New Cyclopenta[*b*]-pyrroles and -pyridines by Reaction of 2-Azido- and 2-Phosphoranylideneaminocyclopent-1-ene-1-carbaldehydes with Aliphatic Esters

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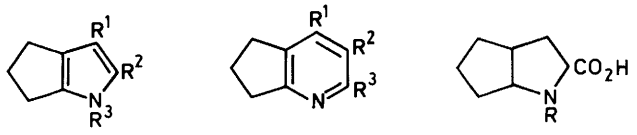
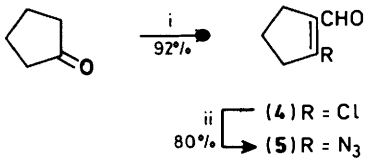
A new cyclopenta[*b*]pyrrole has been synthesized by reaction of 2-azidocyclopent-1-ene-1-carbaldehyde with ethyl acetate and subsequent thermal cyclisation. Dicyclopenta[*b,e*]pyrazines have been isolated from a similar reaction with ethyl propionate or t-butyl propionate. Condensation of the corresponding iminophosphorane from 2-azidocyclopent-1-ene-1-carbaldehyde with ethyl acetate and cyclisation of the dienic iminophosphorane so obtained gave a cyclopenta[*b*]pyridine. The products were characterized on the basis of ^{1}H n.m.r., i.r., and mass spectrometric results.

Cyclopenta[*b*]-pyrroles and pyridines (**1**) and (**2**) are of interest both with regard to the chemistry of natural products [1] and the pharmacological properties [2] of several of their derivatives. Moreover, the cyclopenta[*b*]pyrroles (**1**; $R^2 = CO_2Et$) are precursors for the synthesis of the tetrahydrocyclopenta[*b*]-pyrroles (**3**) which have been recently studied as potential angiotensin converting enzymes [3] and dipeptidyl carboxy-peptidase inhibitors.[4] Thus, Urbach and Henning [5] have prepared the pyrrolidine (**3**; R = H) by hydrogenation of the pyrrole (**1**; R^1 = H, $R^2 = CO_2Et$, $R^3 = CH_2Ph$) obtained from 2-chlorocyclopent-1-ene-1-carbaldehyde (**4**).



(**1**) (**2**) (**3**)

We now report a new method for the synthesis of (**1**) and (**2**) involving condensation of active methylene aliphatic esters with the aldehyde group of the 2-azidocyclopent-1-ene-1-carbaldehyde (**5**), or the corresponding iminophosphorane (**8**), followed by thermal cyclization. The cyclization step can be performed either by nitrene attack on the unsaturated side-chain,[6] or by an intramolecular aza-Wittig reaction,[7] starting from (**5**) and (**8**) respectively. In a previous communication,[8] we described a very efficient preparation from cyclopentanone of the azide (**5**) (see Scheme 1), noting that the latter is more stable than its



Scheme 1. *Reagents and reaction conditions:* i, $POCl_3$–DMF, CH_2Cl_2, 0 °C; ii. NaN_3, DMSO, +10 °C

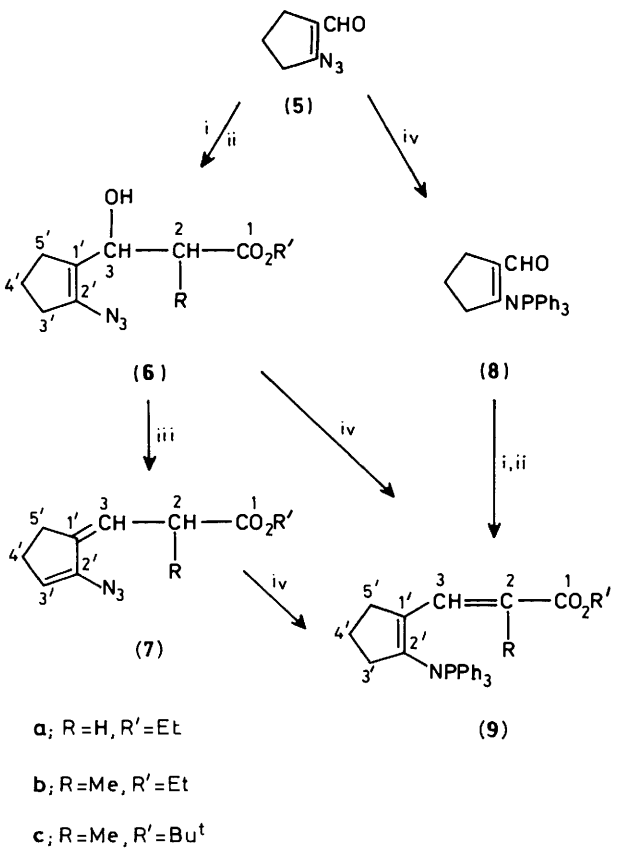
precursor (**4**) and, furthermore, can be converted in 80% yield into the iminophosphorane (**8**) (see Scheme 2).

