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Conjugated Heterocumulenes. Synthesis of Conjugated Carbodiimides and their Facile Conversion *via* Intramolecular Cycloaddition into Nitrogen Heterocycles, Quinoline and Pyrido[2,3-*b*]indole (α-Carboline) Derivatives

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A convenient method is described for the synthesis of conjugated carbodiimides and their application to nitrogen heterocycle synthesis *via* electrocyclisation–intramolecular Diels–Alder reaction.

Previously we reported an efficient method for the synthesis of conjugated heterocumulenes, carbodiimides[1] and ketenimines,[2] *via* a Wittig-type reaction and their facile conversion into a variety of hetero(carbo)cycles, *e.g.* dihydropyridines, quinolines, isoquinolines, tetrahydropyrimidines and fluoranthenes *via* electrocyclic ring closure or intermolecular hetero Diels–Alder reaction.[1,2] As part of our continuing interest in these key heterocumulenic species, we have extended this methodology to the preparation of other new types of conjugated carbodiimides **4–9** and **19–24** and to their synthetic application to nitrogen heterocycles, *viz*. 2-aminoquinolines and α-carbolines, *via* the intramolecular cycloadditions outlined in Schemes 1 and 2.

The carbodiimides **4–9** and **19–24** possess 2-aza-1,3-diene

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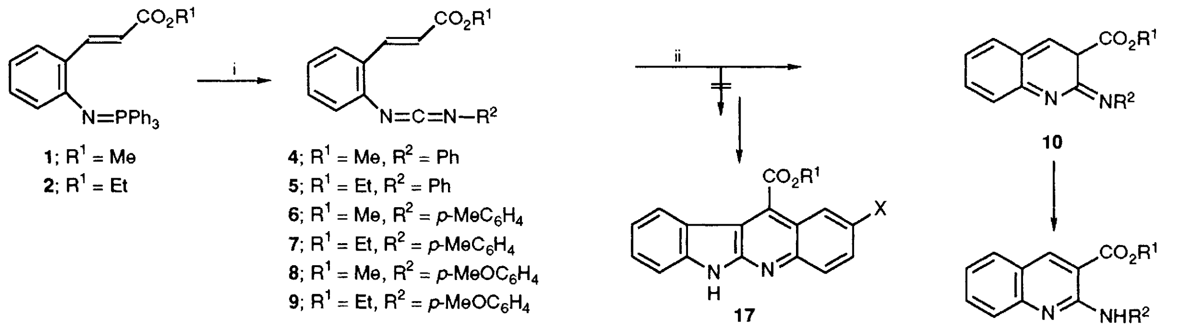

Scheme 1 *Reagent and conditions*: i, O=C=N–R^2 **3**, room temp., 1 h, in benzene; ii, 140 °C in xylene, 3–5 h

units of (X)=C=N–C=C structure (including the aromatic ring) capable of undergoing Diels–Alder reaction either inter- or intra-molecularly. There are some examples of conjugated isocyanates, isothiocyanates, ketenimines and carbodiimides incorporating such structural units taking part as 1,3-diene components in Diels–Alder reactions.[1–4] Otherwise, it is possible for the carbodiimides **4–9** and **19–24** to undergo electrocyclisation using, *e.g.* the conjugated system consisting of C=C(unsaturation)–C=C(*o*-phenylene)–N=C(one cumulene bond). Thus, peri- and site-selectivity in the cycloadditions of these conjugated carbodiimides are also of interest, as well as application to heterocycle synthesis.

Iminophosphoranes **1** and **2**, readily available by the Staudinger reaction from *o*-azidocinnamates and triphenylphosphine, underwent a Wittig-type reaction with isocyanates **3** to give the carbodiimides **4–9** (Scheme 1). The carbodiimides could be obtained as oily monomers in good yields and characterized spectroscopically (Table 1).† On heating **4–9** at 140 °C in xylene, electrocyclisation took place with complete site- and peri-selectivities to produce 2-aminoquinolines **11–16**† *via* prototropic aromatisation of **10**. No other probable product could be detected (TLC, NMR): *e.g.*, 6*H*-indolo[2,3-*b*]quinolines **17** which, in the light of Molina's case, might have been produced.‡

Table 1 Yields of carbodiimides **4–9** and quinolines **11–16**

Carbodiimide	Yield (%)	Cycloadduct	Yield (%)
4	96	**11**	81
5	81	**12**	76
6	93	**13**	74
7	82	**14**	70
8	89	**15**	80
9	85	**16**	72

While the conjugated carbodiimides **19–24** could be isolated by similar treatment of **1** and **2** with isocyanates **18**, they were conveniently converted by a one-pot procedure into the corresponding heterocycles **26–33** *via* cycloaddition (Scheme 2). In contrast to the above results, carbodiimides **19–22** underwent intramolecular Diels–Alder reaction to afford eventually pyrido[2,3-*b*]indoles (α-carbolines) **26–29**† on heating at 140 °C in xylene in the presence of activated MnO_2 or nitrobenzene, or followed by treatment with DDQ–$NaCO_3$ (Table 2).‡ Without the dehydrogenation agents, **26–29** were obtained in lower yields and accompanied by mixtures of intermediates of the initial cycloadducts **25**.

