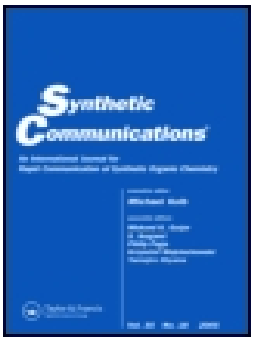

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Synthesis of novel 3-phenyl-2-oxido/sulfido-1,3,4,2-benzoxadiazaphosphepines

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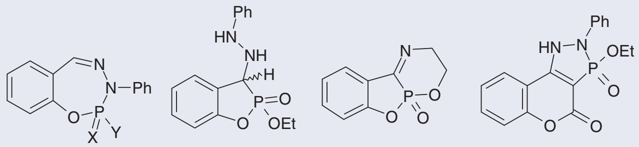
ABSTRACT

An efficient and facile synthetic approach towards a series of novel 3-phenyl-2-oxido/sulfido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepines **2**–**7** was described. The method depended on the cyclocondensation of equimolar ratios of salicylaldehyde phenylhydrazone (**1**) with different examples of phosphorus halides and phosphorus sulfides in toluene containing triethylamine as a catalyst. In the same manner, the fusion of salicylaldehyde phenylhydrazone (**1**) with triethyl phosphate in the presence of DBU afforded the 2-ethoxy-1,3,4,2-benzoxa-diazaphosphepine **8**, while a fusion of compound **1** with diethyl phosphite and tris(2-chloroethyl)phosphite led to the formation of new examples of 1,2-benzoxaphospholes **9** and **10**, respectively. Interestingly, the reaction of compound **1** with diethyl ethoxycarbonyl phosphonate in ethanol containing DBU as a catalyst furnished the chromeno[3,4-*d*][1,2,3]diazaphosphole derivative **12** as a regioselective product.

GRAPHICAL ABSTRACT



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1,3,4,2-Benzoxadiazaphosphepine; 1,2-benzoxaphosphole; 1,2,3-diazaphosphole; salicylaldehyde phenylhydrazone

Introduction

During the last years, phosphorus heterocycles attracted the interest of both industrial and pharmaceutical researchers.[1–7] Different applications for phosphorus heterocycles were developed,[8,9] for example, they served as pesticide,[10] anticancer,[11] and antineoplastic agents.[12] In the course of developing our previous studies, we have synthesized some

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bioactive fused phosphorus seven-membered rings such as 1,2,4-triazino[4,3-*f*][1,5,6,2]thiadiazaphosphepine (**A**), 1,2,4-triazino[4,3-*f*][1,2,5,6,3]tetrazaphosphepine (**B**),[13] and chromono[2,3-*e*][1,2,4,3]triazaphosphepines (**C**)[14] (Fig. 1). Also, a series of 1,3,4,2-oxadiazaphosphepino[6,7-*c*]quinolinones (**D**) as first examples of 1,3,4,2-oxadiazaphosphepine rings was constructed in our last article[15] (Fig. 1). In continuation of an ongoing program on the synthesis of novel phosphorus heterocycles,[16–18] we planned to synthesize a novel class of 1,3,4,2-benzoxadiazaphosphepine heterocycles *via* the treatment of salicylaldehyde phenylhydrazone with different examples of phosphorus halides, phosphorus sulfides, and phosphorus esters.

Experimental

The melting points were determined in an open capillary tube on a digital Stuart SMP-3 apparatus. Infrared spectra were measured on FT-IR (Nicolet IS10) spectrophotometer using KBr disks and Perkin-Elmer 293 spectrophotometer using KBr disks. ^{1}H and ^{13}C NMR spectra were measured on Gemini-300BB spectrometer (400 and 100 MHz), using DMSO-d_6 as a solvent and TMS as an internal standard. ^{31}P NMR spectra were measured on a Bruker (162 MHz) spectrophotometer using DMSO-d_6 as a solvent, TMS as an internal standard and 85% H_3PO_4 as an external reference. Mass spectra were recorded on a Gas Chromatographic GCMSqp 1000 ex Shimadzu instrument at 70 eV. Elemental microanalysis was performed Perkin-Elmer 2400II at the Chemical War department, Ministry of Defense. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) and elemental microanalysis.