Results and Discussion

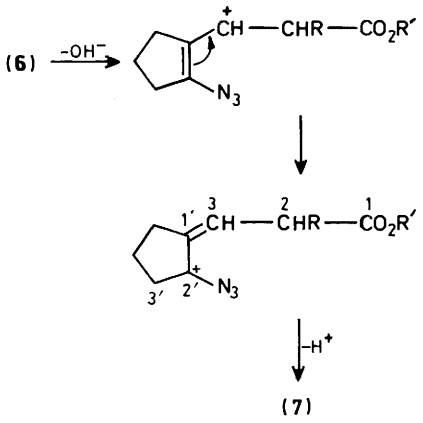
Condensations.—Nucleophilic addition of the lithium enolate of acetic and propionic esters to the azide (**5**) at −78 °C in tetrahydrofuran (THF), followed by acid hydrolysis affords the azides (**6**) (see Scheme 2). The ^{1}H n.m.r. spectrum of (**6a**) showed two diastereotopic groups corresponding to the methylene protons 2-H_2 and 5′-H_2 closest to the asymmetric carbon atom. Simplification of the 3-H multiplet to a doublet of doublets upon treatment of the compound with D_2O enabled us to establish the coupling constants between 3-H and the two C-2 protons (*J* 9.3 and 3.6 Hz). The observation of two resonances of nearly equal intensities for most of the signals of (**6b**) indicated the presence of a mixture of two diastereoisomers. In contrast, single resonances for all the signals of (**6c**) as well as 11 carbon resonances in the ^{13}C n.m.r. spectrum suggested that the product was a single diastereoisomer. This change could be explained by the replacement of the Et group by the Bu^t group.

Since an unsaturated side-chain was required for cyclization, dehydration of the azides (**6**) was then carried out in benzene at 0 °C by an equimolar mixture of phosphorus oxychloride and pyridine. Unexpectedly, the final products were the non-conjugated dienic azides (**7**). Their structures were deduced from spectroscopic results. Such data showed a weak coupling constant (*J ca.* 0.7 Hz) between the two protons in the olefinic region of the ^{1}H n.m.r. spectrum of the three derivatives (**7**) as well as only two methylene residues and a doublet for the 2-Me in the spectrum of (**7b**) and (**7c**). Moreover, the observation of a diastereotopic group for the methylene protons 5′-H_2 of (**7b**) and (**7c**) established the presence of an asymmetrical carbon and confirmed the existence of a cyclic double bond. The migration of the double bond during the dehydration is readily explained by the rearrangement of the initially formed secondary cation into the more stable tertiary one (see Scheme 3).

Condensation of the iminophosphorane (**8**) with the same esters was achieved under identical conditions and produced the dehydrated derivatives (**9**). The latter were also obtained by addition of triphenylphosphine to the azides (**7**) or (**6a**) at room temperature in toluene. Under the same conditions, (**6b**) and (**6c**) produced an inseparable mixture of hydrated and dehydrated derivatives. It is noteworthy that formation of the iminophosphorane was accompanied by dehydration of (**6a**) or a C-2 to C-3′ 1,5-sigmatropic hydrogen shift for (**7**). The very mild conditions in which the latter rearrangement was observed can probably be explained by the lability of the 2-H protons adjacent to the ester group. The ^{1}H n.m.r. spectra showed a large coupling constant (*J* 15.2 Hz) between the two olefinic protons of (**9a**) and a singlet for the methyl groups on C-2 of (**9b**) and (**9c**). These data allowed us definitely to eliminate an isomeric structure showing one cyclic double bond. In addition,



Scheme 2. *Reagents and reaction conditions:* i, LDA, THF, −78 °C; ii, RCH_2CO_2R'; iii, $POCl_3$, pyridine, benzene, 0 °C; iv, PPh_3, toluene, room temp.



Scheme 3.

the value of the above coupling constant indicated that the exocyclic double bond of (**9a**) adopts the *trans* configuration. The distance between the nitrogen atom and the ester carbonyl group is, therefore, very large and does not promote a further cyclization.

