New insights on the reaction of trialkyl phosphites with 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide: an indolic nitrone. Crystal structures of 1-diethylphosphoryl-2-phenyl-3-phenylamino-1*H*-indole and 2-phenyl-4-phenylimino-4*H*-3,1-benzoxazine

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Received (in Cambridge, UK) 20th September 1999, Accepted 21st January 2000

2-Phenyl-3-phenylimino-3*H*-indole *N*-oxide (an indolic nitrone) reacts with triethyl and triisopropyl phosphite in refluxing xylene and *tert*-butylbenzene to give 2-phenyl-3-phenylimino-3*H*-indole (indolenine) in very good yield. The same reaction carried out in refluxing phosphite gave rise to a series of compounds which in part derive from the thermal rearrangement of the starting nitrone and in part from the interaction of the indolenine with phosphites. The formation of the products arising from the reduction of the indolenine is explained by an electron transfer process between this intermediate and the phosphite; whereas the formation of the phosphorylated products is interpreted through the evolution of the intermediate zwitterion generated by the nucleophilic attack of the phosphite on carbon-2 of the indolenine. The formation of this intermediate is also discussed in terms of an electron transfer process. Crystal structures of 1-diethylphosphoryl-2-phenyl-3-phenylamino-1*H*-indole and 2-phenyl-4-phenylimino-4*H*-3,1-benzoxazine are also described.

2-Phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**)[1] is a precursor of a series of stable aminoxyls,[2] which, on the basis of their stability, are useful models to study the chemical behaviour of aromatic aminoxyls,[3–9] and excellent antioxidants in the prevention of oxidative damage in biological systems.[10–14] The most important series of these products is obtained by 1,2-addition of Grignard's reagents to the cyclic nitrone (**1**).[2] Other properly functionalised aminoxyls are prepared from **1** using different kinds of nucleophiles.[15] In the present work the cyclic nitrone (**1**) was reacted with trialkyl phosphites, which are good nucleophiles,[16] in order to obtain aminoxyls phosphorylated at carbon-2 of the indole nucleus. The studied reactions did not give rise to the expected compounds; however, it has given new insights on the reactivity of cyclic nitrones (**1**) with trialkyl phosphites. Aminoxyls were also not obtained when the more nucleophilic diethyl phosphite anion was reacted with nitrone (**1**); in fact, in this case, the main reaction product was 2-phosphorylated indoloxyls.[17]

Results

The products obtained from the reaction of nitrone (**1**) with trialkyl phosphites are reported in Scheme 1. All reactions were carried out using different ratios of the reagents and different solvents under reflux; in some cases (runs 1, 2 and 6, Table 1) the solvent was the phosphite itself.

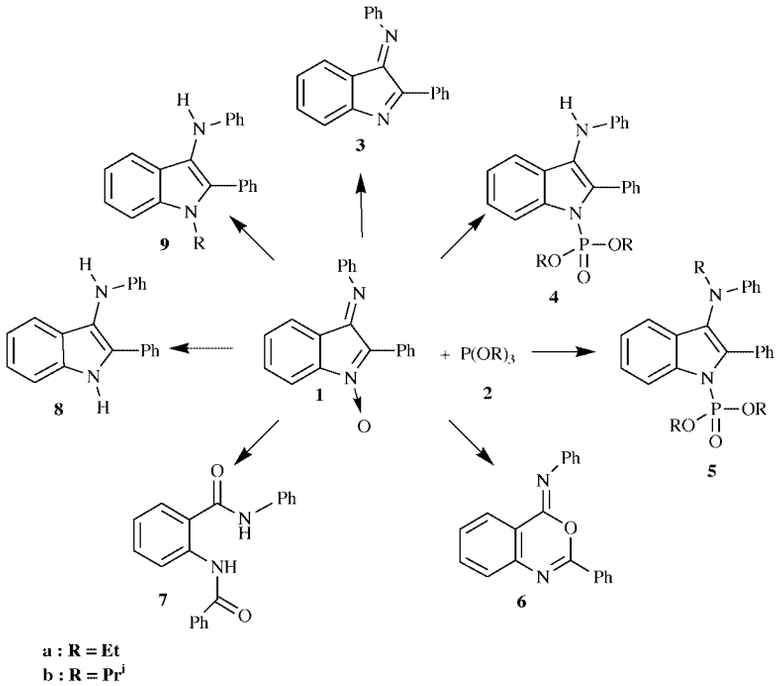
In all studied reactions, the first step led to the formation of 2-phenyl-3-phenylimino-3*H*-indole (**3**): the deoxygenated product of **1**. When the reactions were performed in xylene (T = 139 °C) with a small excess of phosphite complete deoxygenation of nitrone (**1**) was observed after 8–10 h, whereas using *tert*-butylbenzene (T = 168 °C) quantitative deoxygenation occurred after 2 h. By increasing the reaction times and the