Synthesis of 2,3-diphenyl-2-oxido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (2)

A solution of phenylphosphonic dichloride (0.35 ml, 2.5 mmol) in toluene (5 ml) was added dropwise to a solution of compound **1** (0.53 g, 2.5 mmol) in toluene (30 ml) in the presence of a catalytic amount of triethylamine (0.35 ml, 5 mmol) at 5–10 °C for 30 min. The mixture was heated under reflux for 10 h. The formed solid was filtered off, washed with water several times and crystallized from diluted dioxane to give pale green solid in 78% yield; mp 236–238 °C. IR (KBr), (ν_{max}, cm^{-1}): 3098 (C–H$_{arom}$), 1609 (C=N), 1530 (C=C), 1199 (P=O), 1089 (O–C). ^{1}H NMR (400 MHz, DMSO-d$_6$): 7.52–7.59 (m, 4H, Ph–H), 7.74 (d, 3H, $J = 5.2$ Hz, Ph–H), 7.85–7.90 (m, 3H, Ph–H), 8.12–8.21 (m, 4H, Ph–H), 8.91 (s, 1H, CH=N). ^{13}C NMR (100 MHz, DMSO-d_6): 116.7

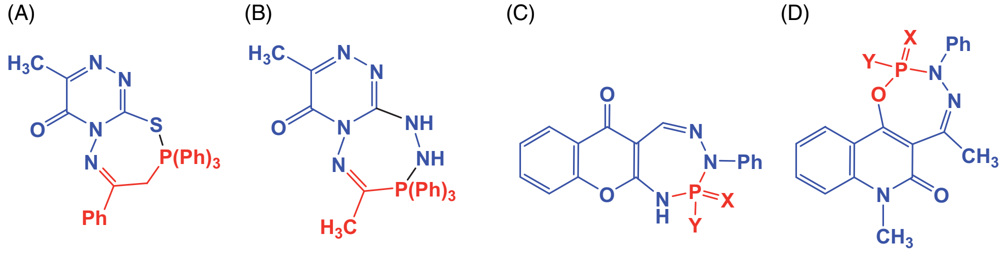


Figure 1. Structures of some bioactive fused phosphorus seven-membered rings.

(C–2′,6′), 118.2 (C–9), 119.4 (C–5a), 120.4 (C–4′), 121.8 (C–7), 124.0 (C–3″,5″), 127.8 (C–2″,6″), 129.6 (C–3′,5′), 130.9 (C–6), 132.3 (C–4″), 136.8 (C–8), 140.0 (d, $J_{PC} = 125$ Hz, C–1″), 142.3 (C–1′), 147.0 (C–5), 159.6 (C–9a). ^{31}P NMR (162 MHz, DMSO-d_6): 35.7 ppm. MS (EI, m/z): 334 (M^+, 6%). Anal. calcd. for $C_{19}H_{15}N_2O_2P$ (334.32): C, 68.26%; H, 4.52%; N, 8.38%. Found: C, 67.91%; H, 4.25%; N, 8.02%.

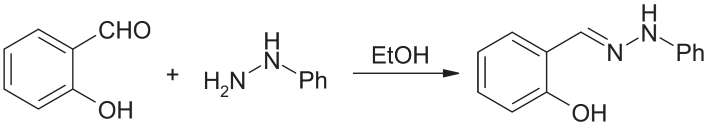
Result and discussion

Salicylaldehyde phenylhydrazone (**1**) as the precursor material was prepared by the reaction of salicylaldehyde with phenylhydrazine in ethanol according to the reported method in the literature (Scheme 1).[19]

The hydroxyl and amino groups are ready-made nucleophilic centers for the synthesis of fused phosphorus heterocyclic rings *via* their reaction with phosphorus halides with eliminating of two molecules of hydrogen halides. Thus, treatment of compound **1** with phenylphosphonic dichloride in toluene containing two equivalent amounts of triethylamine led to the formation of 2,3-diphenyl-2-oxido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (**2**) in 78% yield (Scheme 2). Similarly, treatment of compound **1** with phosphorus oxychloride and phosphorus tribromide in toluene containing triethylamine furnished the intermediates **A** and **B**, respectively, which underwent hydrolysis to give the isolated product **3** and **4**, respectively (Scheme 2).

