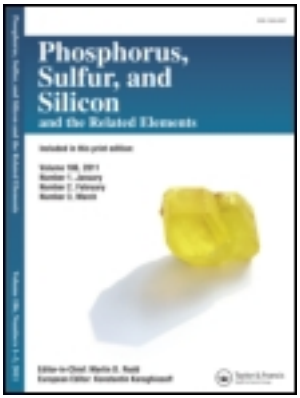

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Synthesis and Molluscicidal Activity of Phosphorus-Containing Heterocyclic Compounds Derived from 5,6-Bis (4-bromophenyl)-3-hydrazino-1,2,4-triazine

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Synthesis and Molluscicidal Activity of Phosphorus-Containing Heterocyclic Compounds Derived from 5,6-Bis (4-bromophenyl)-3-hydrazino-1,2,4-triazine

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Novel N^1-(phosphoryl moiety)-N^2-(1,2,4-triazin-3-yl)hydrazines 4, 6, 8, 9 and 12, iminophosphorane 3, iminophosphane 5, 1,2,4-triazinyldiazaphospholine 7, 1,2,4,3-triazaphospholinotriazines 2, 10, 11, and 1,2,4-triazino[3,2-c][1,2,4,5] triazaphosphine **13** *have been obtained via treatment 5,6-bis(4-bromophenyl)-3-hydrazino-1,2,4-triazine (1) with various polyfunctional phosphorus reagents by stirring at room temperature or refluxing for long time in tetrahydrofuran. Structures of these compounds have been deduced upon the basis of elemental and spectral data. Molluscicidal activity of the prepared compounds against Biomphalaria Alexandrina snails (the intermediate host of Schistosoma mansoni) showed considerable activities.*

Keywords Molluscicidal activity; phosphorus; synthesis; 1,2,4-triazine

INTRODUCTION

1,2,4-Triazines have recently been exploited as anti-AIDS,[1] anticancer,[2] and antimicrobial activities,[3] which are attributed to the nature of substituents in 1,2,4-triazine ring. Furthermore, 5,6-diphenyl-3-hydrazino-1,2,4-triazine was shown to be useful starting material for synthesis of great variety of functionalized heteropolycyclic system.[4] On the other hand, it is known that phosphorus containing heterocyclic compounds are very interesting biologically active.[5] Synthesis of several phosphono substituted 1,2,4-triazines, triazinylphosphoramidates[6,7] and series of stable phosphorus ylides incorporating 1,2,4-triazine moiety as

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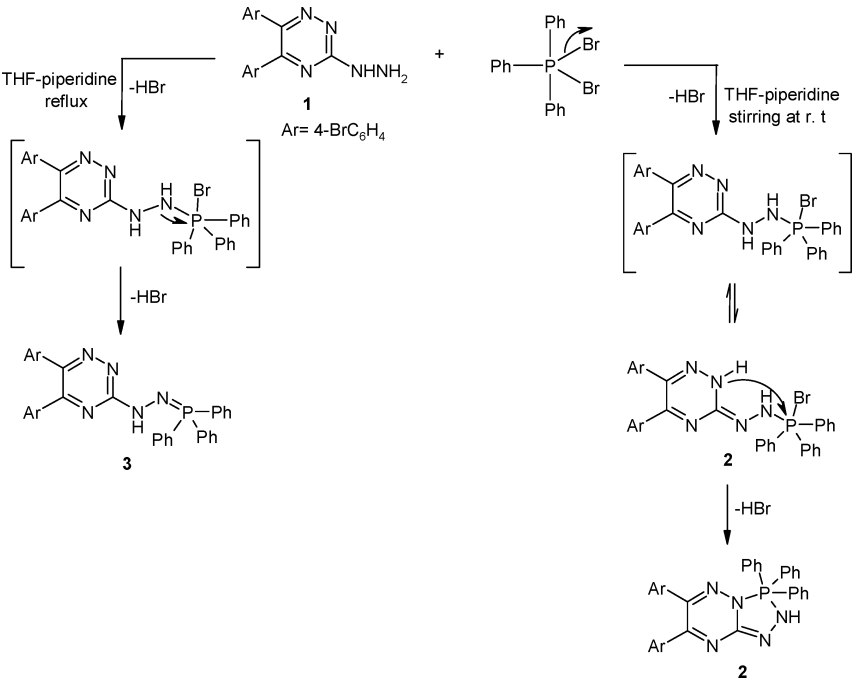
accessible intermediates for preparing new 1,2,4-triazine derivatives of therapeutically potencies have been reported.[8,9] It is conceivable that molecular modification of 1,2,4-triazine rings introducing organophosphorus functionalities might be expected to exhibit the potential activities, depending on the position of the phosphoryl group to 1,2,4-triazine ring. The present work describes synthesis of phosphorus containing fused and isolated heterocyclic systems via reaction of 5,6-bis(4-bromophenyl)-3-hydrazino-1,2,4-triazines (**1**) with some phosphorus reagents in nonpolar solvent under different temperatures. Molluscicidal activity of the prepared compounds against *Biomphalaria Alexandrina* snails (the intermediate host of Schistosoma mansoni) showed considerable activities.

