Reaction of 2-amino- and 2-(substituted amino)-1-azaazulenes with chloro-, phenyl- and diphenyl-ketene

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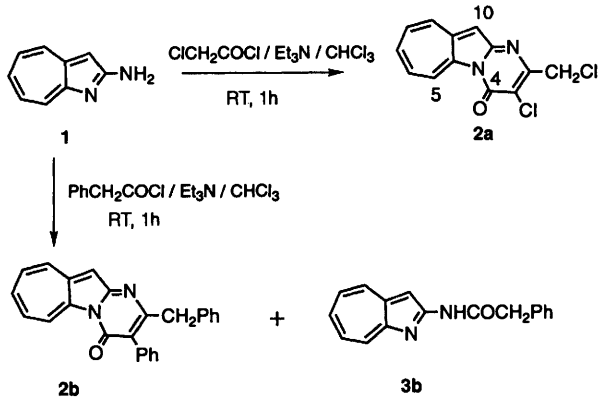
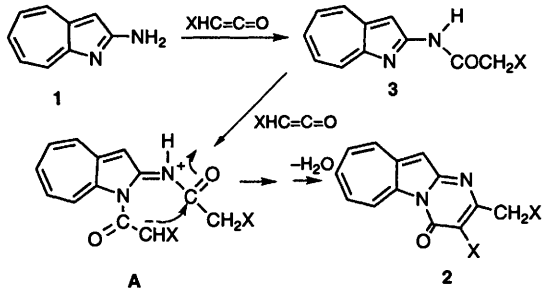
Chloro- and phenyl-ketene react with 2-amino-1-azaazulene 1 to give 4,4a-dihydro-1,4a-diazacyclopent[*a*]azulen-4-one derivatives 2a and 2b as cycloadducts. With 2-alkylamino-1-azaazulenes 4 chloroketene reacts to give *anhydro*-3-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide derivatives 5, whereas phenylketene gives 1-alkyl-4-benzyl-4-hydroxy-1,2,3,4-tetrahydro-1,10-diazabenz[*a*]azulen-2-ones 6, 2-alkylamino-3-phenylacetyl-1-azaazulenes 7 and 1-alkyl-4-benzyl-1,2-dihydro-1,10-diazabenz[*a*]azulen-2-ones 8. The structures of compounds 5a, 6a and 8a are deduced by X-ray structural analysis. These reactions are interpreted in the terms of the hard-soft-acid-base principle.

The azaazulenes have attracted much attention as a result of their interesting chemical and physical properties for the synthesis of hetero-fused heterocycles.[1–9] Cycloadditions have been of great use,[10–16] those of 1-azaazulenes affording a wide variety of cycloadducts depending on the nature of the substituents on the 1-azaazulenes and the reaction conditions employed.[17–25] Such reactions proceeded mainly *via* an extended dipolar intermediate; in particular, 2-amino-1-azaazulene derivatives behaved both like amino enamines and like amidines and reacted with acetylenic ester and diphenylcyclopropenone to give a variety of cycloadducts.[20,22,24,25] Since ketenes undergo cycloadditions to give versatile products,[16,26–27] we have examined their reactions with 2-amino-1-azaazulenes and found that they give rise to novel fused heterocycles.



Scheme 1



Scheme 2

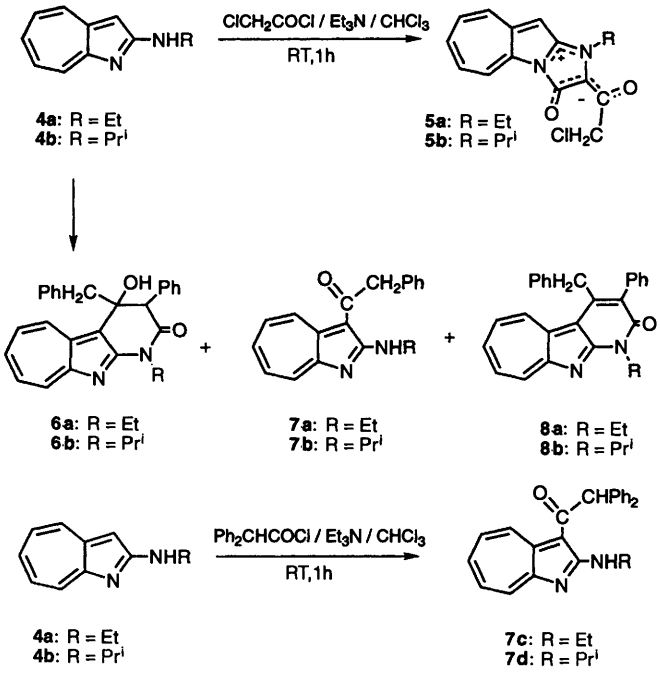
Results and discussion

In the reactions of 2-amino-1-azaazulenes with chloro-, phenyl- and diphenyl-ketene, the ketene was generated *in situ* by the treatment of an appropriate acyl chloride with triethylamine in chloroform. Thus, treatment of 2-amino-1-azaazulene **1** with chloroketene at room temperature for 1 h afforded the cycloadduct 3-chloro-2-chloromethyl-4,4a-dihydro-1,4a-diazabenz[*a*]azulen-4-one **2a** (34%), the IR spectrum of which showed carbonyl (1680 cm^{-1}) but no NH absorption. In its ^1H NMR spectrum, **2a** showed a low resonating 1 H proton (at δ 9.70–9.75), which would be deshielded by the carbonyl group at C-4 and was assigned to H-5, with a 1 H singlet, assigned as H-10, at δ 6.95. These observations are appropriate for the 4,4a-dihydro-1,4a-diazabenz[*a*]azulen-4-one system.[28]