The structures of products **2**, **3**, and **4** were deduced from the analytical and spectroscopic data. The ^{1}H NMR spectra of these compounds revealed the presence of the aromatic protons in region δ 6.92–8.24 ppm, while the P–H proton of compound **4** was observed as a doublet at δ 7.74 with coupling constant 667 Hz. The ^{31}P NMR spectrum of compound **2** showed a singlet at δ 35.7 ppm while compound **4** exhibited a signal at δ 7.8 ppm.[20] Moreover, the mass spectra of compounds **2**, **3**, and **4** recorded their molecular ion peaks at m/z 334, 274, and 258, respectively. Although compound **4** may have two tautomeric forms because of phosphite–phosphonate tautomerism, but the only phosphonate form was found in the IR, ^{1}H, and ^{31}P NMR spectra.

Also, we studied the reaction of compound **1** with three examples of phosphorus sulfides. Thus, 3-phenyl-2-sulfanyl-2-sulfido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (**5**) was isolated as an orange solid when compound **1** reacted with equivalent amount of phosphorus decasulfide in toluene (Scheme 3).[21] 2-Ethoxy-3-phenyl-2-sulfido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (**6**) was also obtained from treatment of compound **1** with *O*,*O*-diethyldithiophosphoric acid (formed *in situ*) in ethanol (Scheme 3). Besides, compound **1** was treated with Lawesson's reagent (LR) in toluene to give a good yield of 2-(4-methoxy-phenyl)-3-phenyl-2-sulfido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (**7**) (Scheme 4). The formation of 2-sulfido-1,3,4,2-benzoxadiazaphosphepine

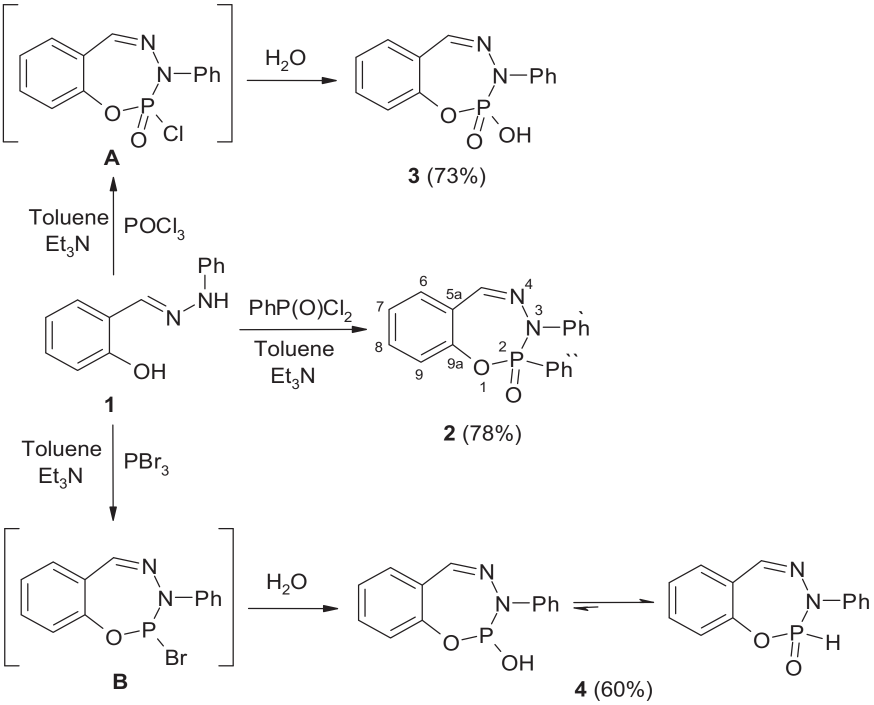


1 (92%)

