The guest molecules are located in isolated cavities. The shape of the acetonitrile molecule can be described as spherical tipped rod when characterizing by the ratios of the inertial moments of volume over those of surface.[5] The total packing coefficient is 0.68 while the local one is 0.38.

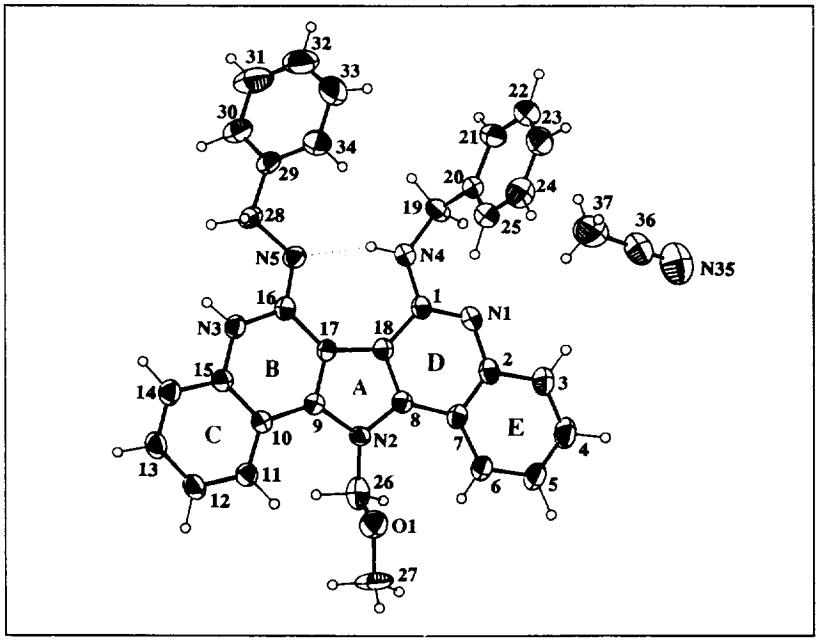


Fig.1.- Molecular structure of the acetonitrile complex of 4b and atomic numbering scheme. Displacement parameters are drawn at the 30% level and the hydrogen atoms are shown as spheres of arbitrary radii. Dotted lines mean hydrogen bonds.

In contrast to the only amino-imino tautomer observed in the solid state for **4b** the compounds **4** show in solution a tautomeric equilibrium between the diamino and amino-imino forms **4A-4B**, which is strongly dependent on the polarity of the solvent. In apolar solvents the tautomer **4A** is the only tautomer observed whereas in polar solvents the tautomer **4B** is found to be the predominant one.

Thus ^{1}H n.m.r. spectra of compound **4b** in $CDCl_3$ or benzene-d_6 indicated only the presence of the tautomer **A** whereas in acetone-d_6 solution both tautomers appeared in 1:1 ratio, and in DMSO-d_6 in a ratio 1:4 wise **B** being the predominant tautomer. Thus for **4b** in $CDCl_3$ the NH protons appeared at 6.36 ppm as a triplet and in DMSO-d_6 two signals appeared, as a triplet at 12.80 ppm and as a singlet at 9.94 ppm, due to the exocyclic and endocyclic NH protons respectively. On the other hand, for compound **4a** we have observed that in $CDCl_3$ only the tautomer **A** is observed whereas in DMSO-d_6 both tautomers appeared in a ratio 1:1. The low solubility of compounds **4c** and **4d** in the usual n.m.r. solvents do not allow us to study their possible tautomeric equilibria.

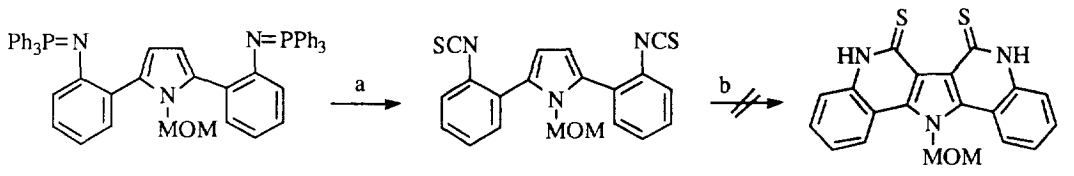
The reaction of bis(iminophosphorane) **3** with aliphatic iso(thio)cyanates and a proton source such as triethylammonium bromide led to the salts **5a-b** as the only reaction products in moderate yields (45-52 %) (Scheme 1). The ^{1}H n.m.r. spectra of **5a-b** in DMSO-d_6 showed a resonance in the range 16.02-16.71 ppm due to

a strong N...H...N hydrogen bridge characteristic of protonated "proton sponges".[6] In addition, both ^{1}H and ^{13}C n.m.r. spectra showed a high degree of symmetry in the molecule, due, probably, to a rapid exchange of the bridging proton between the two exocyclic nitrogens, which confirms the proposed structure **5a-b**. The reaction of bis(iminophosphorane) **3** with aromatic isocyanates in the presence of the same proton source did not give the expected salts **5c-d**. The basic behaviour of compounds **4a-b** could be explained by the fact that they are vinylogue of pentasubstituted biguanides, which display a high basic strength.[7] No protonation of compounds **4c-d** by the action of triethylammonium bromide may be ascribed to the fact that in the related biguanides alkylderivatives are stronger bases than are arylbiguanides. We should finally note that the transprotonation of **5a-b** with 1,8-bis(dimethylamino)naphthalene gives **4a-b**.

Table 1. Selected geometrical parameters (Å, °).

N1-C1	1.323(6)	N1-C2	1.388(6)	N2-C8	1.371(5)
N2-C9	1.403(5)	N3-C15	1.394(6)	N3-C16	1.361(6)
N4-C1	1.365(3)	N4-C19	1.437(6)	N5-C16	1.304(6)
N5-C28	1.471(6)	O1-C26	1.368(7)	O1-C27	1.459(6)
C1-C18	1.427(6)	C7-C8	1.437(6)	C8-C18	1.395(6)
C9-C10	1.431(6)	C9-C17	1.376(6)	C10-C15	1.421(6)
C16-C17	1.466(6)	C17-C18	1.445(6)	N35-C36	1.134(11)
C36-C37	1.431(18)				
C9-N2-C26	125.3(4)	C8-N2-C26	123.6(4)	C1-N4-C19	122.7(4)
C16-N5-C28	119.7(4)	C26-O1-C27	110.6(4)	N1-C1-N4	119.8(4)
N4-C1-C18	119.2(4)	N1-C1-C18	121.0(4)	N3-C16-N5	121.6(4)
N5-C16-C17	122.8(4)	N3-C16-C17	115.5(4)	N2-C26-O1	109.0(4)
N35-C36-C37	178.8(10)				
C8-N2-C26-O1	100.0(5)	C19-N4-C1-N1	8.4(7)	C1-N4-C19-C20	-95.4(5)
C28-N5-C16-N3	-0.1(7)	C16-N5-C28-C29	-173.6(4)	C27-O1-C26-N2	-178.2(4)
N4-C1-C18-C17	3.2(7)	N5-C16-C17-C18	1.5(8)	C16-C17-C18-C1	2.5(8)
N4-C19-C20-C25	19.6(7)	N5-C28-C29-C34	-51.1(7)		
Hydrogen interactions					
X-H...Y		X-H	X...Y	H...Y	X-H...Y
N4-H4...N5		0.89(4)	2.766(5)	1.92(4)	158(4)
C6-H6...O1		0.96(4)	3.303(6)	2.48(4)	143(3)
C11-H11...O1		0.99(4)	3.353(6)	2.50(4)	145(3)
N3-H3N...N35(-x+1, -y, -z)		0.93(6)	3.694(9)	2.78(6)	170(5)

Bis(iminophosphorane) **3** also reacted with carbon disulfide in benzene solution at reflux temperature to give the corresponding bis(isothiocyanate) **6** in 69 % yield, which was recovered unaltered after prolonged heating at 160 °C in a sealed tube (Scheme 2).