Similar treatment of **1** with phenylketene gave 2-benzyl-3-phenyl-4,4a-dihydro-1,4a-diazabenz[*a*]azulen-4-one **2b** (10%) together with 2-phenylacetylamino-1-azaazulene **3b** (32%).

A reasonable mechanism for this reaction is shown in Scheme 2 in which attack of the ketene occurs initially at the amino group of **1** to give **3**. Subsequent attack of a second molecule of the ketene on **3** at N-1 gives a dipolar intermediate **A**, the successive cyclization of which furnishes **2**.

The reactions of 2-alkylamino-1-azaazulenes with chloro- and phenyl-ketene showed rather different features from those of 2-amino-1-azaazulene **1**. Thus, treatment of 2-ethylamino-1-azaazulene **4a** with chloroketene at room temperature for 1 h afforded an extremely stable mesoionic compound **5a**, *anhydro*-2-chloroacetyl-1-ethyl-3-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide, (36%) which was unaffected by treatment with dil. hydrochloric acid or aq. sodium hydroxide at room temperature. The mass spectrum (*m*/*z* 290 and 288, M^+) of **5a** together with its elemental analysis show that it has the molecular formula $C_{15}H_{13}N_2O_2Cl$; in its ^1H NMR spectrum, CH_2CH_3 protons resonate at rather low field (δ 4.53) whilst a CH_2 singlet appears at δ 4.82 (2 H, s) and the seven-membered ring protons at δ 7.20–7.40 (m, H-5, 6 and 7), 7.77 (d, *J* 11.0 Hz, H-8) and 8.71 (d, *J* 8.5 Hz, H-4); a 1 H singlet at δ 6.45 was assigned to H-9. The divergence of coupling constants for the seven-membered ring protons suggests that compound **5a** is a heptafulvene rather than a tropylium cation. The electronic absorption spectrum of **5a** shows a strong band at 468 nm (log ε 4.07) which is in agreement with the conclusions drawn from the ^1H NMR evidence. A single-crystal X-ray structural analysis (Fig. 1) confirmed these conclusions with bond



Scheme 3

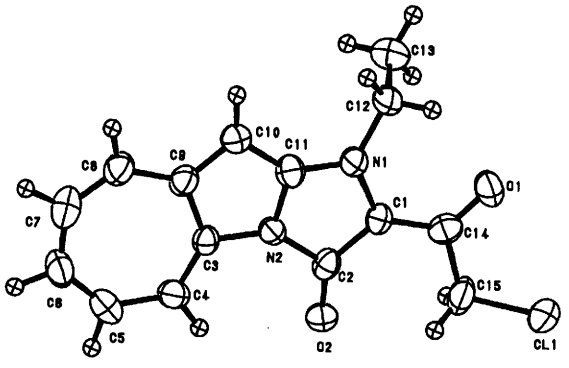


Fig. 1 ORTEP drawing of **5a** with thermal ellipsoid plot (50% probability). Selected bond lengths (Å): N(1)–C(1) 1.431(4), N(1)–C(11) 1.325(4), C(1)–C(2) 1.426(5), C(2)–N(2) 1.425(4), N(2)–C(11) 1.366(4), N(2)–C(3) 1.390(4), C(3)–C(9) 1.472(4), C(9)–C(10) 1.384(5), C(10)–C(11) 1.402(4), C(3)–C(4) 1.353(5), C(4)–C(5) 1.417(5), C(5)–C(6) 1.355(6), C(6)–C(7) 1.411(6), C(7)–C(8) 1.354(5), C(8)–C(9) 1.422(4).

alternation in the seven-membered ring (1.355–1.422 Å), consistent with a heptafulvene structure.

The reaction of **4a** with phenylketene failed to give a mesoionic compound, instead three compounds, 4-benzyl-1-ethyl-4-hydroxy-1,2,3,4-tetrahydro-1,10-diazabenz[*a*]azulen-2-one **6a** (11%), 2-ethylamino-3-phenylacetyl-1-azaazulene **7a** (43%) and 4-benzyl-1-ethyl-1,2-dihydro-1,10-diazabenz[*a*]-azulen-2-one **8a** (13%) were obtained. Structural assignments were made on the basis of spectroscopic evidence as well as elemental analyses. In the ^{1}H NMR spectrum of **7a**, the NH proton appears at δ 7.47 but there is no H-3 signal; the seven-membered ring protons appearing in the region expected, it is concluded that the phenylacetyl group is at C-3 of the 1-azaazulene ring. Compounds **6a** and **8a** are 1:2-adducts of **4a** and phenylketene from the evidence of their elemental analyses and mass spectra. Treatment of **7a** with phenylketene gave **6a** (10%) and **8a** (13%) along with recovered **7a** (12%). This shows that compounds **6a** and **8a** are secondary products produced from **7a** and phenylketene. In the ^{1}H NMR spectrum of **6a**, there are two AB doublets at δ 3.18 and 3.30 (J 13.4, benzylic H), a singlet at δ 4.18 (methine H), a broad singlet at δ 6.75; signals for the protons of the phenyl group and seven-membered ring appear in the expected range. In the IR