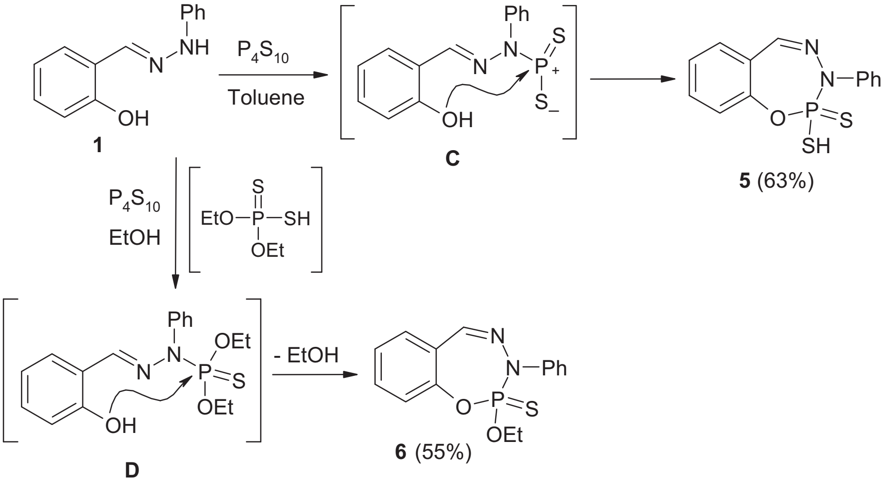
Scheme 1. Preparation of salicylaldehyde phenylhydrazone (**1**).

rings can be explained on the basis of phosphorylation of the NH group by phosphorus sulfide reagent to give the nonisolable intermediates **C**, **D**, and **E**, respectively. These intermediates underwent fast intramolecular cyclization *via* attack of OH group through addition or elimination reactions as shown in Schemes 3 and 4.

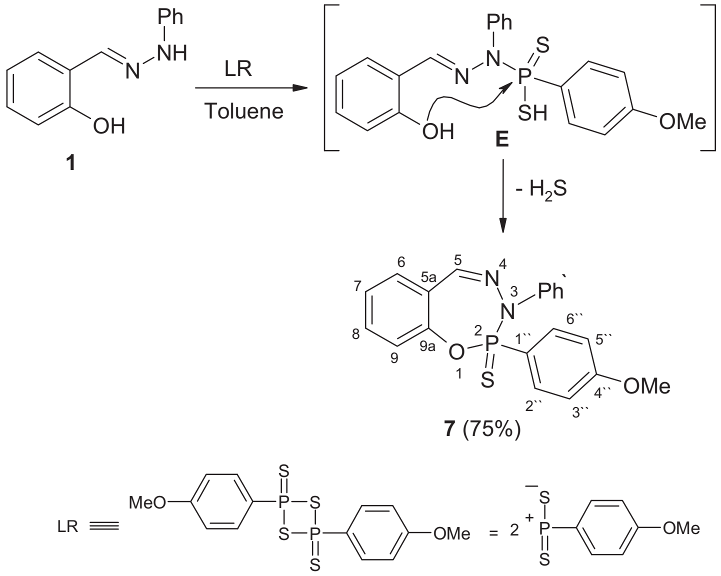
In the mass spectra of compounds **5**–**7**, they showed their expected molecular ion peaks (M^+) which supported the proposed structures. The most characteristic signals in their ^{1}H NMR spectra were those of the sulfanyl, ethoxy, and methoxy protons. They



Scheme 2. Reaction of compound **1** with some phosphorus halides.



Scheme 3. Reaction of compound **1** with phosphorus decasulfide and *O*,*O*-diethyldithiophosphoric acid.



