Synthesis of 1,6-Methano[10]annulenopyridines by Tandem Aza-Wittig Reaction/Electrocyclisation

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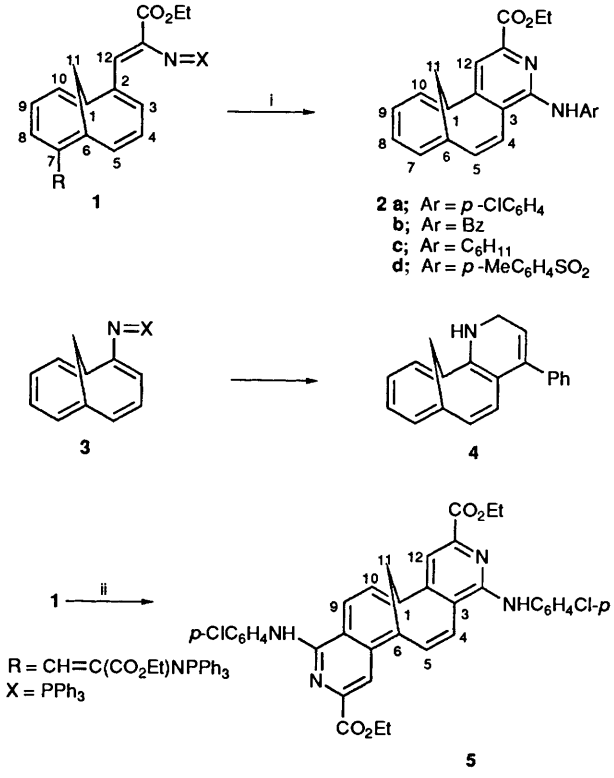
Iminophosphoranes **1** (X = PPh_3) derived from the corresponding 1,6-methano[10]annulenes have been made to react with isothiocyanates and also with aromatic aldehydes to give, by an aza-Wittig reaction followed by cyclisation, novel 1,6-methano[10]annulenopyridines of structural types **2** and **6**. Aza-Wittig reactions of the 2-triphenylphosphoranylideneamino derivative **3** (X = PPh_3) with aromatic aldehydes or isothiocyanates led to the Schiff's bases **3** (X = CHAr) or carbodiimides (X = C=NAr) respectively. The latter on treatment with enamines gave, by a Diels–Alder cyclisation, the annuleno[2,3-b]pyridines **12**.

Annelation of ring systems with N-heterocycles by means of an aza-Wittig reaction has recently been widely utilised because of the availability of functionalised iminophosphoranes.[1] In continuation of our interest in the heteroannelation of 1,6-methano[10]annulenes[2] we have explored tandem aza-Wittig cyclisations for the synthesis of annulenopyridines (*e.g.*, **5** and **12**). Examples of pyridine-fused annulenes of types **2** and **4** made by mediation of iminophosphoranes have been reported.[2,3]

In a Staudinger reaction we converted the 2,7-bis(azidoacrylate) **1** [X = N_2, R = CH=C(CO_2Et)N_3] by treatment with triphenylphosphine into the bisphosphorane **1** [X = PPh_3, R = CH=C(CO_2Et)NPPh_3]. On being made to react with excess of *p*-chlorophenyl isothiocyanate in toluene the dipyridino compound **5** (56%) was obtained. Ring closure had occurred in tandem with a double aza-Wittig reaction between the bis-iminophosphorane and the isothiocyanate to give **5** (see Scheme 1). Extending the scope of one of our previous approaches[2] we prepared a series of the annulenopyridines **2** (Ar = *p*-ClC_6H_4, COC_6H_5, C_6H_{11} and *p*-$MeC_6H_4SO_2$) from the required isothiocyanates and the phosphorane **1** (X = PPh_3, R = H). Aliphatic isocyanates or isothiocyanates did not react under similar conditions (hot toluene). The ^1H NMR spectra of these yellow annulated pyridines **2** are as expected for an aromatic 14π system. The two bridge protons appear upfield as doublets at δ_H 0.23–0.83 and −0.38 to −0.24 (*J* 9.5 Hz) while the bridge C-atom resonates as a triplet in the region of δ_C 34.1–32.0. The diagnostic carbonyl and imine stretching bands were observed at ~1700 and ~3400 cm^{-1} respectively. When CS_2 was made to react with compound **1** (X = PPh_3, R = H) a stable isothiocyanate **1** (X = CS, R = H) was produced which could not be made to cyclise to give a pyridine. This observation is borne out by other workers[4] who found that similar isothiocyanates could not be cyclised. Its structure **1** (X = CS, R = H) is supported by a characteristic band at 2025 cm^{-1} (-NCS) as well as by the presence of the bridge protons at δ_H −0.38 and −0.22.

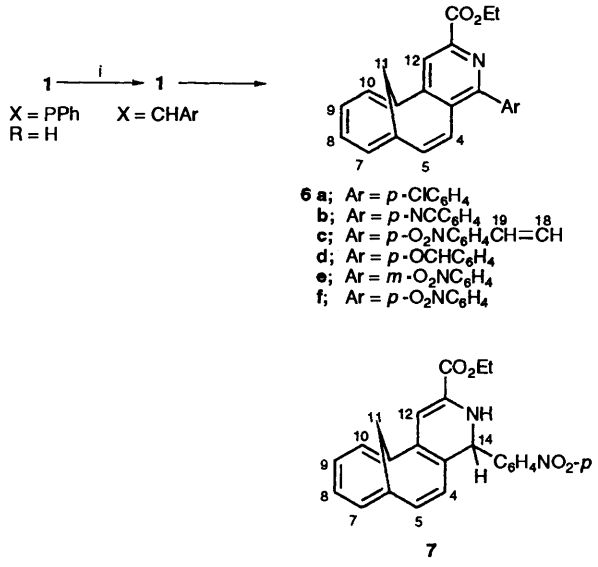
The reaction of aryl aldehydes (ArCHO) with the iminophosphorane **1** (X = PPh_3, R = H) in hot toluene under argon afforded, *via* non-isolable imines **1** (X = CHAr), a series of novel 1,6-methano[10]annuleno[3,2-*c*]pyridines **6** (see Scheme 2). In the case of the *p*-nitrobenzaldehyde an inseparable mixture of the pyridoannulene **6** (Ar = *p*-$NO_2C_6H_4$) and the dihydro compound **7** was obtained. Its composition was clearly



Scheme 1 *Reagents:* i, ArNCS; ii, *p*-ClC_6H_4NCS. Note non-systematic numbering scheme for compounds **1**, **2**, **5**, used for the NMR data only.