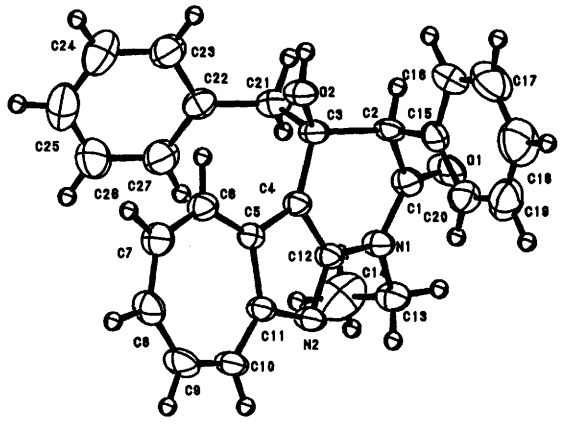


Fig. 2 ORTEP drawing of **6a** with thermal ellipsoid plot (50% probability)

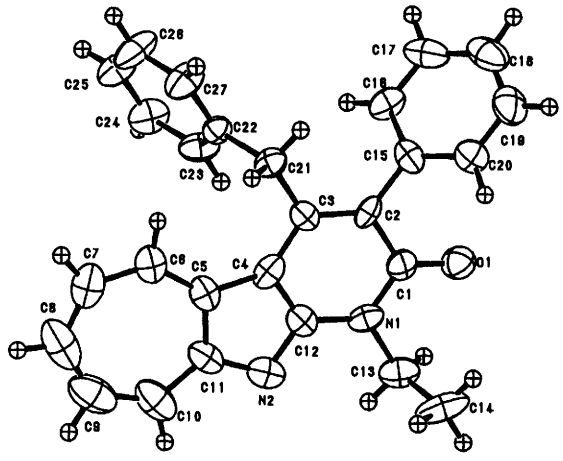


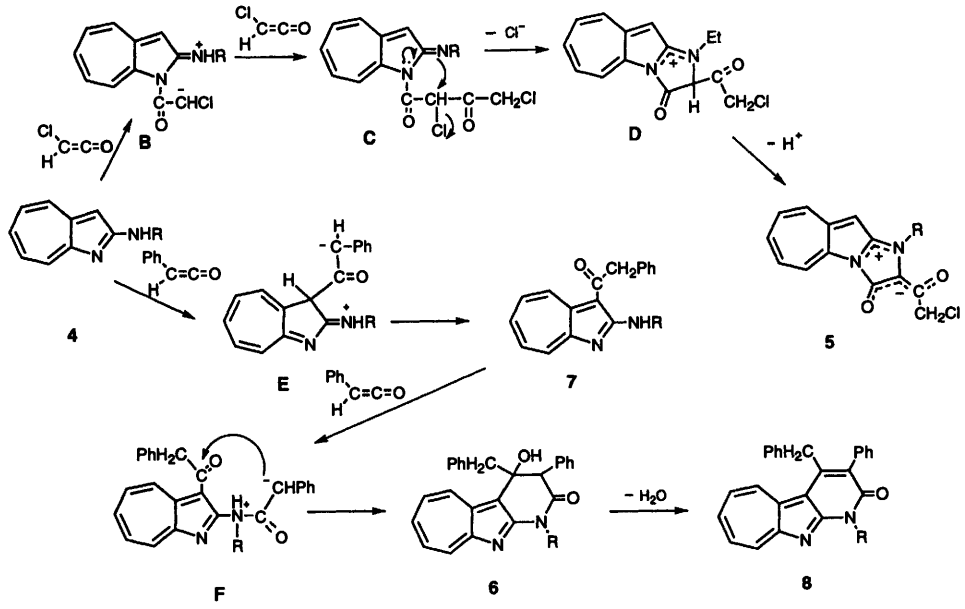
Fig. 3 ORTEP drawing of **8a** with thermal ellipsoid plot (50% probability)

spectrum of **6a**, OH and carbonyl absorption appears at 3340 and 1644 cm^{-1}, respectively, although for **8a** there is a carbonyl (at 1634 cm^{-1}) and no OH absorption. In its ^{1}H NMR spectrum **8a** showed a 2 H singlet at δ 4.39 (benzylic H) to lower field than the corresponding resonance for **6a**. Structures **6a** and **8a** were assigned on the basis of this spectral evidence and were finally confirmed by single-crystal X-ray structural analysis (Figs. 2 and 3).