Table 1 Reaction of nitrone **1** with phosphite **2a** and **2b** experimental conditions, isolated products and yields

					Products and yields (%)						
Run	Reagents	Eq.[a]	T/°C[b]	t/h[c]	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	**1** + **2a**	6	**2a**	1 h 15′		(6.7)	(53.5)		(10)	(traces)	
2	**1** + **2a**	6	**2a**[d]	1 h 15′		(43)					(35)
3	**1** + **2a**	1.4	Xylene	10	(74)						
4	**1** + **2a**	1.8	Xylene	8	(87)						
5	**1** + **2a**	3.6	Bu^{t}Ph	13	(9.4)		(51.7)				
6	**1** + **2b**	6	**2b**	1 h 15′				(8)	(10)	(6)	(7)
7	**1** + **2b**	1.8	Xylene	8	(76)						
8	**1** + **2b**	1.8	Bu^{t}Ph	2	(91)						
9	**1** + **2b**	3.6	Bu^{t}Ph	13	(9)		(30)		(11)	(1.4)	
10	**3** + **2a**	6	**2a**	1 h 15′		(4)	(33)		(11.3)	(2.5)	

[a] Equivalents of phosphites for equivalents of nitrone **1**. [b] The reaction temperature corresponds to the boiling point of the solvent. [c] Reaction time. [d] In the presence of ethanol.

DOI: 10.1039/a907601h



Scheme 1

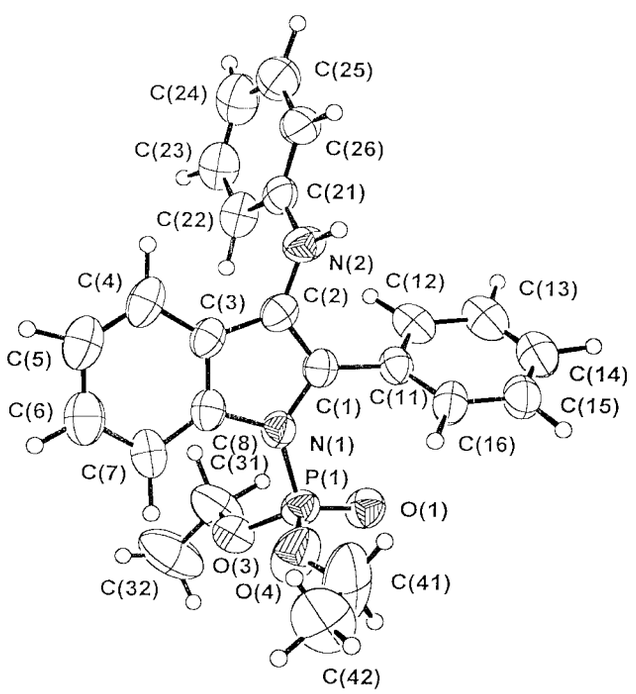


Fig. 1

concentration of phosphite, other products were formed besides the indole (**3**). Runs 1, 2 and 6 were carried out in phosphite as solvent; under these conditions, where there was a large excess of phosphite and the temperature was higher, the deoxygenation process was fast and complete in about 10 min. Under longer reaction times the indole (**3**) afforded the mixture of products shown in Scheme 1.

Compound **3** was identified by comparison with an authentic sample.[18] The structure of compound **4a** was demonstrated by X-ray analysis (Fig. 1) and its spectroscopic data are in agreement with the found structure (see Experimental section). In the case of triisopropyl phosphite, product **4b** was not isolated. The structure of compound **5a** was determined by comparing its spectroscopic data with those of compound **4a**, which were strictly similar: the ^{1}H-NMR spectrum of **5a** showed only an additional ethyl group with respect to that of **4a**, which is the

