159. Synthesis of 1,2-Five-Ring-Annellated Barrelenes *via* the Intramolecular *Diels-Alder* Reaction of Acetylenic Derivatives

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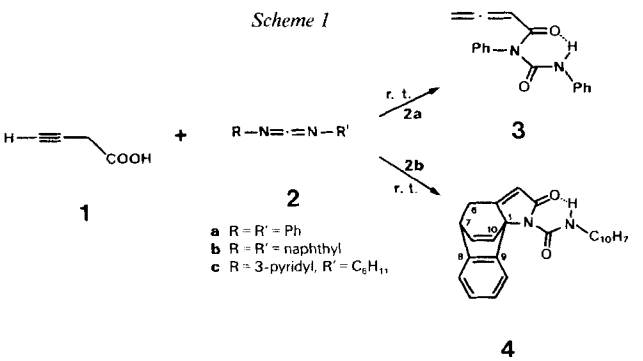
The intramolecular *Diels-Alder* reaction conducted with acetylenic acylureas, obtained from carbodiimides, and the acetylenic acid **5** and its derivatives **13** gave the 1,2-annellated barrelene **14** (from **13a**) and the benzobarrelenes **8** (from **5**) and **15** (from **13b**); in the case of 3-butynoic acid (**1**), [1,3]-H shifts were observed. The formation of the azabarrelenes **16** (from **13c**) as an intermediate is postulated which looses HCN to afford the indolinone **17**. The acylureas **6** and **9** underwent isocyanate cleavage instead of [4 + 2] cyclization.

Intramolecular *Diels-Alder* reactions employing acetylenes as dienophiles have received considerable attention [1–6]. The intermolecular version of this reaction has also been employed for the preparation of barrelenes (=bicyclo[2.2.2]octa-2,5,7-trienes) [7] [8] and of benzobarrelenes (=1,4-dihydro-1,4-ethenonaphthalenes) [9]. Not long ago, we reported the [4 + 2] cycloaddition of allenic acylureas and -amides proceeding under surprisingly mild conditions [10]. The known similarity in reactivity of allenes and acetylenes [11] led us to examine the utility of this approach in the synthesis of barrelenes.

Treatment of 3-butynoic acid (**1**) with the carbodiimides **2a, b** afforded at room temperature, the allenic acylurea **3** and the benzofused tricyclic compound **4**, respectively *(Scheme 1)*. The isolation of **4** rather than of the expected barrelene derivative (double

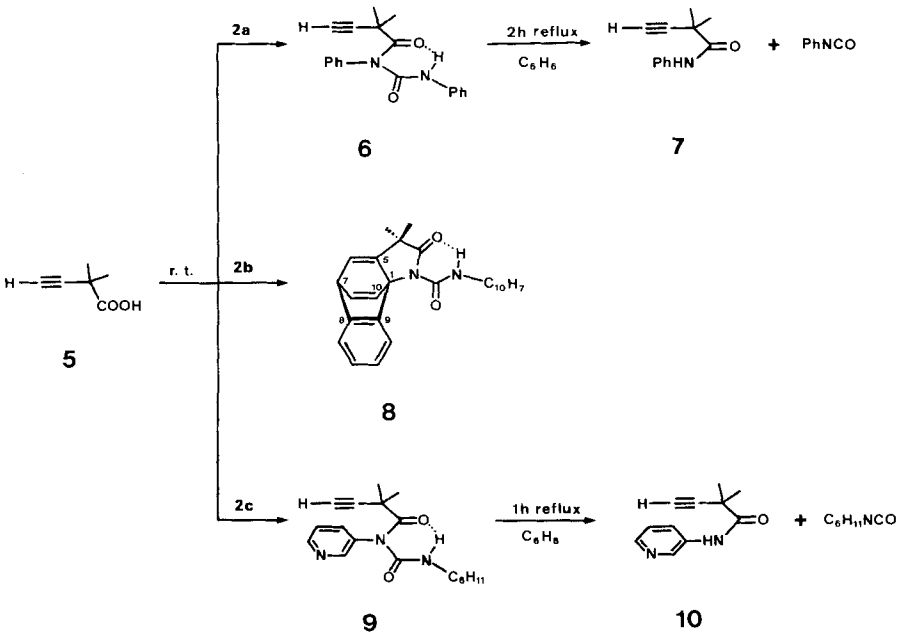
Scheme 1



bond between C(5) and C(6)) can be easily explained with the [1,3]-H shift leading to the conjugated double bond in **4**. However, another route to **4** *via* the naphthalene derivative analogous to **3** is also feasible. On the grounds of the presently available data, a choice between the two cannot be made.