RESULTS AND DISCUSSION

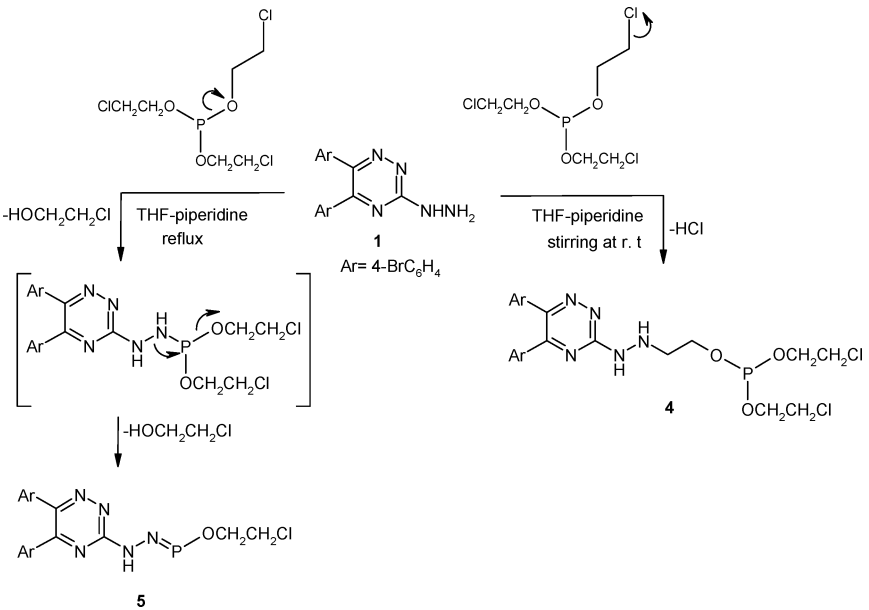
The synthesis of heterocyclic systems containing a 1,2,4-triazine moiety has gained much attention because of their rapid effect in various diseases.[10] Thus, a facile route to synthesize of 6,7-bis(4-bromophenyl)-2,3-dihydro-3,3,3-triphenyl-3-λ^5-1,2,4,3-triazaphosph-olino[4,5-b][1,2,



SCHEME 1

4]triazine (**2**) was deduced from stirring 5,6-bis(4-bromophenyl)-3-hydrazino-1,2,4-triazine (**1**) with dibromotriphenylphosphorane in THF containing piperidine at room temperature for 24 hours, while that reaction when carried out under refluxing conditions yielded 5,6-bis(4-bromophenyl)-3-[2-(triphenylphosphoranylidene)hydrazine]-1,2,4-triazine (**3**) (Scheme 1). Formation of **2** may be occurred via heterocyclization of the intermediate N^1, N^2-disubstituted hydrazine through $N-2$ of a triazine moiety, while compound **3** is formed via iminophosphorane mechanism. The ^{31}P NMR spectrum of compound **2** showed singlet signal at δ 29.61 ppm.[11] Also, IR spectrum of iminophosphorane **3** showed N=P group as strong band at 1399 cm^{-1} while its ^{31}P NMR spectrum appeared at δ 15.87 ppm.[12]

We note that when phosphorus atom found in trivalent phosphine behaves as powerful nucleophile. Thus, stirring of 3-hydrazinotriazine **1** with tris(2-chloroethoxy)phosphine in THF containing piperidine at room temperature gave the corresponding hydrazidophosphite **4** which is formed via attacking of NH_2 group at the carbon atom which carries partial positive charge according to Horner-Emmons reactions (Scheme 2).[13,14] On the other hand, refluxing of **1** with tris(2-chloroethoxy)phosphine in boiling THF and piperidine resulted

