Pergamon

Tetrahedron 56 (2000) 4079–4084

TETRAHEDRON

# Isolation, Reactivity and Intramolecular Trapping of Phosphazide Intermediates in the Staudinger Reaction of Tertiary Phosphines with Azides

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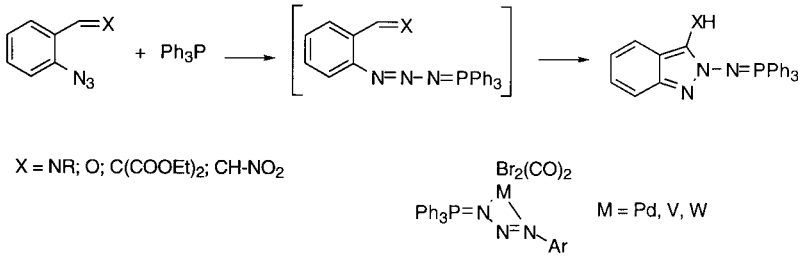
Received 3 February 2000; revised 28 March 2000; accepted 13 April 2000

**Abstract**—The Staudinger reaction of the *N*-substituted *o*-azidobenzamide **1** with triphenylphosphine or diphenylmethylphosphine allows the isolation of the intermediate phosphazides as crystalline solids, which have been characterized by spectroscopic methods. These compounds react in aza Wittig type fashion with isocyanates to give unexpectedly the corresponding 1,2,3-benzotriazinone derivative. Trapping of a *Z*-phosphazide by intramolecular aza Wittig reaction is reported for the first time. © 2000 Elsevier Science Ltd. All rights reserved.

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction, which has proved to be a very useful reaction in synthetic organic chemistry.[1] The primary imination products, phosphazides (triazenophosphoranes or triazaphosphadienes), are sometimes isolable and stable,[2,3] but as a rule they lose nitrogen at room temperature or even at lower temperature to give the corresponding iminophosphorane compound in practically quantitative yields. The only six isolated phosphazides have been formed from sterically hindered components or the electronic effects of substituents have been such as to increase the electron density on the phosphorus atom or decrease it on the N-α atom of the azide.[4–7] The *E*-geometry observed in the isolable phosphazides probably accounts for their stability by making more difficult ring-closure to the four-membered transition state necessary for nitrogen elimination and iminophosphorane formation.

In spite of the important role of iminophosphoranes in heterocyclic synthesis,[8–10] the chemistry of their elusive precursors phosphazides has been poorly studied, primarily due to their rapid conversion to iminophosphoranes.

In this context, we have reported the first trapping of phosphazides,[11,12] from the reaction of *o*-azidobenzaldimines with triphenylphosphine to give iminophosphoranes derived from 2-aminoindazoles. This conversion involves formation and further electrocyclization of the intermediate phosphazide across the central nitrogen atom. Similar behaviour has also been observed with aryl azides bearing an unsaturated functionality at the *ortho*-position: *o*-azidobenzaldehyde,[13,14] diethyl(*o*-azidobenzyliden malonate and 2-(*o*-azidophenyl) nitroethylene.[15] Phosphazides derived from aryl azides and triphenylphosphine have also been trapped through formation of transition metal (Pd, V or W) complexes[16–18] (Scheme 1).




**Scheme 1.**

*Keywords*: Staudinger reaction; azides; phosphines; aza Wittig reaction.