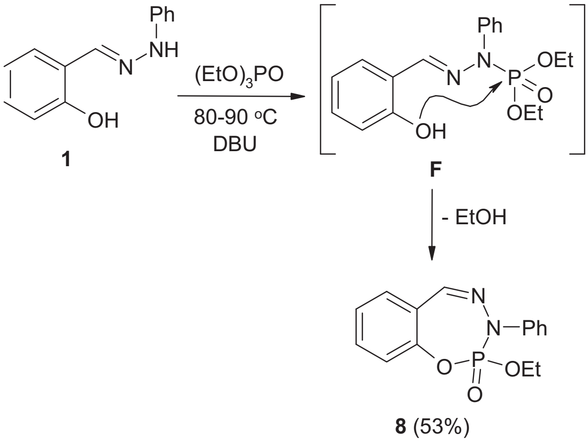
Scheme 4. Reaction of compound **1** with Lawesson's reagent.

were displayed at δ 3.33 (SH), 1.03, 4.01 (CH_3CH_2O), and 3.74 (OCH_3) ppm. In the ^{13}C NMR spectra, the specific carbon atoms of CH_3CH_2O and OCH_3 groups of compounds **6** and **7** were observed at δ 14.3, 59.6, and 55.6 ppm, respectively. Moreover, the ^{31}P NMR spectrum of compound **7** showed a singlet at δ 57.2 ppm.[22]

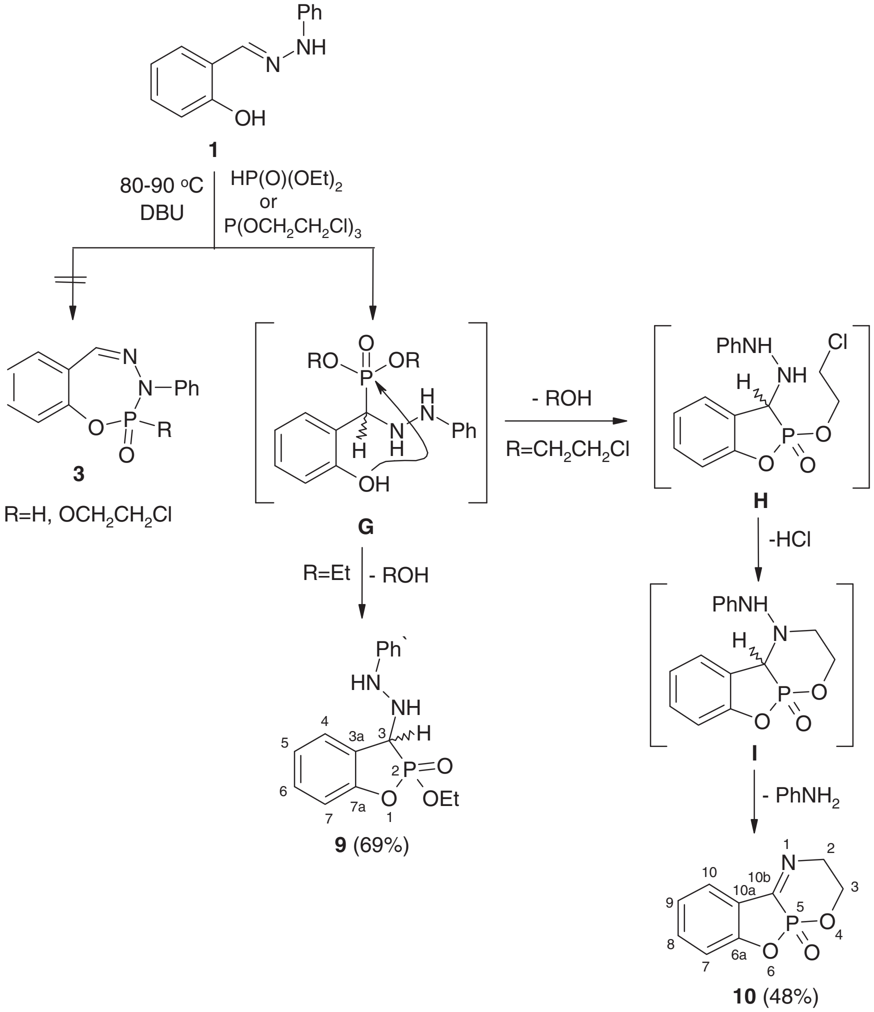
Next, the present work was extended to investigate the chemical behavior of the hydrazone **1** towards four examples of phosphorus esters. Thus, when compound **1** was fused with triethyl phosphate at 80–90 °C in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst, the 2-ethoxy-3-phenyl-2-oxido-2,3-dihydro-1,3,4,2-benzoxadiazaphosphepine (**8**) was separated *via* the removal of two ethanol molecules (Scheme 5).