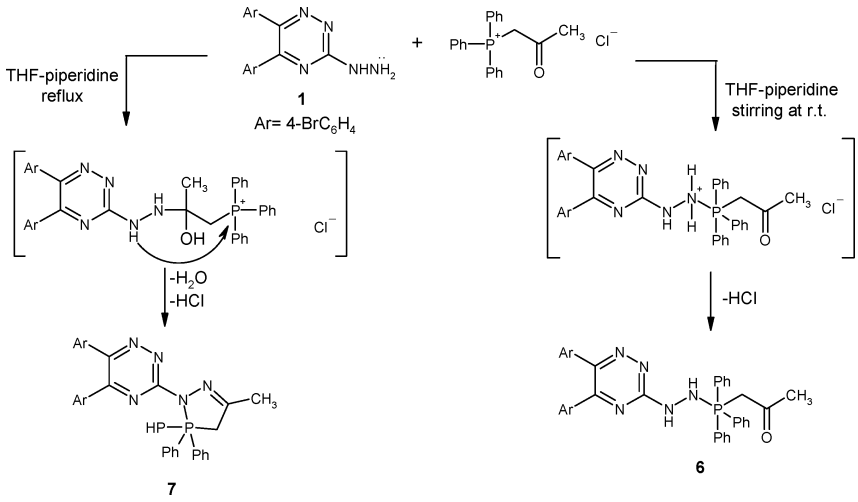


SCHEME 2

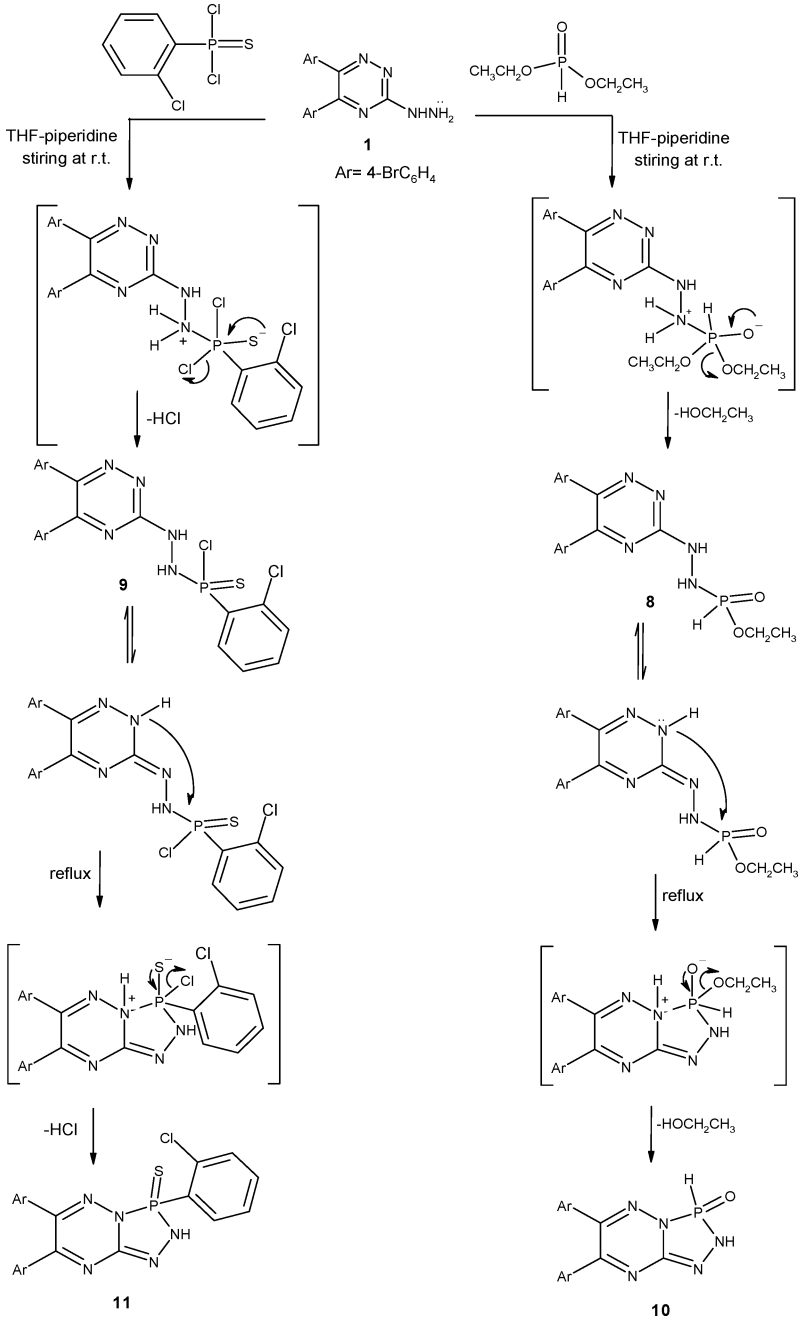
iminophosphane **5** (Scheme 2). The ^{1}H and ^{31}P NMR spectra of compounds **4** and **5** supported the postulated structures.[11]