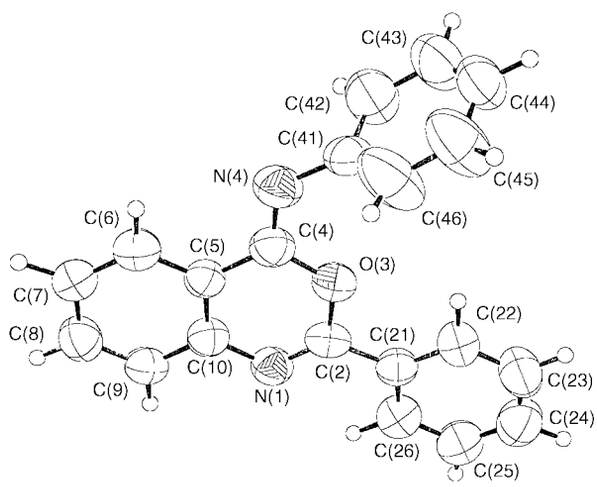


Fig. 2

one bonded to the exocyclic nitrogen. Compound **5b** was identified by comparing its spectroscopic data with those of compound **5a**; the compounds show identical absorptions in the aromatic region. Compound **6** was identified by X-ray analysis (Fig. 2). This compound was also compared with that obtained by an independent route and already described in literature.[19] Compound **7**, isolated in almost all reactions, was identified by comparing its spectroscopic data with those of a sample obtained by a different route.[19,20] Compound **8** was identified by comparison with a sample obtained from the reaction of **3** with phenylhydrazine.[21] Compound **9** was identified by comparing its ^{1}H-NMR and MS spectra with a sample synthesised by reacting compound **8** in DMSO with ethyl bromide in the presence of KOH.

Molecular geometry of 1-diethylphosphoryl-2-phenyl-3-phenylamino-1*H*-indole (4a) and 2-phenyl-4-phenylimino-4*H*-3,1-benzoxazine (6)

Selected bond distances and angles are given in Table 2 and perspective views with the arbitrary numbering scheme used in the crystal analysis for compounds **4a** and **6** are shown in Figs. 1 and 2, respectively. The intramolecular bond lengths and angles are in line with the hybridisation expected for the

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses for compounds **4a** and **6**

Compound **4a**			
P(1)–O(1)	1.454(3)	N(1)–C(1)	1.436(5)
P(1)–O(3)	1.557(3)	N(1)–C(8)	1.425(5)
P(1)–O(4)	1.558(4)	N(2)–C(2)	1.410(5)
P(1)–N(1)	1.663(5)	N(2)–C(21)	1.387(6)
O(3)–C(31)	1.463(6)	C(1)–C(2)	1.355(6)
O(4)–C(41)	1.317(11)	C(3)–C(8)	1.394(6)
O(1)–P(1)–O(3)	116.5(2)	P(1)–O(4)–C(41)	129.8(6)
O(1)–P(1)–O(4)	118.1(2)	C(1)–N(1)–C(8)	106.2(4)
O(1)–P(1)–N(1)	112.9(2)	N(1)–C(1)–C(2)	109.1(4)
O(3)–P(1)–O(4)	97.4(2)	C(1)–C(2)–C(3)	108.8(3)
O(3)–P(1)–N(1)	105.3(2)	C(2)–C(3)–C(8)	107.4(4)
O(4)–P(1)–N(1)	104.6(2)	N(1)–C(8)–C(3)	108.4(3)
P(1)–O(3)–C(31)	119.7(3)		
Compound **6**			
O(3)–C(2)	1.384(6)	N(4)–C(41)	1.424(7)
O(3)–C(4)	1.394(7)	C(2)–C(21)	1.474(9)
N(1)–C(2)	1.263(8)	C(4)–C(5)	1.436(8)
N(1)–C(10)	1.407(8)	C(5)–C(10)	1.397(8)
N(4)–C(4)	1.278(7)		
C(2)–O(3)–C(4)	119.5(4)	O(3)–C(4)–C(5)	117.1(5)
C(2)–N(1)–C(10)	117.7(6)	C(4)–C(5)–C(10)	118.1(5)
C(4)–N(4)–C(41)	122.4(4)	N(1)–C(10)–C(5)	121.8(5)
O(3)–C(2)–N(1)	125.8(5)		

atoms involved; the short single bond O(4)–C(41) 1.317(11) Å in **4a** is related to the high thermal motion of the C(41) atom.

In compound **4a** the fused two-ring system, as expected, is almost planar, the dihedral angle between the mean planes of the two individual rings being 2.4(2)°. As far as the orientation of the phenyl substituent at position 2 and the aminic phenyl at position 3 is concerned, the dihedral angles that their mean planes form with respect to the indolic moiety are 58.5 and 76.4(2)° respectively, in line with those found in similar compounds previously studied;[22,23] the C(1)–C(2)–N(2)–C(21) torsion angle is 111.2(6)°.