A plausible mechanism for the described reaction is shown in Scheme 4 in which chloroketene reacts with **4** initially at N-1 to give the dipolar species **B**, followed by successive addition of a further molar equivalent of chloroketene to **B** to give **C**. Intramolecular S_N2 reaction of **C** leads to a cyclized intermediate **D**, successive deprotonation of which furnishes **5**. Initially, attack of phenylketene on **4** at C-3 would give **7** *via* the dipolar species **E**. Further attack of phenylketene on the amino group of **7** gives **F**, the successive cyclization of which gives **6**; dehydration of this then affords **8**. In reactions of 2-amino-1-azaazulenes, it is known that acetylation with acetic anhydride, considered a hard acid, occurs at the amino group,[20] whilst alkylation with phenacyl bromide, considered a soft acid, occurs at N-1;[29] thiocyanation with bromothiocyanate, considered a softer acid, occurs at C-3.[30] From these considerations, it is reasonable to assume that initially attack of the harder chloroketene occurs at the amino group with attack of the softer phenylketene occurring at C-3.

Similarly, 2-isopropylamino-1-azaazulene **4b** reacted with chloroketene to give **5b** (41%), and with phenylketene to give **6b** (13%), **7b** (32%) and **8b** (16%).

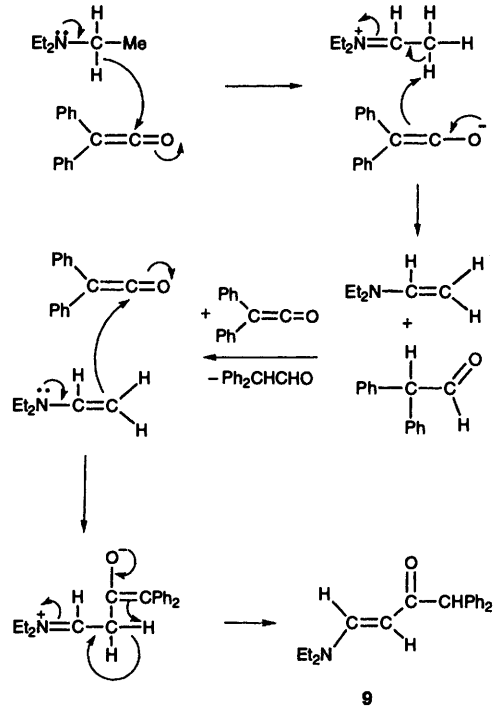
Treatment of diphenylketene with **4a** and **4b** gave no cycloadduct but 2-diethylamino-3-diphenylacetyl-1-azaazulene **7c** (70%) and 2-diisopropylamino-3-diphenylacetyl-1-azaazulene **7d** (82%).



Scheme 4

Interestingly, when the reaction was carried out in refluxing chloroform, (*E*)-4-diethylamino-1,1-diphenylbut-3-en-2-one **9** (9%) was obtained besides **7c** (47%).

The mass sp4ectrum (*m*/*z* 293, M^+) and elemental analysis of **9** show that it has the molecular formula $C_{20}H_{23}NO$. In its ^1H NMR spectrum, **9** showed two AB doublets at δ 5.16 and 7.64 (*J* 12.8 Hz) together with signals for two ethyl group protons and a diphenylmethyl group; its electronic absorption spectrum shows strong absorption at 318 nm (log ε 4.72), which suggested the presence of a strongly conjugated enone system. Since it was considered that **9** could be formed from diphenylketene and triethylamine, diphenylacetyl chloride was treated with excess triethylamine in refluxing chloroform in the absence of 1-azaazulene; compound **9** was isolated. A plausible reaction mechanism for this reaction is shown in Scheme 5. In particular,



Scheme 5

formation of the enamino ketone by the reaction of ketene is of interest.

Experimental

Melting points are uncorrected. ^1H NMR spectra (250 MHz) were recorded on a Hitachi R-250 H spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an internal standard; *J* values are recorded in Hz. Electronic spectra were taken with a Hitachi 220 A spectrophotometer using ethanol as a solvent. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer for Nujol mulls. Mass spectra were taken with a JEOL JMS-01SG-2 spectrometer. Kieselgel 60 was used for column chromatography.

Reaction of 2-amino-1-azaazulene 1 with chloroketene

To a solution of 2-amino-1-azaazulene **1** (0.577 g, 4.0 mmol) and triethylamine (4.86 g, 48.0 mmol) in dry chloroform (20 ml) was added dropwise over a period of 30 min chloroacetyl chloride (2.71 g, 24.0 mmol) in dry chloroform (10 ml) under argon. After being stirred for 1 h at room temperature, the mixture was poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give 3-chloro-2-chloromethyl-4,4a-dihydro-1,4a-diazabenz[*a*]azulen-4-one **2a** (0.358 g, 34%) as brown needles (from ethanol–dichloromethane), mp 256–258 °C; δ_H 4.78 (2 H, s), 6.95 (1 H, s), 7.20–7.45 (5 H, m), 7.89 (1 H, d, *J* 11.0) and 9.80–9.85 (1 H, m); ν_{max}/cm^{-1} 1680 (C=O); λ_{max}/nm (log ε) 259 (4.50), 270 (4.43, sh), 288 (4.20, sh), 300 (4.10, sh), 406 (4.04), 430 (4.06), 500 (3.79), 520 (3.79), 565 (3.64, sh) and 615 (3.17, sh) (Found: C, 55.7; H, 3.0; N, 9.8. Calc. for $C_{13}H_8N_2OCl_2$: C, 55.9; H, 2.9; N, 10.0%).