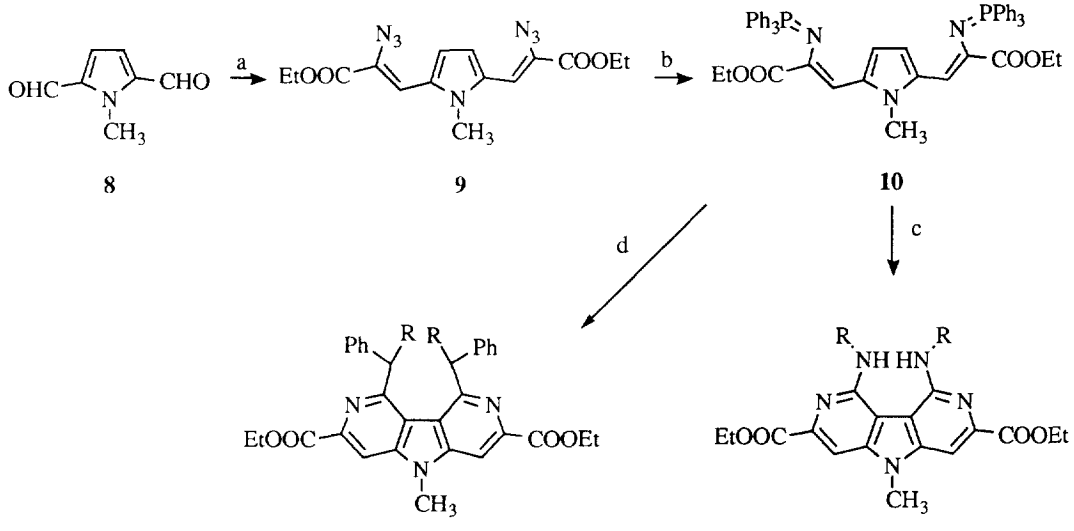


3 6 7

Reagents and Conditions (a) CS_2, benzene, reflux; (b) toluene, sealed tube, 160 °C.

Scheme 2

This bispyrido annulation reaction allows the preparation of dipyrido[4,3-*b*:3',4'-*d*]pyrroles **11** and **12**, structurally related to 9-azaellipticines but differing by deletion of a cycle, which exhibit good cytotoxicity on L1210 cultured cells and significant antitumor properties in the in vivo P388 leukemia system.[8] Only two methods for the preparation of this tricyclic ring system have been described. The first involves Fischer indole reaction of



8 9 10

12

R = C_6H_5, C_2H_5.

11

R = $C_6H_5.CH_2$, 4-Cl. C_6H_4, 4-$CH_3.C_6H_4$.

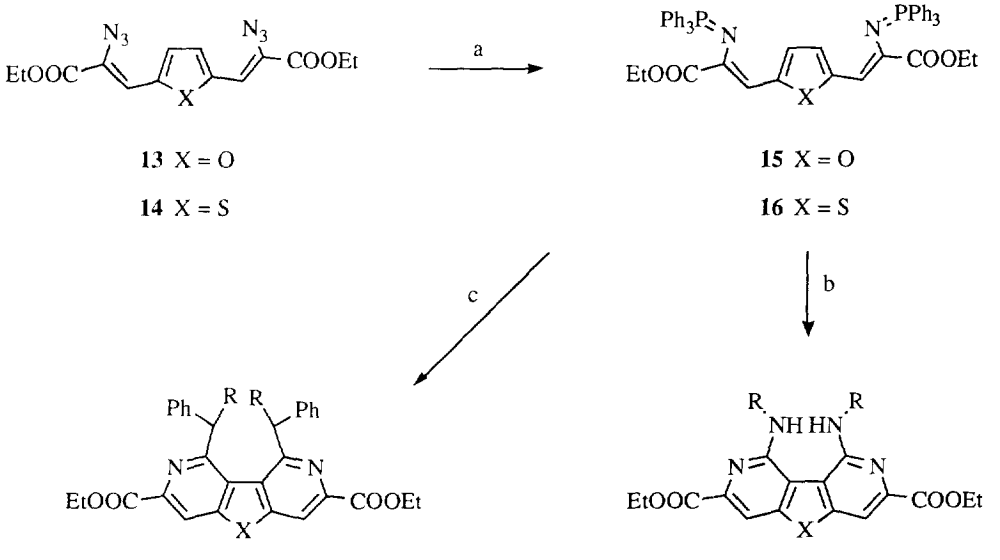
Reagents and Conditions (a) N_3CH_2COOEt, NaOEt, EtOH, - 10 °C; (b) PPh_3, CH_2Cl_2/Et_2O, r.t.; (c) 2 R-NCO, toluene, sealed tube, 160 °C; (d) 2 PhRCCO, toluene, r.t.

Scheme 3

4-hydrazino pyridine derivatives with *N*-acetyl piperidone and further dehydrogenation.[9] The second method is based on a pyrido annulation reaction onto a preformed pyrrolo[3,2-*c*]pyridine.[10]

Our approach is based on the simultaneous construction of the two pyridine rings by using the so-called aza Wittig/electrocyclic ring closure process. The pyrroledicarboxaldehyde **8**, readily available by reaction of *N*-methylpyrrole with α-dicarbonyl compounds and subsequent oxidation with periodate,[11] was subjected to reaction with ethyl azidoacetate at - 10 °C to give the bis(vinylazide) **9** in moderate yield (47 %). Staudinger reaction of compound **9** with triphenylphosphine in dichloromethane/diethyl ether at room temperature provided the key intermediate bis(iminophosphorane) **10** in almost quantitative yield (97 %). Bis(iminophosphorane) **10** reacted with two equivalents of isocyanates at 160 °C in a sealed tube for 8 h to give the tricyclic compounds **11** in 71-80 % yields, whereas the reaction with ketenes at room temperature gave **12** in 72-87 % yields (Scheme 3).

A logical step in this study was to extend this methodology to the preparation of the otherwise not readily available tricyclic compounds derived from furan and thiophene. The only method described for the preparation of furo[3,2-*c*:4,5-*c*']dipyridines involves formation of a pyridine ring onto a preformed appropriately substituted furo[3,2-*c*]pyridine.[12] Perhalogenated thieno[3,2-*c*:4,5-*c*']dipyridines have been prepared by photodehalogenation of perhalogenated 4-(4-pyridylthio)pyridines.[13]



13 X = O

14 X = S

15 X = O

16 X = S

19 X = O R= C_6H_5, C_2H_5.

20 X = S R = C_6H_5.

17 X = O R = $C_6H_5.CH_2$, 4-Cl.C_6H_4, 4-CH_3.C_6H_4.

18 X = S R = $C_6H_5.CH_2$, 4-CH_3.C_6H_4, 4-CH_3O.C_6H_4.

Reagents and Conditions (a) PPh_3, CH_2Cl_2/Et_2O, r.t.; (b) 2 R-NCO, toluene, sealed tube, 160 °C; (c) 2 PhRCCO, toluene, r.t.

Scheme 4

Bis(iminophosphoranes) **15** and **16** were prepared as described for compound **10**. 2,5-Furandicarboxaldehyde[14] was converted into the bis(vinylazide) **13** in 36 % yield by reaction with ethyl azidoacetate, and further treatment with triphenylphosphine provided **15** in 91 % yield. Similarly, bis(vinylazide)[15] **14** afforded the bis(iminophosphorane) **16** in 98 % yield. The reaction of bis(iminophosphoranes) **15** and **16** with isocyanates yielded the furodipyridines **17** (73-86 %) and thienodipyridines **18** (50-80 %) respectively. With ketenes at room temperature the tricyclic compounds **19** (45-61 %) and **20** (67 %) were obtained (Scheme 4).

EXPERIMENTAL.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as nujol emulsions or films on a Nicolet 5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz) or a Varian Unity 300 (300 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer and the FAB in a Autospec 5000VG Fisons instrument. Microanalyses were performed on a Perkin-Elmer 240C instrument. Thermogravimetric analysis was recorded on a Mettler TG-50 thermobalance.

X-Ray Analysis.- A summary of data collection and refinement process is given in Table 2. The structure was solved by direct methods (SIR92)[16] and refined by least-squares procedures on Fobs. All hydrogens were obtained from difference Fourier synthesis and included and refined isotropically in the last cycles. The scattering factors were taken from the International Tables for X-Ray Crystallography.[17] Table 3 list the final atomic coordinates and equivalent thermal factors for non-hydrogen atoms. The calculations were carried out with the XTAL,[18] PESOS[19] and PARST[20] set of programs running on a VAX 6410 computer.