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PII: S0040-4020(00)00322-7

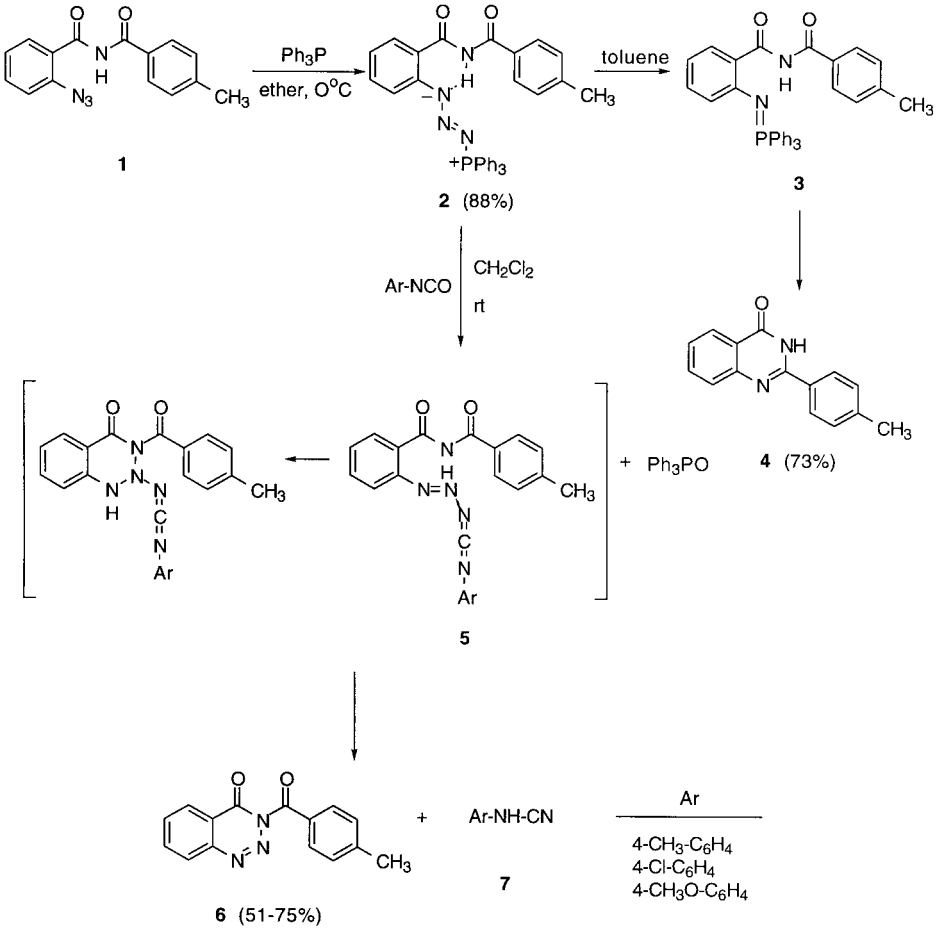
We wish to report here the isolation of a new type of phosphazide and its chemical behaviour in aza Wittig type reactions.

## Results

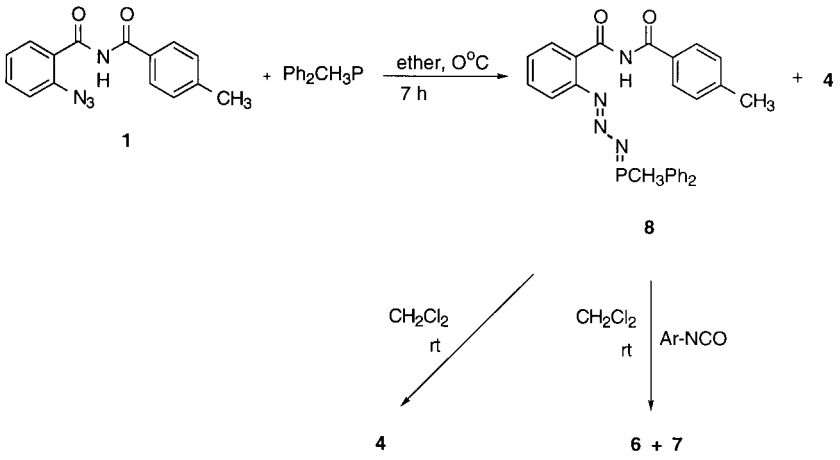
Azide **1**, readily available in 72% yield from the reaction of 4-methylbenzamide with *o*-azidobenzoyl chloride[19] in the presence of sodium hydride, reacted with triphenylphosphine in dry dichloromethane at 0°C to give the phosphazide **2** as a crystalline solid in 88% yield. Compound **2** can be stored for several weeks without any signs of decomposition. The first indication of the phosphazide nature was provided by its $^{13}C$ NMR spectrum in which coupling between the phosphorus atom and the aromatic carbon atoms of the *o*-azidobenzamide residue was not observed as occurs in typical *N*-aryliminophosphoranes. In addition, the $^{31}P$ NMR spectrum displayed only one signal at 25.5 ppm which is in good agreement with previously reported values for this type of compound,[20] and in the MS spectrum in $FAB^+$ mode appeared a fragment at *m/z* 543 corresponding to the $M^+ + 1$. Unfortunately, we were not able to obtain suitable crystals for X-ray diffraction studies.