Reaction of 1 with phenylketene

To a solution of **1** (0.432 g, 3.0 mmol) and triethylamine (3.64 g, 36.0 mmol) in dry chloroform (20 ml) was added dropwise over a period of 30 min phenylacetyl chloride (2.78 g, 18.0 mmol) in dry chloroform (10 ml) under argon. After being stirred for 1 h at room temperature, the mixture was poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give 2-benzyl-3-phenyl-4,4a-dihydro-1,4a-diazabenz[*a*]azulen-4-one **2b** (0.113 g, 10%) and 2-phenylacetylamino-1-azaazulene **3** (0.251 g, 32%), successively.

Compound **2b**: brown needles (from hexane–dichloromethane), mp 247–248 °C; δ_H 3.99 (2 H, s), 6.87 (1 H, s), 7.00–7.60 (13 H, m), 7.79 (1 H, d, *J* 9.8) and 9.70–9.75 (1 H, m); ν_{max}/cm^{-1}

1680 (C=O); λ_{max}/nm (log ε) 259 (4.50), 294 (4.16), 304 (4.15, sh), 409 (4.02), 430 (4.03), 492 (3.73), 520 (3.70), 564 (3.51, sh) and 613 (3.05, sh); *m/z* (rel. intensity) 362 (M^+, 100), 361 (77) and 242 (15) (Found: C, 82.6; H, 5.2; N, 7.5. Calc. for $C_{25}H_{18}N_2O$: C, 82.9; H, 5.0; N, 7.7%).

Compound **3**: orange needles (from hexane), mp 153–154 °C; δ_H 3.81 (2 H, s), 7.20–7.40 (5 H, m), 7.50–7.75 (3 H, m), 7.87 (1 H, s), 8.24 (1 H, d, *J* 10.4), 8.38 (1 H, d, *J* 9.8) and 9.50–9.70 (1 H, br); ν_{max}/cm^{-1} 1702 (C=O); λ_{max}/nm (log ε) 232 (4.31), 272 (4.77, sh), 279 (4.83), 304 (4.50), 335 (4.01), 350 (4.11), 364 (3.83, sh), 457 (3.48), 475 (3.44, sh) and 510 (3.05, sh); *m/z* (rel. intensity) 262 (M^+, 56), 143 (72), 116 (30) and 91 (100) (Found: C, 77.6; H, 5.5; N, 10.7. Calc. for $C_{17}H_{14}N_2O$: C, 77.8; H, 5.4; N, 10.9%).

Reaction of 2-ethylamino-1-azaazulene 4a and 2-isopropylamino-1-azaazulene 4b with chloroketene

To a solution of 2-ethylamino-1-azaazulene **4a** (0.780 g, 4.53 mmol) and triethylamine (5.504 g, 54.4 mmol) in dry chloroform (20 ml), chloroacetyl chloride (3.07 g, 27.2 mmol) in dry chloroform (10 ml) was added dropwise over a period of 30 min under argon. After being stirred for 1 h at room temperature, the mixture was poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give *anhydro*-2-chloroacetyl-1-ethyl-3-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide **5a** (0.476 g, 36%).

In a similar manner, the reaction of 2-isopropylamino-1-azaazulene **4b** with chloroketene gave *anhydro*-2-chloroacetyl-1-isopropyl-3-hydroxy-1,3a-diazacyclopent[*a*]azulenium hydroxide **5b** (41%).

Compound **5a**: brown prisms (from hexane–dichloromethane), mp 202–203 °C (decomp.); δ_H 1.46 (3 H, t, *J* 7.0), 4.53 (2 H, q, *J* 7.0), 4.82 (2 H, s), 6.45 (1 H, s), 7.20–7.40 (3 H, m), 7.77 (1 H, d, *J* 11.0) and 8.71 (1 H, d, *J* 8.5); ν_{max}/cm^{-1} 1672, 1612 (C=O) and 1596 (C=C); λ_{max}/nm (log ε) 262 (4.29), 320 (4.20) and 468 (4.07); *m/z* (rel. intensity) 290 (M^+, 16), 288 (M^+, 47) and 155 (100) (Found: C, 62.6; H, 4.7; N, 9.4. Calc. for $C_{15}H_{13}N_2O_2Cl$: C, 62.4; H, 4.5; N, 9.7%).

Compound **5b**: brown prisms (from hexane–dichloromethane), mp 202–204 °C (decomp.); δ_H 1.59 (6 H, d, *J* 6.6), 4.85 (2 H, s), 5.99 (1 H, sep, *J* 6.6), 6.53 (1 H, s), 7.15–7.40 (3 H, m), 7.77 (1 H, dm, *J* 11.0) and 8.78 (1 H, d, *J* 8.5); ν_{max}/cm^{-1} 1668, 1604 (C=O) and 1596 (C=C); λ_{max}/nm (log ε) 260 (4.46), 320 (4.34) and 468 (4.18); *m/z* (rel. intensity) 304 (M^+, 9), 303 (19), 302 (M^+, 42), 260 (30) and 155 (100) (Found: C, 63.2; H, 5.0; N, 9.2. Calc. for $C_{16}H_{15}N_2O_2Cl$: C, 63.5; H, 5.0; N, 9.3%).

