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

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2-Phenyl-3-phenylimino-3H-indole N-oxide (an indolic nitrene) reacts with triethyl and triisopropyl phosphite in refluxing xylene and tert-butylbenzene to give 2-phenyl-3-phenylimino-3H-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 nitrene 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-1H-indole and 2-phenyl-4-phenylimino-4H-3,1-benzoxazine are also described.

2-Phenyl-3-phenylimino-3H-indole N-oxide (1) is a precursor of a series of stable aminoxyls, which, on the basis of their stability, are useful models to study the chemical behaviour of aromatic aminoxyls and excellent antioxidants in the prevention of oxidative damage in biological systems. The most important series of these products is obtained by 1,2-addition of Grignard’s reagents to the cyclic nitrene (2). Other properly functionalised aminoxyls are prepared from 1 using different kinds of nucleophiles. In the present work the cyclic nitrene (1) was reacted with trialkyl phosphites, which are good nucleophiles, in order to obtain aminoxyl 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 nitrene (1); in fact, in this case, the main reaction product was 2-phosphorylated indoloxyl.

Results

The products obtained from the reaction of nitrene (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-3H-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 nitrene (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 nitrene 1 with phosphite 2a and 2b experimental conditions, isolated products and yields

<table>
<thead>
<tr>
<th>Run</th>
<th>Reagents</th>
<th>Eq.a</th>
<th>T°C.b</th>
<th>t/h.c</th>
<th>Products and yields (%)</th>
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<td></td>
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<td>3 4 5 6 7 8 9</td>
</tr>
<tr>
<td>1</td>
<td>1 + 2a</td>
<td>6</td>
<td>2a</td>
<td>1 h 15’</td>
<td>(6.7) (53.5) (10) (traces)</td>
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<tr>
<td>2</td>
<td>1 + 2a</td>
<td>6</td>
<td>2a</td>
<td>1 h 15’</td>
<td>(43)</td>
</tr>
<tr>
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<td>(74)</td>
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<tr>
<td>5</td>
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<td>Bu/Ph</td>
<td>13</td>
<td>(9.4) (51.7)</td>
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<tr>
<td>6</td>
<td>1 + 2b</td>
<td>6</td>
<td>2b</td>
<td>1 h 15’</td>
<td>(8) (10) (6) (7)</td>
</tr>
<tr>
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<td>1.8</td>
<td>Xylene</td>
<td>8</td>
<td>(76)</td>
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<td>6</td>
<td>2a</td>
<td>1 h 15’</td>
<td>(4) (35) (11.3) (2.5)</td>
</tr>
</tbody>
</table>

a Equivalents of phosphites for equivalents of nitrene 1. b The reaction temperature corresponds to the boiling point of the solvent. c Reaction time.


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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. 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 trisopropyl 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 1H-NMR spectrum of 5a showed only an additional ethyl group with respect to that of 4a, which is the 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. Compound 7, isolated in almost all reactions, was identified by comparing its spectroscopic data with those of a sample obtained by a different route. Compound 8 was identified by comparison with a sample obtained from the reaction of 3 with phenylhydrazine. Compound 9 was identified by comparing its 1H-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-1H-indole (4a) and 2-phenyl-4-phenylimino-4H-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
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 aminec 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)–(C2)–(N2)–(C21) torsion angle is 11.2(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) Å] and single P–O [1.557(3) and 1.538(4) Å] bonds of the phosphonilic group. Packing is determined by a long hydrogen bond of the type N⋯O involving the amine nitrogen and the phosphonilic oxygen in the 2–x, ½+y, ½–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 previously reported structures of 3,1-benzoxazine25 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 conformation26 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.

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(4)–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) 1.358(6) |
| O(4)–C(41) 1.317(11) C(3)–C(8) 1.394(6) |

| 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) |

| Scheme 2 | 1 + 2a 2b  |
| Scheme 3 | 12 |

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-3H-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.

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 trialkylphosphite.

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 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 in UV-irradiation of nitrones (1)17 and 2-phenyl-3H-indol-3-one N-oxide (phenylisatoen),30 through the formation of an oxaziridine ring11,31 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 nitrene 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 compound possesses good oxidising power and is easily reduced by hydrazobenzene and by phenylhydrazine to 8. To our knowledge, there are no analogues in the literature of reduction of quinonediazidine derivatives with trialkyl phosphites, even if Olah, years ago, described the reduction of the carbonyl group to CH₂ by trisopropyl phosphite. Moreover, the reduction of indole (3) with trialkyl phosphites could be explained through an electron transfer reaction between compound 3 and the phosphate at high temperature, even if the redox potentials of the reagents would exclude this possibility at room temperature. 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 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; δₙ (CDCl₃) 7.1--7.0 (dt, 1H, aromatic), 7.7--7.2 (tt, 1H, aromatic), 8.0--7.9 (m, 2H, aromatic), 8.2 (b, 1H, NH), 8.7 (dd, 1H, aromatic), 11.7 (b, 1H, NH); MS (70 eV, EI): m/z: 316 (M⁺, 3%), 224 (M⁺ -- NHPh, 10%), 93 (NH₃Ph, 100%); IR νₚₑₚₑ⁻¹ 2060; 1320 (C=O), 3260 (N--H); Anal. Calc. for C₂₃H₂₆N₂O₃ (M⁺ 316): C, 51.1; H, 75.93; N, 8.85; Found: C, 50.9; H, 75.84; N, 8.9%. Compound 9a. Mp 144--146°C; δₙ (CDCl₃) 1.2 (t, 6H, OCH₂CH₃), 1.7 (t, 1H, aromatic), 7.4--7.1 (m, 6H, aromatic), 7.3--7.6 (m, 7H, aromatic); δp (CDCl₃) 4.38; MS (70 eV, EI): m/z: 420 (M⁺, 56%), 283 (M⁺ -- PO(OEt)₂), base peak; IR νₚₑₚₑ⁻¹ 1279 (P=O), 1016 (P=O=C); Anal. Calc. for C₂₃H₂₆N₂O₃P (M⁺, 448): C, 69.63; H, 6.52; N, 6.25; Found: C, 69.72; H, 6.48; N, 6.30%.