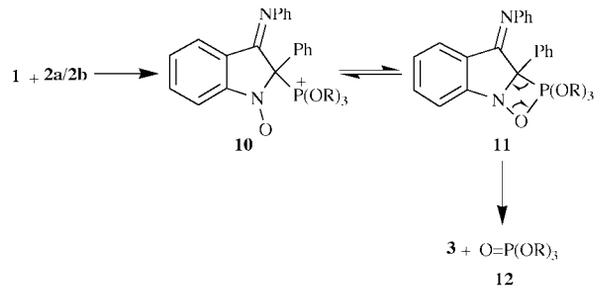
The value of the P–N bond [1.663(5) Å] compares well with analogous ones reported in the literature,[24] as well as the double P=O [1.454(3)] and single P–O [1.557(3) and 1.558(4) Å] bonds of the phosphonyl group. Packing is determined by a long hydrogen bond of the type N···O involving the aminic nitrogen and the phosphonilic oxygen in the $2 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$ position [N(2)···O(1) 3.076(7), H(2)···O(1) 2.21(5) Å; N(2)–H(2)···O(1) 170(4)°]. Other contacts are consistent with van der Waals interactions.

In compound **6**, the benzoxazine system has a bonding geometry similar to that found in previously reported structures of 3,1-benzoxazine[25] and in particular with that reported in ref. 26, in which a phenyliminic substituent in position 4 is present. Bond lengths indicate a double bond character at N(1)–C(2) [1.263(8) Å] and N(4)–C(4) [1.278(7) Å] while N(1)–C(10) [1.407(8) Å] has a value characteristic of a relevant degree of single bond.

The conformational analysis of the molecule indicates that the two condensed ring system is almost planar, the dihedral angle between the two mean planes being 1.4(2)°. The oxazine ring adopts a boat conformation[27] with N(1) and C(4) out of the mean plane through the other four atoms by 0.017(5) and 0.023(6) Å, respectively. The attached phenyl ring is nearly coplanar with the benzoxazine moiety, the angle between the respective mean planes being 10.1(2)°. The phenyl of phenyliminic group is rotated with respect to the central system by 102.4(2)°, the O(3)–C(4)–N(4)–C(41) torsion angle is 1.2(8)°. Molecular packing is consistent with van der Waals interactions.

Discussion

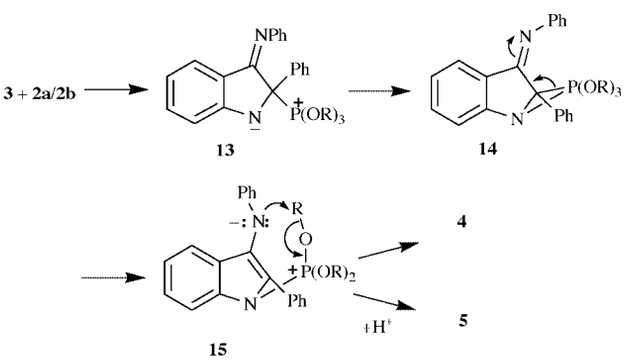
The results of the reaction of cyclic nitrone (**1**) with trialkyl phosphites (**2a** and **2b**) demonstrate that the first product formed is the 2-phenyl-3-phenylimino-3*H*-indole (**3**). The formation of **3** could be explained by the attack of the phosphite on carbon 2 with subsequent deoxygenation through the steps shown in Scheme 2.



Scheme 2

The steps reported in Scheme 2 are in agreement with the mechanism already described.[28] When **3** is reacted for longer periods of time with trialkyl phosphites, products **4**–**9** are isolated (Scheme 1). Compounds **4** and **5** are the main reaction products and could be explained by the reaction of indole **3** with trialkyl phosphite.

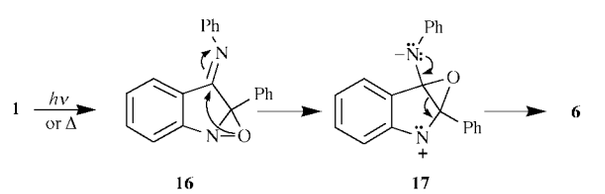
The nucleophilic attack of the phosphite at carbon-2 of the indole (**3**) could give rise to the intermediate (**14**), as shown in Scheme 3, which rearranges affording compound **4** through an



Scheme 3

intermolecular Arbuzov reaction,[29] and compound **5** through the protonation of the exocyclic nitrogen and elimination of an alkyl group from the phosphite moiety. The formation of intermediates such as **14** and **15** is confirmed by the fact that compound **5** is replaced by compound **4** when the reaction is carried out in the presence of a proton source (see Experimental section, run 2).