On contrary, the fusion of compound **1** with diethyl phosphite or tris(2-chloroethyl) phosphite under the same reaction conditions, did not give the expected 1,3,4,2-benzoxadiazaphosphepines **3** (Scheme 6). These reactions occurred *via Michael* addition of phosphorus atom at the azomethine bond to form the nonisolable dialkyl α-hydrazinophosphonates **G**. The latter intermediate (R=Et) was spontaneously cyclized by losing of ethanol molecule to give the isolated compound **9** (Scheme 6).[23] On the other hand, the intermediate **G** ($R=OCH_2CH_2Cl$) underwent double cyclizations by elimination of 2-chloroethanol and hydrogen chloride molecules giving the nonisolable intermediate **I**, that removed aniline molecule to yield the novel 2,3-dihydro[1,2]benzoxaphospholo[2,3-*b*][1,4,2]oxazaphosphinine 5-oxide (**10**) (Scheme 6).

The IR spectrum of compound **9** showed the absorption bands of NH and P=O groups at 3415–3162 and 1230 cm^{-1}, respectively. The presence of the molecular ion peak for this compound at *m/z* 304 in its mass spectrum confirmed the cyclization process. However, the characteristic hydrogen and carbon atoms of compound **9** were observed in their ^1H and ^{13}C NMR spectra. For example, the P–CH proton was shown as a doublet at δ 5.32 ppm ($J = 15.2$ Hz) and the CH_3CH_2O protons were resonated as triplet and quartet at δ 0.77 (CH_3) and 3.95 (CH_2) ppm, while the two D_2O-exchangeable



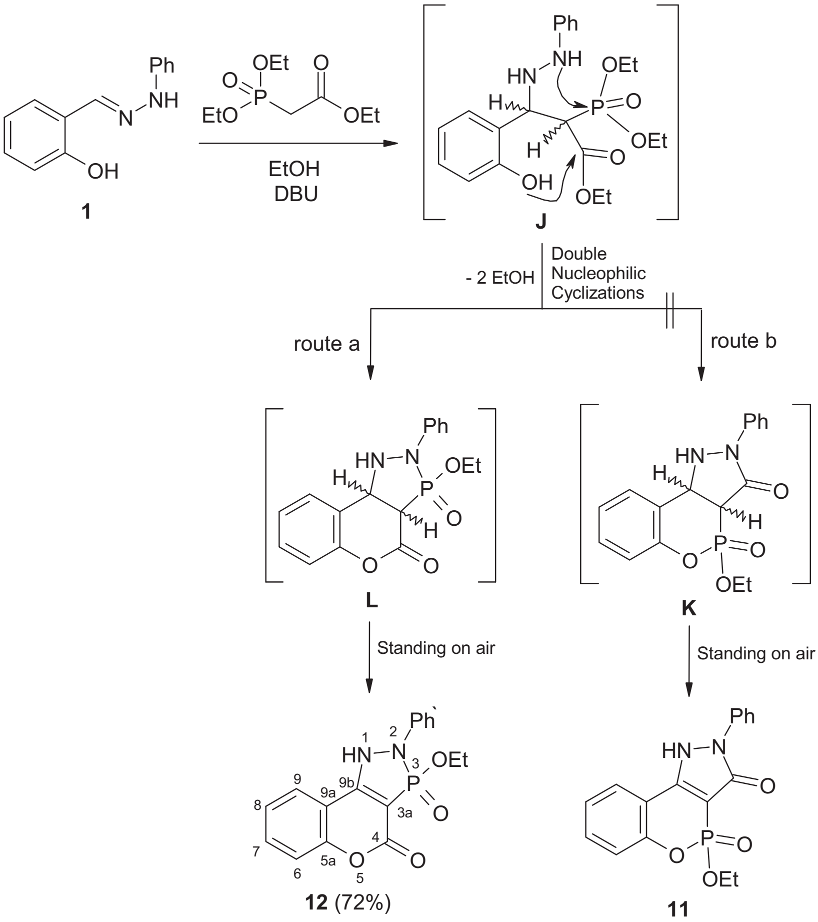
Scheme 5. Reaction of compound **1** with triethyl phosphate.