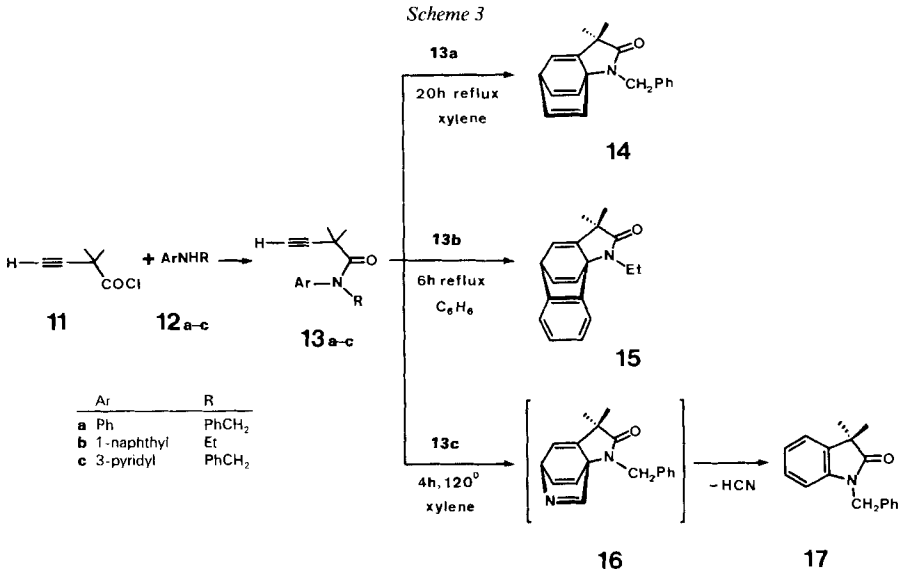
As more suitable model systems were chosen the derivatives of the 2,2-dimethyl-3-butynoic acid (**5**) in which the acetylene→allene rearrangement is precluded. Thus,

Scheme 2



treating **5** with carbodiimides **2a, c** gave the acetylenic acylureas **6** and **9**, respectively *(Scheme 2)*. Refluxing the latter in benzene produced the corresponding acetylenic amides **7** and **10**, and not the desired barrelenes; the latter failed to form even on prolonged reflux in xylene of **7** and **10**. In order to obtain a more reactive aromatic diene for the [4 + 2] reaction, we employed dinaphthylcarbodiimide **2b**. The barrelene **8** was formed in this case, as expected, even at room temperature.

Scheme 3



The structure of the barrelene **8** is supported by the signal for H–C(7) (*td* at 5.00 ppm, J = 5.8, 1.3) in the ^{1}H-NMR spectrum and by the signals for C(1) (75.2 ppm) and C(7) (48.7 ppm) in the ^{13}C-NMR spectrum.

The failure of the acetylenic acylureas **6** and **9** to cyclize led us to the use of the *N*-arylamides **13** as starting compounds in the intramolecular cyclization to barrelenes. Heating **13a, b** gave the barrelene **14** and the benzobarrelene **15**, respectively *(Scheme 3)*. These two compounds showed similar spectral characteristics to the ones of **8** (see *Exper. Part*).

The attempt to synthesize in a similar way the azabarrelene **16** from the amide **13c** was unsuccessful, the reaction product being the 2-indolinone **17** resulting from the *retro-Diels-Alder* cleavage of HCN from the likely intermediate **16**.

Experimental Part

General. See [10].