Compound **6** could be explained by the thermal rearrangement of **1**. In fact, this product is formed when the reaction temperature is very high, as when carried out in refluxing phosphites; in refluxing xylene (runs 3 and 4) the reaction does not give compound **6**. It is well known that this kind of isomerisation also occurs upon UV-irradiation of nitrone (**1**)[19] and 2-phenyl-3*H*-indol-3-one *N*-oxide (phenylisatogen),[30] through the formation of an oxaziridine ring[31,32] of the intermediate (**16**) (Scheme 4).

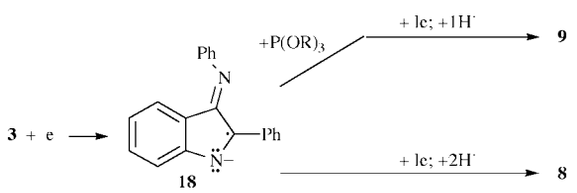


Scheme 4

The mechanistic proposal reported in Scheme 4 could be supported by the fact that the phenyl group of the phenylimino moiety in compound **6** is oriented in the opposite direction (Fig. 2) with respect to that of the starting nitrone **1**.[1]

Compound **7** is formed by hydrolysis of **6**, as demonstrated by reacting compound **6** in ethanol with traces of hydrochloric acid.

Compound **8** is the reduction product of the indole **3**; this latter compound possesses good oxidising power[33] and is easily reduced by hydrazobenzene and by phenylhydrazine to **8**.[21] To our knowledge, there are no examples in the literature of reduction of quinonediimino derivatives with trialkyl phosphites, even if Olah, years ago, described the reduction of the carbonyl group to CH_2 by triisopropyl phosphite.[34] Moreover, the reduction of indole (**3**) with trialkyl phosphites could be explained through an electron transfer reaction between compound **3** and the phosphite at high temperature, even if the redox potentials of the reagents ($E_{red} = -0.67$ V *vs.* NHE in DMF and triethyl/triisopropyl phosphite and E_{ox} *ca.* 1.7 V *vs.* NHE in *tert*-butylbenzene)[35] would exclude this possibility at room temperature.[36] Amongst all products isolated, the formation of compound **8** could easily be explained through a reductive process. Although the reduction potentials of the reagents are not in agreement with an electron transfer process, it may be assumed that the radical anion (**18**) (Scheme 5) could be



Scheme 5

formed in some way at very high reaction temperatures. This intermediate would also justify the formation of compound **9** through an intermolecular Arbuzov reaction with triethyl phosphite according to Scheme 5. The reaction of indole (**3**) with phosphite (**2a**) (run 10) clearly shows that **3** is the precursor of compounds **4**, **5**, **8** and **9**.

Experimental

General

Melting points were measured on an Electrothermal apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer and δ are referred to $SiMe_4$. ^{31}P-NMR were recorded on a Bruker AMDX 300 at 121.5 MHz and δ are referred to H_3PO_4 (85%). IR spectra were measured on a Nicolet 20SX FT-IR spectrometer. Mass spectra were recorded in EI mode on a Carlo Erba QMD 1000 GS-MS spectrometer equipped with a direct probe apparatus. Triethyl phosphite, triisopropyl phosphite, xylene and *tert*-butyl benzene were purchased from Aldrich and were of ACS grade; 2-phenyl-3-phenylimino-3*H*-indole 1-oxide was synthesised as reported in the literature.[18]

Reaction procedures and product analyses

Run 1: Reaction between triethyl phosphite (2a) and 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (1). 2-Phenyl-3-phenylimino-3*H*-indole 1-oxide (**1**) (2.25 g, 7.6 mmol) and 11 ml (64 mmol) of triethyl phosphite were refluxed for 1 h and 15 min. The reaction solution was cooled and then washed with 10% aqueous $NaHCO_3$, extracted with dichloromethane, separated, dried on Na_2SO_4 and then chromatographed on a column of silica gel, eluting first with cyclohexane–ethyl acetate (9 : 1) and then increasing the polarity to cyclohexane–ethyl acetate 1 : 1. The isolated products, whose yields are reported in Table 1, were eluted in the order: **7** (240 mg), **4a** (214 mg) and **5a** (1.82 g).