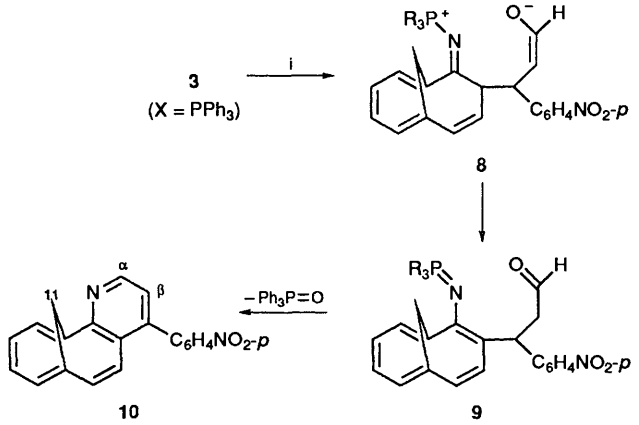
indicated by an analysis of its ^1H and ^{13}C NMR spectra (see Experimental section).

The phosphorane **3** (X = PPh_3) obtained from the corresponding 2-azido compound[2] by a Staudinger reaction with triphenylphosphine was converted into the 1,6-methano[10]-annuleno[2,3-*b*]pyridine **10** when made to react with *p*-nitrocinnamaldehyde in benzene in the presence of Pd/C. In contrast to the iminophosphorane[3] **3** (X = PBu_3) the phenyl analogue **3** (X = PPh_3) is unstable and has to be allowed to react *in situ* with the reagent. It was found to be unreactive towards unsaturated ketones. The formation of compound **10** can be visualised to involve, first, an enaminic type of alkylation



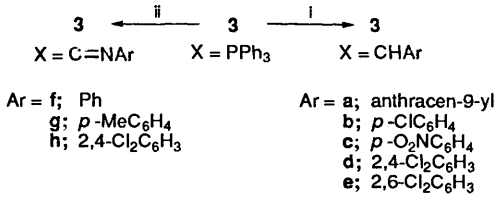
Scheme 2 *Reagents and conditions:* i, ArCHO, toluene, reflux. Note non-systematic numbering schemes for NMR data.

of the iminophosphorane to give intermediate **8**. This is followed by a proton transfer to give the intermediate **9**. Cyclisation by an intramolecular aza-Wittig reaction leads to a dihydropyridine which is dehydrogenated (Pd/C) to give the product **10** (see Scheme 3).



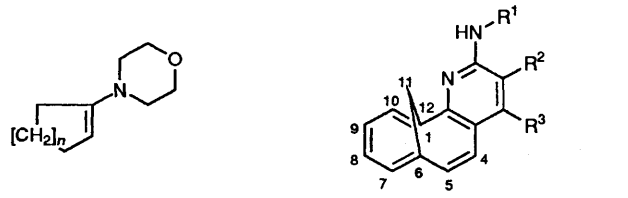
Scheme 3 *Reagents:* i, *p*-$O_2NC_6H_4CH$=CHCHO, Pd/C (10%), benzene. Note non-systematic NMR numbering for **10**.

The phosphorane **3** (X = PPh_3) could also be made to react in good yield with aromatic aldehydes to give the imines (Schiff's bases) **3** (X = CHAr) and with aryl isothiocyanates to give the not very stable diimides **3** (X = C=NAr) (see Scheme 4).



Scheme 4 *Reagents and conditions:* i, ArCHO, $CHCl_3$, 60 °C; ii, ArNCS, C_6H_6, reflux

Analogous reactions on other phosphoranes are known.[5] The imines showed a peak at δ_C 155 due to the iminocarbon in structures **3** (X = CHAr), and the diimides **3** (X = C=NAr) displayed bands at 2133–2135 cm^{-1} and resonances at δ_C 135–138 typical for unsymmetric carbodiimides.[6] The carbodiimides **3** (X = C=NAr) reacted speedily in hot bromobenzene with the electron-rich enamines **11** (*n* = 1 or 2) in a Diels–Alder cyclisation with inverse electron demand[7] to give the annuleno-pyridines **12**. The bridge protons show up characteristically at



Non-systematic NMR numbering scheme is shown for compounds **12**

δ_H ~1 and ~ −0.3 while the NH proton is to be found in the region δ_H 6.2–6.5. All other resonances correspond to heteroannulenes of a 14π aromatic character. Attempts to bring about a cyclisation with the imines **3** (X = CHAr) using electron-rich vinyl ethers[8] gave intractable residues. The diene reactivity of these Schiff's bases for cyclisation is lacking in this case.

Experimental

M.p.s were recorded on a Reichert melting-point microscope and are uncorrected. IR spectra were measured on a Perkin-Elmer 325 spectrometer, ^1H NMR spectra with a Bruker HX-90E (W.M.-250 MHz) and ^{13}C spectra with a Bruker W.M. 250 (62.89 MHz); δ-values are given relative to tetramethylsilane. *J*-Values are given in Hz. NMR locants refer to the numbering schemes shown in the structural formulae. Mass spectra were measured on a Varian MAT 311A spectrometer. For column chromatography silica gel 60 (63–200 μm) (Merck) or neutral alumina 90, grade 1 (63–200 μm) (Fluka) was employed. Solvents were dried by the usual methods. All isocyanates and isothiocyanates are commercially available. Unstable compounds were analysed by peak matching.