_N_-Methoxymethyl-2,5-bis(_o_-nitrophenyl)pyrrole 1.

To a solution of 2,5-bis(*o*-nitrophenyl)pyrrole[2] (0.618 g, 2 mmol) in dry benzene (25 ml) potassium hydroxide (5 mmol) and 18-crown-6 (30 mg) were added. The resultant mixture was stirred at reflux temperature for 2 h. Then, a solution of chloromethyl methyl ether (0.402 g, 5 mmol) in dry benzene (10 ml) was added dropwise and the new solution stirred at reflux temperature for 4 h. After cooling at room temperature the reaction mixture was filtered over celite, which was washed with benzene (2 x 5 ml). The solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (7:3) to give **1** in 85 % yield as orange prisms, m.p. 118-119 °C. (Found: C, 61.00; H, 4.32; N, 11.75. $C_{18}H_{15}N_3O_5$ requires: C, 61.19; H, 4.28; N, 11.89); i.r. (nujol): 1610, 1573, 1522, 1355, 1151, 1102, 919, 852, 788, 756, 720, 703 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.95 (s, 3 H), 4.84 (s, 2 H), 6.25 (s, 2 H), 7.54-7.65 (m, 6 H), 7.95 (dd, 2 H, J = 0.60, 7.80 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 55.4, 76.0, 110.8, 124.2, 127.3, 129.3, 130.3, 132.3, 133.8, 150.1; m/z (%): 353 (M^+, 5), 104 (11), 77 (7), 45 (100).

Table 2. Crystal analysis parameters at room temperature.

Crystal data			
Chemical formula	$C_{34}H_{29}N_5O.C_2H_3N$	Crystal system	Monoclinic
Mr	564.69	Space group	$P2_1/c$
a (Å)	11.4605(5)	α (°)	90
b (Å)	8.8523(8)	β (°)	90.105(8)
c (Å)	28.9376(41)	γ (°)	90
Z	4	*Dx* (gr/cm³)	1.28
V (Å³)	2935.8(5)	Radiation	CuKα
Wavelength (Å)	1.5418	No. of reflections for	
θ range for lattice parameters (°)	2-45	Lattice parameters:	67
Absorption coefficient (cm^{-1})	5.91	Temperature (K)	295
Crystal colour	Dark yellow	Crystal description	Prism
Crystal size (mm)	0.46 x 0.17 x 0.17		
Data collection			
Diffractometer type	Philips PW1100, four circle. Graphite oriented monocromator.		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θmax (°)	65
No. of standard reflections (interval)	2 (90 min.). 46% decay	Scan width (°)	1.5
No. of independent reflections	5013	No. of observed reflections, I>3σ(I)	3104
Refinement			
Treatment of hydrogen atoms	See experimental part Refinement: Least-Squares of *Fo*. Full matrix		
Secondary extintion correction (10^4)	0.25(3)		
R	0.076	No. of parameters refined	516
*w*R	0.081	Degrees of freedom	2588
$(\Delta\rho)_{max}$ (e/Å³)	0.44	Ratio of freedom	6.0
<Shift/error>	0.14	Max. thermal value (Å²) U11[C33]= 0.23(1)	
Weighting scheme: Empirical as to give no trends in $<\omega\Delta^2F>$ vs. <|Fobs|> and $<\sin\theta/\lambda>$.			

***N*-Methoxymethyl-2,5-bis(*o*-aminophenyl)pyrrole 2.**

To a solution of *N*-methoxymethyl-2,5-bis(*o*-nitrophenyl)pyrrole **1** (0.706 g, 2 mmol) in ethanol (30 ml) was added 10 % Pd on charcoal (0.075 g), and the reaction mixture was stirred at room temperature under hydrogen at 2 atm for 4 h. The reaction mixture was filtered on celite, which was washed with ethanol (2 x 10 ml). The filtrate and the ethanolic extracts were combined and concentrated to dryness under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl ether (3:7) to give **2** in 81 % yield as a viscous oil. (Found: C, 73.78; H, 6.45; N, 14.37. $C_{18}H_{19}N_3O$ requires: C, 73.69; H, 6.53; N, 14.32); i.r. (neat): 3461, 3365, 1619, 1488, 1453, 1384, 1301, 1149, 1086, 916, 756 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.93 (s, 3 H), 4.05 (br s, 4 H), 4.92 (s, 2 H), 6.31 (s, 2 H), 6.73-6.81 (m, 4 H), 7.14-7.24 (m, 4 H); ^{13}C n.m.r. δ ($CDCl_3$): 55.5, 75.3,

109.9, 115.4, 118.1, 118.5, 129.3, 131.9, 132.0, 145.7; m/z (%): 293 (M^+, 33), 260 (54), 231 (35), 155 (72), 144 (97), 131 (100), 94 (58), 77 (27).

Bis(iminophosphorane) 3.

To a cooled at 0 °C solution of triphenylphosphine (1.311 g, 5 mmol) in dry benzene (30 ml), bromine (0.799 g, 5 mmol) in the same solvent (20 ml) was added dropwise. The mixture was allowed to warm at room temperature and then *N*-methoxymethyl-2,5-bis(*o*-aminophenyl)pyrrole **2** (0.733g, 2.5 mmol) and triethylamine (1.012 g, 10 mmol) were added. The resultant mixture was refluxed for 8 h. After cooling, the precipitated solid was separated by filtration, the filtrate was concentrated to dryness and the residual material was recrystallized from benzene/ *n*-hexane to give the bis(iminophosphorane) **3** in 76 % yield as colourless prisms, m.p. 245-247 °C. (Found: C, 79.80; H, 5.51; N, 5.21. $C_{54}H_{45}N_3OP_2$ requires: C, 79.69; H, 5.57; N, 5.16); i.r. (nujol): 1590, 1435, 1362, 1314, 1113, 1083, 1026, 753, 742, 722, 693 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.68 (s, 3 H), 5.22 (s, 2 H), 6.32 (s, 2 H), 6.56 (d, 2 H, J = 7.86 Hz), 6.68 (t, 2 H, J = 7.36 Hz), 6.88 (dd, 2 H, J = 1.63, 7.55 Hz), 7.30-7.50 (m, 20 H), 7.62-7.73 (m, 12 H); ^{31}P n.m.r. δ ($CDCl_3$): - 2.12.

General Procedure for the Preparation of Diquino[4,3-*b*:3',4'-*d*]pyrroles 4.

To a solution of the bis(iminophosphorane) **3** (0.407 g, 0.5 mmol) in dry toluene (20 ml) a solution of the appropriate iso(thio)cyanate (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was heated at reflux temperature for 6 h. After cooling, the product was isolated by one of the following procedures: a) the solvent was concentrated to dryness under reduced pressure and the residual material was chromatographed on a silica gel column using ethanol as solvent (for **4a**); b) the solvent was removed under reduced pressure and the resulting material was treated with cold ethanol, the precipitated solid was filtered and recrystallized (for **4b**); or c) the precipitated solid was filtered and recrystallized (for **4c** and **4d**).

4a (R = CH_3) (79 %), m.p. 216-217 °C (from ethanol/diethyl ether as colourless prisms). (Found: C, 71.05; H, 5.65; N, 18.81. $C_{22}H_{21}N_5O$ requires: C, 71.14; H, 5.70; N, 18.85); i.r. (nujol): 3365, 1613, 1570, 1533, 1519, 1239, 1228, 1202, 1087, 971, 852, 761 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.11 (br s, 6 H), 3.53 (s, 3 H), 5.21 (s, 3 H), 5.92 (br s, 2 H), 7.10 (t, 2 H, J = 7.48 Hz), 7.29 (t, 2 H, J = 7.60 Hz), 7.67 (d, 2 H, J = 7.08 Hz), 7.76 (d, 2 H, J = 7.35 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 28.9, 54.7, 78.8, 105.6, 113.9, 120.8, 122.1, 127.1, 127.6, 140.8, 146.2, 152.4; m/z (%): 371 (M^+, 58), 327 (24), 326 (100), 297 (13), 283 (8), 268 (9).