Some five–membered organophosphorus heterocyclic compounds have been synthesized by Mannich-type reactions of guanidine derivatives with phenyldichlorophsphine and ketones and/or aminoheterocyclic with aryl phosphoryl dichloride and aromatic aldehydes.[15,16] Similarly, phosphorylation of 3-hydrazinotriazine **1** via treatment with acetonyltriphenylphosphonium chloride under stirring in THF and few drops of piperidine for 24 hours at room temperature achieved 1-[{2-[5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl] hydrazino}(triphenylphosphoranyl)]acetone (**6**) (Scheme 3). Formation of **6** may due to that phosphorus reagent such as phosphonium salt in which phosphorus atom is more electrophilic than carbon when one of the five groups is good leaving group. Also, the reaction of **1** with acetonyltriphenylphosphonium chloride in boiling THF-piperidine afforded 5,6-bis (4-bromophenyl)-3-[(3,3,3-triphenyl)-5-methyl-3,4-dihydro-2H-1,2,3-λ^5-diazaphosphol-2-yl] -1,2,4-triazine (**7**) (Scheme 3). Formation of **7** may be occurred via nucleophilic attack of hydrazine moiety at carbonyl group to loss molecule of water followed by leaving of HCl.

Abdel-Rahman,[3] reported that refluxing of 3-hydrazino-1,2,4-triazine derivatives with α,β-bifunctional groups especially haloketone and/or oxoketone produced hydrazone. Thus, one of the most important of the present investigation is treatment of 3-hydrazinotriazine **1** with diethyl phosphite and/or 2-chlorophenyldichlorothiophosphate in



SCHEME 3



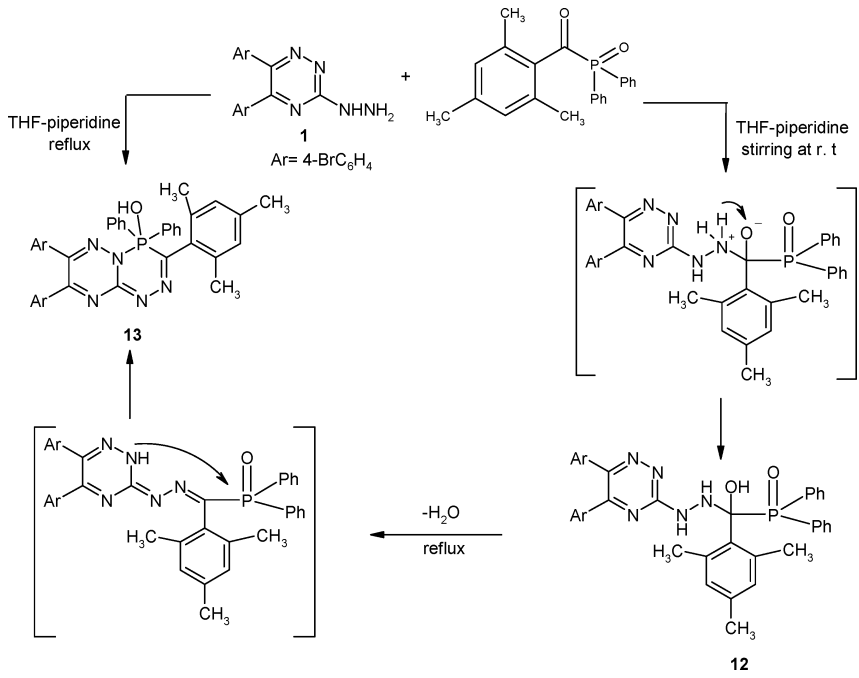
SCHEME 4

THF containing few drops of piperidine at room temperature yielded phosphonohydrazide **8** and phosphonohydrazidothioic acid **9**, respectively (Scheme 4). Also, repeat the same reactions under refluxing led to the direct formation of the 1,2,4,3-triazaphospholo[4,5-b] [1,2,4]triazine derivatives **10** and **11**, respectively. Formation of **10** and **11** may be occurred via nucleophilic attack of the primary NH_2 group of hydrazine on phosphorus atom to remove ethoxy and/or chlorine atom as good leaving groups followed by heterocyclization by loss one molecule of ethanol and/or HCl. The ^{1}H NMR spectra of **10** and **11** showed signals of NH protons at δ 10.92 and 10.34 ppm, respectively, while their ^{31}P NMR spectra recorded signals at δ 14.52 and 47.72 ppm, respectively.[17–19]