1. Reaction of 3-Butynoic Acid (1) with Carbodiimides 2a, b. – A soln. of **1** [12] (1 mmol) and *N,N*-diphenyl- or *N,N*-di(1-naphthyl)carbodiimide (**2a** or **2b**, resp., 1.2 mmol) in dry benzene (2 ml) was kept at r. t. for 2 or 4 days, resp. The mixture was subjected to prep. TLC (5 plates) with petroleum ether/Et_2O/$CHCl_3$ 65:27:8. The UV (254 nm)-active zone was eluted with $CHCl_3$, the solvent evaporated, and the oily residue recrystallised from benzene/hexane to give pure **3** (33%) or **4** (26%), resp.

N-(2,3-Butadienoyl)-N,N'-diphenylurea (**3**). M.p. 115–116.5° (dec.). IR ($CHCl_3$): 3230*m*, 3180*m*, 3135*m*, 3030*m* (br.), 1965*s*, 1930*m*, 1715*s*, 1640*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 11.58 (*s*, NH); 7.60–7.45 (*m*, 5 arom. H); 7.40–7.20 (*m*, 4 arom. H); 7.10 (*t*, J = 7.4, arom. H); 5.51 (*t*, J = 6.3, H–C(2)); 5.28 (*d*, J = 6.3, CH_2(4)). MS: 278 (16, M^+), 159 (100, M^+ – PhNCO), 130 (28), 119 (70, $PhNCO^+$), 94 (90). HR-MS: 278.1042 ($C_{17}H_{14}N_2O_2$, calc. 278.1025).

(1RS,7SR)-2-[N-(1-Naphthyl)carbamoyl]-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one (**4**). M.p. 191–194.5°. IR ($CHCl_3$): 3220*m* (br.), 3020*m* (br.), 1715*s*, 1680*m*, 1640*m* (sh), 1630*m*, 1560*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 11.60 (*s*, NH); 8.41 (*d*, J = 7.7, H–C(8')); 8.25 (*d*, J = 8.3, H–C(5')); 7.91 (*d*, J = 8.3, H–C(4')); 7.7–7.5 (*m*, 4 arom. H); 7.3–7.1 (*m*, 4 arom. H); 6.8–6.6 (*m*, H–C(10), H–C(11)); 5.96 (br. *s*, H–C(7)); 2.70, 2.53 (*AB*, J = 17.8, CH_2 (6)): MS: 378 (4, M^+), 209 (39, M^+ – $C_{10}H_7NCO$), 180 (32), 169 (100, $C_{10}H_7NCO^+$), 141 (22, 140 (21).

2. Reaction of 2,2-Dimethyl-3-butynoic Acid (5) with Carbodiimides 2a–c. – A soln. of **5** (3 mmol) and **2a**, **2b**, or **2c** (3.5 mmol) in dry benzene (3 ml) was kept at r.t. for 20 h, 4 days or 3 days, resp. Evaporation of the solvent in the first case and recrystallisation of the residue from hexane gave pure **6** (67%). In the case of **2b**, the mixture was subjected directly to column chromatography on silica gel with petroleum ether/Et_2O/CH_2Cl_2 70:23:7. The fraction containing **8** was evaporated and the red oily residue recrystallised from petroleum ether/Et_2O to afford pure **8** (23%) as colourless needles. In the case of **2c**, the crystals formed were filtered off and washed with benzene/hexane 1:1 yielding **9**. The mother liquor was evaporated and the residue chromatographed on 7 prep. TLC plates with petroleum ether/(i-Pr)$_2$O/2-butanone/AcOEt 61:13:13:13. The product eluted from the UV (254 nm)-active zone at R_f 0.3 was recrystallised from hexane/Et_2O to give an additional amount of **9** (total 49%).

N-(2,2-Dimethyl-3-butynoyl)-N,N'-diphenylurea (**6**). M.p. 106.5–108°. IR ($CHCl_3$): 3415*w*, 3300*m*, 3225*w*, 3175*w*, 2980*w*, 2930*w*, 2860*w*, 1705*s*, 1645*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 10.79 (*s*, NH); 7.52 (*d*, J = 8.1, 2 H); 7.50–7.35 (*m*, 5 arom. H); 7.30 (*t*, J = 8.4, 2 arom. H); 7.09 (*t*, J = 7.4, arom. H_p); 2.07 (*s*, H–C(4)); 1.51 (*s*, 2 CH_3). MS: 306 (20, M^+), 212 (8), 211 (10), 187 (53, M^+ – PhNCO), 120 (33), 119 (100, $PhNCO^+$), 93 (33), 92 (31), 91 (59), 77 (40), 68 (68), 67 (73, $C_5H_7^+$).