4b (R = $C_6H_5.CH_2$) (59 %), m.p. 186-188 °C (from ethanol as colourless prisms). (Found: C, 77.78; H, 5.56; N, 13.41. $C_{34}H_{29}N_5O$ requires: C, 77.99; H, 5.58; N, 13.37); i.r. (nujol): 3324, 1635, 1609, 1569, 1544, 1513, 1223, 1080, 1031, 963, 752, 715, 699 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.64 (s, 3 H), 4.61 (d, 4 H, J = 4.46 Hz), 5.48 (s, 2 H), 6.36 (t, 2 H, J = 4.46 Hz), 7.14-7.36 (m, 14 H), 7.74 (d, 2 H, J = 7.87 Hz), 7.93 (d, 2 H, J = 7.87 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 46.1, 54.8, 79.1, 105.6, 114.3, 120.9, 122.5, 127.2, 127.4, 127.8, 128.6, 139.7, 141.4, 146.2, 151.4; m/z (%): 523 (M^+, 25), 478 (35), 432 (44), 283 (34), 209 (27), 118 (100), 91 (56), 77 (31).

4c (R = 4-$CH_3.C_6H_4$) (64 %), m.p. 299-300 °C (from toluene as colourless prisms). (Found: C, 77.71; H, 5.52; N, 13.09. $C_{34}H_{29}N_5O$ requires: C, 77.99; H, 5.58; N, 13.13); i.r. (nujol): 3390, 1681, 1628, 1604, 1569, 1511, 1089,

971, 828, 753, 716 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$ + CF_3COOH) (tautomers ratio 3:1): 2.33 (s, Ar.CH_3, minor tautomer), 2.36 (s, Ar.CH_3, major tautomer), 2.42 (s, Ar.CH_3, minor tautomer), 3.87 (s, CH_3OCH_2, minor tautomer), 3.91 (s, CH_3OCH_2, major tautomer), 5.86 (s, CH_3OCH_2, minor tautomer), 5.97 (s, CH_3OCH_2, major tautomer), 7.05-8.44 (m, aromatic, major and minor tautomers); HRMS (FAB$^+$) M^++1 524.2457, theor. 524.2450.

4d (R = 4-$CH_3O.C_6H_4$) (72 %), m.p. 237-238 °C (from toluene as colourless prisms). (Found: C, 73.41; H, 5.20; N, 12.64. $C_{34}H_{29}N_5O_3$ requires: C, 73.49; H, 5.26; N, 12.60); i.r. (nujol): 3387, 1668, 1629, 1572, 1550, 1504, 1246, 1085, 1037, 830, 748 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$ + CF_3COOH) (tautomers ratio 2.5:1): 3.84 (s), 3.88 (s), 3.92 (s), 5.89 (s, CH_3OCH_2, minor tautomer), 5.97 (s, CH_3OCH_2, major tautomer), 6.99-8.45 (m, aromatic, major and minor tautomers); HRMS (FAB$^+$) M^++1 556.2342, theor. 556.2348.

General Procedure for the Preparation of Diquino[4,3-*b*:3',4'-*d*]pyrrole Hydrobromides 5.

To a mixture of the bis(iminophosphorane) **3** (0.407 g, 0.5 mmol) and triethylammonium bromide (0.5 mmol) in dry toluene (20 ml), a solution of the appropriate iso(thio)cyanate (1 mmol) in the same solvent (5 ml) was added at once . The reaction mixture was heated at reflux temperature for 6 h. After cooling, the precipitated solid was filtered, washed with cold water (2.5 ml) and dried. An analytical sample was obtained by recrystallization.

5a (R = CH_3) (45 %), m.p. 280-282 °C (from ethanol as colourless prisms). (Found: C, 58.40; H, 4.95; N, 14.93. $C_{22}H_{21}N_5O.HBr$ requires: C, 58.41; H, 4.90; N, 15.48); i.r. (nujol): 3193, 1648, 1593, 1333, 1307, 1252, 1206, 1085, 974, 772, 753, 741 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.95 (s, 6 H), 3.52 (s, 3 H), 5.21 (s, 2 H), 7.15 (t, 2 H, J = 7.23 Hz), 7.38-7.47 (m, 4 H), 7.75 (d, 2 H, J = 8.12 Hz), 10.59 (s, 2 H), 16.02 (s, 1 H); ^{13}C n.m.r. δ (DMSO-d_6): 31.1, 54.6, 77.6, 109.4, 111.3, 117.2, 121.4, 123.2, 129.4, 137.0, 137.6, 148.5; MS (FAB$^-$) 452 (M^+, 54).

5b (R= $C_6H_5.CH_2$) (52 %), m.p. 244-246 °C (from ethanol as colourless prisms). (Found: C, 67.37; H, 5.06; N, 11.52. $C_{34}H_{29}N_5O.HBr$ requires: C, 67.55; H, 5.00; N, 11.58); i.r. (nujol): 3166, 1634, 1595, 1301, 1247, 1203, 1110, 1085, 973, 752, 704 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 3.64 (s, 3 H), 4.43 (s, 4 H), 5.58 (s, 2 H), 7.16-7.25 (m, 10 H), 7.36 (t, 2 H, J = 7.81 Hz), 7.56 (t, 2 H, J = 7.81 Hz), 7.85 (d, 4 H, J = 8.12 Hz), 11.12 (s, 2 H), 16.71 (s, 1 H); ^{13}C n.m.r. δ (DMSO-d_6): 47.3, 54.9, 78.2, 110.0, 112.0, 117.6, 122.2, 123.9, 127.2, 127.5, 128.6, 130.1, 137.3, 138.1, 139.2, 148.4; MS (FAB$^+$) 524 (M^+ - Br, 97).

Reaction of Bis(iminophosphorane) 3 with Carbon Disulfide.

A mixture of bis(iminophosphorane) **3** (0.407 g, 0.5 mmol), dry benzene (15 ml) and carbon disulfide (4 ml) was refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with petroleum ether/dichloromethane (1:1) to give **6** in 69 % yield, as colourless prisms, m.p. 124-125 °C. (Found: C, 63.59; H, 4.09; N, 11.19. $C_{20}H_{15}N_3OS_2$ requires: C, 63.64; H, 4.00; N, 11.13); i.r (nujol): 2173, 2114, 1600, 1568, 1331, 1230, 1162, 1081, 949, 923, 753 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.89 (s, 3 H), 4.99 (s, 2 H), 6.44 (s, 2 H), 7.31-7.38 (m, 6 H), 7.58-7.61 (m, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 55.5, 75.6, 112.2, 126.1, 127.3, 129.1, 130.6, 131.4, 131.6, 132.1, 136.6; m/z (%): 377 (M^+, 100), 287 (17), 274 (72), 257 (26), 242 (18).

Table 3. Final atomic coordinates and Ueq=(1/3)Σ[Uij.a_i*.a_j*.a_i.a_j.cos(a_i,a_j)]x10^3

