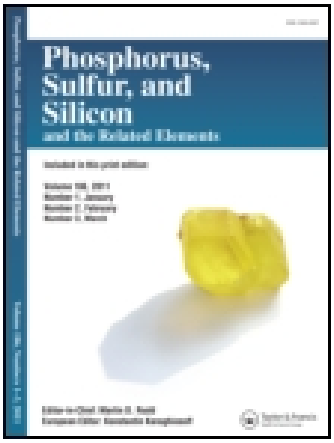

Phosphorus, Sulfur, and Silicon and the Related Elements

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# Scope and Limitation of the Reactions of 3-Imino Derivatives of Pentane-2,4-Diones with Organophosphorus Reagents

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# SCOPE AND LIMITATION OF THE REACTIONS OF 3-IMINO DERIVATIVES OF PENTANE-2,4-DIONES WITH ORGANOPHOSPHORUS REAGENTS

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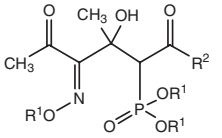
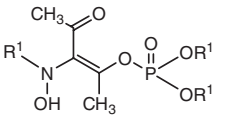
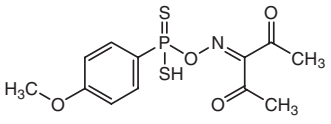
## GRAPHICAL ABSTRACT



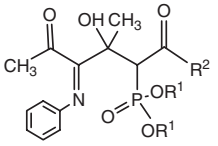
**10a,** $R^1 = C_2H_5$, $R^2 = OC_2H_5$
**10b,** $R^1 = CH_3$, $R^2 = OCH_3$



**12a,** $R^1 = CH_3$
**b**, $R^1 = C_2H_5$



**13**



**16**, $R^1 = C_2H_5$
$R^{2=} OC_2H_5$

**Abstract** *3-(Hydroxyimino)pentane-2,4-dione reacts with phosphonium ylides, Wittig–Horner reagents, trialkyl phosphites, and Lawesson's reagents to give the olefinic and cyclic products, the phosphonate adducts, the dialkyl phosphate products, the phosphinodithioic acid, and 2,4-dithione products, respectively. Furthermore, the reaction of 3-(phenylimino)pentane-2,4-dione with Wittig, Wittig–Horner reagents and trialkyl phosphite resulted in the formation of 2,5-diendioate, diethoxy phosphoryl hexanoate and the phosphate products. Possible reaction mechanisms are considered and the structural assignments are based on analytical and spectroscopic results. The antibacterial and antifungal activities for some of the new compounds are also reported.*

**Keywords** 3-Substituted pentane-2,4-diones; alkyl phosphites; ylides; *Wittig–Horner* reagents; Lawesson's reagent

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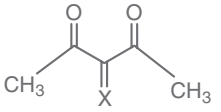
## INTRODUCTION

Several different nitrogen—containing heterocycles such as oxazolines, oxazines, and isoquinolines were synthesized directly from the reaction of $\alpha$-benzoinmonoxime with stabilized—and reactive ylides.[1] Furthermore, the reaction of 2-phenylimino–1,2,3–indantrione with phosphonium ylides gave the new phosphorane products.[2] Recently, several nitrogen containing heterocycles were synthesized from the reaction of triketoindane-2-oxime with different types of phosphoryl carbanions.[3] In view of this and in continuation of our work in organophosphorus chemistry,[4–12] it was of considerable interest to investigate the behavior of 3-(hydroxyimino)-(**1a**), 3-(phenylimino)pentane-2,4-diones **(1b)** toward phosphonium ylides **2a–d**, *Wittig–Horner* reagents **3a–c**, trialkyl phosphites **4a**, **b**, and Lawesson's reagents **5a**, **b** (Scheme 1). The purpose of this study was to determine the preferential site of attack by these reagents and to synthesize new phosphonate adducts with anticipated biological activities.