The stability showed by the phosphazide **2** could be due to the essential zwitterionic character of phosphazides,[1,2] in which the phosphorus atom has partial phosphonium character and the negative charge is on the nitrogen atom linked to the aromatic ring. Probably this fact allows a very strong intramolecular hydrogen bonding between this nitrogen atom and the amide proton (evidenced in the IR spectrum by a strong absorption band in the region 3500–2900 $cm^{-1}$), which prevents the $E \rightarrow Z$ isomerization necessary for the nitrogen elimination. It has been reported[21] that the stability of a phosphazide molecule is determined by electronic (a conjugative delocalization of the cationic charge on phosphorus) and steric factors (screening of the phosphorus atom by bulky substituents). Stabilization of phosphazide **2** by intramolecular hydrogen bonding is closely related to those found in some *N*-aryl, heteroaryl iminophosphoranes bearing an amide group at the *ortho*-position, which even inhibits the aza Wittig reaction, due to conformational restriction and lowered nucleophilicity of the imino nitrogen atom.[22,23] The unusual stability of **2** gave us the opportunity to gain more of an insight into the reactivity of phosphazides, especially in aza Wittig-type reactions. Note that so far the chemical reactivity of phosphazides remains almost unexplored and only the regio- and stereo-specific *N*-alkylation with retention of the nitrogen triad has been reported.[24]

When compound **2** was heated in toluene at reflux temperature the 4(3*H*)-quinazolinone **4** was isolated in 73% yield along with triphenylphosphine oxide. This conversion takes



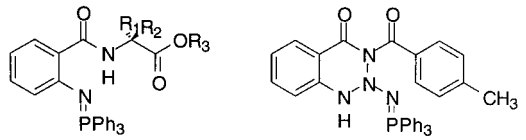

**Scheme 2.**




**Scheme 3.**

place by nitrogen elimination of the phosphazide **2** to give the iminophosphorane **3**, which under the reaction conditions undergoes an intramolecular aza Wittig reaction involving the carbonyl group of the amide functionality to give **4**.

This conversion deserves some comments. First, the high reactivity of the iminophosphorane **3** with respect to the related iminophosphoranes A, which undergo intramolecular aza Wittig reaction across the more reactive carbonyl group of the ester functionality under harsher reaction conditions[22] (6 h, 110°C versus 16–84 h, 140°C). Second, and perhaps more importantly, these conversions support the proposed structure of the phosphazide **2** and rule out the cyclic structure B, originated from **2** by an intramolecular nucleophilic attack of the NH amide group on the central nitrogen atom of the phosphazide moiety.



