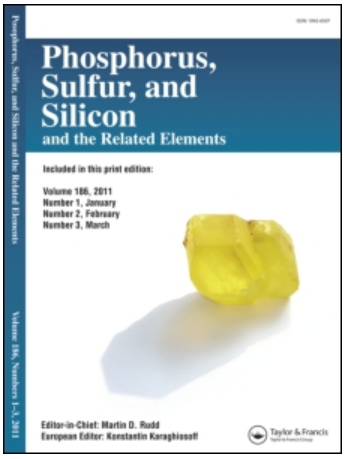

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SYNTHESIS AND REACTIONS OF 1,2,4-TRIAZINE AZIDES WITH TRIPHENYLPHOSPHINE, TRIALKYL PHOSPHITES AND DIALKYL PHOSPHONATES

Yehia O. El-khoshnieh[a]
[a] National Research Centre, Dokki, Cairo, Egypt

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SYNTHESIS AND REACTIONS OF 1,2,4-TRIAZINE AZIDES WITH TRIPHENYLPHOSPHINE, TRIALKYL PHOSPHITES AND DIALKYL PHOSPHONATES

YEHIA O. EL-KHOSHNIEH

National Research Centre, Dokki, Cairo, Egypt

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3-Azido-5,6-diphenyl-1,2,4-triazine (**1**) and 3-azidophenanthro[9,10-e]-1,2,4-triazine (**2**) are synthesized in high yield (~75%), **1** and **2** react with triphenylphosphine to afford phosphazenes **5** and **6** with a covalent structure. Reactions of **1** and **2** with trialkyl phosphites **3b,c** produce phosphazenes **7a,b** and **8a,b** which have the phosphonium dipolar ion structure, **1** reacts with diethyl phosphonate (**4a**) to give the phosphoramidate **10a**, dissociating to the corresponding amine **11** on reaction with dimethyl phosphonate. Possible reaction mechanisms are proposed for the formation of the new adducts.

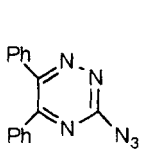
Keywords: 1,2,4-Triazine azides; triphenylphosphine; trialkyl phosphites; 1,2,4-triazine phosphazenes

INTRODUCTION

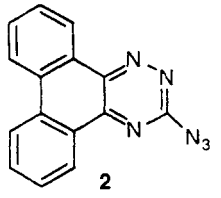
Synthetic studies of heterocyclic compounds deserve considerable attention because of their potential biological activities. Among them triazines are one of the most important classes. They are useful as antiphlogistic, cytostatic, antiviral and immunosuppressive agents.[1–6] Recently,[7] the synthesis of several phosphono-substitiuted triazines and triazine-phosphoramidites have been reported. The synthesis of a series of stable phosphorus ylides have been reported[8], incorporating 1,2,4-triazine moiety as accessi-

ble intermediates for preparing new 1,2,4-triazine-derivatives of therapeutical potencies.

The present investigation describes the results of the studies concerning the preparation of 3-azido-5,6-diphenyl-1,2,4-triazine (**1**), 3-azidophenan-thro [9,10-e]-1,2,4-triazine (**2**), and its behavior toward some trivalent phosphorus reagents namely triphenylphosphine (**3a**), trialkyl phosphites **3b,c** and dialkyl phosphonates **4a,b.**



1



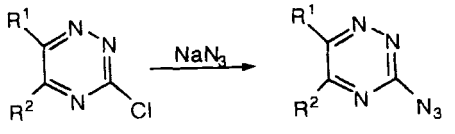
2

PR_3
3a, R=Ph
b, R=OC_2H_5
c, R=OCH_3

$(RO)_2P\text{-}OH \rightleftharpoons (RO)_2\overset{O}{\overset{\|}{P}}\text{-}H$
4a, R=C_2H_5
b, R=CH_3

RESULTS AND DISCUSSION

The required 3-azido-5,6-diphenyl-1,2,4-triazine (**1**) and 3-azidophenanthro[9,10-e]-1,2,4-triazine (**2**) have been prepared *via* the reaction of the corresponding chlorotriazine with aq. NaN_3in acetone or dimethylformamide, respectively (Equation 1). Structures **1,2** are confirmed by correct elemental analyses, IR and mass spectra, whereas, their IR spectra reveal the presence of strong bands at 2137.3 cm^{-1} (**1**) and 2135.3 cm^{-1}(**2**) which ascribed to the N_3 absorption.[9]