Cyclizations.—The azides (**7**) in refluxing xylene afforded the cyclopenta[*b*]pyrrole (**12**) or the dicyclopentapyrazines (**14**) and (**15**) depending on the nature of the substituent on C-2 (see Scheme 4). Since the side chains of (**14**) and (**15**) were unaffected by the reaction, the formation of these compounds can be rationalized by assuming initial decomposition of the azide (**7**). The coupling of the resulting nitrene (**10**) gives a dihydropyrazine intermediate (**13**), which is spontaneously oxidized as previously reported.[9] When the substituent on C-2 is an hydrogen atom, the conjugated nitrene (**11a**) is presumably formed as an intermediate since only conjugated vinyl azides cyclize into pyrrole derivatives,[6] the non-conjugated ones decomposing into azirines.[10] This hypothesis is strongly supported by the fact that the 1,5-sigmatropic rearrangement of the nitrene (**10**) to give the nitrene (**11a**) is closely similar to that observed for the preparation of (**9**) from the same starting material (**7**). The latter rearrangement failed to occur when there was a 2-methyl group, probably because of the reduced lability of 2-H in (**7b**) and (**7c**). The ^1H n.m.r. spectra of (**14**) and (**15**) established the symmetrical nature of the products. In the case of (**15**), the Bu^t and the Me groups gave rise to two signals of nearly equal intensity corresponding to two diastereoisomers. We compared the broadband decoupled and the INEPT spectra of (**15**) to show that a dihydropyrazine structure is not possible. The disappearance of five signals in the INEPT spectrum showed the presence of five quaternary carbons. Among the latter, the signals at 82 and 175 p.p.m. were readily assigned to the quaternary carbon of the Bu^t group and to the carbonyl carbon. Therefore, the three quaternary carbon signals in the region 140—160 p.p.m. remained to be assigned. In addition, according to the value of coupling constants (*J* 132 and 164 Hz), the two doublet signals (δ 42.8 and 125.9 p.p.m.) in the INEPT spectrum were attributable to two CH residues. These signals unambiguously assigned to C-1′ and C-2′ established the pyrazine structure. Indeed, three CH residues and only four quaternary carbons would be expected in the dihydropyrazine structure.

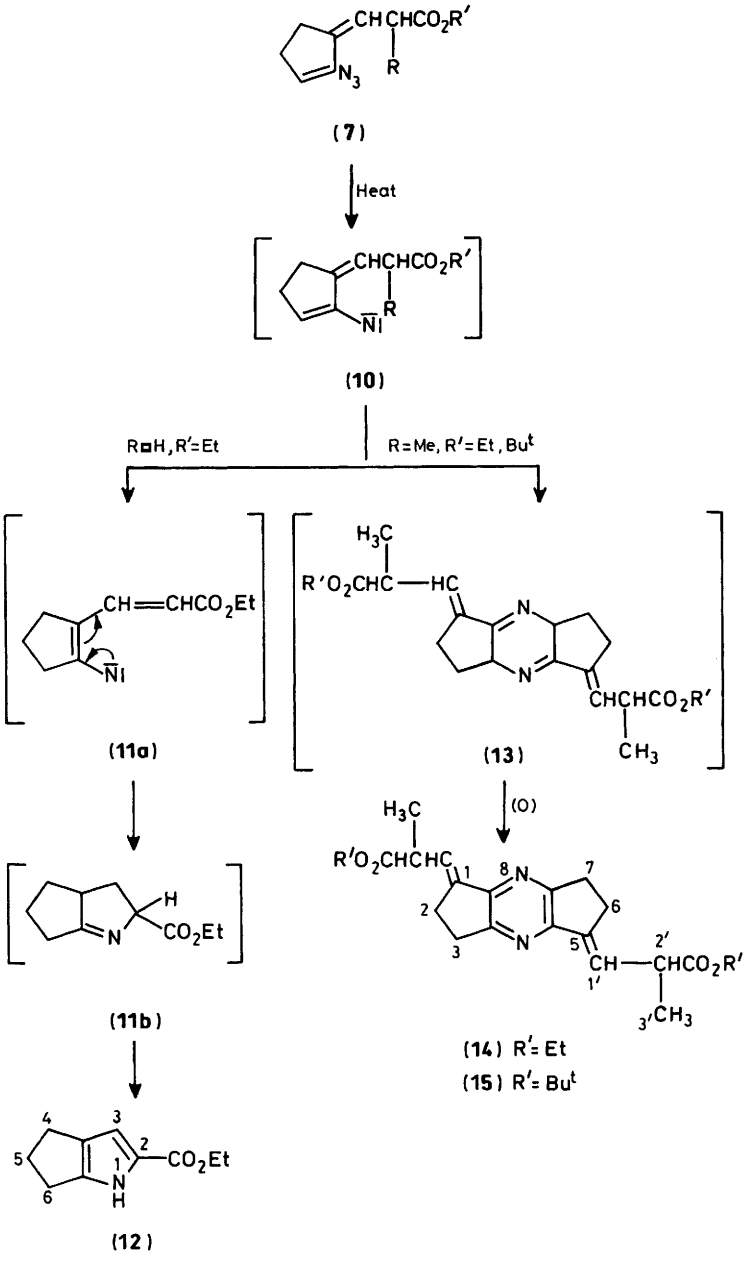
Attempted cyclizations of the iminophosphoranes (**9**) under the usual conditions were unsuccessful, a failure expected in the case of (**9a**) in view of its previously demonstrated unfavourable configuration. Replacement of 2-H by a Me group for compounds (**9**) failed to change their configuration: compounds of suitable products are reported[11] to undergo aza-Wittig reactions under relatively mild conditions. In spite of the unfavourable configuration of (**9a**), the desired cyclopentapyridine (**16**) was obtained by using tetralin (b.p. 207 °C) as solvent (see Scheme 5).