Scheme 6. Reaction of compound **1** with diethyl phosphite and tris(2-chloroethyl) phosphite.

NH were observed at δ 4.68 and 9.08 ppm. Furthermore, the carbon atoms of CH_3CH_2O moiety were resonated at δ 17.2 and 59.6 ppm, whereas the P–CH carbon atom was observed as a doublet at δ 48.5 ppm ($J_{PC} = 148$ Hz). The ^{31}P NMR spectrum of compound **9** recorded a singlet at δ 19.7 ppm. Similarly, the ^1H and ^{13}C NMR spectra of product **10** gave strong evidence for the proposed structure. Its ^1H NMR spectrum displayed four aromatic protons in region δ 6.81–7.68 ppm, whereas its ^{13}C NMR spectrum confirmed the suggested structure by recording only nine carbon atoms (see Experimental section). Furthermore, its mass spectrum displayed the molecular ion peak at *m/z* 209 that proved for the cyclized structure.

The more interesting point in this work was the reaction of hydrazone **1** with diethyl ethoxycarbonyl phosphonate in ethanol containing DBU as a catalyst. The annulated triheterocyclic system **12** was obtained as a regioselective product without any traces of the other product **11** (Scheme 7). A possible explanation for the course of the formation of compound **12** is shown in Scheme 7. The reaction proceeded *via Michael*-addition of phosphonoacetate at azomethine bond of compound **1** with help of a basic catalyst forming the intermediate **J**. The latter intermediate underwent easily double cyclizations with removal of two ethanol molecules *via* double nucleophilic attacks of NH at $P(O)(OEt)_2$



Scheme 7. Reaction of compound **1** with diethyl ethoxycarbonyl phosphonate.

and OH at COOEt (route a) to form the nonisolable chromeno[3,4-*c*][1,2]azaphosphinine **L**. The oxidation of the intermediate **L** by air led to the formation the product **12**.

The chromenodiazaphosphole structure **12** was established by the analytical and spectroscopic tools. In its IR spectrum, the NH and C=O groups were observed at 3270 and 1733 cm^{-1}, respectively, which supported its existence in lactonic form and not amidic form in structure **11**.[24] Also, in the ^{1}H NMR spectrum of compound **12**, the protons of CH_3CH_2O group were observed at δ 1.29 and 4.34 ppm. In addition, its ^{13}C NMR spectrum displayed the carbon atoms of CH_3CH_2O and C=O groups at δ 15.8, 60.0, and 175.1 ppm, respectively. Finally, its ^{31}P NMR spectrum exhibited a singlet at δ 25.3 ppm, whereas the mass spectrum recorded the molecular ion peak at *m/z* 342.

Conclusion

In summary, we have successfully synthesized a novel class of 1,3,4,2-benzoxadiazaphosphepines in one step by the treatment of salicylaldehyde phenylhydrazone with different examples of phosphorus halides and phosphorus sulfides under mild reaction conditions. In addition, two new examples of 1,2-benzoxaphospholes were obtained *via* the fusion of hydrazone with some alkyl phosphites. The annulated chromeno[3,4-*d*][1,2,3]diazaphosphole structure was also isolated as a regioselective product from the treatment of hydrazone with diethyl ethoxycarbonyl phosphonate in basic medium. The obtained results enrich the library of organophosphorus heterocycles and provide an efficient approach to the preparation of phosphorus heterocycles incorporating N–P–O, O–P–O, and C–P–O scaffolds.

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