Phosphorus compounds with a nitrogen or oxygen heteroatom on the carbon α to phosphorus very often exhibited interesting biological properties.[20] Thus, introducing of P–C–O or P–C–N pattern into heterocyclic structure was achieved by interaction between 3-hydrazinotriazine **1** and diphenyl(2,4,6-trimethylbenzoyl)phosphorus oxide under stirring in THF at room temperature resulting (diphenylphosphoryl){[2-[5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]hydrazino} (2′,4′,6′-trimethoxyphenyl)methanol (**12**), while on refluxing afforded 7,8-bis(4-bromophenyl)-4,4-diphenyl-3-(2′,4′,6′-trimethylphenyl)-4H-4λ^5-1,2,4-triazino[3,2-c][1,2,4,5]triazaphosphinin-4-ol (**13**) (Scheme 5). Due to driving force of P=O bond is strong and phenyl groups are bad leaving groups, the nucleophilic attack of hydrazino moiety may be carried out at carbonyl group then P=O group. Structures of **12** and **13** were determined on basis of elemental analysis and spectral methods.

MOLLUSCICIDAL ACTIVITY

Schistosomiasis (also called Bilharziasis) is the most important trematode disease in human. It is an endemic disease in many tropical and subtropical regions. The intermediate host of Schistosoma mansoni, which affects the intestinal system, is *Biomphalaria Alexandrina* snails (average shell diameter 6–8 mm) in Giza governorate in Egypt. The Snails were adapted to laboratory conditions three weeks before being used in toxicity, tests to be sure that the snails are strong and healthy. Snails were kept in plastic aguaria filled with dechlorinated tap water at room temperature 25–27°C. Dried lettuce leaves were added daily, and the water was changed weakly. Stock solution of the investigated compounds (500 ppm) were dissolved in the least amount of ethanol and diluted with dechlorinated tap water based on weight/volume. Series of dilutions of each compound were prepared.[21–24] Table I indicates that under the employed experimental conditions the quantitative structure



SCHEME 5

activity relationship studies of these compounds. It is obvious that most of the prepared compounds on the tested snails depend on the type of N–P moieties which inter of their structures. Generally, the effect of the synthesized compounds is attributed to the following.

1. The presence of a phosphorus atom bound to nitrogen, which contains the backbone of the skeleton.
2. The strong effect of the compounds **2**, **7**, **10**, **11**, and **13** on the tested snails appears in the cases of phosphorus heterobicyclic systems, due to facile donation and back donation in *d*-orbital of phosphorus atom.
3. The medial effect of the compounds **4**, **6**, **8**, and **12** on the tested snail exhibited in the cases, which recorded a conjugation system created.
4. A lethal effect of the evaluated compounds **3**, **5**, and **9** on the tested snail was deduced in the case where weak interactions between N—P were a poor donation and back donation is recorded.
5. In most cases, the total electron barrier of molecular structure of the evaluated compounds led to inhibition enzymatic effect on living

TABLE I The Molluscicidal Activity of the Prepared Compounds against *Biomphalaria Alexandrina* Snails

	Mortality % of snails at concentration		
Compound no.	100 ppm	50 ppm	25 ppm
2	100	30	20
3	0	0	0
4	30	20	10
5	0	0	0
6	20	20	10
7	60	20	10
8	30	20	10
9	10	0	0
10	100	20	10
11	100	30	30
12	20	10	10
13	80	30	20
Baylucide (reference standard)	100	100	100

processes for the tested snail via the contribution between apoenzyme and coenzyme, which may be loose that it and can be broken by a simple process of snails.

CONCLUSION

Synthesis of phosphorus containing fused and isolated heterocyclic systems as molluscicidal agents against *Biomphalaria Alexandrina* snails have been achieved via reaction of 5,6-bis(4-bromophenyl)-3-hydrazino-1,2,4-triazines (**1**) with some polyfunctional phosphorus reagents in tetrahydrofuran under stirring and reflux.

EXPERIMENTAL

Melting points were determined on Boetius apparatus and were uncorrected. IR spectra in KBr were recorded on a Perkin-Elmer 293 FT spectrophotometer (λ_{max} cm^{-1}). UV absorption spectra in DMF were recorded on a Perkin-Elmer, Lambda 4B controller accessory interface. UV-VIS spectrophotometer (λ_{max} in nm). ^{1}H NMR spectra were recorded on an EM NMR spectrometer 300 MHz PMR using $CDCl_3$ as a solvent and TMS as internal reference (chemical shift in ppm). ^{31}P NMR spectra of were registered on a Varian Inova 500 MHz spectrometer at room temperature using TMS as internal standard and

85% H_3PO_4 as external reference. Mass spectrum recorded on a Gas Chromatographic GCMSqp 1000 ex Schimadzu instrument at 70 eV. Elemental analysis was carried out at microanalytical center, Cairo university. 5,6-Bis(4-bromophenyl)-3-hydrazino-1,2,4-triazine (**1**) was prepared according to the published method in literature.[25]