That (**9b**) and (**9c**) failed to cyclize under these conditions is explicable in conformational terms (see Scheme 6). Thus, whereas conformation (**B**) is the major one for (**9b**) and (**9c**) because of the steric hindrance between the methyl and the iminophosphorane group, two conformations, (**A**) and (**B**), are possible for (**9a**). The phosphorus–nitrogen bond of the iminophosphoranes being strongly polarized,[12] several mesomeric forms are to be considered (see Scheme 7). Thus, the formula corresponding to a negative charge located on C-2 enables cyclization *via* the *cis* isomer. The relative stabilities of carbanions compared to the starting compound bearing the negative charge on the nitrogen atom explain that a high temperature is required to induce the cyclization.

Mass and ^1H n.m.r. spectra are in good agreement with the proposed structures. In particular, besides the molecular ion at 163 and the $[M - C_2H_4]^+$ ion at 135 the mass spectrum of (**16**) showed one peak at 107, resulting from the usual loss[13] of the ring carbonyl from the parent ion at 135, to give the 5,6-dihydro-4*H*-cyclopenta[*b*]pyrrole ion. The sole ambiguity in the n.m.r. spectrum of (**16**) concerned the assignments of the triplet signals at 2.90 and 2.83 corresponding to the cyclic methylene groups (5-H_2 or 7-H_2). The doublet signals at 6.47 and 7.38 have been assigned to 3-H and 4-H by comparison of their chemical shifts with those of known 2-alkoxypyridines.[14]

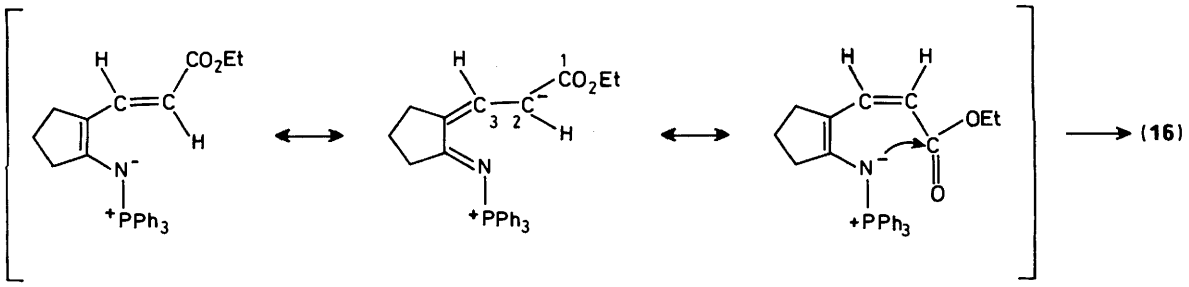
Experimental

M.p.s were determined on a Kofler heated stage, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 580 B



Scheme 4.

[redacted] spectrophotometer. N.m.r. spectra were obtained at 400.13



Scheme 7.

at −78 °C, after which a solution of the azide (**5**) (822 g, 60 mmol) in dry THF (40 ml) was injected slowly, causing the colour of the whole to turn immediately orange. The reaction mixture was stirred at the same temperature for 2.5 h, after which hydrochloric acid (2M; 55 ml) was added and the solution was allowed to warm to room temperature. The mixture was extracted with diethyl ether and the extracts were washed with water, dried, and evaporated under reduced pressure. Chromatography of the residue over silica gel eluting with ether–heptane (2:3) gave the azides (**6**).

(a) *With ethyl acetate: ethyl* 3-(2-*azidocyclopent*-1-*enyl*)-3-*hydroxypropionate* (**6a**). A colourless oil, yield 67% (Found: C, 53.55; H, 6.7. $C_{10}H_{15}N_3O_3$ requires C, 53.32; H, 6.71%); $\nu_{max.}$(film) 3 446 (OH), 2 111 (N_3), 1 735 (CO), 1 668 (C=C), and 1 145 cm^{-1} (OEt); $\delta_H(CDCl_3)$ 1.28 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 1.95 (2 H, m, 4′-H_2), 2.37 (1 H, m, 5′-H), 2.46 (1 H, dd, *J* 16.1 and 3.6 Hz, 2a-H), 2.51 (1 H, m, 5′-H), 2.60 (2 H, m, 3′-H_2), 2.61 (1 H, m, 2b-H), 2.96 (1 H, d, disappears on D_2O shake, *J* 4.0 Hz, OH), 4.17 (2 H, q, *J* 7.2 Hz, CH_2CH_3), and 4.84 (1 H, m, collapses to a dd, *J* 9.3 and 3.6 Hz, upon deuteriation, 3-H).