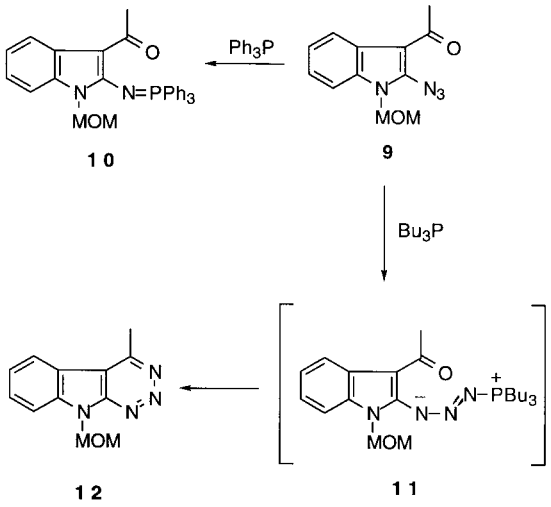
**A** **B**

Reaction of phosphazide **2** with 1 equiv. of aryl isocyanate (phenyl, *p*-methyl or *p*-metoxyphenyl) in dichloromethane at room temperature for 7 h gave directly the 1,2,3-benzotriazine-4-one **6** in yields ranging from 51 to 75%, the corresponding arylcyanoamide **7** and triphenylphosphine oxide. However, when the less reactive aryl isothiocyanate were used instead of arylisocyanate the starting phosphazide **2** together with a small amount of **4** (15%) were isolated. The structure of these compounds have been confirmed by their spectroscopic data and mass spectrometry (Scheme 2).

Similar results, which also confirm the open-chain structure of **2**, were obtained when the triazaphosphadiene adduct pathway[20] was used to study the behaviour of the *N*-(*p*-methylbenzoyl)-*o*-azidobenzamide **1** in aza Wittig reactions towards aryl isocyanates. In this way, the reaction is carried out with the isocyanate present before addition of the triphenylphosphine. Addition of a solution of triphenylphosphine to a mixture of **2** and an arylisocyanate in dichloromethane at room temperature, led to the formation of **6** and **7** in almost the same yields.

Azide **1** also reacted with the more reactive diphenylmethylphosphine under the same conditions to give a mixture of **4** in 33% yield and the new phosphazide **8** in 42% yield (Scheme 3). We have also found that the ratio **4**:**8** strongly depends on the reaction time. Short reaction times improve the yield of **8** although starting material remains unchanged, and longer period of times increase the yield of **4**. These results suggest that the formation of compound **4** arises from **8** by nitrogen elimination and subsequent intramolecular aza Wittig reaction of the resulting very reactive diphenylmethyliminophosphorane. This assumption was confirmed by isolation of **4** in almost quantitative yield after stirring a solution of **8** in dichloromethane at 0°C for 24 h. As the formation of **4** from **2** requires heating in toluene whereas the conversion of **8** into **2** takes place under extremely mild reaction conditions, we conclude that the factors which determine the stability of this kind of phosphazides are not only hydrogen-bonding interactions but also steric factors which impose conformational restrictions to the nitrogen evolution (*E*-configuration). Spectroscopic data of compound **8** are in good agreement with the proposed structure and are quite similar to those observed for phosphazide **2**. The $^{1}H$ and $^{13}C$ NMR were quite similar to those observed for phosphazide **2**. The $^{31}P$ NMR spectrum displayed a signal at $\delta$ 29.13 ppm and the MS ($FAB^{+}$) showed a fragment at *m*/*z* 481 ppm. The chemical behaviour of the phosphazide **8** in aza Wittig reactions towards arylisocyanates is similar to that observed for compound **2** to give the benzotriazinone **6** (42–49%), the corresponding cyanoamide **7** and diphenylmethylphosphine oxide (Scheme 3).

Formation of the 1,2,3-benzotriazine-4-one **6** from the reaction of phosphazides **2** or **8** with aryl isocyanates could be understood by an initial aza Wittig reaction across the nitrogen atom directly linked to the phosphorus atom to give the aza Wittig adduct **5** and the corresponding phosphine oxide. The very reactive intermediates **5** undergo intramolecular nucleophilic attack of the amido group on the central nitrogen atom of the remaining azide framework followed by a retro-ene reaction with concomitant




**Scheme 4.**

elimination of the corresponding arylcyanoamide **7** to give **4** (Scheme 2).

It is worth noting that we have previously described[25] a similar type of carbodiimide fragmentation by a retro-ene reaction to give arylcyanoamides, although under stronger reaction conditions (toluene, 140°C, sealed tube, 36 h).