(1RS, 7SR)-4,4-Dimethyl-2-[N-(1-naphthyl)carbamoyl]-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-5,8,10-trien-3-one (**8**). M.p. 212–213° (dec.). IR ($CHCl_3$): 3400*w*, 3220*m* (br.), 3050*w*, 2960*m*, 2920*w*, 1715*s*, 1685*m*, 1625*m*, 1550*s* (br.). ^{1}H-NMR (250 MHz, $CDCl_3$): 11.76 (*s*, NH); 8.43 (*d*, J = 7.8, H–C(8')); 8.22 (*d*, J = 8.2, H–C(5')); 7.91 (*d*, J = 7.9, H–C(4')); 7.75–7.50 (*m*, 4 arom. H); 7.30–7.20 (*m*, 3 arom. H); 7.00–6.95 (*m*, H–C(10), H–C(11), 1 arom. H); 6.65 (*d*, J = 5.8, H–C(6)); 5.00 (*td*, J = 5.8, 1.3, H–C(7)); 1.40 (*s*, CH_3); 1.22 (*s*, CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 183.0 (*s*, C(3)); 154.0 (*s*, C(5)); 150.2 (*s*, C(1')); 145.2, 145.0 (2*s*, C(8), C(9)); 138.9, 137.7 (2*d*, C(10), C(11)); 134.1, 132.7 (2*s*, C(4a'), C(8a')); 129.3, 128.8, 126.5, 125.9, 124.6, 124.0, 123.6, 121.9, 120.5, 119.4, 117.9 (11*d*, C(6), CH(arom.)); 75.2 (*s*, C(1)); 48.7 (*d*, C(7)); 44.2 (*s*, C(4)); 26.9, 25.9 (2 *q*, 2 CH_3). MS: 406 (38, M^+), 237 (72, M^+ – $C_{10}H_7NCO$), 222 (26), 209 (42), 169 (100, $C_{10}H_7NCO^+$).

N-*Cyclohexyl*-N'-*(2,2-dimethyl-3-butynoyl)*-N'-*(3-pyridyl)urea* (**9**). M.p. 116.5–119°. IR ($CHCl_3$): 3290*m*, 2970*m*, 2915*s*, 2840*m*, 1700*s*, 1647*m*, 1585*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.73 (*d*, *J* = 1.7, H–C(2')); *ca.* 8.7 (br. *s*, NH); 8.63 (*d*, *J* = 3.8, H–C(6')); 7.67 (*dd*, *J* = 7.5, 3.8, H–C(5')); 7.40–7.25 (*m*, H–C(4')); 3.75–3.60 (*m*, HC–N); 2.08 (*s*, H–C(4)); 2.0–1.9 (*m*, 2 H); 1.47 (*s*, 2 CH_3); 1.80–1.20 (*m*, 8 H). MS: 314 (1), 313 (1, $M^{+\cdot}$), 286 (2, $M^{+\cdot}$ – HCN), 232 (4), 224 (4), 209 (6), 188 (100, $M^{+\cdot} - C_6H_{11}NCO$), 173 (11), 161 (33), 121 (80), 97 (16), 94 (26), 68 (74), 67 (98).

3. Thermolysis of 6 and 9. – The acylurea **6** or **9** (0.5 mmol) in dry benzene (2 ml) was refluxed for 2 or 1 h, resp. The solvent was evaporated and the residue recrystallised from hexane to afford **7** (88%) or **10** (54%).