Compound 7. Mp 293–294 °C; δ_H ($CDCl_3$) 7.1–7.0 (dt, 1H, aromatic), 7.2–7.1 (tt, 1H, aromatic), 7.6–7.3 (m, 9H, aromatic), 8.0–7.9 (m, 2H, aromatic), 8.2 (b, 1H, N*H*), 8.7 (dd, 1H, aromatic), 11.7 (b, 1H, N*H*); MS (70 eV, EI): *m*/*z*: 316 (M^+, 3%), 224 ($M^+ - NHPh$, 10%), 93 (NH_2Ph, 100%); IR ν_{max}/cm^{-1} 1640 (C=O), 3260 (N–H); Anal. Calc. for $C_{20}H_{16}N_2O_2$ (M_w: 316): C, 5.1; H, 75.93; N, 8.85; Found: C, 5.09; H, 75.84; N, 8.9%.

*Compound **4a**.* Mp 144–146 °C; δ_H ($CDCl_3$) 1.2 (t, 6H, OCH_2CH_3, $J = 7.1$ Hz), 4.2 (m, 4H, OCH_2CH_3), 5.2 (b, 1H, N*H*), 6.8–6.6 (m, 3H, aromatic), 7.4–7.1 (m, 10H, aromatic), 8.2 (d, 1H, aromatic); δ_P ($CDCl_3$) −1.22; MS (70 eV, EI): *m*/*z*: 420 (M^+, 56%), 283 ($M^+ - PO(OEt)_2$, base peak); IR ν_{max}/cm^{-1} 1274 (P=O), 1016 (P–O–C); Anal. Calc. for $C_{24}H_{25}N_2O_3P$ (M_w: 420): C, 68.73; H, 5.77; N, 6.68; Found: C, 68.69; H, 5.74; N, 6.72%.

*Compound **5a**.* Mp 123–125 °C; δ_H ($CDCl_3$) 1.1 (b, 6H, OCH_2CH_3), 1.3 (t, 3H, NCH_2CH_3, $J = 7$ Hz), 3.8 (b, 4H, OCH_2CH_3), 4.1 (q, 2H, NCH_2CH_3, $J = 7$ Hz), 6.9 (m, 1H, aromatic), 7.3–7.1 (m, 6H, aromatic), 7.3–7.6 (m, 7H, aromatic); δ_P ($CDCl_3$) 4.38; MS (70 eV, EI): *m*/*z*: 448 (M^+, 4%), 312 ($M^+ - PO(OEt)_2$, 40%), 282 ($M^+ - (PO(OEt)_2 + Et)$, 34%); IR ν_{max}/cm^{-1} 1270 (P=O), 1010 (P–O–C); Anal. Calc. for $C_{26}H_{29}N_2O_3P$ (M_w: 448): C, 69.63; H, 6.52; N, 6.25; Found: C, 69.72; H, 6.48; N, 6.30%.

Run 2. The reaction was performed and worked up as described above using 1 g (4.3 mmol) of 2-phenyl-3-phenylimino-3*H*-indole 1-oxide (**1**), 5 ml (29 mmol) of triethyl phosphite (**2a**) and 0.5 ml of ethanol. Compound **9a** (1.09 g) and compound **4a** (1.37 g) were isolated by chromatography.

*Compound **9a**.* Mp 122–124 °C; δ_H ($CDCl_3$) 1.3 (t, 3H, $J = 7$ Hz, CH_2CH_3), 4.2 (q, 2H, $J = 7$ Hz, CH_2CH_3), 5.2 (b, 1H, N*H*), 6.6–6.7 (m, 2H, aromatic), 6.8–6.9 (m, 1H, aromatic), 7.15–7.05 (m, 3H, aromatic), 7.2–7.4 (m, 8H, aromatic); MS (70 eV, EI): *m*/*z*: 312 (M^+, 18%), 283 ($M^+ - C_2H_5$, 16%); IR ν_{max}/cm^{-1} 3401 (N–H); Anal. Calc. for $C_{22}H_{20}N_2$ (M_w: 312): C, 84.58; H, 6.45; Found: C, 84.62; H, 6.41%.

Run 3. The reaction was performed and worked up as described above using 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**), 0.6 ml (3.5 mmol) of triethyl phosphite (**2a**) in 30 ml of refluxing xylene, for 10 h. The excess xylene was removed by distillation and the residue purified by chromatography on a column of silica gel eluting with cyclohexane–ethyl acetate (8 : 2). Indole **3** (521 mg) was the only product obtained.

Run 4. The reaction was performed and worked up as described above using 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**), 0.77 ml (4.5 mmol) of triethyl phosphite (**2a**) in 30 ml of refluxing xylene for 8 h. The solution was evaporated to dryness and the residue was purified by chromatography on a column of silica gel eluting with cyclohexane–ethyl acetate (8 : 2). Indole **3** (613 mg) was the only product obtained.