On the other hand, we have found that the reaction of *N*-methoxymethyl-3-acetyl-2-azidoindole **9** with triphenylphosphine in ether at 0°C led to the expected iminophosphorane **10** in 90%. However, when tri-*n*-butylphosphine was used instead of triphenylphosphine under the same reaction conditions the triazino[4,5-b] indole derivative **12** was isolated in 78% yield as the sole reaction product (Scheme 4).

The different behaviour of the azido compound **9** towards triphenyl- and tri-*n*-butylphosphine could be due not only to electronic effects but also to steric effects. In the proposed intermediate *Z*-phosphazide **11** the adequate geometrical disposition of the substituent on the phosphazide framework, being the highly reactive tri-*n*-butylphosphinimino group loosely connected to the carbonyl group, allows the intramolecular aza Wittig reaction to give **12** to be faster than the nitrogen elimination. For the case of the phosphazide derived from triphenylphosphine the more sterically hindered triphenylphosphonium group prevents such a geometrical disposition and nitrogen elimination through the *E*-configuration is the only reaction pathway.

## Conclusion

These results clearly demonstrate that the chemistry of phosphazides is not only restricted to nitrogen evolution, giving the corresponding iminophosphoranes but also they are able to undergo aza Wittig reaction. In this context, two unprecedented aspects have surfaced from this work. First, the aza Wittig adduct resulting from the reaction of tertiary phosphines with azides and aza Wittig reagents do not always lose nitrogen to give the expected aza Wittig products, in some cases decomposition of this kind of reactive intermediate takes place by a different way to give products containing two nitrogen atoms which originate from the starting azide. Secondly, for the first time a phosphazide has been trapped with an unusual *Z*-configuration by an intramolecular aza Wittig reaction giving rise to a product which retains the three nitrogen atoms of the starting azide.

## Experimental

### General methods

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 Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). Mass spectra were recorded on a Hewlett–Packard 5993C spectrometer or a Fisons AUTOSPEC 500 VG. Microanalyses were performed on a Perkin–Elmer 240C instrument.

***N*-(4-Methylbenzoyl)-*o*-azidobenzamide 1.** To a well-stirred suspension of sodium hydride (2.87 g, 120 mmol) in anhydrous dioxane (45 mL) was added under nitrogen in portions 4-methylbenzamide (1.62 g, 12 mmol) at such rate that the temperature remained below 10°C. Then a solution of *o*-azidobenzoylchloride (2.17 g, 12 mmol) in the same solvent (10 mL) was added dropwise. The resulting reaction mixture was stirred at room temperature for 7 h. After cooling, the solvent was removed under reduced pressure and the residue was poured into a cooled 5% HCl solution (150 mL) and then extracted with dichloromethane (3×100 mL). The combined organic layers were washed with brine (3×75 mL) and then dried over anhydrous $MgSO_4$. Filtration and elimination of the solvent gave a crude product which was chromatographed on a silica gel column with ethyl acetate/hexane (1:1) as eluent to give **1** (2.96 g, 88%); mp. 104–106°C (colourless prisms). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=2.43 (s, 3H, C*H*$_3$–Ar), 7.23–7.33 (m, 4H), 7.59 (td, 1H, *J*=7.8, 1.5 Hz), 7.84 (d, 2H, *J*=8.2 Hz), 8.57(dd, 1H, *J*=7.8, 1.5 Hz), 10.54 (bs, 1H, N*H*). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$=21.6 (*C*H$_3$), 118.4, 124.5 (q), 125.6, 129.4, 129.6, 130.6 (q), 132.9, 133.7, 137.1 (q), 143.9 (q), 163.1 (C=O), 165.1 (C=O). IR (Nujol) $\nu$=3289 (m), 2142 (s), 1730 (vs), 1498 (s), 757 (m) cm$^{-1}$. MS: *m*/*z* (%) (EI positive): 280 ($M^+$, 5), 252 (5), 119 (100), 91 (47). Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 63.98; H, 4.34; N, 20.11.