2,2-Dimethyl-N-*phenyl-3-butynamide* (**7**). M.p. 119.5–120.5°. IR ($CHCl_3$): 3385*m*, 3300*m*, 2975*m*, 2935*w*, 2880*w*, 2105*vw*, 1680*s*, 1590*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.51 (*s*, NH); 7.57 (*d*, *J* = 7.7, arom. H_o); 7.33 (*t*, *J* = 8.2, arom. H_m); 7.12 (*t*, *J* = 7.4, arom. H_p); 2.62 (*s*, H–C(4)); 1.56 (*s*, 2 CH_3). MS: 187 (36, $M^{+\cdot}$), 120 (27, $PhNHCO^+$), 119 (37, $PhNCO^+$), 93 (30), 92 (19, $PhNH^+$), 77 (34), 68 (100, $C_5H_8^+$), 67 (66, $C_5H_7^+$).

2,2-Dimethyl-N-*(3-pyridyl)-3-butynamide* (**10**). M.p. 111–114°. IR ($CHCl_3$): 3385*m*, 3295*m*, 2965*m*, 2935*m*, 2865*m*, 2105 *vw*, 1685*s*, 1585*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.62 (br. *s*, H–C(2'), H–C(6')); 8.24 (br. *d*, *J* = 8.0, H–C(4'), H–C(5')); *ca.* 7.55 (br. *s*, NH); 2.65 (*s*, H–C(4)); 1.60 (*s*, 2 CH_3). HR-MS: 188.0959 ($C_{11}H_{12}N_2O$, calc. 188.0950).

4. Amides 13a–c. – To a soln. of **12** (20 mmol in the case of **12a, b** and 10 mmol in the case of **12c**) in dry Et_2O (50 ml) was added **11** [13] (10 mmol) in dry Et_2O (5 ml) at 0°. After stirring for 5 h at r.t., H_2O was added and the Et_2O layer washed with dil. HCl soln., H_2O and dil. $NaHCO_3$ soln. (for **13a, b**) or with dil. $NaHCO_3$ soln. and H_2O (for **13c**), dried (Na_2SO_4), and the solvent evaporated. The residue **13a** was recrystallised from petroleum ether/Et_2O to give pure product (81%). The residue **13b** (78%) was an oil (pure by TLC and spectroscopy) and used without further purification. The residue **13c** was chromatographed on 12 prep. TLC plates with petroleum ether/2-butanone/AcOEt/Et_3N 65:14:14:7. The UV(254 nm)-active zone at R_f 0.3 was eluted with $CHCl_3$ to give, after evaporation of the solvent, **13c** (27%) as an oil which was not further purified.

3-(Benzylamino)pyridine (**12**). To a soln. of 3-(benzylidenamino)pyridine [14] (18.6 g, 0.1 mol) in abs. MeOH (100 ml) was added $NaBH_4$ (4.0 g, 0.11 mol) at 0°. After stirring at r.t. overnight, the solvent was evaporated, the residue dissolved in H_2O and extracted with Et_2O (2 × 100 ml). The Et_2O layer was washed with H_2O, dried (Na_2SO_4), and the solvent evaporated. The residue was recrystallised from petroleum ether/Et_2O to give **12c** (15 g, 75%) as colourless prisms. M.p. 88–89°. IR ($CHCl_3$): 3435*m*, 3410*m*, 3050*w*, 2955*m*, 2850*w*, 1580*s*, 1565*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.04 (*d*, *J* = 2.9, H–C(2)); 7.94 (*dd*, *J* = 4.7, 1.3, H–C(6)); 7.35–7.25 (*m*, 5 arom. H); 7.04 (*dd*, *J* = 8.4, 4.7, H–C(5)); 6.84 (*ddd*, *J* = 8.4, 2.9, 1.3, H–C(4)); 4.32 (*s*, CH_2). MS: 184 (47, $M^{+\cdot}$), 91 (100, $C_7H_7^+$), 78 (5), 65 (13). HR-MS: 184.0995 ($C_{12}H_{12}N_2$, calc. 184.1000).