Run 5. The reaction was performed and worked up as described above using 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**), 0.77 ml (4.5 mmol) of triethyl phosphite (**2a**) in 30 ml of refluxing *tert*-butylbenzene for 13 h. The solvent was removed by distillation. Indole **3** (66 mg) and compound **5a** (579 mg) were isolated by chromatography from the residue.

Run 6. The reaction was performed in refluxing triisopropyl phosphite for 1 h 15 min starting from 0.894 g (3 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**), 5 ml (20 mmol) of triisopropyl phosphite (**2b**). The reaction mixture was then worked up as described above. Compounds **9b** (68 mg),

6 (71 mg), **8** (52 mg) and **7** (199 mg) were isolated by chromatography.

Compound ***9b***. δ_H ($CDCl_3$) 1.62 (d, 6H, $CH(CH_3)_2$, J = 7 Hz), 4.60 (m, 1H, $CH(CH_3)_2$, J = 7 Hz), 6.72–6.82 (m, 3H, aromatic), 6.85–6.89 (m, 3H, aromatic), 7.0–7.48 (m, 10H, aromatic); MS (70 eV, EI): *m*/*z*: 326 (M^+, 92%), 283 ($M^+ - CH(CH_3)_2$, 100%); Anal. Calc. for $C_{23}H_{22}N_2$ (M_w: 326): C, 84.63; H, 6.76; Found: C, 84.66; H, 6.72%.

Compound ***6***. Mp 122 °C; δ_H ($CDCl_3$) 7.14–7.28 (m, 2H, aromatic), 7.36–7.6 (m, 8H, aromatic), 7.66 (ddd, 1H, aromatic), 7.98–8.04 (m, 2H, aromatic), 8.31 (dd, 1H, aromatic); MS (70 eV, EI): *m*/*z*: 297 (M^+, 100%), 220 (M^+ − phenyl); IR ν_{max}/cm^{-1} 1660 (C=N), 1620 (C=N); Anal. Calc. for $C_{20}H_{14}N_2O$ (M_w: 297): C, 80.52; H, 4.73; N, 9.39; Found: C, 80.50; H, 4.76; N, 9.41%.

Run 7. The reaction was performed and worked up as described above starting from 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**) and 1.1 ml (4.5 mmol) of triisopropyl phosphite (**2b**) in 30 ml of boiling xylene for 8 h. The solvent was removed by distillation and the residue was purified by chromatography on a column of silica gel eluting with cyclohexane–ethyl acetate (8 : 2). Indole **3** (536 mg) was the only product obtained.

Run 8. The reaction was performed and worked up as described above starting from 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**) and 1.1 ml (4.5 mmol) of triisopropyl phosphite (**2b**) in 30 ml of boiling *tert*-butylbenzene. After 2 h the solvent was removed by distillation and the residue was purified by chromatography on a column of silica gel eluting with cyclohexane–ethyl acetate (8 : 2). Only indole **3** (641 mg) was obtained.

Run 9. The reaction was performed and worked up as described above starting from 0.745 g (2.5 mmol) of 2-phenyl-3-phenylimino-3*H*-indole *N*-oxide (**1**) and 2.2 ml (9 mmol) of triisopropyl phosphite (**2b**) in 30 ml of refluxing *tert*-butylbenzene (T = 168 °C). After 13 h the solvent was removed by distillation and the residue purified by chromatography on a column of silica gel eluting with cyclohexane–ethyl acetate. Indole **3** (64 mg), compounds **8** (57 mg), **7** (87 mg) and **5b** (368 mg) were isolated by elution in the reported order.

Compound ***5b***. Mp 135–140 °C; δ_H ($CDCl_3$) 1.9 (b, 12 H, $O=P(OCH(CH_3)_2)$, 1.6 (d, 6H, $NCH(CH_3)_2$), 3.9 (b, 1H, $NCH(CH_3)_2$), 4.5 (m, 2H, $O=P(OCH(CH_3)_2)_2$), 6.9 (m, 1H, aromatic), 7.0–7.2 (m, 6H, aromatic), 7.35–7.6 (m, 7H, aromatic); δ_P ($CDCl_3$) 2.16; MS (70 eV, EI): *m*/*z*: 491 (M^+, 94%), 448 ($M^+ - CH(CH_3)_2$, 52%), 406 ($M^+ - 2\ CH(CH_3)_2$, 97%), 326 ($M^+ - PO(OR)_2$, 96%); IR ν_{max}/cm^{-1} 1270 (P=O), 995 (P–O–C); Anal. Calc. for $C_{29}H_{35}N_2O_3P$ (M_w: 491): C, 71; H, 7.19; N, 5.71; P, 6.31; Found: C, 70.88; H, 7.21; N, 5.80; P, 6.41%.