### General procedure for the preparation of phosphazides 2 and 8

To a solution of *N*-(4-methylbenzoyl)-*o*-azidobenzamide **1** (0.62 g, 2.3 mmol) in dry dichloromethane (8 mL) was added dropwise a solution of the appropriate phosphine (2.3 mmol) in the same solvent (8 mL) at 0°C under nitrogen. The solution was stirred at room temperature for 7 h.

For **2**. The solvent was removed under reduced pressure at room temperature and solid residue was slurried with diethyl ether and filtered to give **2** (1.10 g, 88%) mp

156–158°C (evolution of $N_2$) (yellow needles). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$=2.33 (s, 3H, C$H_3$), 7.13 (d, 2H, $J$=8.1 Hz), 7.23–7.37 (m, 4H), 7.53–7.81 (m, 15H), 8.42 (d, 2H, $J$=8.1 Hz), 13.98 (bs, 1H, N$H$). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$=21.5 (*C*$H_3$), 116.5, 125.4 (q), 125.9, 126.1 (d, $^1J_{P,C}$=95.3 Hz, C*i*), 128.9, 129.1, 129.2 (d, $^3J_{P,C}$=11.6, C*m*), 131.4 (q), 132.0, 132.7, 133.2, (d, $^4J_{P,C}$=2.5 Hz, C*p*), 133.5, (d, $^2J_{P,C}$=9.1 Hz, C*o*), 142.5 (q), 150.1 (q), 164.9 (C=O), 165.7 (C=O). $^{31}$P NMR (200 MHz, $CDCl_3$): $\delta$=25.5. IR (Nujol) $\nu$: 3500–2900 (m), 1724 (s), 1506 (s), 1468 (m), 1440 (m), 1262 (m), 1224 (m), 1160 (s), 1120 (m), 1104 (m) cm$^{-1}$. MS: *m*/*z* (%) (FAB positive, NBA) 543 (M+H)$^+$ (35), 278 (46), 236 (22), 119 (100), 90 (18). Anal. Calcd for $C_{33}H_{27}N_4O_2P$: C, 73.05; H, 5.02; N, 10.33. Found: C, 72.74; H, 5.27: N, 10.19.

For **8**. The precipitated solid formed was separated by filtration, washed with diethylether and identified as **4** (33%). The filtrate was concentrated to dryness under reduced pressure at room temperature. The crude solid was slurried with dry diethylether to give **8** (0.46 g, 42%) mp 162–164°C (evolution of $N_2$) (yellow needles) $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 2.33 (s, 3H, C$H_3$), 2.45 (s, 3H, C$H_3$–P), 7.13 (d, 2H, $J$=8.1 Hz), 7.25–7.43 (m, 4H), 7.55–7.84 (m, 10H), 8.39 (d, 2H, $J$=8.1 Hz), 13.48 (bs, 1H, N$H$). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$: 12.1 (*C*H$_3$–P, $^1J_{P,C}$=64.57), 21.5 (*C*$H_3$), 116.5, 125.4 (q), 125.9, 127.1 (d, $^1J_{P,C}$=94.5 Hz, C*i*), 128.9, 129.0, 129.3 (d, $^3J_{P,C}$=12.1, C*m*), 131.4 (q), 131.9 (d, $^2J_{P,C}$=9.2 Hz, C*o*), 132.0, 132.6, 133.3 (d, $^4J_{P,C}$=2.3 Hz, *Cp*), 142.6 (q), 150.0 (q), 164.9 (C=O), 165.7 (C=O). $^{31}$P NMR (200 MHz, $CDCl_3$): $\delta$=29.13. IR (Nujol) $\nu$: 3500–2900 (m), 1724 (s), 1500 (s), 1467 (m), 1439 (m), 1265 (m), 1221 (m), 1162 (s), 1115 (m), 1098 (m) cm$^{-1}$. MS: *m*/*z* (%) (FAB positive, NBA) 481 (M+H)$^+$ (23), 303 (61), 275 (12), 237 (40), 200 (100), 119 (33), 90 (18). Anal. Calcd for $C_{28}H_{25}N_4O_2P$: C, 69.99; H, 5.24; N, 11.66. Found: C,69.71; H, 5.22 N, 11.50.