Atom	x	y	z	Ueq	Atom	x	y	z	Ueq
N1	0.2495(3)	-0.0505(4)	0.0610(1)	54(1)	C17	0.4951(3)	0.2183(5)	0.0300(1)	44(1)
N2	0.4086(3)	0.1977(4)	-0.0407(1)	45(1)	C18	0.3948(3)	0.1201(5)	0.0327(1)	46(1)
N3	0.6657(3)	0.3640(4)	0.0470(1)	56(1)	C19	0.3423(4)	-0.0405(6)	0.1507(2)	62(2)
N4	0.3820(3)	0.0524(5)	0.1131(1)	57(1)	C20	0.2479(4)	0.0312(6)	0.1784(2)	56(2)
N5	0.5836(3)	0.2227(4)	0.1065(1)	56(1)	C21	0.2281(5)	-0.0265(7)	0.2226(2)	72(2)
O1	0.3351(3)	0.2873(5)	-0.1102(1)	81(1)	C22	0.1405(5)	0.0348(9)	0.2490(2)	88(2)
C1	0.3400(3)	0.0383(5)	0.0692(2)	49(1)	C23	0.0746(5)	0.1522(9)	0.2327(2)	91(3)
C2	0.2025(4)	-0.0607(5)	0.0168(2)	54(2)	C24	0.0924(5)	0.2093(7)	0.1889(2)	85(2)
C3	0.1068(4)	-0.1585(6)	0.0095(2)	68(2)	C25	0.1796(4)	0.1488(6)	0.1623(2)	65(2)
C4	0.0505(5)	-0.1684(7)	-0.0331(2)	80(2)	C26	0.4064(4)	0.1794(6)	-0.0915(2)	72(2)
C5	0.0844(4)	-0.0791(7)	-0.0695(2)	76(2)	C27	0.3279(7)	0.2697(8)	-0.1602(2)	101(3)
C6	0.1789(4)	0.0133(6)	-0.0637(2)	64(2)	C28	0.6762(4)	0.2749(6)	0.1379(2)	64(2)
C7	0.2416(3)	0.0233(5)	-0.0212(2)	51(1)	C29	0.6678(4)	0.1954(6)	0.1833(2)	61(2)
C8	0.3441(3)	0.1108(5)	-0.0110(1)	45(1)	C30	0.7628(5)	0.1227(7)	0.2030(2)	76(2)
C9	0.4991(3)	0.2650(5)	-0.0153(1)	45(1)	C31	0.7586(8)	0.0444(9)	0.2436(2)	123(3)
C10	0.5857(3)	0.3685(5)	-0.0316(1)	45(1)	C32	0.6565(11)	0.0385(14)	0.2657(3)	154(5)
C11	0.5922(4)	0.4302(5)	-0.0761(2)	55(2)	C33	0.5601(10)	0.1046(14)	0.2481(3)	144(5)
C12	0.6804(4)	0.5282(6)	-0.0877(2)	65(2)	C34	0.5632(6)	0.1914(9)	0.2062(2)	96(3)
C13	0.7647(4)	0.5664(6)	-0.0545(2)	69(2)	N35	-0.0789(7)	-0.4833(9)	0.1095(3)	140(4)
C14	0.7595(4)	0.5131(6)	-0.0102(2)	63(2)	C36	-0.0161(7)	-0.3935(10)	0.1223(3)	100(3)
C15	0.6700(4)	0.4151(5)	0.0015(2)	50(1)	C37	0.0622(14)	-0.2780(18)	0.1378(4)	145(5)
C16	0.5828(4)	0.2683(5)	0.0636(2)	50(2)					

Preparation of Bis(azides) 9 and 13.

A mixture of ethyl azidoacetate (10.32 g, 80 mmol) and *N*-methyl-2,5-pyrroledicarboxaldehyde[11] or 2,5-furandicarboxaldehyde[14] (10 mmol) was added dropwise to a well-stirred solution containing sodium (1.84 g, 80 mmol) in dry ethanol (100 ml), under nitrogen at - 10 °C. The reaction mixture was stirred at - 10 °C for 5 h and for 1 h at 0 °C. Then, it was poured into saturated aqueous ammonium chloride (200 ml) and extracted with diethyl ether (3 x 100 ml). The organic layers were washed with water (2 x 150 ml) and dried over $MgSO_4$. The $MgSO_4$ was removed by filtration and the solvent concentrated to dryness. The resulting solid was treated with cold ethanol and recrystallized.

9 (47 %), m.p. 121-124 °C (from ethanol as yellow needles). (Found: C, 50.03; H, 4.71; N, 27.35. $C_{15}H_{17}N_7O_4$ requires: C, 50.14; H, 4.77; N, 27.28); i.r. (nujol): 2107, 1699, 1598, 1261, 1141, 1098, 1075, 772, 748 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.39 (t, 6 H, *J* = 7.04 Hz), 3.61 (s, 3 H), 4.36 (q, 4 H, *J* = 7.04 Hz), 6.84 (s, 2 H), 7.26 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.3, 30.4, 62.2, 112.2, 116.6, 122.6, 130.6, 163.5; m/z (%): 359 (M^+, 5), 230 (77), 184 (62), 158 (100), 131 (44), 90 (29), 54 (42).

13 (36 %), m.p. 92-96 °C (from ethanol as yellow needles). (Found: C, 48.49; H, 4.11; N, 24.36. $C_{14}H_{14}N_6O_5$ requires: C, 48.56; H, 4.07; N, 24.27); i.r. (nujol): 2125, 1712, 1613, 1289,1230, 1192, 1083, 1017, 794, 754

cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.38 (t, 6 H, J = 7.02 Hz), 4.35 (q, 4 H, J = 7.02 Hz), 6.81 (s, 2 H), 7.21 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.2, 62.4, 112.3, 117.8, 124.4, 150.4, 162.9; m/z (%): 346 (M^+, 6), 146 (13), 145 (100), 90 (16), 69 (13), 57 (9).

Preparation of Bis(iminophosphoranes) 10, 15 and 16.

To a solution of triphenylphosphine (1.31 g, 5 mmol) in a mixture of diethyl ether/dichloromethane (2:1) the corresponding bis(azide) **9**, **13** or **14**[15] (2.5 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 12 h, and the separated solid was filtered and recrystallized.

10 (97 %), m.p. 223-225 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 73.92; H, 5.76; N, 5.00. $C_{51}H_{47}N_3O_4P_2$ requires; C, 73.99; H, 5.72; N, 5.08); i.r. (nujol): 1685, 1579, 1408, 1247, 1209, 1107, 788, 752, 717, 696 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 0.88 (t, 6 H, J = 7.20 Hz), 3.53 (s, 3 H), 3.77 (q, 4 H, J = 7.20 Hz), 6.70 (d, 2 H, $J_{H\text{-}P}$ = 7.19 Hz), 7.24 (s, 2 H), 7.37-7.55 (m, 18 H), 7.63-7.69 (m, 12 H); ^{31}P n.m.r. δ (DMSO-d_6): 5.65.

15 (91 %), m.p. 222-223 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 73.63; H, 5.38; N, 3.46. $C_{50}H_{44}N_2O_5P_2$ requires: C, 73.70; H, 5.44; N, 3.44); i.r. (nujol): 1691, 1583, 1263, 1206, 1169, 1109, 746, 717, 695 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.01 (t, 6 H, J = 7.03 Hz), 3.87 (q, 4 H, J = 7.03 Hz), 6.87 (d, 2 H, $J_{H\text{-}P}$ = 7.00 Hz), 7.11 (br s, 2 H), 7.34-7.46 (m, 18 H), 7.69-7.80 (m, 12 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.2, 60.6, 107.7 (d, J = 20.8 Hz), 113.6, 128.1 (d, J = 12.1 Hz), 130.9 (d, J = 2.6 Hz), 132.5 (d, J = 9.3 Hz), 133.1 (d, J = 102.4 Hz), 133.8 (d, J = 6.7 Hz), 152.7, 167.3 (d, J = 6.5 Hz); ^{31}P n.m.r δ ($CDCl_3$): 8.27; m/z (%): 407 (5), 263 (40), 262 (69), 201 (29), 183 (100), 145 (61), 108 (79), 69 (31), 57 (48).

16 (98 %), m.p. 231-232 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 72.19; H, 5.39; N, 3.31. $C_{50}H_{44}N_2O_4P_2S$ requires: C, 72.28; H, 5.34; N, 3.37); i.r. (nujol): 1685, 1570, 1438, 1402, 1233, 1209, 1109, 1042, 744, 717, 695 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.98 (t, 6 H, J = 7.21 Hz), 3.82 (q, 4 H, J = 7.21 Hz), 6.98 (d, 2 H, $J_{H\text{-}P}$ = 7.20 Hz), 7.32-7.40 (m, 18 H), 7.53 (s, 2 H), 7.70-7.77 (m, 12 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.0, 60.5, 112.8 (d, J = 20.6 Hz), 126.9, 127.9 (d, J = 12.1 Hz), 130.7 (d, J = 3.0 Hz), 132.4 (d, J = 9.6 Hz), 132.7 (d, J = 102.7 Hz), 133.7 (d, J = 7.0 Hz), 140.4, 167.2 (d, J = 6.5 Hz); ^{31}P n.m.r. δ ($CDCl_3$): 9.58; m/z (%): 496 (5), 415 (5), 262 (92), 183 (100), 149 (18), 108 (37), 77 (19).