Reaction of 4a and 4b with phenylketene

(a) To a solution of **4a** (0.690 g, 4.00 mmol) and triethylamine (4.86 g, 48.0 mmol) in dry chloroform (20 ml), phenylacetyl chloride (3.71 g, 24.0 mmol) in dry chloroform (10 ml) was added dropwise over a period of 30 min under argon. After being stirred for 1 h at room temperature, the mixture was poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give 4-benzyl-1-ethyl-4-hydroxy-1,2,3,4-tetrahydro-1,10-diazabenz[*a*]azulen-2-one **6a** (0.186 g, 11%), 2-ethylamino-3-phenylacetyl-1-azaazulene **7a** (0.495 g, 43%), 4-benzyl-1-ethyl-1,2-dihydro-1,10-diazabenz[*a*]azulen-2-one **8a** (0.196 g, 13%) and recovered **4a** (0.112 g, 16%), successively.

In a similar manner, the reaction of **4b** (0.800 g) with phenylketene (from 0.800 g of phenylacetyl chloride and 0.522 g of triethylamine) gave 4-benzyl-4-hydroxy-1-isopropyl-1,2,3,4-tetrahydro-1,10-diazabenz[*a*]azulen-2-one **6b** (0.231 g, 13%), 2-isopropylamino-3-phenylacetyl-1-azaazulene **7b** (0.418 g, 32%), 4-benzyl-1-isopropyl-1,2-dihydro-1,10-diazabenz[*a*]azulen-2-one **8b** (0.278 g, 16%) and **4b** (0.132 g, 17%).

(b) To a solution of **4a** (0.690 g, 4.00 mmol) and triethylamine (4.86 g, 48.0 mmol) in dry chloroform (20 ml), phenylacetyl chloride (3.71 g, 24.0 mmol) in dry chloroform (10 ml) was added dropwise over a period of 30 min under argon. The mixture was refluxed for 1 h, and then poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give **6a** (0.469 g, 29%), **8a** (0.448 g, 29%) and recovered **4a** (0.150 g, 22%), successively.

Compound **6a**: orange prisms (hexane–dichloromethane), mp 186–187 °C; δ_H 1.21 (3 H, t, *J* 7.3), 3.18 (1 H, d, *J* 13.4), 3.30 (1 H, d, *J* 13.4), 4.12 (1 H, dq, *J* 6.7 and 7.3), 4.18 (1 H, s), 4.23 (1 H, dq, *J* 6.7 and 7.3), 6.75 (1 H, br), 6.82 (2 H, d, *J* 6.7), 7.00–7.30 (9 H, m), 7.45–7.65 (2 H, m), 8.23 (1 H, d, *J* 10.4) and 8.35 (1 H, d, *J* 10.4); ν_{max}/cm^{-1} 3340 (OH) and 1644 (C=O); λ_{max}/nm (log ε) 285 (4.35), 296 (4.38), 305 (4.33), 344 (3.48), 360 (3.51), 464 (3.25), 485 (3.20, sh) and 520 (2.82, sh) (Found: C, 79.6; H, 6.1; N, 6.7. Calc. for $C_{27}H_{24}N_2O_2$: C, 79.4; H, 5.9; N, 6.9%).

Compound **7a**: orange needles (hexane–dichloromethane), mp 90–91 °C; δ_H 1.32 (3 H, t, *J* 7.3), 4.20 (2 H, s), 4.28 (2 H, q, *J* 7.3), 7.15–7.35 (5 H, m), 7.47 (1 H, br s), 7.50–7.75 (3 H, m), 8.35 (1 H, d, *J* 9.8) and 8.42–8.48 (1 H, m); ν_{max}/cm^{-1} 1690 (C=O); λ_{max}/nm (log ε) 246 (4.20, sh), 275 (4.57, sh), 282 (4.60), 305 (4.31), 344 (3.89, sh), 354 (3.90) and 465 (3.35) (Found: C, 78.60; H, 6.36; N, 9.26. Calc. for $C_{19}H_{18}N_2O$: C, 78.60; H, 6.25; N, 9.65%).

Compound **8a**: red prisms (hexane–dichloromethane), mp 224–225 °C; δ_H 1.55 (3 H, t, *J* 7.0), 4.39 (2 H, s), 4.58 (2 H, q, *J* 7.0), 7.10–7.40 (10 H, m), 7.49 (1 H, t, *J* 10.4), 7.73 (1 H, dd, *J* 10.4 and 9.8), 7.83 (1 H, dd, *J* 10.4 and 9.8), 8.42 (1 H, d, *J* 9.8) and 8.65 (1 H, d, *J* 9.8); ν_{max}/cm^{-1} 1634 (C=O); λ_{max}/nm (log ε) 322 (4.73), 342 (4.27, sh), 365 (3.88), 408 (3.42) and 488 (3.55) (Found: C, 83.4; H, 5.8; N, 6.9. Calc. for $C_{27}H_{22}N_2O$: C, 83.1; H, 5.7; N, 7.2%).