1,2,4,3-Triazaphospholinotriazine 2, N^1-(phosphoryl moiety)-N^2-(1,2,4-triazin-3-yl)hydrazines 4, 6, 8, 9, and 12—General Method

A mixture of 3-hydrazinotriazine **1** (5 mmol) and phosphorus reagents such as dibromotriphenylphosphorane, tris(2-chloroethoxy) phosphine, acetonyltriphenyl phosphonium chloride, diethyl phosphite, 2-chlorophenyldichlorothiophosphate and/or diphenyl-(2,4,6-trimethylbenzoyl)phosphorus oxide (5 mmol) in THF (50 ml) containing few drops of piperidine was stirred at room temperature (25–30°C) for 24 h. The solid separated was collected, washed with diethyl ether and crystallized from a suitable solvent affording the corresponding products **2**, **4**, **6**, **8**, **9**, and **12**, respectively.

6,7-Bis(4-bromophenyl)-2,3-dihydro-3,3,3-triphenyl-3-λ^5-1,2,4,3-triazaphospholo [4,5-b][1,2,4]triazine (2)

Brown crystals from ethanol,23% yield, m.p. = 130–131°C. IR (υ/cm^{-1}): 3420 (NH), 1578 (C=N). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.26–7.70 (m, 23H, Ar–H), 11.60 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 29.61 ppm. MS (m/z, %): 681 (M+1, 10.23%), 680 (M^+, 11.36), 550 (18.18), 456 (14.77), 388 (15.91), 362 (13.64), 277 (72.73), 183 (100), 157 (59.09), 75 (59.09). Anal. calcd. for $C_{33}H_{24}Br_2N_5P$ (681.37): C, 58.17; H, 3.55; P, 4.55%. Found: C, 57.82; H, 3.19; P, 4.32%.

Bis(2-chloroethyl) N-[(5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]hydrazido-phosphite (4)

Yellow crystals from ethanol, 35% yield, m.p. = 170–171°C. IR (υ/cm^{-1}): 3298, 3218 (NHNH), 1582 (C=N), 1067, 1006 (P–O–C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.56–1.66 (m, 4H, CH_2), 1.90 (br, 4H, CH_2), 3.13 (br, 4H, CH_2Cl), 6.32 (s, 1H, NH), 7.20–7.84 (m, 8H, Ar–H), 9.45 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 19.50 ppm. MS (m/z, %): 654 (M^+, 75%), 313 (75), 185 (87.50), 156 (43.75), 137 (81.26), 74 (100). Anal. calcd. for $C_{21}H_{22}Br_2Cl_2N_5O_3P$ (654.13): C, 38.56; H, 3.39; P, 4.74 %. Found: C, 37.99; H, 3.11; P, 4.66%.

1-[{2-[5,6-Bis(4-bromophenyl)-1,2,4-triazin-3-yl]hydrazino}(triphenylphosphor-anyl)]acetone (6)

Yellow crystals from methanol, 42% yield, m.p. = 220–222°C. IR ($\acute{\upsilon}$/cm^{-1}): 3318, 3209 (NHNH), 1685 (C=O), 1587 (C=N). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.92 (s, 3H, CH_3), 3.35 (br, 2H, CH_2), 6.32 (s, 1H, NH), 7.18–7.89 (m, 23H, Ar–H), 9.62 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 20.43 ppm. MS (m/z, %): 739 (M^+, 55.56%), 616 (55.56), 610 (55.56), 556 (55.56), 536 (55.56), 390 (72.22), 263 (72.22), 196 (61.11), 77 (100). Anal. calcd. for $C_{36}H_{30}Br_2N_5OP$ (739.46): C, 58.48; H, 4.09; P, 4.19%. Found: C, 57.94; H, 3.85; P, 3.69%.

Ethyl N-[(5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]phosphonohydrazide (8)

Yellow crystals from ethanol, 25% yield, m.p. = 133–135°C. UV λ_{max} (ε): 210 (0.95), 280 (0.80), 320 (1.00), 385 (0.10). IR ($\acute{\upsilon}$/cm^{-1}): 3409 (br, NHNH), 1585 (C=N), 1216 (P=O), 1071 (P-O-C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.32 (t, 3H, J = 6.9 Hz, CH_3), 3.82 (q, 2H, J=7 Hz, CH_2), 6.5 (br, 1H, P–H), 6.33 (s, 1H, NH), 7.19–7.86 (m, 8H, Ar–H), 9.52 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 7.28 ppm. MS (m/z, %): 529 (M+O, 20.41%), 513 (M^+, 28.57), 460 (22.45), 453 (24.49), 367 (20.41), 324 (24.49), 257 (34.69), 185 (61.22), 155 (100), 90 (65.31). Anal. calcd. for $C_{17}H_{16}Br_2N_5O_2P$ (513.13): C, 39.39; H, 3.14; P, 6.04%. Found: C, 38.98; H, 3.02; P, 5.67%.