**1a,** X= NOH
**b,** X= N-Ph

$Ph_3P{=}CHCOR$

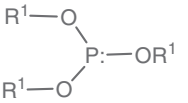
**2a**, R= $OC_2H_5$
**b,** R= $OCH_3$
**c,** R= CH3

$Ph_3P{=}N\text{-}Ph$

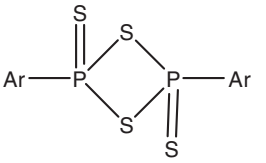
**2d**

$(R^1O)_2P(O)CH_2R^2$

**3a,** $R^1 = C_2H_5$, $R^2 = COOC_2H_5$
**b,** $R^1 = CH_3$, $R^2 = COOCH_3$
**c,** $R^1 = C_2H_5$, $R^2 = CN$



**4a,** $R^1{=}CH_3$
**b**, $R^1 = C_2H_5$



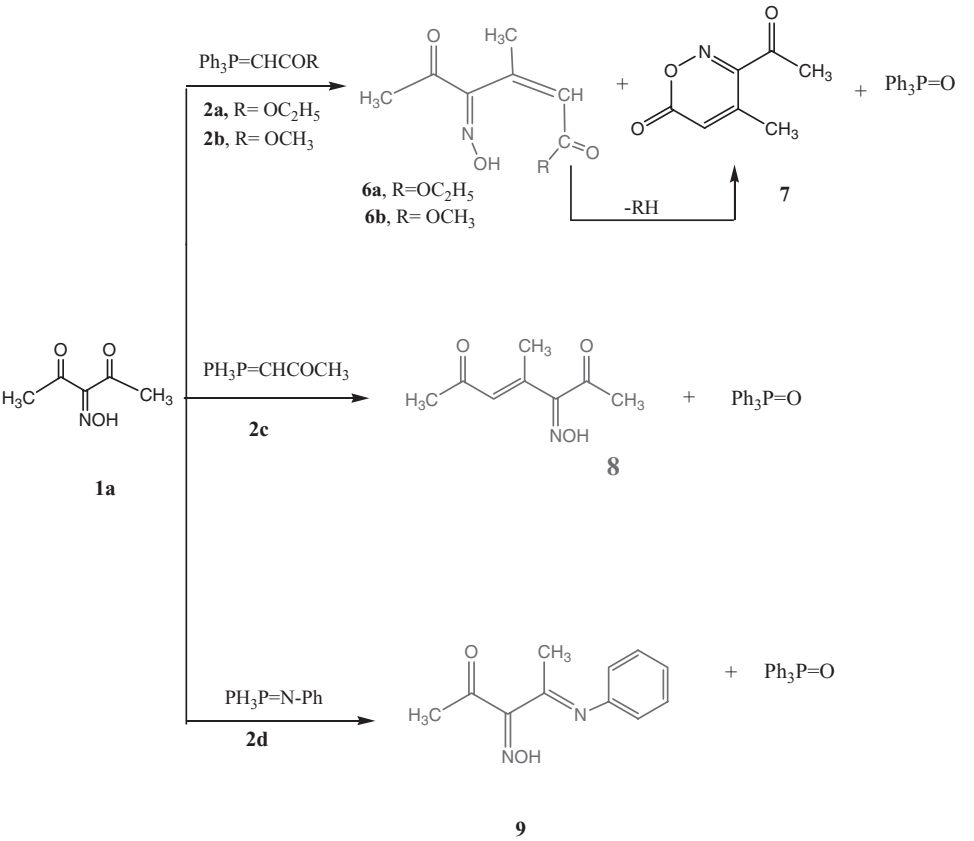
**5 a**, Ar = 4 - $H_3COC_6H_5$
**b**, Ar = S - $C_6H_5$ (also named Japanese reagent)

**Scheme 1**

## RESULTS AND DISCUSSION

We have found that 3-(hydroxyimino)pentane-2,4-dione (**1a**) reacted with two mol equivalents of ethoxycarbonylmethylenetriphenylphosphorane (**2a**) in refluxing toluene to

give chromatographically pure adducts formulated as ethyl-4-(hydroxyimino)-3-methyl-5-oxohex-2-enoate (**6a**) (25% yield), and 3-acetyl-4-methyl-6*H*-1,2-oxazin-6-one (**7**) (65%, yield). Triphenylphosphane oxide was also isolated from the reaction medium and identified (Scheme 2).