Compound **6b**: orange prisms (hexane–dichloromethane), mp 180–182 °C; δ_H 1.50 (6 H, d, *J* 6.7), 3.18 (1 H, d, *J* 13.4), 3.32 (1 H, d, *J* 13.4), 4.13 (2 H, s), 5.36 (1 H, sep, *J* 6.7), 6.70 (1 H, br), 6.85 (2 H, d, *J* 6.7), 7.00–7.40 (9 H, m), 7.70 (1 H, t, *J* 9.8), 7.80 (1 H, t, *J* 9.8), 8.22 (1 H, d, *J* 9.8) and 8.30 (1 H, d, *J* 9.8); ν_{max}/cm^{-1} 3340 (OH) and 1644 (C=O) (Found: C, 79.6; H, 5.9; N, 7.0. Calc. for $C_{28}H_{26}N_2O_2$: C, 79.6; H, 6.2; N, 6.6%).

Compound **7b**: red needles (hexane–dichloromethane), mp 94–95 °C; δ_H 1.25 (6 H, d, *J* 6.7), 3.64 (2 H, s), 5.07 (1 H, sep, *J* 6.7), 7.00–7.25 (6 H, m), 7.69 (1 H, t, *J* 9.8), 7.82 (1 H, t, *J* 9.8), 7.91 (1 H, t, *J* 9.8), 8.49 (1 H, d, *J* 9.8) and 8.67 (1 H, d, *J* 9.8); ν_{max}/cm^{-1} 1652 (C=O) (Found: C, 79.0; H, 6.6; N, 9.0. Calc. for $C_{20}H_{20}N_2O$: C, 78.9; H, 6.6; N, 9.2%).

Compound **8b**: red prisms (hexane–dichloromethane), mp 145–146 °C; δ_H 1.81 (6 H, t, *J* 6.7), 4.36 (2 H, s), 5.97 (1 H, sep, *J* 6.7), 7.10–7.40 (10 H, m), 7.46 (1 H, t, *J* 9.8), 7.73 (1 H, t, *J* 9.8), 7.80 (1 H, dd, *J* 10.4 and 9.8), 8.41 (1 H, d, *J* 10.4) and 8.61 (1 H, d, *J* 9.8); ν_{max}/cm^{-1} 1638 (C=O) (Found: C, 83.0; H, 6.4; N, 6.6. Calc. for $C_{28}H_{24}N_2O$: C, 83.1; H, 6.0; N, 6.9%).

Reaction of 7a with phenylketene

To a solution of **7a** (0.360 g, 1.24 mmol) and triethylamine (1.51 g, 14.9 mmol) in dry chloroform (20 ml), phenylacetyl chloride (1.15 g, 7.44 mmol) in dry chloroform (10 ml) was added dropwise over a period of 30 min under argon. The mixture was refluxed for 1 h, and then poured into ice–water (200 ml) and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give **6a** (0.051 g, 10%), recovered **7a** (0.042 g, 12%) and **8a** (0.063 g, 13%), successively.

Reaction of 4a and 4b with diphenylketene

(a) To a solution of **4a** (0.515 g, 3.00 mmol) and triethylamine (3.659 g, 36.1 mmol) in dry chloroform (20 ml) was added diphenylacetyl chloride (4.154 g, 18.0 mmol) in dry chloroform (10 ml) dropwise over a period of 30 min. After being stirred for 1 h at room temperature, the mixture was poured into ice–water

(200 ml) and extracted with dichloromethane. The extract was washed with 1 M aqueous sodium hydroxide and brine, dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give 2-ethylamino-3-diphenylacetyl-1-aza-azulene **7c** (0.764 g, 70%).

In a similar manner, the reaction of **4b** (0.559 g, 3.00 mmol) with diphenylketene (from 4.115 g of diphenylacetyl chloride and 3.656 g of triethylamine) gave 2-isopropylamino-3-diphenylacetyl-1-azaazulene **7d** (0.937 g, 82%).

(b) To a solution of **4a** (0.515 g, 3.00 mmol) and triethylamine (3.632 g, 36.0 mmol) in dry chloroform (20 ml) was added diphenylacetyl chloride (4.154 g, 18.0 mmol) in dry chloroform (10 ml) dropwise over a period of 30 min. After being heated under reflux for 1 h at room temperature, the mixture was worked up as above. The residue was chromatographed with chloroform to give 2-ethylamino-3-diphenylacetyl-1-azaazulene **7c** (0.513 g, 47%) and **9** (0.049 g, 9%).