### 2-(4-Methylphenyl)-3*H*-quinazoline-4-one 4 from phosphazides 2 and 8

**Procedure A.** A solution of phosphazide **2** (0.3 g, 0.55 mmol) in dry toluene (10 mL) was treated at reflux temperature for 6 h. After cooling the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:1) to give **4** (0.09 g, 73%) mp 240–242°C (colourless prisms). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 2.46 (s, 3H, C$H_3$), 7.38 (d, 2H, $J$=7.8 Hz), 7.94 (ddd, 1H, $J$=8.1, 6.3, 2.1 Hz), 7.79–7.81 (m, 2H), 8.16 (d, 2H, $J$=7.8 Hz), 8.33 (d, 1H, $J$=7.5 Hz), 11.67 (bs, 1H, NH). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$: 21.5 (*C*$H_3$), 120.8 (q, C-4a), 126.4 (C-8), 126.5 (C-6), 127.3, 27.9 (C-5), 129.7, 130.0 (q), 134.7 (C-7), 142.1 (q), 149.7(q, C-8a), 151.7 (q, C-2), 163.8 (C=O). MS: *m*/*z* (%) (EI positive) 236 (M$^+$, 21), 119 (100). IR (Nujol) $\nu$: 3178 (m), 1667 (vs), 1660 (s), 1599 (s), 1562 (m), 1343 (m), 771 (m) cm$^{-1}$. Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.97; H, 5.27: N, 12.07.

**Procedure B.** A solution of phosphazide **8** (0.24 g, 0.5 mmol) in dry diethyl ether was stirred at room temperature for 24 h. The precipitated solid formed was separated by filtration, air-dried and identified as **4** (0.11 g, 95%).

### Reaction of phosphazides 2 and 8 with aryl isocyanates

To a solution of the phosphazide **2** or **8** (1 mmol) in dry dichloromethane (10 mL) was added a solution of the corresponding aryl isocyanate (1 mmol) in the same solvent (5 mL). The mixture was stirred at room temperature under nitrogen for 7 h. The solvent was removed under reduced pressure at room temperature. The crude product was chromatographed on a silica gel column with ethyl acetate/hexane (2:1) as eluent to give **6** (0.13–0.20 g, 51–75%) mp 157–160°C (colourless prisms). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 2.45 (s, 3H, C$H_3$), 7.31 (d, 2H, $J$=8.1 Hz), 7.79–7.91 (m, 3H), 8.04 (t, 1H, $J$=8.0 Hz), 8.25 (d, 1H, $J$=8.0 Hz), 8.40 (d, 1H, $J$=8.0 Hz). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$: 21.9 (*C*$H_3$), 120.4 (C-4a), 125.6, 128.7 (C-1′), 129.0, 129.7, 131.2, 133.3, 135.8, 143.4 (C-4′), 146.4 (C-8a), 155.0 (C-4), 169.3 (C=O). MS: *m*/*z* (%) (FAB positive, NBA) 266 (M+H)$^+$ (65). IR (Nujol) $\nu$: 1730 (vs), 1703 (vs), 1607 (s) cm$^{-1}$. Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.46; H, 4.29; N, 15.62. and **7** (Ar=4-$H_3C$–$C_6H_4$; IR (:3304 (s), 2236 (s) cm$^{-1}$ MS: *m*/*z* (%) (EI positive) 132 (M$^+$, 100), 106 (25), 105 (68), 91 (54).