General Procedure for the Preparation of Dipyrido[4,3-*b*:3',4'-*d*]pyrroles 11, Furo[3,2-*c*:4,5-*c*']-dipyridines 17 and Thieno[3,2-*c*:4,5-*c*']dipyridines 18.

To a suspension of the corresponding bis(iminophosphorane) **10**, **15** or **16** (0.5 mmol) in dry toluene (25 ml) the isocyanate (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was heated at 80 °C for 30 min and then 8 h at 160 °C in a sealed tube. After cooling, the solvent was removed under reduced pressure and the residual material was treated with cold ethanol (5 ml), the separated solid was filtered and recrystallized.

11a (R = $C_6H_5.CH_2$) (77 %), m.p. 172-173 °C (from ethanol as yellow prisms). (Found: C, 69.31; H, 5.74; N, 13.00. $C_{31}H_{31}N_5O_4$ requires: C, 69.26; H, 5.81; N, 13.03); i.r. (nujol): 3381, 3364, 3256, 1735, 1715, 1569, 1242, 1206, 1189, 1115, 780, 756, 706 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.47 (t, 6 H, J = 7.08 Hz), 3.75 (s, 3 H), 4.45 (q, 4 H,

J = 7.08 Hz), 4.63 (d, 4 H, J = 5.51 Hz), 6.05 (t, 2 H, J = 5.51 Hz), 7.15-7.36 (m, 10 H), 7.63 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.3, 29.7, 46.6, 61.4, 99.8, 106.7, 127.2, 128.5, 128.6, 139.4, 142.8, 146.2, 152.2, 166.1; m/z (%): 537 M^+, 6), 446 (16), 298 (22), 209 (6), 91 (100), 65 (14).

11b (R = 4-Cl.C_6H_4) (71 %), m.p. 299-301 °C (from ethanol as orange prisms). (Found: C, 60.15; H, 4.31; N, 12.07. $C_{29}H_{25}Cl_2N_5O_4$ requires: C, 60.22; H, 4.36; N, 12.11); i.r. (nujol): 3359, 1717, 1706, 1636, 1601, 1566, 1271, 1180, 1094, 828, 759, 726 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$ + CF_3COOH): 1.44 (t, 6 H, J = 7.15 Hz), 4.23 (s, 3 H), 4.55 (q, 4 H, J = 7.15 Hz), 7.33 (d, 4 H, J = 8.68 Hz), 7.56 (d, 4 H, J = 8.68 Hz), 8.08 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$ + CF_3COOH): 13.5, 32.1, 65.7, 103.7, 108.5, 125.0, 131.6, 131.8, 132.8, 136.2, 147.8, 149.0, 159.4.

11c (R = 4-CH_3.C_6H_4) (80 %), m.p. 282-283 °C (from ethanol as orange prisms). (Found: C, 69.21; H, 5.77; N, 13.10. $C_{31}H_{31}N_5O_4$ requires: C, 69.26; H, 5.81; N, 13.03); i.r. (nujol): 3349, 1732, 1704, 1631, 1513, 1287, 1238, 1195, 1028, 760 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$ + CF_3COOH): 1.42 (t, 6 H, J = 7.21 Hz), 2.44 (s, 6 H), 4.21 (s, 3 H), 4.52 (q, 4 H, J = 7.21 Hz), 7.28 (d, 4 H, J = 7.40 Hz), 7.40 (d, 4 H, J = 7.40 Hz), 8.01 (s, 2 H): ^{13}C n.m.r. δ ($CDCl_3$ + CF_3COOH): 13.5, 21.0, 31.9, 65.2, 103.2, 108.1, 123.7, 129.9, 132.1, 132.2, 140.7, 148.1, 148.5, 159.3.

17a (R = C_6H_5.CH_2) (82 %), m.p. 176-177 °C (from ethanol as yellow prisms). (Found: C, 68.60; H, 5.32; N, 10.74. $C_{30}H_{28}N_4O_5$ requires: C, 68.69; H, 5.38; N, 10.68); i.r. (nujol): 3322, 3243, 1739, 1716, 1604, 1422, 1312, 1299, 1237, 1114, 1027, 781, 753, 725 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.45 (t, 6 H, J = 7.21 Hz), 4.42 (q, 4 H, J = 7.21 Hz), 4.62 (d, 4 H, J = 5.41 Hz), 5.93 (t, 2 H, J = 5.41 Hz), 7.27-7.32 (m, 10 H), 7.73 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.3, 46.6, 61.7, 102.1, 108.0, 127.4, 128.6, 138.8, 145.2, 152.5, 162.0, 165.0; m/z (%): 524 (M^+, 7), 433 (10), 359 (5), 285 (7), 196 (6), 106 (5), 91 (100), 65 (10).

17b (R = 4-Cl.C_6H_4) (73 %), m.p. 251-253 °C (from ethanol as orange prisms). (Found: C, 59.55; H, 3.96; N, 9.87. $C_{28}H_{22}Cl_2N_4O_5$ requires: C, 59.48; H, 3.92; N, 9.91); i.r. (nujol): 3354, 1714, 1643, 1606, 1593, 1496, 1287, 1254, 1220, 1029, 835, 767 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$ + CF_3COOH): 1.40 (t, 6 H, J = 7.11 Hz), 4.46 (q, 4 H, J = 7.11 Hz), 7.18 (d, 4 H, J = 8.59 Hz), 7.48 (d, 4 H, J = 8.59 Hz), 7.57 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$ + CF_3COOH): 13.7, 64.6, 101.9, 114.6, 123.6, 131.3, 133.2, 133.8, 136.5, 146.9, 159.9, 161.5; m/z (%): 568 (M^+ + 4, 4), 566 (M^+ + 2, 25), 564 (M^+, 40), 455 (20), 381 (20), 127 (40), 111 (100), 77 (48), 68 (44), 55 (44).

17c (R = 4-CH_3.C_6H_4) (86 %), m.p. 232-233 °C (from ethanol as orange prisms). (Found: C, 68.64; H, 5.31; N, 10.61. $C_{30}H_{28}N_4O_5$ requires: C, 68.69; H, 5.38; N, 10.68); i.r. (nujol): 3357, 1711, 1658, 1604, 1512, 1290, 1254, 1220, 1105, 1031, 814, 767 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$ + CF_3COOH): 1.43 (t, 6 H, J = 7.21 Hz), 2.44 (s, 6 H), 4.53 (q, 4 H, J = 7.21 Hz), 7.24 (d, 4 H, J = 8.40 Hz), 7.41 (d, 4 H, J = 8.40 Hz), 8.05 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$ + CF_3COOH): 13.4, 20.9, 65.8, 104.3, 111.0, 123.7, 129.6, 132.3, 135.3, 141.4, 148.7, 158.8, 164.8; m/z (%): 524 (M^+, 10), 421 (13), 376 (14), 285 (10), 188 (17), 149 (17), 91 (95), 69 (56), 55 (100).

18a (R = C_6H_5.CH_2) (50 %), m.p. 171-172 °C (from ethanol as yellow prisms). (Found: C, 66.60; H, 5.31; N, 10.30. $C_{30}H_{28}N_4O_4S$ requires: C, 66.65; H, 5.22; N, 10.36); i.r. (nujol): 3362, 1735, 1725, 1571, 1548, 1274, 1219, 1038, 856, 782, 704 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.44 (t, 6 H, J = 7.22 Hz), 4.41 (q, 4 H, J = 7.22 Hz), 4.62 (d, 4 H, J = 5.25 Hz), 6.03 (t, 2 H, J = 5.25 Hz), 7.28 (s, 10 H), 7.94 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.4, 46.7, 61.7, 110.3, 117.8, 127.6, 128.7, 128.8, 138.7, 142.9, 149.1, 152.3, 165.3; m/z (%): 540 (M^+, 13), 450 (27), 449 (100), 375 (42), 301 (64), 91 (35).