(b) *With ethyl propionate: ethyl* 3-(2-*azidocyclopent*-1-*enyl*)-3-*hydroxy*-2-*methylpropionate* (**6b**). A yellow oil, yield 70% (Found: C, 55.2; H, 7.1; O, 20.4. $C_{11}H_{17}N_3O_3$ requires C, 55.22; H, 7.16; O, 20.06%); $\nu_{max.}$(film) 3 462 (OH), 2 111 (N_3), 1 732 (CO), 1 668 (C=C), and 1 127 cm^{-1} (OEt); $\delta_H(CDCl_3)$ [mixture (1:1) of the two diastereoisomers] 1.04 and 1.19 (2 × 3 H, 2 × d, *J* 7.2 Hz, 2-Me), 1.25 and 1.27 (2 × 3 H, 2 × t, *J* 7.2 Hz, CH_2CH_3), 1.92 and 1.94 (2 × 2 H, 2 × m, 4′-H_2), 2.24—2.69 (2 × 5 H, 2 × m, 2-H, 3′-H_2, and 5′-H_2), 2.71 and 2.74 (2 × 1 H, 2 × d, disappears on D_2O shake, *J* 5.5 Hz, OH), 4.13 and 4.17 (2 × 2 H, 2 × q, *J* 7.2 Hz, CH_2CH_3), and 4.52 and 4.58 (2 × 1 H, 2 × m, collapses to 2 d, *J* 5.5 and 9.1 Hz, upon deuteriation, 3-H).

(c) *With t-butyl propionate: t-butyl* 3-(2-*azidocyclopent*-1-*enyl*)-3-*hydroxy*-2-*methylpropionate* (**6c**). Yellow needles, yield 66%, m.p. 32 °C (from heptane) (Found: C, 58.45; H, 7.85; O, 18.05. $C_{13}H_{21}N_3O_3$ requires C, 58.41; H, 7.92; O, 17.95%); $\nu_{max.}$(KBr) 3 466 (OH), 2 104 (N_3), 1 732 (CO), 1 668 (C=C), and 1 151 cm^{-1} (OBu^t); $\delta_H(CDCl_3)$ 1.02 (3 H, d, *J* 7.2 Hz, 2-Me), 1.46 (9 H, s, Bu^t), 1.95 (2 H, m, 4′-H_2), 2.28 (1 H, m, 5′-H), 2.48 (1 H, qd, *J* 8.8 and 7.2 Hz, collapsing to a d, *J* 8.8 Hz, on irradiation at 1.02 p.p.m., 2-H), 2.52 (1 H, m, 5′-H), 2.61 (2 H, m, 3′-H_2), 2.93 (1 H, d, disappears on D_2O shake, *J* 4.6 Hz, OH), and 4.49 (1 H, dd, *J* 8.8 and 4.6 Hz, collapses to a d, *J* 8.8 Hz, upon deuteriation, 3-H); δ_C (100.6 MHz, $CDCl_3$, broadband decoupled spectrum) 14.7, 21.0, 30.3, 31.8 (C-3′, C-4′, C-5′, or $CHCH_3$), 28.7 [$C(CH_3)_3$], 45.4 (C-2), 69.7 (C-3), 81.7 [$C(CH_3)_3$], 126.7, 134.6 (C-1′ or C-2′), and 175.8 (CO_2Bu^t).

Dehydration of the Azides (**6**): *General Procedure.*—To a stirred solution of the azide (**6**) (14 mmol) in dry benzene (45 ml) at room temperature was added rapidly pyridine (3.4 ml, 42 mmol). After dropwise addition of phosphorus oxychloride (4 ml, 42 mmol) at 0 °C, and stirring for 5 h at the same temperature, hydrochloric acid (2M; 100 ml) was added slowly. The solution was then allowed to warm to room temperature after which it was extracted with diethyl ether. The extracts were washed with water, dried, and evaporated under reduced pressure. Chromatography of the residue over silica gel eluting with ether–heptane (1:3) gave the dienic azides (**7**).

Dehydration of (**6a**): *ethyl* 3-(2-*azidocyclopent*-2-*enylidene*)-*propionate* (**7a**). Yellow oil, yield 74% (Found: C, 57.85; H, 6.4; O, 15.75. $C_{10}H_{13}N_3O_2$ requires C, 57.96; H, 6.32; O, 15.44%); $\nu_{max.}$(film) 2 117 (N_3), 1 732 (CO), 1 618 (cyclic C=C), 1 598 (exocyclic C=C), and 1 157 cm^{-1} (OEt); $\delta_H(CDCl_3)$ 1.26 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 2.52 (2 H, m, 4′-H_2), 2.58 (2 H, m, 5′-H_2), 3.06 (2 H, d, *J* 7.4 Hz, 2-H), 4.14 (2 H, q, *J* 7.2 Hz, CH_2CH_3), 5.51 (1 H, m, collapses to a t, *J* 2.6 Hz, on irradiation at 2.58 p.p.m., 3-H), and 5.69 (1 H, m, 3′-H).