N-*Benzyl-2,2-dimethyl*-N-*phenyl-3-butynamide* (**13a**). M.p. 58–60°. IR ($CHCl_3$): 3295*m*, 2975*m*, 2935*m*, 2865*w*, 2100*vw*, 1630*s*, 1585*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.30–7.15 (*m*, 8 arom. H); 7.15–7.05 (*m*, 2 arom. H); 4.93 (*s*, CH_2); 1.93 (*s*, H–C(4)); 1.49 (*s*, 2 CH_3). MS: 278 (16), 277 (39, $M^{+\cdot}$), 276 (22), 262 (32), 234 (15), 210 (15), 91 (100, $PhCH_2^+$).

N-*Ethyl-2,2-dimethyl*-N-*(1-naphthyl)-3-butynamide* (**13b**). Oil. IR ($CHCl_3$): 3285*m*, 3070*m*, 3020*m*, 2980*w*, 2960*w*, 1630*s*, 1590*m*, 1570*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.95–7.80 (*m*, 3 arom. H); 7.60–7.30 (*m*, 4 arom. H); 4.50, 4.43 (2 *q*, *J* = 7.0, total 2 H, CH_2); 3.12 (br. *s*, H–C(4)); 1.54 (*s*, CH_3); 1.35 (*s*, CH_3); 1.17 (*t*, *J* = 7.0, CH_3CH_2). MS: 265 (37, $M^{+\cdot}$), 250 (6, $M^{+\cdot} - CH_3$), 198 (100, $M^{+\cdot} - C_5H_7$). 154 (17), 142 (19), 177 (28), 122 (63), 67 (14, $C_5H_7^+$). HR-MS: 265.1468 ($C_{18}H_{19}NO$, calc. 265.1467).

N-*Benzyl-2,2-dimethyl*-N-*(3-pyridyl)-3-butynamide* (**13c**). Oil. IR ($CHCl_3$): 3290*m*, 2970*m*, 2935*m*, 2860*w*, 2100*w*, 1645*s*, 1580*m*, 1570*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.51 (*dd*, *J* = 4.9, 1.4, H–C(6')); 8.36 (*d*, *J* = 2.3, H–C(2')); 7.40–7.10 (*m*, H–C(4'), H–C(5'), C_5H_5); 4.96 (*s*, CH_2); 1.99 (*s*, H–C(4)); 1.52 (*s*, 2 CH_3). MS: 278 (4, $M^{+\cdot}$), 277 (5), 263 (3, $M^{+\cdot} - CH_3$), 251 (7), 212 (6), 157 (9), 91 (100, $C_7H_7^+$). HR-MS: 278.1389 ($C_{18}H_{18}N_2O$, calc. 278.1419).

5. Thermolysis of Amides 13a–c. – *2-Benzyl-4,4-dimethyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-5,8,10-trien-3-one* (**14**). A soln. of **13a** (1.20 g, 4.33 mmol) in xylene (10 ml) was refluxed for 20 h. The mixture was chromatographed on 12 prep. TLC plates with petroleum ether/2-butanone/AcOEt 90:5:5 (twofold). The UV(254 nm)-active zone at R_f 0.45 was eluted with $CHCl_3$, the solvent evaporated, and the residue recrystallised from petroleum ether/Et_2O to give **14** (0.70 g, 58%) as colourless prisms. M.p. 141.5–142.5°. IR ($CHCl_3$): 2985*m*, 2960*m*, 2915*w*, 2860*w*, 1685*s*, 1665*s*, 1590*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.25 (*m*, 5 arom. H); 6.65 (*t*, *J* = 6.1, H–C(8), H–C(11)); 6.44 (*dd*, *J* = 6.7, 1.5, H–C(9), H–C(10)); 6.33 (*d*, *J* = 5.6, H–C(6)); 4.88 (*s*, CH_2); 4.80–4.70 (*m*, H–C(7)); 1.20 (*s*, 2 CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 180.5 (*s*, C(3)); 159.0 (*s*, C(5)); 140.1, 139.2 (2*d*, C(8), C(9), C(10), C(11));

138.3 (*s*, C(arom.)); 128.7, 128.2, 127.7, 127.5 (4*d*, C(6), CH(arom.)); 77.8 (*s*, C(1)); 48.2 (*d*, C(7)); 45.2 (*t*, CH_2); 41.2 (*s*, C(4)); 25.7 (*q*, 2 CH_3). MS: 277 (53, $M^{+\cdot}$), 262 (4, $M^{+\cdot} - CH_3$), 251 (40, $M^{+\cdot} - C_2H_4$), 158 (34), 91 (100, $PhCH_2^+$). HR-MS: 277.1474 ($C_{19}H_{19}NO$, calc. 277.1467).