18b (R = 4-CH_3.C_6H_4) (76 %), m.p. 228-230 °C (from ethanol as orange prisms). (Found: C, 66.71; H, 5.17; N, 10.39. $C_{30}H_{28}N_4O_4S$ requires: C, 66.65; H, 5.22; N, 10.36); i.r. (nujol): 3339, 1736, 1707, 1599, 1509, 1252, 1223, 1197, 865, 833, 762, 728 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 1.38 (t, 6 H, *J* = 7.05 Hz), 2.24 (s, 6 H), 4.36 (q, 4 H, *J* = 7.05 Hz), 7.03 (d, 4 H, *J* = 8.16 Hz), 7.52 (d, 4 H, *J* = 8.16 Hz), 8.33 (s, 2 H), 9.45 (s, 2 H); ^{13}C n.m.r. δ (DMSO-d_6): 14.1, 20.4, 61.1, 111.5, 118.9, 119.1, 128.9, 130.5, 138.6, 141.9, 149.3, 149.4, 164.5; m/z (%): 540 (M^+, 100), 539 (53), 467 (17), 465 (25), 451 (44), 437 (56), 393 (20), 91 (21).

18c (R = 4-CH_3O.C_6H_4) (80 %), m.p. 249-250 °C (from ethanol as orange prisms). (Found: C, 62.85; H, 4.98; N, 9.74. $C_{30}H_{28}N_4O_6S$ requires: C, 62.93; H, 4.93; N, 9.78); i.r. (nujol): 3335, 1735, 1706, 1665, 1606, 1508, 1300, 1248, 1033, 837, 760, 731, 694 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 1.37 (t, 6 H, *J* = 6.93 Hz), 3.75 (s, 6 H), 4.36 (q, 4 H, *J* = 6.93 Hz), 6.84 (d, 4 H, *J* = 8.71 Hz), 7.61 (d, 4 H, *J* = 8.71 Hz), 8.32 (s, 2 H), 9.30 (s, 2 H); ^{13}C n.m.r. δ (DMSO-d_6): 14.3, 55.3, 61.2, 111.2, 113.8, 118.7, 120.7, 134.4, 142.0, 149.2, 149.7, 154.5, 164.7; m/z (%): 573 (M^+, 35), 467 (65), 449 (73), 304 (38), 301 (61), 170 (91), 149 (65), 91 (100), 77 (50).

General Procedure for the Preparation of Dipyrido[4,3-*b*:3',4'-*d*]pyrroles 12, Furo[3,2-*c*:4,5-*c'*]dipyridines 19 and Thieno[3,2-*c*:4,5-*c'*]dipyridines 20.

To a suspension of the corresponding bis(iminophosphorane) **10**, **15** or **16** (0.5 mmol) in dry toluene (25 ml) the ketene (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was stirred at 80 °C for 30 min and then 8 h at room temperature. The solvent was removed under reduced pressure and the residual material was treated with cold ethanol (5 ml), the separated solid was filtered and recrystallized (for **12a**, **19a** and **20**) or the residual material was chromatographed on a silica gel column using *n*-hexane/ethyl acetate (3:2) as eluent (for **12b** and **19b**).

12a (R = C_6H_5) (87 %), m.p. 282-283 °C. (Found: C, 78.21; H, 5.59; N, 6.39. $C_{43}H_{37}N_3O_4$ requires: C, 78.28; H, 5.65; N, 6.37); i.r. (nujol): 1721, 1578, 1297, 1268, 1164, 1033, 983, 877, 787, 737, 703 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.41 (t, 6 H, *J* = 7.17 Hz), 3.95 (s, 3 H), 4.39 (q, 4 H, *J* = 7.17 Hz), 6.15 (s, 2 H), 6.98-7.03 (m, 8 H), 7.16-7.26 (m, 12 H), 8.10 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.2, 29.7, 56.7, 61.5, 103.8, 119.4, 126.4, 127.8, 130.2, 144.0, 144.2, 147.6, 156.6, 165.8; m/z (%): 660 (M^+, 60), 418 (12), 330 (17), 201 (21), 167 (86), 166 (41), 165 (100), 152 (67), 91 (47), 77 (60).

12b (R = C_2H_5) (72 %) diastereomeric ratio 2:1. (Found: C, 74.52; H, 6.69; N, 7.42. $C_{35}H_{37}N_3O_4$ requires: C, 74.58; H, 6.62; N, 7.45); i.r. (nujol): 1738, 1714, 1596, 1549, 1295, 1268, 1175, 981, 867, 789, 740, 702 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.65 (t, CH_2CH_3, major diastereomer), 0.86 (t, CH_2CH_3, minor diastereomer), 1.48 (t, OCH_2CH_3, major diastereomer), 1.49 (t, OCH_2CH_3, minor diastereomer), 2.27-2.40 (m, CH_2CH_3, both diastereomers), 2.56-2.69 (m, CH_2CH_3, both diastereomers), 3.91 (s, NCH_3, minor diastereomer), 3.92 (s, NCH_3, major diastereomer), 4.49 (q, OCH_2CH_3, both diastereomers), 5.04 (t, -*CH*PhEt, both diastereomers), 7.11-7.44 (m, aromatic, both diastereomers), 8.05 (s, H_4 and H_6, minor diastereomer), 8.06 (s, H_4 and H_6, major diastereomer); ^{13}C n.m.r. δ ($CDCl_3$) (both diastereomers): 12.3, 12.6, 14.1, 14.3, 29.6, 29.9, 31.3, 52.8, 61.6, 103.5, 103.7, 119.3, 126.2, 126.3, 128.0, 128.1, 128.6, 129.0, 142.9, 143.5, 144.0, 147.4, 158.6, 158.8, 165.8, 165.9; m/z (%): 563 (M^+, 75), 548 (63), 535 (50), 472 (35), 444 (64), 342 (20), 282 (31), 179 (24), 91 (100).

19a (R = C_6H_5) (61 %), m.p. 279-280 °C (from ethanol as yellow prisms). (Found: C, 78.07; H, 5.25; N, 4.39. $C_{42}H_{34}N_2O_5$ requires: C, 78.00; H, 5.30; N, 4.33); i.r. (nujol): 1718, 1582, 1547, 1311, 1245, 1108, 1028, 889, 792, 739, 699 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.39 (t, 6 H, J = 7.12 Hz), 4.38 (q, 4 H, J = 7.12 Hz), 6.11 (s, 2 H), 6.95-6.98 (m, 8 H), 7.21-7.23 (m, 12 H), 8.25 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.1, 56.6, 61.7, 106.9, 120.7, 126.7, 128.0, 130.0, 143.3, 146.8, 157.3, 162.7, 164.6; m/z (%): 646 (M^+, 36), 405 (8), 210 (15), 165 (88), 152 (57), 92 (71), 91 (100), 77 (50).

19b (R = C_2H_5) (45 %) diastereomeric ratio 3:1. (Found: C, 74.09; H, 6.27; N, 5.01. $C_{34}H_{34}N_2O_5$ requires: C, 74.16; H, 6.22; N, 5.09); i.r. (nujol): 1743, 1723, 1560, 1310, 1286, 1215, 1100, 788, 733, 699 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.48 (t, CH_2CH_3, major diastereomer), 0.86 (t, CH_2CH_3, minor diastereomer), 1.37 (t, OCH_2CH_3, major diastereomer), 1.38 (t, OCH_2CH_3, minor diastereomer), 2.03-2.18 (m, $CH_aH_bCH_3$, major diastereomer), 2.20-2.32 (m, $CH_aH_bCH_3$, minor diastereomer), 2.42-2.76 (m, $CH_aH_bCH_3$, both diastereomer), 4.39 (q, OCH_2CH_3, both diasteromers), 4.93 (t, CHPhEt, both diastereomers), 7.02-7.35 (m, aromatic, both diastereomers), 8.09 (s, H_4 and H_6, minor diastereomer), 8.14 (s, H_4 and H_6, major diastereomer); ^{13}C n.m.r. δ ($CDCl_3$) (both diastereomers): 12.2, 12.6, 14.2, 29.6, 30.2, 31.0, 52.5, 52.8, 61.8, 106.6, 106.9, 120.3, 120.9, 126.4, 126.5, 128.1, 128.3, 129.0, 142.1, 143.1, 146.4, 146.5, 159.3, 159.4, 162.5, 164.7; m/z (%): 551 (M^+, 13), 536 (13), 523 (12), 431 (12), 283 (12), 173 (13), 91 (100), 77 (17).