Compound **7c**: orange needles (hexane–dichloromethane), mp 137.5–139.5 °C; δ_H 1.35 (3 H, t, *J* 7.3), 4.30 (2 H, br q, *J* 7.3), 5.80–6.15 (1 H, br), 7.10–7.40 (11 H, m), 7.50–7.75 (3 H, m), 8.31 (1 H, d, *J* 9.8) and 8.42–8.48 (1 H, m); ν_{max}/cm^{-1} 1662 (C=O); λ_{max}/nm (log ε) 282 (4.54), 310 (4.24, sh), 342 (3.82), 354 (3.86) and 464 (3.31) (Found: C, 81.6; H, 6.2; N, 7.5. Calc. for $C_{25}H_{22}N_2O$: C, 81.9; H, 6.1; N, 7.6%).

Compound **7d**: red needles (hexane–dichloromethane), mp 142–144 °C; δ_H 1.24 (6 H, d, *J* 6.7), 5.10 (1 H, sep, *J* 6.7), 5.19 (1 H, s), 6.81 (1 H, s), 7.10–7.25 (10 H, m), 7.66 (1 H, t, *J* 9.8), 7.82 (1 H, t, *J* 9.8), 7.90 (1 H, t, *J* 9.8), 8.39 (1 H, d, *J* 9.8) and 8.69 (1 H, d, *J* 9.8); ν_{max}/cm^{-1} 1652 (C=O); λ_{max}/nm (log ε) 272 (4.54), 330 (3.76) and 474 (3.16) (Found: C, 81.8; H, 6.5; N, 7.3. Calc. for $C_{26}H_{24}N_2O$: C, 82.1; H, 6.4; N, 7.4%).

Compound **9**: pale yellow prisms (hexane–dichloromethane), mp 94–95 °C; δ_H 1.00–1.25 (6 H, m), 3.05–3.35 (4 H, m), 5.04 (1 H, s), 5.16 (1 H, d, *J* 12.8), 7.15–7.40 (10 H, m) and 7.64 (1 H, d, *J* 12.8); ν_{max}/cm^{-1} 1660 (C=O) and 1564 (C=C); λ_{max}/nm (log ε) 318 (4.72); *m/z* (rel. intensity) 293 (M^+, 6), 165 (100) and 128 (47) (Found: C, 82.2; H, 8.0; N, 4.9. Calc. for $C_{20}H_{23}NO$: C, 81.9; H, 7.9; N, 4.8%).

Heating of diphenylketene with triethylamine

To a solution of triethylamine (1.821 g, 18.0 mmol) in dry chloroform (10 ml) was added diphenylacetyl chloride (2.052 g, 9.0 mmol) in dry chloroform (5 ml) dropwise over a period of 30 min. After being heated under reflux for 1 h at room temperature, the mixture was poured into ice–water (100 ml) and extracted with dichloromethane. The extract was washed with 1 M aqueous sodium hydroxide and brine, dried (Na_2SO_4) and evaporated. The residue was chromatographed with chloroform to give **9** (0.142 g, 6%).

X-Ray structure determinations

Crystal data for 2a. Brown prism, $C_{15}H_{13}N_2O_2Cl$, M = 288.73, monoclinic, space group $P2_1/n$, a = 7.678(4), b = 11.717(2), c = 14.920(3) Å, β = 93.86(2)°, V = 1339.1(7) Å^3, Z = 4, D_c = 1.432 g cm^{-3}, crystal dimensions 0.24 × 0.32 × 0.80 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total of 3459 reflections (3225 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using 1455 observed reflections [$I > 3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final R and R_w values were 0.046 and 0.049. The maximum peak and minimum peak in the final difference map were 0.19 e Å^{-3} and −0.27 e Å^{-3}.

Crystal data for 6a. Orange prism, $C_{27}H_{24}N_2O_2$, M = 408.50, monoclinic, space group $P2_1/a$, a = 10.157(3), b = 20.838(3), c = 10.617(4) Å, β = 102.25(3)°, V = 2196(1) Å^3, Z = 4, D_c = 1.235 g cm^{-3}, crystal dimensions 0.20 × 0.52 × 0.58 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total of 5468 reflections (5187 unique) were collected using the ω-2θ scan technique to a maximum 2θ value of 55.0°. The structure was solved by direct methods and refined by full-matrix least-squares method using 2418 observed reflections [$I > 3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final R and R_w values were 0.051 and 0.055. The maximum peak and minimum peak in the final difference map were 0.22 e Å^{-3} and −0.32 e Å^{-3}.

Crystal data for 8a. Red needle, $C_{27}H_{22}N_2O$, M = 390.48, orthorhombic space group *Pbca*, a = 22.11(3), b = 23.58(2), c = 8.140(8) Å, V = 4244(5) Å^3, Z = 8, D_c = 1.222 g cm^{-3}, crystal dimensions 0.08 × 0.18 × 0.88 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total of 8345 reflections (4479 unique) were collected using the ω–2θ scan technique to a maximum 2θ value of 54.8°. The structure was solved by direct methods and refined by a full-matrix least-squares method using 1030 observed reflections [$I > 3.00\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. The weighting scheme $\omega = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final R and R_w values were 0.068 and 0.092. The maximum peak and minimum peak in the final difference map were 0.22 e Å^{-3} and −0.27 e Å^{-3}.

Atomic coordinations, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Centre and are available on request.† Any such request should be accompanied by a full bibliographic reference for this paper together with the reference no. 207/44.

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† For details see Instructions for Authors (1996), *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

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