1,2

(Equation 1)

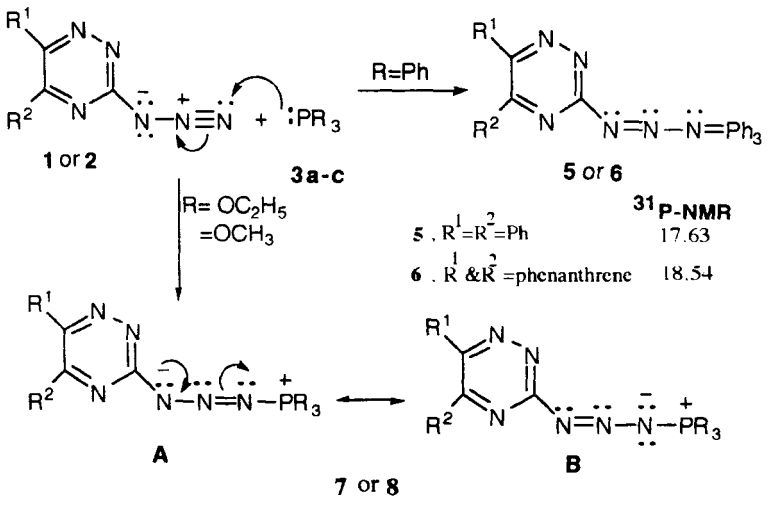
3-Azidotriazine **1** reacts with triphenylphosphine (**3a**) in refluxing dry benzene to give a yellow crystalline product formulated as **5** [Scheme 1]. The phosphazene structure **5** is assigned for the following reasons : (a) Correct elemental analysis and molecular weight determination (MS) correspond to $C_{33}H_{25}N_6P$. (b) Its ^{31}P-NMR spectrum has one signal at δ = 17.6 ppm (*vs.* 85% H_3PO_4) which clearly indicates an iminophosphorane structure.[10] (c) The IR spectrum of **5** reveals the presence of an absorption band at 1345.4 cm^{-1}characteristic for N=P group absorption[11] and the absence of N_3 group absorption which is recorded in the starting material at 2137.3 cm^{-1}. (d) The ^{1}H-NMR spectrum ($CDCl_3$) showed only a multiplet in the range δ 7.25–7.98 ppm (Ar-**H**).

Similarly, azidotriazine **2** reacts with triphenylphosphine **(3a)** to give the phosphazene **6** based on correct elemental, spectroscopic data and by analogy with **5** [*cf.* Experimental].

The reaction of azidotriazine **1** with triethyl phosphite **3b**, in refluxing dry benzene, affords the phosphazene **7a**. Its structure may have one of the two dipolar resonance forms **A** or **B** (Scheme 1). Structure for adduct **7a** was confirmed by the following evidence : (a) Correct elemental analysis and molecular weight determination (MS) of **7a** correspond to $C_{21}H_{25}N_6O_3P$. (b) Its ^{31}P-NMR spectrum has only one signal at δp = 6.6 ppm (*vs.* 85% H_3PO_4) indicating that **7a** exists only in one form of **A** or **B** and not as conformers **A**↔**B**.[10] (c) The ^{1}H-NMR spectrum of **7a** showed signals at δ 1.32 (t, 6H, -CC**H**$_3$, J_{HH} = 6.8 Hz); 1.49 (t, 3H, C-C**H**$_3$, J_{HH} = 6.8 Hz); 4.19 (qt, 4H, OC**H**$_2$, J_{HP} = 7.4 Hz); 4.33 (qt, 2H, OC**H**$_2$, J_{HP} = 7.4 Hz); 7.17–7.56 (m, 10H, Ar-**H**). (d) The IR spectrum of **7a** showed an absorption band at 1337.2 ($\overset{\cdot}{N} - \overset{+}{P}$), and the absence of the absorption band at 2137.3 (N3), a phenomenon that had previously been noted in the case of the reaction of sulfonyl azides with triphenylphosphine.[12]

7b was likewise obtained from the reaction of **1** and trimethyl phosphite (**3c**). Assignment of **7b** was based on analytical, spectroscopic data and by analogy with **7a**. The ^{31}P-NMR measurement of **7b** exhibited one signal at δp = 6.8 ppm (*vs.* 85% H_3PO_4).