20 (R = C_6H_5) (67 %), m.p. 316 °C (from ethanol as yellow prisms). (Found: C, 76.07; H, 5.11; N, 4.20. $C_{42}H_{34}N_2O_4S$ requires: C 76.11; H, 5.17; N, 4.23); i.r. (nujol): 1717, 1494, 1302, 1181, 1159, 1119, 1020, 746, 734, 707 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.42 (t, 6 H, J = 7.06 Hz), 4.45 (q, 4 H, J = 7.06 Hz), 6.01 (s, 2 H), 7.12 (s, 20 H), 8.38 (s, 2 H); ^{13}C n.m.r. δ ($CDCl_3$): 14.4, 57.4, 61.8, 116.4, 126.7, 127.9, 130.0, 130.3, 143.1, 144.6, 149.8, 158.6, 164.8.

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Peroxydicarbonate-Mediated Oxidation of *N*-(*ortho*-Aryloxyphenyl) and *N*-(*ortho*-Arylaminophenyl)aldimines

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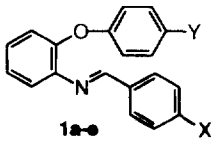
Abstract: Imidoyl radicals **5**, obtained from imines **1** by hydrogen abstraction with di-*iso*-propyl peroxydicarbonate (DPDC), give dibenzoxazepines through 7-membered ring closure. A competitive 6-membered cyclisation leads to intermediate spirocyclohexadienyl radicals that rearrange to aryloxy radicals; this process entails a novel 1,5-aryl radical translocation from an oxygen to a carbon atom and leads to benzophenones, benzoxazoles, and biphenyls. The possibility that the oxazepines arise from rearrangement of the 6-membered-ring-closure intermediates is discussed. With imine **1e**, the formation of **5e** occurs to a minor extent owing to a side-reaction of the *iso*-propoxycarbonyloxy radicals, which give rise to an intermolecular aromatic *ipso*-substitution on the benzenic ring linked to the two oxygen atoms. The 1,5-aryl migration can also be observed with imidoyl radicals generated by radical addition to 2-phenoxyisocyanobenzene. In contrast, the reactions of imines **2** with DPDC do not afford imidoyl radicals, as abstraction of the iminic hydrogen is slower than oxidation of the methyl group: this process entails the formation of carbamoyl radicals, which cyclise onto the carbon-nitrogen double bond, furnishing quinoxalinone derivatives, or loose carbon monoxide to yield benzimidazoles through ring closure of aminyl radicals. A novel cyclisation of a nitrogen-centred radical onto a formamido group could account for the formation of a benzimidazolinone derivative.

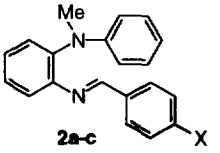
INTRODUCTION

In the last decade we have dedicated our attention to imidoyl radicals, mainly from a synthetic point of view. These species have been generated by hydrogen abstraction from imines by means of di-*iso*-propyl peroxydicarbonate (DPDC). This is the way we synthesised many heterocyclic derivatives, either through intramolecular cyclisation onto an aromatic ring,[1] or *via* intermolecular addition to alkynes,[2] alkenes,[3] and diethyl azodicarboxylate[4] followed by ring closure of the intermediate radical adduct. In the literature other papers have appeared dealing with intramolecular addition to carbon-carbon double bonds[5] and 4 + 1 homolytic annulations;[6] in these cases imidoyls have been generated by treating the corresponding seleno-imidates with tin radicals and by addition of carbon-centred radicals to isonitriles, respectively. Recently, we have also observed that imidoyl radicals can give rise to an intramolecular substitution, *i.e.* S_Hi, at the sulfur atom of a phenylsulfide group, which leads to benzothiazoles.[7] This last result suggested us to direct our attention to imidoyl radicals bearing aryloxy or arylamino moieties; since no S_Hi at the heteroatom can occur, we aimed at investigating the possibility of cyclisation on the aromatic ring. Here we report the full details and further progress on the reactivity of *N*-arylidene-2-aryloxybenzenamines **1**[8] and *N*-arylidene-*N'*-methyl-*N'*-phenylbenzen-1,2-diamines **2** when treated with DPDC.



1a-e

a: X = H, Y = H;
b: X = Cl, Y = H;
c: X = OMe, Y = H;
d: X = H, Y = Cl;
e: X = H, Y = OMe.

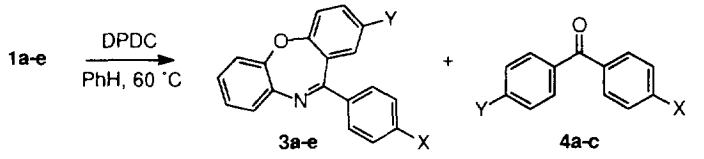


2a-c

a: X = H;
b: X = Cl;
c: X = OMe.

RESULTS AND DISCUSSION

When the imines **1a-e** (1 mmol) were allowed to react with DPDC (2 or 4 mmol) at 60 °C in benzene solution, complicated mixtures of products were obtained, the main ones being dibenzoxazepines **3** and benzophenones **4** (Scheme 1 and Table 1).

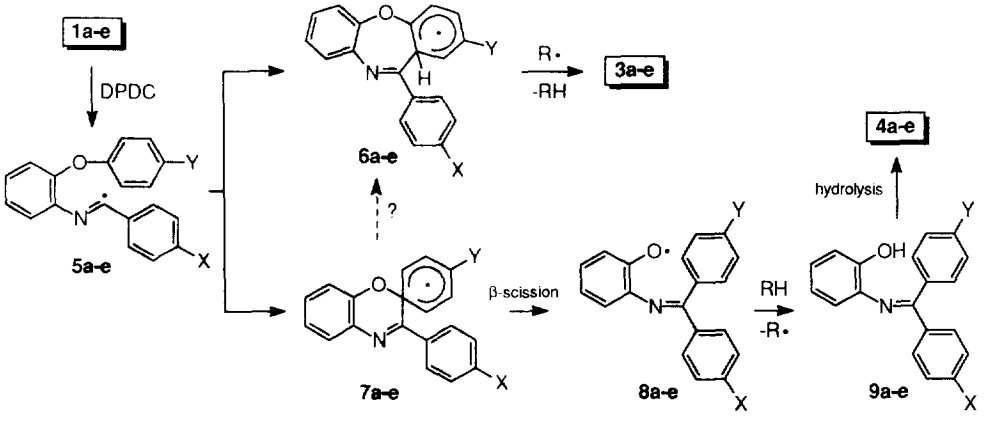


Scheme 1. Main products of the reaction of imines **1a-e** with DPDC.

Comp.	X	Y	t (h)[a]	**3** (%)[a]	**4** (%)[a]	t (h)[b]	**3** (%)[b]	**4** (%)[b]
1a	H	H	47	12	11	25	10	9
1b	Cl	H	70	17	11	48	8	8
1c	OMe	H	24	19	14	6	17	18
1d[c]	H	Cl	54	11	16	30	14	13
1e[c]	H	OMe	-	-	-	48	3	4

Table n. 1. All yields are for the starting imines and were determined by GC analysis using the internal standard method and authentic specimens of the reaction products prepared according to reported procedures.
a) Reactions carried out with 2 mmol of DPDC. b) Reactions carried out with 4 mmol of DPDC.
c) Compounds **4d** and **4e** are the same as **4b** and **4c**, respectively.

Compounds **3** and **4** can be accounted for through the intermediacy of imidoyl radicals **5**. Particularly, benzoxazepines **3** can arise from 7-membered homolytic aromatic substitution of **5** on the benzenic ring of the *ortho* substituent; benzophenones **4** are probably the result of a competitive 6-membered *ipso*-substitution on the same ring, leading to the phenoxy radicals **8** *via* the spirocyclohexadienyls **7**; the oxygen-centred radicals **8** can give hydrogen abstraction furnishing the ketimines **9**, which are converted into phenones **4** by hydrolysis in the reaction mixture[9] (Scheme 2).



Scheme 2. Reaction mechanism of imidoyl radicals **5a-e**.