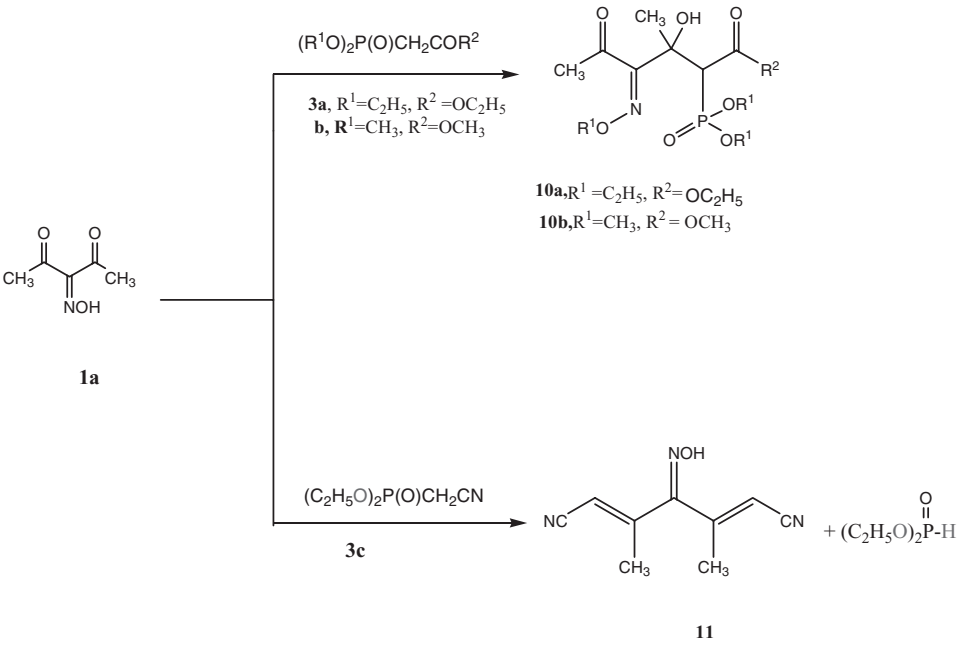

**Scheme 2**

Similarly, methoxycarbonylmethylenetriphenylphosphorane (**2b**) reacts with (**1a**) (**2b**:**1a** = 2:1), in refluxing toluene to give products **6b** (30% yield) and **7** (60% yield). Triphenylphosphane oxide was also isolated from the reaction mixture (Scheme 2).

Structures **6a**, **6b**, and **7** were deduced from correct microanalysis, IR, $^{1}H$, $^{13}C$ NMR, and mass spectral (MS) data (*cf. Experimental*). We propose the reaction course depicted in Scheme 2. The reaction was assumed to form the olefinic compounds **6a, b** with expulsion of triphenylphosphane oxide. Then, the reaction was accompanied by elimination of one molecule of alcohol under the applied reaction conditions to afford the cyclic 3-acetyl-4-methyl-6*H*-1,2-oxazin-6-one (**7**). Worthy to mention is that only one isomer of **6a** and **6b** was isolated. The course of cyclization of **6a** and **6b** to **7** suggested the *cis* isomer since the cyclization process occurs only in case of *E*-isomer.[13] Furthermore, when **6a** or **6b** were heated in refluxing xylene for 4 h, product **7** was obtained in 75% yield.

Next, when **1a** was treated with 1 mol equivalent of acetylmethylenetriphenylphosphorane (**2c**) in refluxing toluene for 8 h, product **8** along with triphenylphosphane

oxide were isolated from the reaction medium (Scheme 2). Compound **8** was obtained irrespective of whether one or two mol equivalents of **2c** were used. Structural elucidation of 5-(hydroxyimino)-4-methylhept-3-ene-2,6-dione (**8**) is based upon elemental and spectroscopic data (IR, $^{1}H$, $^{13}C$, $^{31}P$–NMR and MS, *cf. Experimental*). When **1a** was allowed to react with 1 mol equivalent of N-(triphenylphosphoranylidene)aniline (**2d**) in refluxing toluene for 3 h, product **9** was isolated in 80% yield. Triphenylphosphane oxide was also isolated from the reaction mixture and identified. The structure of 3-(hydroxyimino)-4-(phenylimino)pentane-2-one (**9**) was deduced on the basis of elemental analysis and spectral studies (Scheme 2, *cf. Experimental*). In addition, the reaction of 3-(hydroxyimino)pentane-2,4-dione (**1a**) with *Wittig–Horner* reagents **3a–b** was studied too. When **1a** was treated with 1 mol equivalent of triethylphosphonoacetate (**3a**), in the presence of alcoholic sodium ethoxide solution at reflux temperature for 2 h, adduct **10a** was isolated (Scheme 3).