Conversely, when azidotriazine **2** was treated with triethyl phosphite (**3b**) the reaction led to the formation of the phosphazene **8a**. Examination of its ^{31}P-NMR spectrum, however, showed the presence of two signals at δp 6.32 ppm (23%) and 8.92 ppm (72%) indicating that **8a** exists in the



	31P-NMR
5, $R^1=R^2$=Ph	17.63
6, R^1 &R^2 =phenanthrene	18.54

	31P-NMR
7a, R=OC_2H_5, $R^1=R^2$=Ph	6.60
7b, R=OCH_3, $R^1=R^2$=Ph	6.83
8a, R=OC_2H_5, R^1&R^2=phenanthrene	6.32 (23%) and 8.92 (77%)
8b, R=OCH_3, R^1&R^2=phenanthrene	8.59

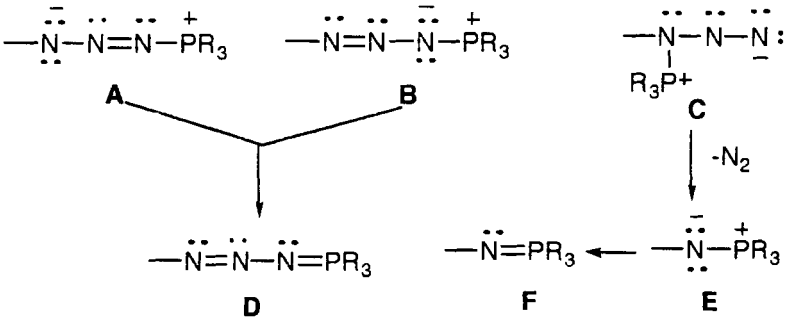
SCHEME 1

two conformers **A↔B.** Pertinent NMR and analytical data are presented in the experimental section.

Reaction of **2** with trimethyl phosphite (**3c**) afforded **8b** which showed only one signal at δp 8.59 ppm in its ^{31}P-NMR spectrum, indicating the presence of **8b**as one conformer **A** or **B**, probably, the other form of that **7a** and **7b** (*cf.* Experimental).

It has been established that[13–15] nucleophilic attack by phosphorus (with its electron pair) can occur on azides to give three dipolar ion structures **A**, **B** and **C** (Scheme II). **A** and **B** are merely resonance forms of the equivalent structure **D** used by Staudinger to depict phosphazenes (which he calls phosphazides).[16–18]

Conformer **C** can not be considered as a contributor for **D**, as it decomposes easily with the evolution of nitrogen to afford structure **E** and/or **F**, and should show the asymmetric azide absorption in IR spectrum, both as a solid and in solution. According to these mechanisms, a possible expla-



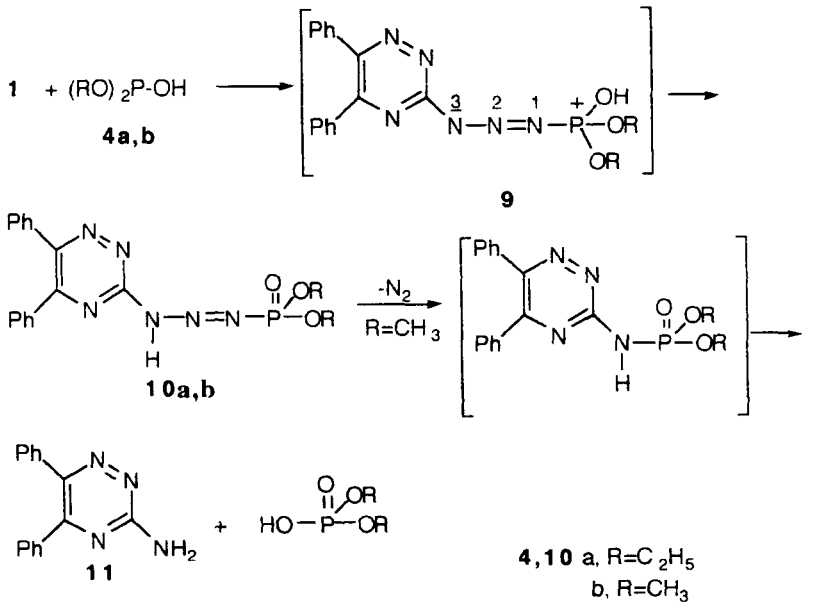
SCHEME 2

nation for the course of the reaction between the triazine azides **1,2** and the above mentioned phosphorus reagents **3a-c** is shown in (Scheme 1). This involves an intitial nucleophilic attack of phosphorus on the terminal nitrogen of the azide to give the imination products **5,6** (**1** or **2** with TPP), **7A** or **7B** (**1** with **3b** or **1** with **3c**), an equilibrium of **8A**↔**8B** (**2** with **3b**) and **8A** or **8B**(**2** with **3c**). Compounds **5,6,7** and **8** are shown to be quite stable under usual conditions.