† The reaction mixture was purified by means of column chromatography and recrystallisation (except for the oily carbodiimides) to give the isolated product(s).

Selected physical data: **9** (yellowish oil): ν_{max}/cm^{-1} 2136 (N=C=N) and 1716 (CO); δ_H ($CDCl_3$) 1.34 (t, 3H, *J* 7.8 Hz, Me), 3.77 (s, 3H, OMe), 4.30 (q, 2H, *J* 7.8 Hz, OCH_2), 6.49 (d, 1H, *J* 16.2 Hz, =CH), 6.71–7.67 (m, 8H, ArH) and 8.14 (d, 1H, *J* 16.2 Hz, CH=); δ_C ($CDCl_3$) 14.33 (Me), 55.29 (OMe), 60.37 (OCH_2) and 114.78–166.62 (CO); *m/z* 322 (M^+, 45%), 277 (10, M^+ – OEt) and 249 (100, M^+ – CO_2Et).

16 (orange rhombs): m.p. 119–120 °C; *m/z* 322.1317, $C_{19}H_{18}N_2O_3$ requires 322.1318; ν_{max}/cm^{-1} 3320 and 3284 (NH) and 1698 (CO); δ_H 1.41 (t, 3H, *J* 7.2 Hz, Me), 3.81 (s, 3H, OMe), 4.41 (q, 2H, *J* 7.2 Hz, OCH_2), 6.79–8.00 (m, 8H, ArH), 8.64 (s, 1H, 4-H) and 10.10 (s, 1H, NH); δ_C 14.22 (Me), 55.46 (OMe), 61.54 (OCH_2) and 110.28–167.08 (CO); *m/z* 322 (M^+, 100%), 321 (43, M^+ –1) and 249 (12, M^+ – CO_2Et).

24 (yellowish oil): ν_{max}/cm^{-1} 2140 (N=C=N) and 1712 (CO): δ_H 1.33 (t, 3H, *J* 7.26 Hz, Me), 4.27 (q, 2H, *J* 7.26 Hz, OCH_2), 6.49 (d, 1H, *J* 16.16 Hz, =CH), 6.73 (dd, 1H, *J* 3.63 and 1.32 Hz, 3′-H), 6.83 (dd, 1H, *J* 5.61 and 3.63 Hz, 4′-H), 6.94 (dd, 1H, *J* 5.61 and 1.32 Hz, 5′-H), 7.13–7.25 (m, 2H, ArH), 7.30–7.36 (m, 1H, ArH), 7.57 (dd, 1H, *J* 7.92 and 1.32 Hz, ArH) and 8.08 (d, 1H, *J* 16.16 Hz, CH=); δ_C 14.32 (Me), 60.58 (OCH_2) and 119.89–166.75 (CO); *m/z* 298 (M^+, 6%), 253 (3, M^+ – OEt) and 225 (47, M^+ – CO_2Et).

31 (yellow needles): m.p. 255–256 °C, *m/z* 296.0622, $C_{16}H_{12}N_2O_2S$ requires 296.0621; ν_{max}/cm^{-1} 3208 (NH) and 1722 (CO); δ_H 1.58 (t, 3H, *J* 7.18 Hz, Me), 4.71 (q, 2H, *J* 7.18 Hz, OCH_2), 7.30 (ddd, 1H, *J* 2.19, 6.23 and 8.06 Hz, 6-H), 7.45 (d, 1H, *J* 6.23 Hz, 3-H), 7.53–7.58 (m, 2H, 7-H and 8-H), 7.73 (d, 1H, *J* 6.23 Hz, 2-H), 8.45 (d, 1H, *J* 8.06 Hz, 5-H) and 9.22 (s, 1H, NH); δ_C (CD_3SOCD_3) 11.06 (Me), 62.06 (OCH_2) and 111.04–166.25 (CO); *m/z* 296 (M^+, 100%), 251 (10, M^+ – OEt) and 223 (33, M^+ – CO_2Et).