N-{[5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]P-[2-chlorophenyl]phosphono-hydrazidothioic chloride (9)}

Yellow crystals from benzene, 36% yield, m.p. = >300°C. IR ($\acute{\upsilon}$/cm^{-1}): 3413, 3278 (NHNH), 1579 (C=N), 755 (P=S). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.38 (s, 1H, NH), 7.20–7.91 (m, 12H, Ar–H), 9.82 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 53.96 ppm. MS (m/z, %): 630 (M^+, 70.59), 619 (56.82), 561 (64.71), 471 (58.82), 389 (64.71), 382 (76.47), 282 (58.82), 256 (64.71), 158 (100), 122 (70.59), 800 (70.59). Anal. calcd. for $C_{21}H_{14}Br_2Cl_2N_5PS$ (630.13): C, 40.03; H, 2.24; P, 4.92%. Found: C, 39.94; H, 2.15; P, 4.52%.

(Diphenylphosphoryl){[2-[5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]hydrazino} (2,4,6-trimethoxyphenyl)methanol (12)

Yellow crystals from methanol, 33% yield, m.p. = 224–226°C. UV λ_{max} (ε): 210–225 (0.95), 275–285 (1.25), 340–360 (0.15), 390 (0.05). IR ($\acute{\upsilon}$/cm^{-1}): 3143 (br, NH, OH), 1583 (C=N), 1211 (P=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.56 (s, 9H, CH_3), 2.12 (br, 1H, OH), 6.25 (br, 1H, NH), 7.08–7.88 (m, 20H, Ar–H), 9.32 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz)

δ: 32.83 ppm. MS (m/z, %): 772 (M+3, 1.66%), 689 (2.15), 622 (1.82), 576 (1.99), 474 (1.99), 406 (2.15), 268 (2.15), 155 (100), 74 (65.23). Anal. calcd. for $C_{37}H_{32}Br_2N_5O_2P$ (769.48): C, 57.75; H, 4.19; P, 4.03%. Found: C, 57.94; H, 4.15; P, 3.72%.

Iminophosphorane 3, Iminophosphane 5, 1,2,4-Triazinyldiazaphospholine 7, 1,2,4,3-Triazaphospholinotriazine 10, 11, and 1,2,4,5-Triazaphosphinine 13—General Method

A mixture of 3-hydrazinotriazine **1** (5 mmol) and dibromotriphenylphosphorane, tris(2-chloroethoxy)phosphine, acetonyltriphenylphosphonium chloride, diethyl phosphite, 2-chlorophenyldichlorothiophosphate and/or diphenyl-(2,4,6-trimethylbenzoyl)phosphorus oxide (5 mmol) in THF (50 ml) containing few drops of piperidine was refluxed for 12 h. The solvent was removed under vacuum, and the residue was treated with methanol or ethyl acetate and crystallized from a suitable solvent to give the corresponding products**3**, **5**, **7**, **10**, **11**, and **13**, respectively.

5,6-Bis(4-bromophenyl)-3-[2-(triphenylphosphoranylidene)hydrazino]-1,2,4-triazine (3)

Yellow crystals from ethanol, 88% yield, m.p. = 240–242°C. IR ($\acute{\upsilon}$/cm^{-1}): 3408 (br, NH), 1584 (C=N), 1399 (N=P). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.45 (br, 1H, NH), 7.23–7.73 (m, 23H, Ar–H). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 15.87 ppm. MS (m/z, %): 683 (M+2, 4.74%), 682 (M+1, 4.01), 681 (M^+, 3.28), 586 (5.47), 462 (3.28), 402 (4.72), 292 (7.30), 277 (100), 199 (25.55), 77 (42.34). Anal. calcd. for $C_{33}H_{24}Br_2N_5P$ (681.37): C, 58.17; H, 3.55; P, 4.55%. Found: C, 57.94; H, 4.29; P, 4.13%.

2-Chloroethyl{2-[5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl]hydrazono} phosphinite (5)

Yellow crystals from toluene, 36% yield, m.p. = 170–171°C. UV λ_{max} (ε): 205 (0.9), 245 (1.15), 290(1.00), 320 (0.65), 330 (0.60). IR ($\acute{\upsilon}$/cm^{-1}): 3218 (NH), 1583 (C=N), 1334 (N=P), 1066 (P-O-C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.60 (br, 2H, CH_2), 3.71 (t, 2H, CH_2), 6.33 (s, 1H, NH), 7.19–7.84 (m, 8H, Ar–H). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 14.45 ppm. MS (m/z, %): 529 (M^+, 5.37%), 527 (5.37), 424 (5.37), 382 (15.12), 313 (4.88), 233 (4.88), 199 (98.05), 155 (100), 76 (62.93). Anal. calcd. for $C_{17}H_{13}Br_2ClN_5OP$ (529.56): C, 38.56; H, 2.47; P, 5.85%. Found: C, 37.98; H, 2.31; P, 5.48%.