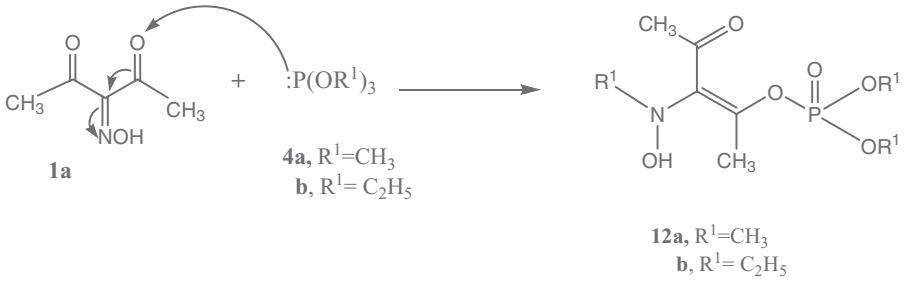

**Scheme 3**

The structure of methyl 2-(diethoxyphosphoryl)-3-hydroxy-4-(ethoxyimino)-3-methyl-5-oxohexanoate (**10a**) was assigned from its analysis, IR, $^{1}H$, $^{13}C$, $^{31}P$ NMR, and MS data. The Infrared (IR) spectrum of **10a** revealed the presence of strong absorption bands at 3498 $cm^{-1}$ (OH), 1252 $cm^{-1}$ (P=O),[14] 1129 $cm^{-1}$ (P–O–$C_2H_5$), and 1739 $cm^{-1}$ (C=O, ester), 1683 $cm^{-1}$ ($COCH_3$). The product **10a** possesses a positive shift in its $^{31}P$ NMR spectrum ($\delta$ = 20.2, 85% $H_3PO_4$) and absorbs in the region characteristic for this class of compounds.[15–17] The structure of compound **10a** was also confirmed from its $^{1}H$, $^{13}C$–NMR, and MS data, *cf. Experimental*). Similarly, trimethylphosphonoacetate (**3b**) reacts with **1a** in the presence of methanolic sodium methoxide solution at reflux temperature for 3 h to give methyl 2-(dimethoxyphosphoryl)-3-hydroxy-4-(methylimino)-3-methyl-5-oxohexan-oate **10b** in 75% yield (Scheme 3). Due to the bulky of the phosphonate groups

in compound **10a**, **b**, *trans* configuration was suggested. The spectroscopic data of product **10b** were in good agreement with the proposed structure (*cf. Experimental*).

Moreover, when 3-(hydroxyimino)pentane-2,4-dione (**1a**) was treated with 2 mol equivalent of diethyl(cyanomethylene)phosphonate (**3c**) in the presence of ethanolic sodium ethoxide solution at 60–70 °C for 5 h, adduct **11** was isolated in good yields (Scheme 3). The structure of 4-(hydroxyimino)-3,5-dimethylhepta-2,5-dienedinitrile (**11**) was deduced from its analysis, IR, $^{1}$H, $^{13}$C NMR, and MS data (*cf. Experimental*).

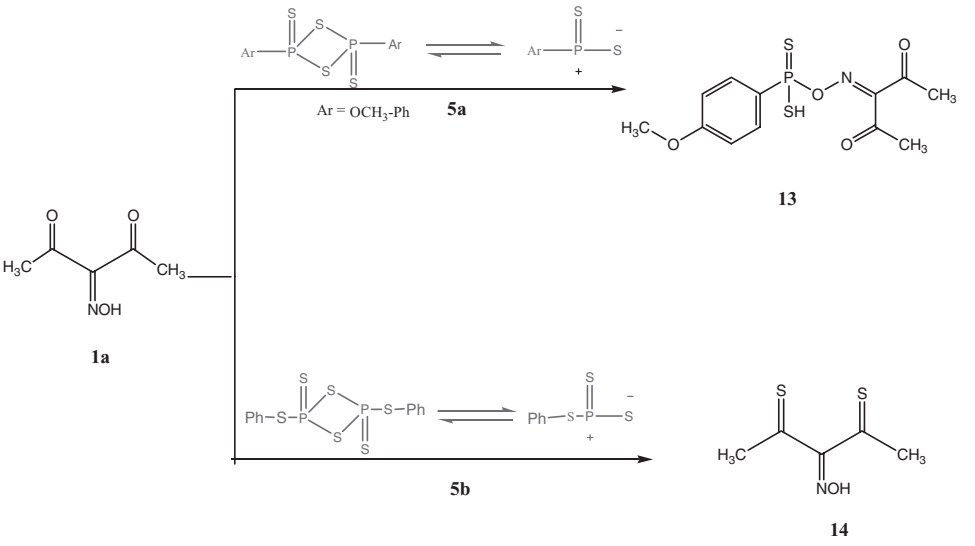
The reaction of **1a** with trialkyl phosphites was also investigated. We have found that the reaction with trimethyl-(**4a**) and/or triethyl (**4b**) phosphites in refluxing benzene gave dimethyl(3-(methyl(hydroxyl)amino-4-oxopent-2-en-2-yl) phosphate **12a** and diethyl(3-(ethyl(hydroxy)amino)-4-oxopent-2-en-2-yl) phosphate **12b**. This is simply explained of initial nucleophilic attack by phosphorus on the carbonyl oxygen, forming zwitterion intermediate of which undergo intramolecular alkyl group transfer to yield products **12a** and **12b**, respectively (Scheme 4).[18,19] Physical and spectroscopic data in Experimental Section.