Diethyl β,β-1,6-*Methanocyclodeca*-1,3,5,7,9-*pentaene*-2,7-*diyl*)-1,α'-(*bistriphenylphosphoranylidenamino*)*acrylate* **1** [X = PPh_3, R = CH=C(CO_2Et)NPPh_3].—To a solution of the azide **1** [X = N_2, R = CH=C(CO_2Et)N_3][2] (0.13 g, 0.31 mmol) in dry CH_2Cl_2 (10 cm^3) was added triphenylphosphine (1.62 g, 0.62 mmol) in small portions. When evolution of gas had ceased the reaction mixture was agitated for 12 h. The precipitate was filtered off and gave, on recrystallisation (CH_2Cl_2–diethyl ether 2:1) red crystals of *compound* **1** [X = PPh_3, R = CH=C-(CO_2Et)NPPh_3] (0.52 g, 93%), m.p. 289 °C; δ_H(CD_2Cl_2) −0.19 (2 H, s, 11-H_A and -H_B), 0.98 (6 H, t, *J* 7.6, OCH_2*Me*), 3.80 (4 H, q, *J* 7.6, OCH_2Me) 6.90 (2 H, t, *J* 10.6, 4- and 9-H), 7.29 (2 H, d, *J* 9.3, 3- and 8-H), 7.47 (2 H, d, *J* 9.3, 5- and 10-H), 8.51 (2 H, d, *J* 10, 12- and 14-H); *m/z* 889 (M^+) (Found: C, 77.1; H, 5.7; N, 3.2; P, 6.8. $C_{57}H_{50}N_2O_4P_2$ requires C, 77.01; H, 5.67; N, 3.15; P, 6.97%).

General Preparation of Ethyl 1-*Arylamino*-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **2a–d**.—(*a*) To a solution of iminophosphorane **1** (X = PPh_3, R = H)[2] (2.38 g, 4.5 mmol) in dry toluene (40 cm^3) was added *p*-chlorophenyl isothiocyanate (0.76 g, 4.5 mmol) and the reaction mixture was agitated for 30 min at 0 °C. This was followed by heating under reflux for 7 h. The mixture was stirred at room temperature for 3 days. The yellow precipitate was filtered off and washed on the filter

(3 × 20 cm^3 hexane) and purified by chromatography (SiO_2; hexane–ethyl acetate 3:2). Recrystallisation (CH_2Cl_2–hexane 1:1) yielded *ethyl* 1-(p-*chloroanilino*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **2a** (Ar = *p*-ClC_6H_4) (1.31 g, 75%), m.p. 162 °C; ν_{max}/cm^{-1} 3431 (NH) and 1679 (CO_2Et); $\delta_H(CDCl_3)$ −0.24 (1 H, d, *J* 9.5 and 1, 11-H_A), 0.80 (1 H, d, *J* 9.5, 11-H_B), 1.49 (3 H, t, *J* 8.4, OCH_2Me), 4.49 (2 H, q, OCH_2Me), 7.05–7.20 (3 H, m, NH + 4- and 7-H), 7.24–7.34 (4 H, m, 2 × ArH + 5- and 8-H), 7.40 (1 H, t, 9-H), 7.50–7.58 (3 H, m, 2 × ArH + 10-H) and 8.59 (1 H, s, 12-H); *m/z* 392 ($M^+ + 2$) and 390 (M^+) (Found: C, 70.6; H, 5.0; N, 7.0. $C_{23}H_{19}ClN_2O_2$ requires C, 70.68; H, 4.90; N, 7.17%).

(*b*) A mixture of benzoyl isothiocyanate (1.08 g, 8 mmol) and iminophosphorane **1** (X = PPh_3)[2] (2.23 g, 8 mmol) in toluene (50 cm^3) was heated under reflux (24 h). The mixture was then stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the oily residue was washed (3 × 20 cm^3 hexane) and purified (SiO_2; hexane–ethyl acetate 5:1) to give *ethyl* 1-*benzoylamino*-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **2b** (Ar = COC_6H_5) (1.93 g, 63%), m.p. 158 °C; ν_{max}/cm^{-1} 3410 (NH) and 1712 (CO_2Et); $\delta_H(CDCl_3)$ −0.38 (1 H, d, *J* 9.4 and 1, 11-H_A), 0.23 (1 H, d, *J* 9.4, 11-H_B), 1.44 (3 H, t, *J* 8.2, OCH_2Me), 4.43 (2 H, q, OCH_2Me), 5.47 (1 H, s, NH), 7.18–7.62 (7 H, m, Ph, 7- and 8-H), 7.69 (1 H, d, *J* 7.3, 9-H), 7.98 (1 H, d, *J* 8.6, 4-H), 8.50 (1 H, d, *J* 6.8, 10-H), 8.51 (1 H, d, *J* 6.8, 5-H), and 8.91 (1 H, d, *J* 9.5, 12-H); *m/z* 384 (M^+) (Found: C, 74.7; H, 5.3; N, 7.35; $C_{24}H_{20}N_2O_3$ requires C, 74.98; H, 5.24; N, 7.29%).

(*c*) A mixture of cyclohexyl isothiocyanate (0.57 g, 4.05 mmol), iminophosphorane **1** (X = PPh_3)[2] (2.09 g, 4.05 mmol) and toluene (15 cm^3) was treated as in (*a*). Purification of the crude product by chromatography (SiO_2; hexane–ethyl acetate 10:1) gave *ethyl* 1-*cyclohexylamino*-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **2c** (Ar = C_6H_{11}) (0.89 g, 61%), m.p. 122 °C; ν_{max}/cm^{-1} 3410 (NH) and 1719 (CO_2Et); $\delta_H(CDCl_3)$ −0.29 (1 H, d, *J* 9.5, 11-H_A), 0.83 (1 H, d, *J* 9.5, 11-H_B), 1.18–1.40 (4 H, m, cyclohexyl), 1.47 (3 H, t, *J* 8.3 OCH_2Me), 1.62–1.88 (4 H, m, cyclohexyl), 2.12–2.29 (2 H, m, cyclohexyl), 4.20–4.32 (1 H, m, $NHCH[CH_2]_5$), 4.45 (2 H, q, OCH_2Me), 4.94 (1 H, br s, NH), 7.0 (1 H, d, *J* 10.6, 7-H), 7.10–7.18 (1 H, m, 4-H), 7.24–7.32 (2 H, m, 5- and 8-H), 7.48 (1 H, d, *J* 9.7, 9-H), 7.70–7.54 (1 H, m, 10-H) and 8.31 (1 H, s, 12-H) (Found: M^+, 362.1996. $C_{23}H_{26}N_2O_2$ requires M, 362.1995).