Experimental

General

Melting points were measured on an Electrothermal apparatus and are uncorrected. H-NMR spectra were recorded on a Varian Gemini 200 spectrometer and δ are referred to SiMe₃. ³¹P-NMR were recorded on a Bruker AMX 300 at 121.5 MHz and δ are referred to H₃PO₄ (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. Trialky phosphite, trisopropyl phosphite, xylene and tert-butyl benzene were purchased from Aldrich and were of ACS grade; 2-phenyl-3-phenylimino-3H-indole 1-oxide was synthesised as reported in the literature.¹⁸

Reaction procedures and product analyses

**Run 1:** Reaction between triethyl phosphate (2a) and 2-phenyl-3-phenylimino-3H-indole N-oxide (1). 2-Phenyl-3-phenylimino-3H-indole 1-oxide (1) (2.25 g, 7.6 mmol) and 11 ml (64 mmol) of triethyl phosphate were refluxed for 1 h and 15 min. The reaction solution was cooled and then washed with 10% aqueous NaHCO₃, extracted with dichloromethane, separated, dried over Na₂SO₄ 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

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

**Compound 9b.** δ$_{x}$ (CDCl$_3$) 1.62 (d, 6H, CH(CH$_3$)$_2$), 2.16 (d, 6H, CH(CH$_3$)$_2$), 6.72 (dd, 1H, aromatic), 7.0-7.4 (m, 10H, aromatic); MS (70 eV, EI): m/z: 291 (M$^+$, 100%), 209 (M$^+$ - phenyl), 123 (M$^+$ - PO$_2$), 79, 63, 31; IR ν$_{max}$ cm$^{-1}$ 1666 (C=O), 1600 (C=N); Anal. Calc. for C$_{14}$H$_{13}$N$_3$O (M$_w$ = 291): C, 70.88; H, 7.21; N, 5.80; Found: C, 70.6; H, 7.32; N, 5.82.

**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-3H-indole (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-3H-indole (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-3H-indole (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$_{x}$ (CDCl$_3$) 1.9 (b, 12 H, O=S=OCH(CH$_3$)$_2$), 1.6 (d, 6H, CH(CH$_3$)$_2$), 3.9 (b, 1H, NCH$_2$(CH$_2$)$_2$), 4.5 (m, 2H, O-P(OCH$_2$(CH$_2$)$_2$)$_2$), 6.9 (m, 4H, aromatic), 7.0-7.2 (m, 6H, aromatic), 7.35-7.6 (m, 7H, aromatic); δ$_{y}$ (CDCl$_3$) 2.16; MS (70 eV, EI): m/z: 491 (M$^+$, 94%), 448 (M$^+$ - CH$_2$(CH$_2$)$_2$), 406 (M$^+$ - 2 CH$_2$(CH$_2$)$_2$), 326 (M$^+$ - PO$_2$), 176; IR ν$_{max}$ cm$^{-1}$ 1270 (P=O), 995 (P-O-C); Anal. Calc. for C$_{14}$H$_{13}$N$_3$O$_2$P (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 phosphate (2a) and 2-phenyl-3-phenylimino-3H-indole (3).** 2-Phenyl-3-phenylimino-3H-indole (0.368 g, 1.1 mmol) and 5 ml (20 mmol) of triethyl phosphate 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$_2$SO$_4$, 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$_2$SO$_4$ and then chromatographed on column silica gel eluting with cyclohexane-ethyl acetate 9:1. The isolated product was 9a (0.125 g, yield 40%).

**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-phenylimino-1H-indole (4a) and 2-phenyl-1-phenylimino-1H-3,1-benzoxazone (6).** Table 3 shows the experimental and crystallographic data for 4a and 6. The intensities $I_{me}$ were determined at room temperature by analysing the reflection profiles using the Lehmann and Larsen procedure. One standard reflection measurement 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. Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Crystallografici, Parma, Italy. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

**Table 3** Experimental data for the X-ray diffractions studies on crystal-line compounds 4a and 6.

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<th>Compound</th>
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<th>6</th>
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a SHELXS86, b SHELX76, c PARST d = Σ|F$_{o}$|/Σ|F$_{c}$|, R = [Σ(|F$_{o}$| - |F$_{c}$|)/Σ|F$_{o}$|]; GOF = [Σ|F$_{o}$| - Σ|F$_{c}$|]/[NO - NV]$^{1/2}$. 

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References


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