The reaction of 3-azido-5,6-diphenyl-1,2,4-triazine (**1**) with dialkyl phosphonates was also studied. **1** was found to react with diethyl phosphonate (**4a**) in benzene solution at reflux temperature for 10 h to give the phosphoramidate **10a** (Scheme III) in ~70% yield. The assignment of structure **10a** for the product was based on the following data : (a) Correct elemental analysis and molecular weight determination (MS) of this adduct correspond to $C_{19}H_{21}N_6O_3P$. (b) The IR spectrum of **10a** revealed the presence of strong-NH absorption band at 3399.6 cm^{-1},[9] 1205.4 cm^{-1} characteristic for P=O group absorption,[11] and 1053.7 cm^{-1} for P-O-C.[11] (c) The ^{1}H-NMR spectrum of **10a** showed signals at δ 1.2 (d, 6H, -C-C**H**$_3$, J_{HH}= 6.2 Hz); 3.85 (qt, 4H, O-C**H**$_2$, J_{HP} = 10.5 Hz); 7.1–7.6 (m, 10H, Ar-**H**) and 9.45 (s, NH, exchangeable with D_2O) which indicates a protonation of the nitrogen separated from phosphorus.

When **1** was treated with dimethyl phosphonate (**4b**) in the same way, the expected phosphoramidate **10b** could not be isolated, instead, the aminotriazine **11** only the reaction product (*cf.* Experimental).

A mechanism which accounts for the reaction of azidotriazine **1** with dialkyl phosphonates **4a,b** is depicted in Scheme 3. The reaction gives first



SCHEME 3

the expected phosphonium dipolar ion **9**, which followed by proton migration to the nitrogen-3 to afford the stable phosphoramidate **10a** in the case of diethyl phosphonate (**4a**). On the other hand, with dimethyl phosphonate (**4b**), the phosphoramidate formed **10b**, however, is unstable and decomposes due to the adversion moisture, to give finally the aminotriazine **11** with expulsion of nitrogen.

Acid- and alkali-hydrolysis were also carried out on the phosphazene product **7a**, whereby, the aminotriazine **11** was only the reaction product (cf. Experimental).

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrophotometer model 197 (Grating) using KBr disk. ^{1}H-NMR spectra were recorded on a Jeol-270 MHz Spectrometer, using

TMS as an internal reference. ^{31}P-NMR were carried out on a Varian CFT-20 Spectrometer (vs. external 85% H_3PO_4). Mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I) Spectrometer provided with a data system. Elemental analyses were done using Perkin-Elmer 2400 CHN Elemental Analysis at the Microanalytical Centre, Faculty of Science, Cairo University. The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques.

Preparation of 3-azido-5,6-diphenyl-1,2,4-triazine *(1)*

A solution of NaN_3 (0.97 g, 0.015 mol) in water (5 ml)was added dropwise to a stirred solution of 3-chlorotriazine[19] (2.6 g, 0.01 mol) in acetone (50 ml) at room temperature and the stirring was continued for 3 h. The reaction mixture was poured into water and the precipitated product was collected (2.46 g, 90%) and recrystallized from chloroform-pet ether (1:1) to give **11** as yellow crystals, m.p. 193 °C. Anal. Calcd. for $C_{15}H_{10}N_6$ (274.28) : C, 65.68; H 3.68: N, 30.64. Found : C, 65.61; H, 3.60; N, 30.54. IR (KBr) : 2137.3 cm^{-1} (N_3). MS : m/z (%) : M^+. 274 (48.21), M^++1, 275 (100).