(*d*) A mixture of toluene-*p*-sulfonyl isocyanate (0.85 g, 4.32 mmol), iminophosphorane **1** (X = PPh_3)[2] (2.23 g, 4.32 mmol) and toluene (50 cm^3) was treated as in (*a*). Repeated chromatography on silica gel with hexane–ethyl acetate (1:1) as developer afforded a pure sample of *ethyl* 1-(p-*tosylsamino*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **2d** (R = *p*-$MeC_6H_4SO_2$) (1.31 g, 71%), m.p. 162 °C; ν_{max}/cm^{-1} 3443 (NH) and 1724 (CO_2Et); $\delta_H(CDCl_3)$ −0.33 (1 H, d, *J* 9.2, 11-H_A), 0.28 (1 H, d, *J* 9.2, 11-H_B), 1.51 (3 H, t, *J* 8.4, OCH_2Me), 2.38 (3 H, s, Ar*Me*), 4.53 (2 H, q, OCH_2Me), 7.17–7.40 (5 H, m, 2 × ArH, 4-, 7- and 8-H), 7.60 (1 H, t, *J* 9.5, 9-H), 7.80 (1 H, d, *J* 8.6, 5-H), 7.97 (2 H, d, 2 × ArH), 8.16 (1 H, s, 12-H), 9.15 (1 H, d, *J* 10.6, 10-H) and 13.23 (1 H, s, NH); *m/z* 434 (M^+) (Found: C, 66.5; H, 5.3; N, 6.5. $C_{24}H_{22}N_2O_4S$ requires C, 66.34; H, 5.10; N, 6.45%).

Under similar conditions a reaction mixture of *p*-chlorophenyl isothiocyanate (0.32 g, 0.93 mmol) and iminophosporane **1** [X = PPh_3, R = $CH{=}C(CO_2Et)NPPh_3$] (0.41 g, 0.47 mmol) in toluene (10 cm^3) after chromatography (SiO_2; hexane–ethyl acetate 10:1) gave *diethyl* 4,11-*bis*-(p-*chloroanilino*)-7,14-*methanocyclodeca*[1,2-c:6,7-c']*dipyridine*-2,9-*dicarboxylate* **5** (1.31 g, 56%), m.p. 242 °C; ν_{max}/cm^{-1} 3442 (NH) and 1700 (CO_2Et); δ_H([$^2H_5$]pyridine) 1.13 (2 H, s, 11-H_A and -H_B), 1.32 (6 H, t, *J* 8.4, OCH_2Me), 4.58 (4 H, q, OCH_2Me), 7.42 (2 H, d, *J* 9.8, 4-and 9-H), 7.46 (2 H, d, *J* 9.6, 5- and 10-H), 7.43–8.17 (8 H, AA'BB' system, 8 × ArH), 8.52 (2 H, s, 12- and 15-H) and 9.12 (2 H, s, NH); *m/z* 642 ($M^+ + 4$), 640 ($M^+ + 2$) and 638 (M^+) (Found: C, 65.85; H, 4.0; N, 9.0. $C_{35}H_{28}Cl_2N_4O_4$ requires C, 65.83; H, 4.38; N, 8.77).

Ethyl α-*Isothiocyanate*-β-(1,6-*methanocyclodeca*-1,3,5,7,9-*pentaen*-2-*yl*)*acrylate* **1** (X = CS, R = H).—A mixture of CS_2 (0.46 g, 6.04 mmol) and iminophosphorane **1** (X = PPh_3)[2] (3.11 g, 6.03 mmol) in toluene (20 cm^3) was heated under reflux (16 h) and was then stirred at room temperature 3 days before the solvent and excess of CS_2 were removed under reduced pressure. The residue was washed (3 × 20 cm^3 hexane) to remove by-products such as triphenylphosphine sulfide, and was then chromatographed (SiO_2; hexane–ethyl acetate 3:1) to yield *title compound* **1** (X = CS, R = H) as an orange oil (1.13 g, 63%); ν_{max}/cm^{-1} 2025 (N=C=S) and 1722 (CO_2Et); $\delta_H(CDCl_3)$ −0.38 (1 H, d, *J* 9.5, 11-H_A), −0.22 (1 H, d, *J* 9.5, 11-H_B), 1.42 (3 H, t, *J* 7.6, OCH_2Me), 4.39 (2 H, q, *J* 7.6, OCH_2Me), 6.94–7.07 (1 H, m, 3-H), 7.10–7.65 (5 H, m, 4-, 5-, 7-, 8- and 9-H), 7.80 (1 H, s, 12-H) and 7.98 (1 H, d, *J* 10.6, 10-H); *m/z* 297 (M^+) (Found: C, 68.6; H, 5.2; N, 4.5. $C_{17}H_{15}NO_2S$ requires C, 68.66; H, 5.08; N, 4.71%).

4-(p-*Nitrophenyl*)-7,12-*methanocyclodeca*[b]*pyridine* **10**.—To a solution of 2-azido-1,6-methanocyclodeca-1,3,5,7,9-diene[2] **3** (X = N_2) (1.55 g, 8.47 mmol) in dry benzene (10 cm^3) was added triphenylphosphine (2.16 g, 8.2 mmol) and the mixture was stirred for 30 min at room temperature to give the iminophosphorane **3** (X = PPh_3).[2] To this solution were added *p*-nitrocinnamaldehyde (0.62 g, 3.5 mmol) and 10% Pd/C (1.75 g, 0.175 mmol), and the mixture was refluxed (18 h). After removal of the solvent the resulting residue was chromatographed (SiO_2; hexane–ethyl acetate 5:1) to give the *title compound* **10** (0.82 g, 32%), m.p. 134 °C; $\delta_H(CDCl_3)$ −0.04 (1 H, d, *J* 9.5 and 1, 11-H_A), 1.18 (1 H, d, *J* 9.5, 11-H_B), 7.02–7.21 (2 H, m, 4- and 7-H), 7.22–7.32 (4 H, m, 2 × ArH + 5- and 8-H), 7.38 (1 H, t, 9-H), 7.49–7.56 (4 H, m, 2 × ArH, 10-H and H^β) and 8.54 (1 H, s, H^α) (Found: M^+, 314.103 24. $C_{20}H_{14}N_2O_2$ requires M, 314.105 54).