(1RS,7SR)-2-Ethyl-4,4-dimethyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-5,8,10-trien-3-one (**15**). A soln. of **13b** (3.25 g, 12.2 mmol) in dry benzene (20 ml) was refluxed for 6 h. The solvent was partially (*ca.* ½) evaporated and hexane (6 ml) added. After staying overnight at r.t., the crystals formed were collected and washed with hexane to yield **15** (2.45 g, 75%) as pale brown plates. M.p. 140–143° (anal. sample, m.p. 142.5–144.0°, from MeOH). IR ($CHCl_3$): 2960*m*, 2915*w*, 2855*w*, 1670*s*, 1650*m*, 1585*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.2–7.1 (*m*, 2 arom. H); 7.0–6.9 (*m*, H–C(11), 2 arom. H); 6.86 (*dd*, *J* = 7.1, 1.6, H–C(10)); 6.49 (*d*, *J* = 5.8, H–C(6)); 4.92 (*td*, *J* = 5.8, 1.6, H–C(7)); 4.14 (*qd*, *J* = 13.5, 7.2, HC–N); 3.62 (*qd*, *J* = 13.5, 7.2, HC–N); 1.52 (*t*, *J* = 7.2, CH_3CH_2); 1.21 (*s*, CH_3); 1.02 (*s*, CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 180.7 (*s*, C(3)); 158.2 (*s*, C(5)); 146.9, 146.6 (2*s*, C(8), C(9)); 139.9, 136.6 (2*d*, C(10), C(11)); 127.7, 124.0, 123.5, 122.0, 118.6 (5*d*, C(6), CH(arom.)); 76.2 (*s*, C(1)); 48.9 (*d*, C(7)); 41.7 (*s*, C(4)); 38.4 (*t*, CH_2); 26.5, 25.7 (2*q*, 2 CH_3–C(4)); 14.8 (*q*, CH_3CH_2). MS: 265 (100, $M^{+\cdot}$), 250 (43, $M^{+\cdot} - CH_3$), 237 (38, $M^{+\cdot} - CO$), 222 (62, $M^{+\cdot} - CH_3 - CO$), 208 (20), 194 (29), 179 (24), 167 (18). HR-MS: 265.1466 ($C_{18}H_{19}NO$, calc. 265.1467).

1-Benzyl-3,3-dimethylindolin-2-one (**17**). A soln. of **13c** (0.38 g, 1.37 mmol) in dry xylene (10 ml) was heated at 120° for 4 h. The solvent was evaporated and the residue chromatographed on 3 prep. TLC plates with petroleum ether/(i-Pr)$_2$O/2-butanone/AcOEt 40:20:20:20. The UV(254 nm)-active zone at R_f 0.75 was eluted with $CHCl_3$, the solvent evaporated and the residue recrystallised from petroleum ether to give **17** (0.302 g, 88%). M.p. 80–81°. IR ($CHCl_3$): 3050*m* (br.), 2965*m*, 2915*m*, 2860*m*, 1695*s*, 1610*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.3–7.2 (*m*, H–C(4), C_6H_5); 7.14 (*td*, *J* = 7.0, 1.4, H–C(5)); 7.02 (*t*, *J* = 7.5, H–C(6)); 6.72 (*d*, *J* = 7.9, H–C(7)); 4.92 (*s*, CH_2); 1.44 (*s*, 2 CH_3). MS: 251 (72, $M^{+\cdot}$), 236 (20, $M^{+\cdot} - CH_3$), 208 (10), 160 (13, $M^{+\cdot} - PhCH_2$), 91 (100, $C_7H_7^+$). HR-MS: 251.1324 ($C_{17}H_{18}NO$, calc. 251.1388).

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