Dehydration of (**6b**): *ethyl* 3-(2-*azidocyclopent*-2-*enylidene*)-2-*methylpropionate* (**7b**). Yellow oil, yield 66% (Found: C, 60.05; H, 6.8; O, 14.25. $C_{11}H_{15}N_3O_2$ requires C, 59.71; H, 6.83; O, 14.46%); $\nu_{max.}$(film) 2 117 (N_3), 1 732 (CO), 1 662 (cyclic C=C), 1 595 (exocyclic C=C), and 1 174 cm^{-1} (OEt); $\delta_H(CDCl_3)$ 1.24 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 1.25 (3 H, d, *J* 7.0 Hz, 2-Me), 2.52 (2 H, m, 4′-H_2), 2.59 and 2.68 (2 H, 2 × m, 5′-H_2), 3.19 (1 H, qd, *J* 7.0 and 9.5 Hz, 2-H), 4.12 (2 H, q, *J* 7.2 Hz, CH_2CH_3), 5.36 (1 H, m, 3-H), and 5.69 (1 H, t, *J* 2.9 Hz, 3′-H).

Dehydration of (**6c**): *t-butyl* 3-(2-*azidocyclopent*-2-*en*-1-*ylidene*)-2-*methylpropionate* (**7c**). Yellow oil, yield 77% (Found: C, 62.65; H, 7.6. O, 12.95. $C_{13}H_{19}N_3O_2$ requires C, 62.63; H, 7.68; O, 12.83%); $\nu_{max.}$(film) 2 117 (N_3), 1 728 (CO), 1 662 (cyclic C=C), 1 598 (exocyclic C=C), and 1 151 cm^{-1} (OBu^t); $\delta_H(CDCl_3)$ 1.21 (3 H, d, *J* 7.1 Hz, 2-Me), 1.43 (9 H, s, Bu^t), 2.52 (2 H, m, 4′-H_2), 2.59 and 2.68 (2 H, 2 × m, 5′-H_2), 3.09 (H, qd, *J* 7.1 and 9.5 Hz, 2-H), 5.34 (1 H, m, 3-H), and 5.68 (1 H, m, 3′-H).

Synthesis of Dienic Iminophosphoranes (**9**): *General procedures.*—(a) *From the iminophosphorane* (**8**). The procedure was performed as previously described for the condensation of esters with the azide (**5**).

(b) *From the azide* (**6a**). A solution of triphenylphosphine (1.15 g, 4.4 mmol) in anhydrous toluene (50 ml) was added dropwise at room temperature to a solution of the azide (**6a**) (4.5 mmol) in the same solvent (50 ml). After the mixture had been stirred for 7 h at room temperature, solvent was evaporated under reduced pressure. Chromatography of the residue over silica gel eluting with ether–heptane (1:1) followed by recrystallization from dichloromethane–heptane (1:1) afforded the dienic iminophosphorane (**9a**).

(c) *From the dienic azides* (**7**). The dienic iminophosphoranes (**9**) were obtained using the procedure described in (b).

Ethyl 3-(2-*triphenylphosphoranylideneaminocyclopent*-1-*enyl*)*propionate* (**9a**). Yield 89% from (**8**), 86% from (**6a**), 98% from (**7a**); m.p. 178 °C (Found: C, 76.2; H, 6.4; N, 3.1; O, 7.2; P, 7.05. $C_{28}H_{28}NO_2P$ requires C, 76.17; H, 6.39; N, 3.17; O, 7.25; P, 7.02%); $\nu_{max.}$(KBr) 1 698 (CO), 1 665 (cyclic C=C), 1 595 (exocyclic C=C), and 1 145 cm^{-1} (OEt); $\delta_H(CDCl_3)$ 1.30 (3 H, t, *J* 7.2 Hz, CH_2CH_3), 1.71 (2 H, quint., *J* 7.3 Hz, 4′-H_2),

1.98 (2 H, t, *J* 7.3 Hz, 3′-H_2 or 5′-H_2), 2.39 (2 H, t, *J* 7.3 Hz, 5′-H_2 or 3′-H_2), 4.20 (2 H, q, *J* 7.2 Hz, CH_2CH_3), 5.37 (1 H, d, *J* 15.2 Hz, 2-H), 7.44—7.75 (15 H, m, ArH), and 8.35 (1 H, d, *J* 15.2 Hz, 3-H); *m/z* 441 (M^+, 17%), 412 (11), 396 (8), 368 (8), 354 (4), 262 (100), and 183 (44).