Preparation of 3-azidophenanthro[9,10-e]1,2,4-triazine *(2)*

A solution of NaN_3(0.97 g, 0.015 mol) in water (5 ml)was added dropwise to a stirred solution of 3-chlorotriazine[19] (2.6 g, 0.01 mol) in dimethylformamaide (50 ml) at 30 °C. The stirring was continued for 3 h. The precipitated material was filtered off, washed with water (1.63 g, 60%) and recrystallized from benzene to give **2** as yellow crystals, m.p. 228 °C. Anal. Calcd. for $C_{15}H_{18}N_6$ (272.27) : C, 66.17; H, 2.96; N, 30.87. Found : C, 66.11; H, 2.88; N, 30.80. IR (KBr) : 2135.3 cm^{-1}(N_3). MS : m/z (%):M^+, 272(19.17), M^++1, 273 (100).

Reaction of 1, 2 with triphenylphosphine, trimethyl- and triethyl phosphites *(3a-c)*

General procedure

A mixture of 3-azidotriazine **1**, **2** (0.01 mol) and **3a-c**(0.01 mol) was refluxed in dry benzene solution (30 ml). After the reaction was completed

(TLC, ≈3 h), the volatile materials were evaporated *in vacuo* and the residual substance was crystallized from the suitable solvent to give the products **5, 6, 7a,b** and **8a,b,** respectively.

Compound **5,** yellow needles (4.66 g, 87%), m.p. 218 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{33}H_{25}N_6P$ (536.58) : C, 73.87; H, 4.70; N, 15.66; P, 5.77. Found : C, 73.81; H, 4.66; N, 15.60; P, 5.71. IR (KBr) cm^{-1} : 1583.4 (N=N), 1345.4 (N=P), 987.9 (P-C, phenyl). ^{31}P-NMR ($CDCl_3$)δ = 17.6 ppm. MS : m/z (%) M^+, 536 (1.66), M^++1, 537 (26.25), $[M^+ + 1]$-N_2, 509 (100).

Compound **6,** yellow needles (3.95 g, 74 %), m.p. 284 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{33}H_{23}N_6P$ (534.56) : C, 74.15; H, 4.34; N, 15.72; P, 5.79. Found : C, 74.09; H, 4.28; N, 15.68; P, 5.71. IR (KBr) cm^{-1} : 1586.3 (N=N), 1355.9 (N=P), 997.2 (P-C, phenyl. ^{31}P-NMR ($CDCl_3$)δ = 18.5 ppm. MS : m/z (%) M^+, 534 (0.21), M^++1, 535 (8.01), $[M^+ + 1]$-N_2, 507 (100).

Compound **7a**, yellow needles (3.52 g, 80%), m.p. 113 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{21}H_{25}N_6O_3P$ (440.44) : C, 57.27; H, 5.72; N, 19.08; P, 7.03. Found: C, 57.20; H, 5.71; N, 19.00; P, 6.97. IR (KBr) cm^{-1} : 1590.2 (N=N). 1377.2 ($\ddot{N}-\dot{P}$), 1032.9 (P-O-C). ^1H-NMR ($CDCl_3$) : δ 1.32 (t, 6H. C-C**H**$_3$, J_{HH} = 6.8 Hz), 1.49 (t, 3H, C-C**H**$_3$, J_{HH} = 6.8 Hz), 4.19 (qt, 4H, OC**H**$_2$, J_{HP}, 7.4 Hz), 4.33 (qt, 2H, OC**H**$_2$,J_{HP} = 7.4 Hz), 7.16–7.56 (m, 10H, Ar-**H**). ^{31}P-NMR ($CDCl_3$)δ = 6.6 ppm MS : m/z (%):M^+, 440 (12.06), M^++1, 441 (18.42), M^+-N_2, 412 (100).

Compound **7b**, yellow needles (2.98 g, 75%), m.p. 134 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{18}H_{19}N_6O_3P$(398.37) : C, 54.27; H, 4.81; N, 21.10; P, 7.77. Found : C, 54.18; H, 4.75; N, 21.00: P, 7.67. IR (KBr) cm^{-1} : 1592 (N=N), 1377.6 ($\ddot{N}-\dot{P}$), 1180.6 (P-O-C). ^1H-NMR ($CDCl_3$):δ 3.79 (d, 9H, OC**H**$_3$, J_{HP} = 10.6 Hz), 7.27–7.53 (m, 10H, Ar-**H**). ^{31}P-NMR ($CDCl_3$)δ = 6.8 ppm. MS : m/z (%): M^++1, 399 (17.87), $[M^+ + 2]$-N_2, 372 (100).