33 (yellow needles): m.p. 85.6–87.4 °C; *m/z* 298.0774, $C_{16}H_{14}N_2O_2S$ requires 298.0777); ν_{max}/cm^{-1} 3296 (NH) and 1690 (CO); δ_H 1.46 (t, 3H, *J* 7.26 Hz, Me), 4.43 (q, 2H, *J* 7.26 Hz, OCH_2), 6.77 (dd, 1H, *J* 1.32 and 3.62 Hz, 3′-H), 6.84 (dd, 1H, *J* 1.32 and 5.44 Hz, 5′-H), 6.92 (dd, 1H, *J* 3.62 and 5.44 Hz, 4′-H), 7.29 (d, 1H, *J* 7.26 Hz, 8-H), 7.64–7.69 (m, 2H, 6-H and 7-H), 7.86 (d, 1H, *J* 8.91 Hz, 5-H), 8.70 (s, 1H, 4-H) and 10.81 (s, 1H, NH); δ_C 14.22 (Me), 61.74 (OCH_2) and 109.74–166.90 (CO); *m/z* 298 (M^+, 100%), 252 (85, M^+ – OEt – H) and 224 (83, M^+ – CO_2Et – H).

Satisfactory elemental analyses were obtained for all new compounds.

‡ Recently Molina *et al.* reported that *ortho*-butadienyl-substituted diaryl- and aryl styryl-carbodiimides both underwent the intramolecular Diels–Alder reaction in a completely periselective fashion, furnishing the corresponding dehydrogenatively aromatized compounds of the initial adducts.[5]

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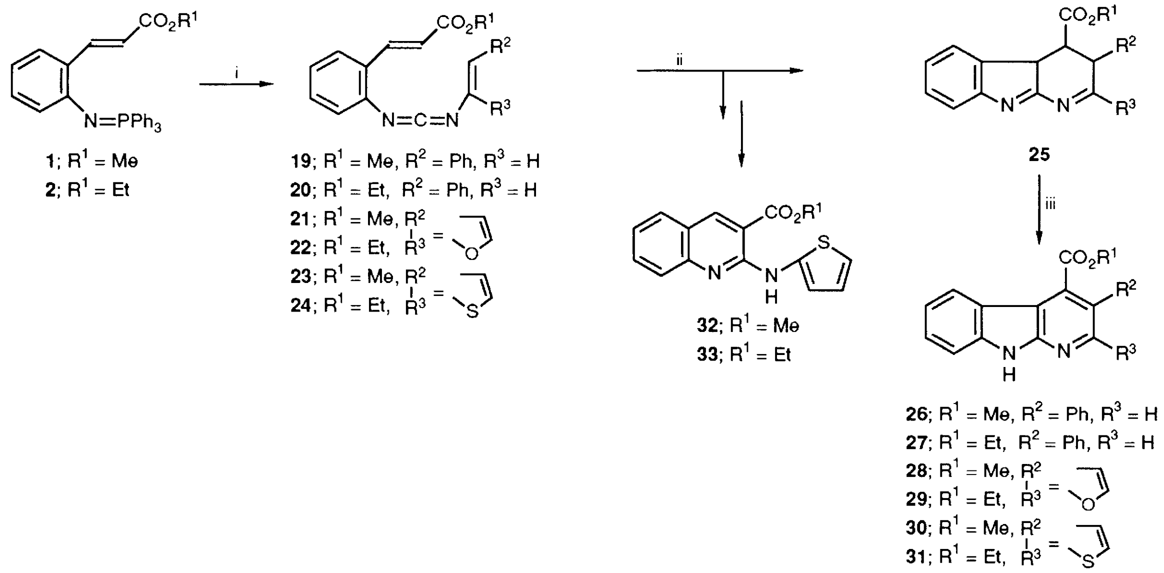

Scheme 2 *Reagents and conditions*: i, O=C=N–CR^3=CHR^2 **18**, room temp., 1 h, in xylene or benzene; ii, 140 °C in xylene, 15–30 min; iii, MnO_2, $PhNO_2$, or DDQ–Na_2CO_3

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Table 2 One-pot synthesis of α-carbolines **26–31** and quinolines **32** and **33** from **1** and **2** + **18** *via* carbodiimides **19–24**

Cycloadduct	Yield (%)[a]	Cycloadduct	Yield (%)[a]
26	45, 19,[b] 43[c]	**30**	55
27	33, 20[b]	**31**	33
28	47[d]	**32**	15
29	45[d]	**33**	13

[a] In the presence of MnO_2. [b] Dichlorodicyanobenzoquinone (DDQ)–Na_2CO_3 (Florisil). [c] In the presence of $PhNO_2$. [d] Based on isolated **21** or **22**.

Interestingly, the thienyl-substituted carbodiimides **23** and **24**, on the similar treatment in the presence of MnO_2, gave both the cycloadducts, **30** and **31**, and **32** and **33** (Table 2).† It is likely that the competition between the electrocyclisation and the intramolecular Diels–Alder reaction depends on the C=C bond character of the diene component, *viz*. relatively more alkenic or more aromatic, in these conjugated carbodiimides with the electron-withdrawing dienophilic C=C–CO_2R group.

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