Ethyl 2-methyl-3-(2-triphenylphosphoranylideneaminocyclopent-1-enyl)propionate (**9b**). Yield 67% from (**8**), 90% from (**7b**); m.p. 186 °C (Found: C, 76.45; H, 6.6; N, 3.05; O, 7.0; P, 6.8. $C_{29}H_{30}NO_2P$ requires C, 76.46; H, 6.64; N, 3.07; O, 7.02; P, 6.80%); $\nu_{max.}$(KBr) 1 672 (CO), 1 632 (cyclic C=C), 1 598 (exocyclic C=C), 1 104 (OEt), 981, 842, and 714 cm^{-1} (aromatic bands); δ_H($CDCl_3$) 1.36 (3 H, t, *J* 7.1 Hz, CH_2CH_3), 1.69 (2 H, m, 4′-H_2), 1.96 (2 H, t, *J* 7.4 Hz, 3′-H_2 or 5′-H_2), 2.07 (3 H, s, 2-Me), 2.76 (2 H, t, *J* 6.9 Hz, 5′-H_2 or 3′-H_2), 4.20 (2 H, q, *J* 7.1 Hz, CH_2CH_3), 7.43—7.76 (15 H, m, ArH), and 8.39 (1 H, s, 3-H); *m/z* 455 (M^+, 17%), 426 (10), 410 (11), 354 (4), 262 (100), and 183 (44).

t-Butyl 2-methyl-3-(2-triphenylphosphoranylideneaminocyclopent-1-enyl)propionate (**9c**). Yield 75% from (**8**), 95% from (**7c**); m.p. 188 °C (Found: C, 77.0; H, 7.0; N, 2.85; O, 6.6; P, 6.45. $C_{31}H_{34}NO_2P$ requires C, 76.99; H, 7.09; N, 2.90; O, 6.62; P, 6.40%); $\nu_{max.}$(KBr) 1 668 (CO), 1 631 (cyclic C=C), 1 588 (exocyclic C=C), 1 104 (OBu^t) 987, 867, and 694 cm^{-1} (aromatic bands); δ_H([$^2H_6$]-DMSO) 1.53 (9 H, s, Bu^t), 1.65 (2 H, m, 4′-H_2), 1.90 (2 H, t, *J* 7.7 Hz, 3′-H_2 or 5′-H_2), 1.95 (3 H, s, 2-Me), 2.69 (2 H, t, *J* 6.8 Hz, 5′-H_2 or 3′-H_2), 7.59—7.78 (15 H, m, ArH), and 8.21 (1 H, s, 3 H); *m/z* 483 (M^+, 8%), 427 (7), 426 (11), 410 (5), 382 (13), 354 (25), 262 (100), and 183 (65).

Cyclization of Dienic Azides (**7**).—*Ethyl cyclopenta*[b]*pyrrole-2-carboxylate* (**12**). A solution of (**7a**) (0.5 g, 2.4 mmol) in dry xylene (100 ml) was refluxed for 16 h. The solvent was then distilled under reduced pressure and the residue was chromatographed over silica gel eluting with dichloromethane–acetone (8:1). Recrystallization from heptane afforded pure title compound (**12**) (0.36 g, 83%) as white needles, m.p. 124 °C (Found: C, 66.95; H, 7.3; N, 7.75; O, 17.8. $C_{10}H_{13}NO_2$ requires C, 67.02; H, 7.31; N, 7.82; O, 17.85%); $\nu_{max.}$(KBr) 3 286 (NH) and 1 665 cm^{-1} (CO); δ_H($CDCl_3$) 1.99 (3 H, t, *J* 7.1 Hz, CH_2CH_3), 2.37 (2 H, m, 5-H_2), 2.56 (2 H, t, *J* 7.0 Hz, 6-H_2), 2.66 (2 H, t, *J* 7.2 Hz, 4-H_2), 4.24 (2 H, q, *J* 7.1 Hz, CH_2CH_3), 6.61 (1 H, d, *J* 1.5 Hz, 3-H), and 8.77 (1 H, br s, NH); *m/z* 179 (M^+, 100%), 178 (9), 134 (48), 133 (98), 106 (31), and 105 (42).