5,6-Bis(4-bromophenyl)-3-[(3,3,3-triphenyl)-5-methyl-3,4-dihydro-2H-1,2,3-λ⁵-diazaphosphol-2-yl]-1,2,4-triazine (7)

Brown crystals from methanol, 22% yield, m.p. = 213–214°C. IR ($\acute{\upsilon}$/cm^{-1}): 3090 (C-H_{arom}), 2810 (C-H_{aliph}), 1586 (C=N). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.54 (s, 3H, CH_3), 3.75 (br, 2H, CH_2), 7.25–8.00 (m, 23H, Ar–H). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 25.90 ppm. MS (m/z, %): 723 (M+2, 58.82%), 722 (M+1, 64.71), 567 (64.71), 534 (94.12), 404 (82.35), 348 (70.59), 279 (82.35), 206 (88.24), 103 (100), 55 (94.12). Anal. calcd. for $C_{36}H_{28}Br_2N_5P$ (721.44): C, 59.94; H, 3.91; P, 4.29%. Found: C, 57.84; H, 3.75; P, 3.90%.

6,7-Bis(4-bromophenyl)-2,3-dihydro-1,2,4,3-triazaphospholo[4,5-b][1,2,4] triazine-3-oxide (10)

Yellow crystals from methanol, 19% yield, m.p. = 198–199°C. UV λ_{max} (ε):220 (1.05), 280 (0.70), 330 (0.75), 390 (0.10). IR ($\acute{\upsilon}$/cm^{-1}): 3415 (NH), 1587 (C=N), 1218 (P=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.61 (br, 1H, P–H), 7.18–7.88 (m, 8H, Ar–H), 10.92 (br, 1H, NH).^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 14.52 ppm. MS (m/z, %): 467 (M^+, 11.96%), 466 (10.87), 419 (11.96), 368 (16.30), 325 (14.13), 269 (16.30), 226 (21.74), 183 (100), 155 (98.91), 76 (75). Anal. calcd. for $C_{15}H_{10}Br_2N_5OP$ (467.06): C, 38.57; H, 2.16; P, 6.63%. Found: C, 38.04; H, 1.95; P, 6.80%.

3-(2-Chlorophenyl)-6,7-bis(4-bromophenyl)-2,3-dihydro-1,2,4,3-triazaphospholo [4,5-b][1,2,4]triazine-3-sulfide (11)

Yellow crystals from methanol, 38% yield, m.p. = 219–220°C. IR ($\acute{\upsilon}$/cm^{-1}): 3309 (NH), 1577 (C=N), 753 (P=S). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.09–7.78 (m, 12H, Ar–H), 10.34 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 47.72 ppm. MS (m/z, %): 592 (M-H, 27.50), 460 (25), 37 (35), 292 (37.50), 213 (35), 178 (100), 151 (37.50), 55 (35). Anal. calcd. for $C_{21}H_{13}Br_2ClN_5PS$ (593.67): C, 42.49; H, 2.21; P, 5.22%. Found: C, 42.05; H, 2.15; P, 4.84%.

7,8-Bis(4-bromophenyl)-4,4-diphenyl-3-(2,4,6-trimethylphenyl)-4H-4λ⁵-1,2,4-triazino[3,2-c][1,2,4,5]triazaphosphinin-4-ol (13)

Brown crystals from methanol, 27% yield, m. p. = 129–130°C. UV λ_{max} (ε): 210 (0.45), 240 (0.95), 280 (1.15), 350 (0.50). IR ($\acute{\upsilon}$/cm^{-1}): 3414 (br, OH), 1581 (C=N), 1070 (P–OH). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.57 (s, 9H, CH_3), 4.19 (s, 1H, OH), 7.09–7.85 (m, 20H, Ar–H). ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ: 25.70 ppm. MS (m/z, %): 752.30 (M+1, 2.43), 644 (3.10), 533 (4.87), 441 (3.32), 334 (6.64), 323 (4.65), 173 (7.30), 82 (100). Anal. calcd. for $C_{37}H_{30}Br_2N_5OP$ (751.47): C, 59.14; H, 4.02; P, 4.12%. Found: C, 58.94; H, 3.88; P, 3.74%.

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