[10]*Annulenopyridines* **6a–f**.—(*a*) A mixture of triphenylphosphoranylideneamine **1** (X = PPh_3)[2] (11.72 g, 22.73 mmol), *p*-chlorobenzaldehyde (9.58 g, 68.19 mmol) and dry *p*-xylene (150 cm^3) was heated under reflux for 24 h. The solvent was removed under reduced pressure. The residue was chromatographed (SiO_2; cyclohexane–benzene–triethylamine 9:0.5:0.5). Recrystallisation (cyclohexane) gave *ethyl* 1-(p-*chlorophenyl*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **6a** (Ar = *p*-ClC_6H_4) (6.69 g, 75%), m.p. 191 °C; ν_{max}/cm^{-1} 1722 (CO_2Et); $\delta_H(CDCl_3)$ −0.12 (1 H, d, *J* 9.5 and 1, 11-H_A), 1.04 (1 H, d, *J* 9.5, 11-H_B), 1.50 (3 H, t, *J* 8.4, OCH_2Me), 4.53 (2 H, q, OCH_2Me), 7.09 (1 H, d, 4-H), 7.12 (1 H, d, 7-H), 7.27–7.38 (3 H, m, 5-, 8- and 9-H), 7.49 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 7.57 (1 H, d, *J* 7.3, 10-H), 7.79 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH) and 8.98 (1 H, s, 12-H); *m/z* 375 (M^+) (Found: C, 73.2; H, 5.1; N, 3.85; Cl, 9.75. $C_{23}H_{18}ClNO_2$ requires C, 73.50; H, 4.83; N, 3.73. Cl, 9.43%).

(*b*) A mixture of iminophosphorane **1** (X = PPh_3)[2] (2.88 g, 5.58 mmol), *p*-cyanobenzaldehyde (2.53 g, 16.75 mmol) and dry *p*-xylene (50 cm^3) was treated as in (*a*). Purification of the crude product by chromatography (SiO_2; cyclohexane–benzene–triethylamine 8:1:1) yielded *ethyl* 1-(p-*cyanophenyl*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **6b** (Ar = *p*-NCC_6H_4) (1.47 g, 72%), m.p. 187 °C; ν_{max}/cm^{-1} 1735 (CO_2Et); $\delta_H(CDCl_3)$ −0.10 (1 H, d, *J* 9.5, 11-H_A), 1.04 (1 H, d, *J* 9.5, 11-H_B), 1.48 (3 H, t, *J* 8.4, OCH_2Me), 4.52 (2 H, q, OCH_2Me), 7.00–7.20 (2 H, m, 4- and 7-H), 7.24–7.47 (3 H, m, 5-, 8- and 9-H), 7.82 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 7.94 (2 H,

d, *J* 7.5, AA'BB'-system, 2 × ArH), 8.12 (1 H, d, *J* 7.3, 10-H) and 9.01 (1 H, s, 12-H); *m/z* 366 (M^+) (Found: C, 78.5; H, 4.8; N, 7.8. $C_{24}H_{18}N_2O_2$ requires C, 78.67; H, 4.95; N, 7.65%).

(*c*) A mixture of iminophosphorane **1** (X = PPh_3)[2] (2.88 g, 5.58 mmol), *p*-nitrocinnamaldehyde (2.96 g, 16.75 mmol) and dry xylene (30 cm^3) was treated as in (*a*). Purification of the crude product by chromatography (SiO_2; cyclohexane–benzene–triethylamine 8:1:1) yielded *ethyl* 1-(p-*nitrostyryl*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **6c** (Ar = *p*-$O_2NC_6H_4CH$=CH) (1.56 g, 68%), m.p. 200 °C; ν_{max}/cm^{-1} 1731 (CO_2Et); $\delta_H(CDCl_3)$ −0.11 (1 H, d, *J* 9.5, 11-H_A), 1.02 (1 H, d, *J* 9.5, 11-H_B), 1.51 (3 H, t, *J* 8.4 OCH_2*Me*), 4.57 (2 H, q, OCH_2Me), 7.15 (1 H, d, 4-H), 7.29–7.58 (6 H, m, 5-, 7-, 8-, 9-, 18- and 19-H), 7.80 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 8.00 (1 H, d, *J* 7.3, 10-H), 8.27 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 8.92 (1 H, s, 12-H); *m/z* 387 (M^+) (Found: C, 72.6; H, 5.0; N, 6.6%; M^+, 412.1423. $C_{25}H_{20}N_2O_4$ requires C, 72.80; H, 4.89; N, 6.79%; M, 412.1423).

(*d*) Terephthalaldehyde (4.76 g, 35.49 mmol) and iminophosphorane **1** (X = PPh_3)[2] (6.1 g, 11.83 mmol) gave, under similar conditions, *ethyl* 1-(p-*formylphenyl*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **6d** (Ar = *p*-$OCHC_6H_4$) (3.01 g, 69%), m.p. 183 °C; ν_{max}/cm^{-1} 1741 (HC=O) and 1708 (CO_2Et); $\delta_H(CDCl_3)$ 0.05 (1 H, d, *J* 9.5, 11-H_A), 1.09 (1 H, d, *J* 9.5, 11-H_B), 1.50 (3 H, t, *J* 8.4, OCH_2*Me*), 4.53 (2 H, q, OCH_2Me), 7.06–7.18 (2 H, m, 4- and 7-H), 7.29–7.48 (3 H, m, 5-, 8- and 9-H), 7.60 (1 H, d, *J* 7.3, 10-H), 7.82–7.98 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 7.98–8.12 (2 H, d, *J* 7.5, AA'BB'-system, 2 × ArH), 9.02 (1 H, s, 12-H) and 10.14 (1 H, s, CHO) (Found: M^+, 369.1366. $C_{24}H_{19}NO_3$ requires M, 369.1365).

(*e*) 3-Nitrobenzaldehyde (2.53 g, 16.75 mmol) and iminophosphorane **1** (X = PPh_3)[2] (2.88 g, 5.58 mmol) gave, under similar conditions, *ethyl* 1-(m-*nitrophenyl*)-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **6e** (Ar = m-$O_2NC_6H_4$) (1.1 g, 51%); ν_{max}/cm^{-1} 1715 (CO_2Et); $\delta_H(CDCl_3)$ −0.09 (1 H, d, *J* 9.5, 11-H_A), 1.07 (1 H, d, *J* 9.5, 11-H_B), 1.50 (3 H, t, *J* 8.4, OCH_2*Me*), 4.57 (2 H, q, OCH_2Me), 7.08 (1 H, d, *J* 10.6, 4-H), 7.13 (1 H, d, *J* 7.3, 7-H), 7.32–7.45 (3 H, m, ArH and 5-H), 7.57–7.76 (2 H, m, 8- and 9-H), 8.19 (1 H, d, *J* 7.0, 10-H), 8.36 (1 H, dd, *m*-ArH), 8.68 (1 H, s, *p*-ArH) and 9.04 (1 H, s, 12-H); *m/z* 387 (M^+) (Found: C, 71.5; H, 4.8; N, 7.1%; M^+, 386.1261. $C_{23}H_{18}N_2O_4$ requires C, 71.49; H, 4.70; N, 7.25%; M, 386.1266).