1,5-*Bis*(2-*ethoxycarbonylpropylidene*)*dicyclopenta*[b,e]-*pyrazine* (**14**). A solution of (**7b**) (0.88 g, 4 mmol) in dry xylene (80 ml) was refluxed for 24 h. The solvent was evaporated under reduced pressure and the residue was chromatographed over silica gel eluting with ether–heptane (4:1). Recrystallization of the residue from heptane afforded the title compound (**14**) (0.32 g, 50%), m.p. 144 °C (Found: C, 68.75; H, 7.3; N, 6.95; O, 16.7. $C_{22}H_{28}N_2O_4$ requires C, 68.73; H, 7.34; N, 7.29; O, 16.64%); $\nu_{max.}$(KBr) 1 725 (CO), 1 662 (C=C), 1 605, and 1 147 cm^{-1} (OEt); δ_H($CDCl_3$) 1.25 (6 H, t, *J* 7.1 Hz, 2 × CH_2CH_3), 1.38 (6 H, d, *J* 7.0 Hz, 2 × $CHCH_3$), 2.78 to 2.95 (8 H, m, cyclic CH_2), 3.42 (2 H, qd, *J* 9.6 and 7.0 Hz, 2 × 2′-H), 4.15 (4 H, q, *J* 7.1 Hz, 2 × CH_2CH_3), and 6.83 (2 H, dt, *J* 9.6 and 2.5 Hz, 2 × 1′-H); *m/z* 384 (M^+, 60%), 339 (100), 311 (65), and 237 (14).

1,5-*Bis*(2-*t-butoxycarbonylpropylidene*)*dicyclopenta*[b,e]-*pyrazine* (**15**). From (**7c**), the above procedure was used to give the title compound (**15**) (0.51 g, 58%), m.p. 184 °C (Found: C, 70.9; H, 8.2; N, 6.3; O, 14.55. $C_{26}H_{36}N_2O_4$ requires C, 70.88; H, 8.24; H, 6.36; O, 14.53%); $\nu_{max.}$(KBr) 1 725 (CO), 1 662 (C=C), 1 605, 1 181, and 1 154 cm^{-1} (OBu^t); δ_H($CDCl_3$) 1.332 and 1.335 (6 H, 2 × d, *J* 7.0 and 6.9 Hz, 2 × CH_2CH_3), 1.43 and 1.44 (18 H, 2 × Bu^t), 2.78 to 2.92 (8 H, m, cyclic CH_2), 3.31 (2 H, qd, *J* 9.6 and 7.0 Hz, 2 × 2′-H), and 6.80 (2 H, m, 2 × 1′-H); δ_C(100.6 MHz, $CDCl_3$, broadband decoupled spectrum) 17.9 (C-3′), 26.5, 26.6 (C-2 or C-3), 28.7 (Me_3), 42.8 (C-2′), 81.2 (CMe_3), 125.9 (C-1′), 139.3, 140.3, 161.2 (C-1, C-3a, or C-8a), and 173.8 (CO_2); δ_C(100.6 MHz, $CDCl_3$, INEPT spectrum) 17.9 (q, *J* 129 Hz, C-3′), 26.5 (t, *J* 133 Hz, C-2), 26.6 (t, *J* 136 Hz, C-3), 28.7 (q, *J* 127 Hz, Me_3), 42.8 (d, *J* 132 Hz, C-2′), and 125.9 (d, *J* 164 Hz, C-1′); *m/z* 440 (M^+, 25%), 384 (29), 349 (50), 339 (36), 284 (52), 283 (56), 240 (39), 239 (63), and 57 (100).

Cyclization of Dienic Iminophosphoranes (**9**).—*2-Ethoxycyclopenta*[b]*pyridine* (**16**). A solution of (**9a**) (1.32 g, 3 mmol) in dry 1,2,3,4-tetrahydronaphthalene (tetralin) (60 ml) was refluxed for 9 h. The solvent was distilled under reduced pressure and the residue was chromatographed over silica gel eluting with ether–heptane (3:1) to give the pure title compound (**16**) (0.34 g, 70%) as a colourless oil (Found: C, 73.65; H, 8.1; N, 8.5; O, 9.85. $C_{10}H_{13}NO$ requires C, 73.59; H, 8.03; N, 8.58; O, 9.80%); $\nu_{max.}$(film) 1 595 (C=N), 1 455, 1 045, and 825 cm^{-1}; δ_H($CDCl_3$) 1.38 (3 H, t, *J* 7.0 Hz, CH_2CH_3), 2.10 (2 H, m, 6-H_2), 2.83 (2 H, t, *J* 7.4 Hz, 7-H_2 or 5-H_2), 2.90 (2 H, t, *J* 7.7 Hz, 5-H_2 or 7-H_2), 4.30 (2 H, q, *J* 7.0 Hz, CH_2CH_3), 6.47 (1 H, d, *J* 8.2 Hz, 3-H) (lit.,[14] 6.37 p.p.m. for 2-butoxypyridine; 6.62 p.p.m. for 2-methoxypyridine), and 7.38 (1 H, d, *J* 8.2 Hz, 4-H) (lit.,[14] 7.48 p.p.m. for 2-butoxypyridine; 7.40 p.p.m. for 2-methoxypyridine); *m/z* 163 (M^+, 24%), 148 (100), 135 (57), 134 (51), 119 (37), 107 (33), and 106 (51).

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