyclopropa[*c*]isoquinoline **11e** (0.03 g, 20%).

4-Ethyl-1,4-dihydro-4-isopropenyl-3-phenylisoquinoline 14g. Compound **11g** (0.05 g, 0.18 mmol) in *p*-xylene (3 cm^3) was heated under reflux for 24 h and gave 4-ethyl-1,4-dihydro-4-isopropenyl-3-phenylisoquinoline **14g** as a yellow oil (45 mg, 90 %) [Found: $(M + 1)^+$, 276.1685. $C_{20}H_{21}N$ requires $(M + 1)^+$, 276.1752]; δ_H(200 MHz, $CDCl_3$) 0.46 (3 H, t, *J* 7.3, CH_3), 1.52 (3 H, d, 0.7, CH_3), 2.03 (2 H, q, *J* 7.3, CH_2), 5.01 (1 H, br s, C=CH_2), 5.05 (2 H, s, CH_2), 5.19 (1 H, br s, C=CH_2), 7.03–7.65 (9 H, m, Ar-H); δ_C(63 MHz, $CDCl_3$) 9.0 (CH_3), 21.5 (CH_3), 30.2 (CH_2), 52.2 (quat.), 53.1 (CH_2), 111.8 (CH), 124.3 (CH), 125.5 (CH), 126.4 (CH), 127.1 (CH), 127.6 (2 × CH), 127.8 (2 × CH), 128.5 (CH), 132.0 (quat.), 135.6 (quat.), 140.7 (quat.), 148.9 (quat.), 169.0 (quat.); ν_{max}(Nujol)/cm^{-1} 1628 (C=N).

4-Methyl-3,5,5-triphenyl-5*H*-2-benzazepine 16h. Compound **11h** (0.05 g, 0.13 mmol) in *p*-xylene (3 cm^3) was heated under reflux for 168 h and gave 4-methyl-3,5,5-triphenyl-5*H*-2-benzazepine **16h** as a yellow oil (0.02 g, 40%) [Found: $(M + 1)^+$, 386.1939. $C_{29}H_{23}N$ requires $(M + 1)^+$, 386.1909]; δ_H(200 MHz, $CDCl_3$) 1.74 (3 H, s, CH_3), 6.78–7.55 (19 H, m, Ar-H), 8.39 (1 H, br, HC=N); and starting material (0.01 g).

The crystal structure of 1,4-dihydro-4-isopropenyl-4-methyl-3-phenylisoquinoline 14d

Crystal data. Crystal data for $C_{19}H_{19}N$, $M = 261.37$, monoclinic, $P2_1/c$, $a = 8.657(6)$, $b = 24.090(18)$, $c = 7.071(8)$ Å, $\beta = 94.95(8)°$, $V = 1469.1$ $Å^3$, $Z = 4$, $D_c = 1.18$ g cm^{-3}, $F(000) = 561.32$ (obtained from the values of the scattering factors at $\theta = 0$), $T = 150$ K, μ(Cu-Kα) = 0.48 mm^{-1}. Colourless block, 0.47 × 0.35 × 0.19 mm^3.

Data collection and processing. The crystals grew in clumps, and despite attempts to cut a single crystal out of the clumps none of the samples selected for study gave a diffraction pattern that could be indexed with reference to one orientation matrix. Indexing was performed using the program DIRAX,[14] but the quality of the sample naturally limited the precision of the final structure determination, which, although it establishes chemical connectivity, is unsuited to more detailed analysis. Data were collected using ω-θ scans with graphite-monochromated Cu-Kα radiation in the range $5 \leqslant 2\theta \leqslant 120°$ on a Stoe Stadi4 diffractometer equipped with an Oxford Cryosystems low temperature device.[15] The structure was solved by direct methods (SIR92)[16] and refined against *F* with anisotropic displacement parameters on all non-H atoms, and H-atoms placed in calculated positions (CRYSTALS).[17] The refinement converged to $R = 9.73\%$ and $R_w = 10.73\%$ using a Chebychev polynomial weighting scheme for 1159 data with $F > 4\sigma(F)$ and 182 parameters. The final difference synthesis max and min were +0.49 and −0.32 e $Å^{-3}$, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/172.

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