***N*-Methoxymethyl-2-acetyl-3-(triphenylphosphoranylidene)aminoindole 10.** To a cooled 0°C solution of triphenylphosphine (0.53 g, 2.04 mmol) in dry diethyl ether (10 mL), a solution of *N*-methoxymethyl-3-acetyl-2-azido indole **9**[26] (0.5 g, 2.04 mmol) in the same solvent (10 mL) was added dropwise under nitrogen. The mixture was allowed to warm to room temperature and stirred for 12 h. After cooling, the precipitated solid was collected by filtration and recrystallized from benzene–*n*-hexane to give **10** (0.88 g, 90%) mp 152–153°C (colourless prisms). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 2.15 (s, 3H, C$H_3$CO), 3.24 (s, 3H, C$H_3$O), 5.62 (s, 2H, C$H_2$O), 7.0–7.15 (m, 2H, H-5+H-6), 7.20–7.33 (m, 1H, H-7), 7.34–7.48 (m, 9H, H*m*+H*p*), 7.49–7.57 (m, 1H, H-4), 7.58–7.72 (m, 6H, H*o*). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$:30.0 (*C*$H_3$CO), 55.8 (*C*$H_3$O), 71.7 (*C*$H_2$O), 100.9 (C-3), 108.7 (C-7), 118.4 (C-4), 120.0 (C-6), 121.2 (C-5), 127.2 (C-3a), 128.1 ($^3J_{P,C}$=12.8 Hz, C*m*), 131.0 ($^4J_{P,C}$=2.9 Hz, C*p*), 132 ($^2J_{P,C}$=9.9 Hz, C*o*), 133.3 ($^1J_{P,C}$=108.4 Hz, C*i*), 133.9 ($J_{P,C}$=1.24 Hz, C-7a), 154.0 ($J_{P,C}$=10.9 Hz, C-2), 189.3 (C=O). $^{31}$P NMR ($CDCl_3$) d 11.74. IR (Nujol) $\nu$: 1619 (vs) cm$^{-1}$. MS: *m*/*z* (%) (EI positive) 480 (M$^+$+2, 6), 479 (M$^+$+1, 32), 478 (M$^+$, 100). Anal. Calcd for $C_{30}H_{27}N_2O_2P$: C, 75.30; H, 5.69; N, 5.85. Found: C, 75.18; H, 5.78; N, 5.69.

**4-Methyl-9-methoxymethyl-triazino[4,5-b]indole 12.** To a cooled solution of compound **9** (0.3 g, 1.2 mmol) in dry diethyl ether (10 mL) a solution of tri-*n*-butylphosphine (0.33 mL, 0.27 g, 1.34 mmol) in the same solvent (5 mL) was added dropwise under nitrogen. The mixture was allowed to warm to room temperature and stirred for 5 h. The solution was concentrated to dryness under reduced pressure and the residue was chromatographed on a silica gel column with diethyl ether/hexane as eluent to give **12** (0.20 g, 73%) mp 128–130°C (colourless prisms). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 3.16 (s, 3H, C$H_3$), 3.37 (s, 3H,

C$H_3$O), 6.05 (s, 2H, C$H_2$O), 7.50–7.58 (ddd, 1H, $J$=8.65, 1.5 Hz), 7.72–7.84 (m, 2H), 8.21 (d, 1H, $J$=7.8 Hz). $^{13}$C NMR (50 MHz, $CDCl_3$)$\delta$: 20.5 (*C*$H_3$), 56.9 (*C*$H_3$O), 43.0 (*C*$H_2$O), 109,3 (q), 111.7, 118.0,(q), 123.2, 124.5, 130.6, 139.4 (q), 150.7 (q), 152.7 (q). IR (Nujol) $\nu$: 1619 (s), 1587 (s), 1095 (vs), cm$^{-1}$. MS: *m/z* (%) (EI positive) 228 ($M^+$, 22), 200 ($M^+$-28, 5), 185 (15), 169 (56), 129 (100). Anal. Calcd for $C_{12}H_{12}N_4O$: C, 63.15; H, 5.30; N, 24.55. Found: C, 62.91; H, 5.42; N, 24.36.

## Acknowledgements

We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (project number PB95-1019).

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