(*f*) Under similar conditions a reaction mixture of iminophosphorane **1** (X = PPh_3)[2] (2.88 g, 5.58 mmol) and *p*-nitrobenzaldehyde (2.53 g, 16.75 mmol) in dry xylene (50 cm^3) gave ethyl 1-(*p*-nitrophenyl)-5,10-methanocyclodeca[*c*]pyridine-3-carboxylate **6f** (Ar = *p*-$O_2NC_6H_4$) and *ethyl* 1-(p-*nitrophenyl*)-1,2-*dihydro*-5,10-*methanocyclodeca*[c]*pyridine*-3-*carboxylate* **7** (Ar = *p*-$O_2NC_6H_4$), as a mixture (0.97 g, 45%), m.p. 193 °C; ν_{max}/cm^{-1} 1712 (CO_2Et); $\delta_H(CDCl_3)$ −0.04 (1 H, d, *J* 9.5 and 1, 11-H_A), 1.11 (1 H, d, *J* 9.5, 11-H_B), 1.57 (3 H, t, *J* 8.4, OCH_2*Me*), 4.59 (2 H, q, OCH_2Me), 7.06–7.27 (2 H, m, 4- and 7-H), 7.33–7.52 (5 H, m, 2 × ArH + 5-, 8- and 9-H), 8.11–8.23 (2 H, m, 2 × ArH), 8.38 (1 H, d, *J* 7.3, 10-H) and 9.09 (1 H, s, 12-H) (for **6f**); −0.30 (1 H, d, *J* 9.5 and 1, 11-H_A), 0.14 (1 H, d, *J* 9.5, 11-H_B), 1.40 (3 H, t, *J* 8.4, OCH_2*Me*), 4.38 (2 H, q, OCH_2Me), 4.99 (1 H, s, NH), 5.99 (1 H, s, 14-H), 6.31 (1 H, d, *J* 7.3, 4-H), 7.06–7.59 (7 H, m, ArH + 5-, 7- and 8-H), 7.58–7.72 (2 H, m, 9- and 10-H) and 8.71 (1 H, s, 12-H) (for **7**); *m/z* 387 (M^+ for **7**) [Found (for **7**): C, 70.5; H, 5.2; N, 7.3. $C_{23}H_{20}N_2O_4$ requires C, 70.31; H, 4.94; N, 7.23%].

Synthesis of Imines **3a–e** (X = CHAr). *General Procedure.*—In a dried, argon-filled Schlenck tube a mixture of the iminophosphorane **3** (X = PPh_3)[2] (2.08 g, 5 mmol), anthracene-9-carbaldehyde (1.03 g, 5 mmol) and chloroform (50 cm^3) was heated for 20 h at 60 °C. After cooling, the solvent was driven off under reduced pressure and the resulting oil was purified by means of silica gel short-column chromatography in hexane–ethyl acetate (10:1) to give N-(*anthracen*-9-*ylmethylene*)*bicyclo*[4.4.1]*undeca*-1(10),2,4,6,8-*pentaen*-2-*ylamine* **3a** (Ar = anthracen-9-yl) (0.78 g, 45%), m.p. 37 °C; $\delta_H(CDCl_3)$ −0.41 (1 H, d, *J* 9.5, 11-H_A), 0.10 (1 H, d, *J* 9.5, 11-H_B), 7.00 (1 H, d, *J* 9.3, 3-H), 7.15 (1 H, d, *J* 9.3, 4-H), 7.19–7.31 (3 H, m, 5-, 8- and 9-H), 7.43 (1 H, d, *J* 9.1, 7-H), 7.44–7.60 (4 H, m, 4 × anthracene H), 7.92 (1 H, d, *J* 7.3, 10-H), 8.02 (2 H, d, 2 × anthracene H), 8.51 (1 H, s, 1 × anthracene H and N=CH) 8.85 (2 H, d, 2 × anthracene H) and 9.37 (1 H, s, 12-H-N=C*H*Ar) (Found: M^+, 345.1518. $C_{26}H_{19}N$ requires M, 345.1517).

N-(4-*Chlorobenzylidene*)*bicyclo*[4.4.1]*undeca*-1(10), 2,4,6,8-*pentaen*-2-*ylamine* **3b** (Ar = *p*-ClC_6H_4). Yellow oil, $\delta_H(CDCl_3)$ −0.48 (1 H, d, *J* 9.5, 11-H_A), −0.07 (1 H, d, *J* 9.5, 11-H_B), 6.81 (1 H, d, *J* 9.3, 3-H), 7.08 (1 H, t, *J* 9.3, 4-H), 7.17–7.23 (2 H, m, 8- and 9-H), 7.35 (1 H, d, *J* 9.3, 5-H), 7.48–7.51 (3 H, m, AA'BB'-system, *J* 7.5, 2 × ArH and 7-H), 7.78–7.92 (3 H, m, AA'BB'-system, 2 × ArH, *J* 7.5 Hz and 10-H) and 8.45 (1 H, s, N=CH (Found: M^+, 279.0808. $C_{18}H_{14}ClN$ requires M, 279.0815, peakmatching because of instability of the product).

N-(4-*Nitrobenzylidene*)*bicyclo*[4.4.1]*undeca*-1(10), 2,4,6,8-*pentaen*-2-*ylamine* **3c** (Ar = *p*-$O_2NC_6H_4$). This compound had m.p. 39 °C; $\delta_H(CDCl_3)$ −0.39 (1 H, d, *J* 9.5, 11-H_A), −0.02 (1 H, d, *J* 9.5, 11-H_B), 6.96 (1 H, d, *J* 9.3, 3-H), 7.17 (1 H, t, *J* 9.3, 4-H), 7.25–7.37 (2 H, m, 8- and 9-H), 7.40–7.54 (2 H, m, 5- and 7-H), 7.93 (1 H, d, *J* 7.3, 10-H), 8.11 (2 H, d, AA'BB'-system, *J* 7.5, 2 × ArH), 8.47 (2 H, d, AA'BB'-system, 2 × ArH, *J* 7.5) and 8.69 (1 H, s, N=CH) (Found: M^+, 290.1055. $C_{18}H_{14}N_2O_2$ requires M, 290.1055).