Run 10: Reaction between triethyl phosphite (2a) and 2-phenyl-3-phenylimino-3*H*-indole (3). 2-Phenyl-3-phenylimino-3*H*-indole (0.368 g, 1.3 mmol) and 5 ml (20 mmol) of triethyl phosphite were refluxed for 1 h and 15 min. The reaction solution was cooled, washed with 10% aqueous $NaHCO_3$, and then extracted with dichloromethane. The organic layer was separated, dried on Na_2SO_4 and chromatographed on a column of silica gel eluting first with cyclohexane–ethyl acetate (9 : 1) and then increasing the polarity to cyclohexane–ethyl acetate 1 : 1. The isolated products, whose yields are reported in Table 1, were eluted in the order: **8** (9 mg), **7** (46 mg), **4a** (22 mg) and **5a** (192 mg).

Synthesis of compound 9a. Ethyl bromide 0.218 g (2 mmol) was added to a stirred solution of **8** (0.284 g, 1 mmol) with two powdered pellets of KOH in 10 ml of DMSO. The reaction mixture was stirred at room temperature for 4 h and then poured into water and extracted with benzene. The organic phase was washed several times with water, dried on Na_2SO_4 and then chromatographed on column silica gel eluting with cyclohexane–ethyl acetate 9 : 1. The isolated product was **9a** (0.125 g, yield 40%).

Table 3 Experimental data for the X-ray diffraction studies on crystalline compounds **4a** and **6**

Compound	**4a**	**6**
Formula	$C_{24}H_{25}N_2O_3P$	$C_{20}H_{14}N_2O$
F_w	420.4	298.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell parameters at 295 K		
a/Å	12.437(3)	10.627(2)
b/Å	9.569(2)	4.667(2)
c/Å	19.543(4)	30.968(3)
α/degrees	90	90
β/degrees	106.9(1)	93.0(1)
γ/degrees	90	90
V/Å^3	2225.4(14)	1533.8(8)
Z	4	4
Linear abs coeff/cm^{-1}	13.0	6.4
Unique total data	4647	3340
Criterion of obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Unique obs data (NO)	2070	850
No. of refined par (NV)	271	208
Overdetermn ratio (NO/NV)	7.7	4.1
R_{int}	0.021	0.046
R	0.044	0.045
R_w	0.049	0.047
GOF	0.339	1.415
Largest shift/esd	0.65	0.75
Largest peak/e Å^{-3}	0.27	0.18
Programs	[a]	[a]

[a] SHELXS86,[39] SHELX76,[40] PARST.[41] $R = \Sigma||\Delta F|/\Sigma|F_o||$, $R_w = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, GOF = $[\Sigma w|\Delta F|^2/(NO - NV)]^{1/2}$.

Independent synthesis of 7 by hydrolysis of compound 6. Compound **6** (0.298 g, 1 mmol) and two drops of 1 M HCl were refluxed for 2 h in 20 ml of ethanol (95%). The reaction solution was then evaporated to dryness. Compound **7** was isolated from the residue in good yield (0.309 g, 97%).

Crystal structures of 1-diethylphosphoryl-2-phenyl-3-phenylamino-1*H*-indole (4a) and 2-phenyl-4-phenylimino-4*H*-3,1-benzoxazine (6). Table 3 shows the experimental and crystallographic data for **4a** and **6**. The intensities I_{hkl} were determined at room temperature by analysing the reflection profiles using the Lehmann and Larsen procedure.[37] One standard reflection measured every 100 collected reflections to monitor crystal decomposition and instrumental linearity showed no significant variations. Corrections for Lorentz and polarization effects were performed; there were no corrections for absorption effects. The structures were solved by direct methods and refined by cycles of full-matrix anisotropic least-squares; the hydrogen atoms were located in the difference map and included in the final structure factors calculation as fixed contributors.

Atomic scattering factors were from the International Tables for X-Ray Crystallography.[38] Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

CCDC reference number 188/220. See http://www.rsc.org/suppdata/p2/a9/a907601h/ for crystallographic files in .cif format.

Acknowledgements

The authors would like to thank the Italian MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica) for financial support and Dr M. Iacussi for help with NMR spectra.

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Paper a907601h