Compound **8a**, yellow needles (3.6 g, 82%), m.p. 104 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{21}H_{23}N_6O_3P$ (438.43) : C, 57.53 ; H, 5.29; N, 19.17; P, 7.06. Found : C, 57.46; H, 5.19; N, 19.12; P, 7.00. IR (KBr) cm^{-1} : 1581.3 (N=N), 1355.8 ($\ddot{N}-\dot{P}$), 1029 (P-O-C). ^1H-NMR ($CDCl_3$):δ 1.40 (t, 9H. C-C**H**$_3$, J_{HH} = 6.8 Hz), 4.37 (qt, 6H, OC**H**$_2$, J_{HP} = 7.2 Hz), 7.26–9.32 (m, 8H. Ar-**H**). ^{31}P-NMR ($CDCl_3$) :

δ = 8.9 ppm (77%) and 6.3 ppm (23%). MS : m/z (%) M^+, 438 (1.60), M^++1, 439(19.41), $[M^+ + 1]$-N_2, 411 (100).

Compound **8b**, yellow needles (3 g, 76%), m.p. 202 °C (chloroform-light petroleum 1:1). Anal. Calcd. for $C_{18}H_{17}N_6O_3P$ (396.35) : C, 54.55; H, 4.32 ; N, 21.20; P, 7.82. Found: C, 54.44; H, 4.25; N, 21.10; P, 7.70. IR (KBr) cm^{-1} : 1573.2 (N=N). 1372.7 ($\ddot{N} - \dot{P}$), 1182.6 (P-O-C). ^{1}H-NMR ($CDCl_3$) : δ 3.89 (d. 9H. OCH_3, J_{HP}= 11.2 Hz), 7.26–9.01 (m, 8H, Ar-**H**). ^{31}P-NMR ($CDCl_3$)δ = 8.59 ppm. MS : m/z (%) M^+, 396 (5.39), M^++1, 397 (12.20), $[M^+ + 2]$-N_2, 370 (100).

Action of hydrochloric acid on 7a

A mixture of the phosphazene **7a** (0.44 g, 0.001 mol) and dilute HCl (7 ml, 5%) was refluxed for 3 h. The reaction mixture was cooled, neutralized with sodium bicarbonate and then extracted with ether. After distilling off the ether, the solid residue (0.23 g, 90%) was crystallized from cyclohexane and identified to be the aminotriazine **11**, m.p., mixed mps (175 °C)[19]and comparative IR spectra.

Action of sodium hydroxide on 7a

A mixture of **7a** (0.44 g, 0.001 mol) and ethanolic sodium hydroxide (7 ml, 5%) was refluxed for 1 h. After cooling, the reaction mixture was neutralized with dil. hydrochloric acid and extracted with ether. The solvent was distilled off and the residue (0.2 g, 80%) was crystallized from cyclohexane and proved to be the aminotriazine (mp, mixed mps and comparative IR spectra).[19]

Reaction of 1 with dialkyl phosphonates 4a,b

A mixture of 3-azidotriazine **1** (2.6g, 0.1 mol) and dialkyl phosphonate **4a** or **4b** (0.01 mol) was refluxed in dry benzene solution (30 ml). After the reaction was completed (TLC, $\approx$ 10 h), the pet-ether (40–60 °C) was added to the reaction mixture, the precipitated material was filtered off and crystallized from the proper solvent.

With diethyl phosphonate (4a)

The reaction produced the phosphoramidate **10a** (3 g, 74%) as yellow crystals, mp 167 °C (chloroform-pet. ether 1:1). Anal. Calcd. for $C_{19}H_{21}N_6O_3P$ (412.39) : C, 55.34: H, 5.13; N, 20.38; P, 7.51. Found : C, 55.25; H, 5.03; N, 20.27; P, 7.40. IR (KBr) cm^{-1} : 3399.6 (NH), 1205.4 (P=O), 1053.7 (P-O-C). ^{1}H-NMR ($CDCl_3$):δ 1.2 (d, 6H, C-C**H**$_3$,J_{HH} = 6.2 Hz), 3.85 (qt, 4H, OC**H**$_2$, J_{HP}= 10.5 Hz), 7.1–7.6 (m, 10H, Ar-**H**), 9.45 (s, NH, exchangeable with D_2O). MS : m/z (%) : M^+, 412 (0.35), M^++1, 413 (7.94), [M^++1]-N_2, 385 (18.86).

With dimethyl phosphonate (4b)

The reaction afforded the aminotriazine **11** (1.75 g, 70%), mp. mixed mps and comparative IR spectra.[19]

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