N-(2,4-*Dichlorobenzylidene*)*bicyclo*[4.4.1]*undeca*-1(10), 2,4,-6,8-*pentaen*-2-*ylamine* **3d** (Ar = 2,4-$Cl_2C_6H_4$). This compound had m.p. 45 °C; $\delta_H(CDCl_3)$ −0.42 (1 H, d, *J* 9.5 and 1.1, 11-H_A), −0.01 (1 H, d, *J* 9.5, 11-H_B), 6.90 (1 H, d, *J* 9.3, 3-H), 7.13 (1 H, t, *J* 9.3, 4-H), 7.22–7.29 (2 H, m, 8- and 9-H), 7.34–7.55 (4 H, m, 3 × ArH, 5-H), 7.89 (1 H, d, *J* 7.0, 7-H), 8.27 (1 H, d, *J* 7.3, 10-H) and 8.97 (1 H, s, N=CH) (Found: M^+, 313.0416. $C_{18}H_{13}Cl_2N$ requires M, 313.0425).

N-(2,6-*Dichlorobenzylidene*)*bicyclo*[4.4.1]*undeca*-1(10), 2,4,-6,8-*pentaen*-2-*ylamine* **3e** (Ar = 2,6-$Cl_2C_6H_3$). Red oil, $\delta_H(CDCl_3)$ −0.47 (1 H, d, *J* 9.5 and 1.1, 11-H_A), −0.02 (1 H, d, *J* 9.5, 11-H_B), 6.87 (1 H, d, *J* 9.3, 3-H), 7.11 (1 H, t, *J* 9.3, 4-H), 7.18–7.50 (7 H, m, 3 × ArH, 5-, 7-, 8- and 9-H), 7.89 (1 H, d, *J* 7.3, 10-H) and 8.80 (1 H, s, N=CH) (Found: M^+, 313.0425).

General Procedure for the Preparation of N-*Aryl*-N'-(1,6-*Methano*[10]*annulenyl*)*carbodiimides* **3f–h** (X = C=NAr).—(*a*) A solution of the iminophosphorane **3** (X = PPh_3)[2] (1.5 g, 3.6 mmol) and phenyl isothiocyanate (0.49 g, 3.6 mmol) in anhydrous benzene (50 cm^3) was refluxed for 3 h. After removal of the solvent under reduced pressure the residual oil was dissolved in hexane and the mixture was filtered to remove insoluble material. The filtrate was concentrated and chromatographed (SiO_2; hexane–ethyl acetate 10:1) to give *N*-aryl-*N'*-(1,6-methano[10]annulenyl)carbodiimides **3f–h** (X = C=NAr).

Compound **3f** (Ar = Ph) was a yellow oil (0.76 g, 82%); ν_{max}/cm^{-1} 2135 (N=C=N); $\delta_H(CDCl_3)$ −0.43 (1 H, d, *J* 9.5, 11-H_A), −0.09 (1 H, d, *J* 9.5, 11-H_B), 7.16 (1 H, d, *J* 9.5, 3-H), 7.18 (1 H, t, *J* 9.1, 4-H), 7.25 (1 H, d, *J* 9.5, 5-H), 7.27–7.42 (5 H, m, Ph), 7.42–7.52 (2 H, m, 8- and 9-H), 7.58 (1 H, d, *J* 9.0, 7-H) and 7.92 (1 H, d, *J* 8.3, 10-H) (Found: M^+, 258.1153. $C_{18}H_{14}N_2$ requires M, 258.1157).

(*b*) *With* p-*tolyl isocyanate.* Under conditions similar to those in (*a*), a solution of iminophosphorane **3** (X = PPh_3)[2] (2.08 g, 5 mmol) in benzene (50 cm^3) and *p*-tolyl isocyanate (0.63 cm^3, 5 mmol) gave the *carbodiimide* **3g** (Ar = *p*-MeC_6H_4) as a yellow oil (1.01 g, 74%); ν_{max}/cm^{-1} 2133 (N=C=N); $\delta_H(CDCl_3)$ −0.60 (1 H, dd, *J* 9.5 and 1.1, 11-H_A), −0.21 (1 H, dd, *J* 9.5, 11-H_B), 2.29 (3 H, s, Ar*Me*), 6.93–7.03 (2 H, m, 3- and 4-H),

7.03–7.22 (6 H, m, ArH, 5- and 9-H), 7.32 (1 H, dd, *J* 8.3, 8-H), 7.41 (1 H, d, *J* 8.3, 7-H) and 7.76 (1 H, d, *J* 8.3, 10-H) (Found: M^+, 272.1314. $C_{19}H_{16}N_2$ requires M, 272.1313).

(*c*) *With 2,4-dichlorophenyl isothiocyanate.* Under similar conditions to those described in (*a*), a solution of iminophosphorane **3** (X = PPh_3)[2] (2.08 g, 5 mmol) in benzene (50 cm^3) and 2,4-dichlorophenyl isocyanate (0.94 g, 5 mmol) gave the *carbodiimide* **3h** (Ar = 2,4-$Cl_2C_6H_3$) as a yellow oil (1.24 g, 76%); ν_{max}/cm^{-1} 2135 (N=C=N); $\delta_H(CDCl_3)$ −0.50 (1 H, dd, *J* 9.5 and 1.1, 11-H_A), −0.14 (1 H, d, *J* 9.5, 11-H_B), 7.03–7.27 (3 H, m, 3- and 4-H, and 1 × ArH), 7.27–7.33 (3 H, m, 2 × ArH and 5-H), 7.33–7.53 (3 H, m, 7-, 8- and 9-H) and 7.80–7.93 (1 H, m, 10-H); *m/z* 330 (M^+ + 4), 328 (M^+ + 2) and 326 (M^+) (Found: C, 65.95; H, 3.5; N, 8.6. $C_{18}H_{12}Cl_2N_2S$ requires C, 66.07; H, 3.70; N, 8.56%).

General Procedure for the Reaction of Carbodiimides **3f, g** (X = NAr *and* Ar = Ph *or* p-MeC_6H_4) *with Enamines* **11a, b** (*n* = 1 *or* 2).—A solution of carbodiimide **3f** or **3g** and enamine **11a** or **11b** (3 mol equiv.) in anhydrous bromobenzene (10 cm^3) was refluxed for 30 min. The reaction mixture was concentrated and the residue was chromatographed (SiO_2; hexane–ethyl acetate 10:1) to yield the pyridine derivatives **12a–d**.

4-*Anilino*-2,3-*dihydro*-1H-6,11-*methanocyclodeca*[b]*cyclopenta*[d]*pyridine* **12a** (R^1 = Ph, R^2R^3 = $-[CH_2]_3^-$) (0.57 g, 41%); ν_{max}/cm^{-1} 3450 (NH); $\delta_H(CDCl_3)$ −0.27 (1 H, dd, *J* 9.5 and 1.1, 11-H_A), 1.12 (1 H, d, *J* 9.5, 11-H_B), 2.17–2.36 (2 H, m, CH_2), 2.87–2.98 (2 H, m, CH_2), 3.19–3.31 (2 H, m, CH_2), 6.27 (1 H, s, NH), 7.03–7.08 (3 H, m, 2 × ArH, 4-H), 7.23–7.33 (4 H, m, 3 × ArH, 7-H), 7.35–7.43 (2 H, m, 8- and 9-H), 7.84 (1 H, d, *J* 7.5, 5-H) and 7.85 (1 H, d, *J* 7.5, 10-H); *m/z* 324 (M^+) (Found: C, 85.0; H, 6.0; N, 8.7%; M^+, 324.1627. $C_{23}H_{20}N_2$ requires C, 85.15; H, 6.21; N, 8.63%; M, 324.1626).

5-*Anilino*-1,2,3,4-*tetrahydro*-7,12-*methanocyclodeca*[c]*isoquinoline* **12b** (R^1 = Ph, R^2R^3 = $-[CH_2]_4^-$) (0.23 g, 37%); ν_{max}/cm^{-1} 3454 (NH); $\delta_H(CDCl_3)$ −0.28 (1 H, dd, *J* 8.5 and 1.1, 11-H_A), 1.05 (1 H, d, *J* 8.5, 11-H_B), 1.28–1.44 (2 H, m, CH_2), 1.47–2.13 (2 H, m, CH_2), 2.61–2.76 (2 H, m, CH_2), 3.02–3.15 (2 H, m, CH_2), 6.44 (1 H, s, NH), 6.97–7.14 (4 H, m, 3 × ArH, 4-H), 7.14–7.24 (3 H, m, 2 × ArH, 7-H), 7.35–7.47 (2 H, m, 8- and 9-H), 7.80 (1 H, d, *J* 9, 5-H) and 7.86 (1 H, d, *J* 9, 10-H); *m/z* 338 (M^+) (Found: C, 85.1; H, 6.5; N, 8.3%; M^+, 338.1777. $C_{24}H_{22}N_2$ requires C, 85.17; H, 6.55; N, 8.28%; M, 338.1783).

4-(p-*Toluidino*)-2,3-*dihydro*-1H-6,11-*methanocyclodeca*[b]*cyclopenta*[d]*pyridine* **12c** (R^1 = *p*-MeC_6H_4, R^2R^3 = $-[CH_2]_3^-$) (0.24 g, 39%); ν_{max}/cm^{-1} 3429 (NH); $\delta_H(CDCl_3)$, −0.34 (1 H, dd, *J* 10 and 1.1, 11-H_A), 1.05 (1 H, d, *J* 10, 11-H_B), 2.16–2.27 (2 H, m, CH_2), 2.29 (3 H, s, Ar*Me*), 2.82–2.92 (2 H, m, CH_2), 3.13–3.25 (2 H, m, CH_2), 6.22 (1 H, s, NH), 6.93 (1 H, d, *J* 7.7, 4-H), 6.97 (1 H, d, *J* 6.8, 7-H), 7.13–7.29 (5 H, m, 2 × ArH, 5-, 8- and 9-H), 7.69 (2 H, d, *J* 8.4, 2 × ArH) and 7.78 (1 H, d, *J* 7.5, 10-H); *m/z* 338 (M^+) (Found: C, 85.0; H, 6.7; N, 8.2%; M^+, 338.1777).

5-(p-*Toluidino*)-1,2,3,4-*tetrahydro*-7,12-*methanocyclodeca*[c]*isoquinoline* **12d** (R^1 = p-MeC_6H_4, R^2R^3 = $-[CH_2]_4^-$) (0.22 g, 34%); ν_{max}/cm^{-1} 3448 (NH); $\delta_H(CDCl_3)$ −0.35 (1 H, d, *J* 9 and 1.1, 11-H_A), 0.98 (1 H, d, *J* 9, 11-H_B), 1.70–1.84 (2 H, m, CH_2), 1.91–2.03 (2 H, m, CH_2), 2.30 (3 H, s, Ar*Me*), 2.52–2.62 (2 H, m, CH_2), 2.95–3.06 (2 H, m, CH_2), 6.31 (1 H, s, NH), 6.93 (1 H, d, *J* 7.7, 4-H), 7.03 (1 H, d, *J* 6.8, 7-H), 7.06–7.19 (3 H, m, 5-, 8- and 9-H), 7.14–7.19 (2 H, d, *J* 7.8, 2 × ArH), 7.57–7.62 (2 H, d, *J* 7.8, 2 × ArH) and 7.77 (1 H, d, *J* 7.7, 10-H); *m/z* 352 (M^+) (Found: C, 84.9; H, 6.8; N, 7.9%; M^+, 352.1937. $C_{25}H_{24}N_2$ requires C, 85.19; H, 6.86; N, 7.95%; M, 352.1939).

Acknowledgements

Support by the Verband der Chemischen Industrie-Fonds der Chemie is gratefully acknowledged. We also thank BASF AG, Bayer AG and Hoechst AG for the donation of chemicals, and ICN-Biomedicals for the donation of silica gel. We are indebted to Mrs. A. Schormann, Mrs. U. Hertle and Dipl.-Chem. P. Meffert for recording the NMR spectra, to Mr. H. Rudy for measuring the mass spectra, and to Mr. P. Weyrich for performing microanalyses and measuring the IR and UV spectra.

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Paper 3/07217G
Received 6th *December* 1993
Accepted 20th *December* 1993