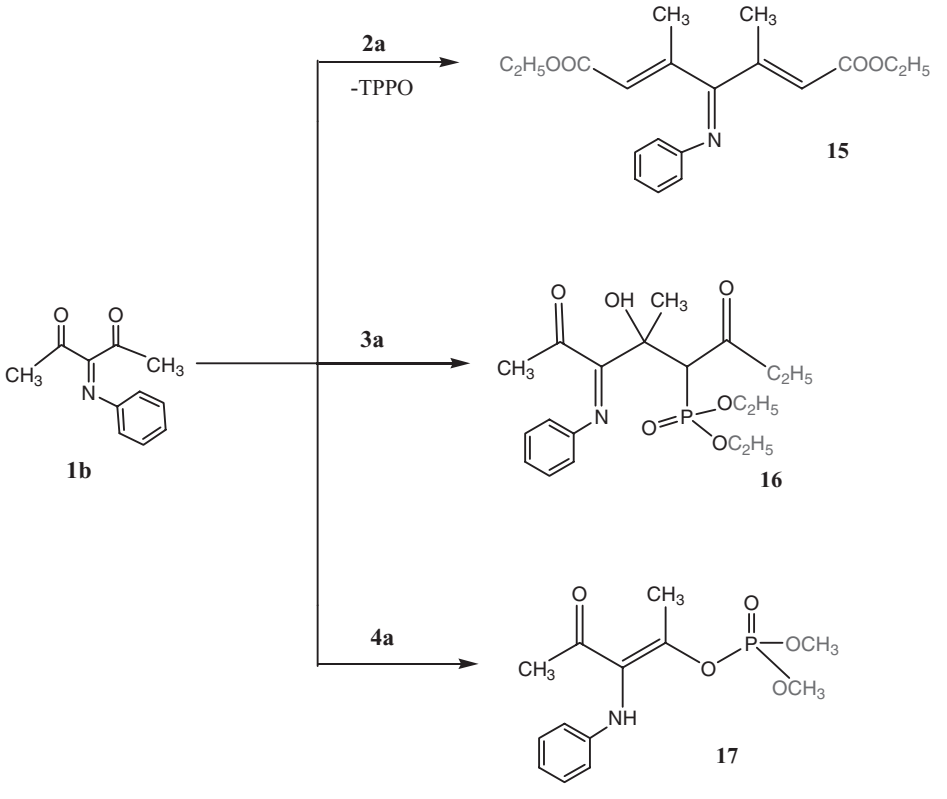

**Scheme 4**

We have also investigated the reaction of **1a** with Lawesson's and Japanese reagents **5a**, **b**. When 3-(hydroxyimino)pentane-2,4-dione (**1a**) was reacted with Lawesson's reagent **5a** in dry benzene at room temperature for 1 h, the corresponding (((2,4-dioxopentan-3-ylidene)amino)oxy)(4-methoxyphenyl)phosphinodithioic acid (**13**) was only obtained in good yield. The elemental microanalysis, $^{1}$H, $^{13}$C, $^{31}$P NMR, and MS data agreed with structure **13** (Scheme 5).

The IR spectrum of **13** revealed the absence of =NOH band that appeared in the starting material at $v = 3384$ and showed bands at 625 cm$^{-1}$ (P=S), 1654 cm$^{-1}$ (C=N), 1673 cm$^{-1}$ (2 $CH_3CO$), 2320 cm$^{-1}$ (SH). The $^{1}$H NMR shifts of compound **13** were 2.05 (s, 6H, $2CH_3$), 3.75 (s, 3H, $OCH_3$), 3.3 (s, 1H, SH, exchangeable with $D_2O$), and 6.94–7.28 (m, 4H, aromatic). The $^{31}$P NMR of **13** appeared at $\delta$ 18.78 ppm.[20] The structure assigned for **13** was based on $^{13}$C NMR spectra that indicates the presence of signals at $\delta = 55.70$ ($OCH_3$), 30.15 ($2CH_3$), 121.5 (P—C—Ph, d, $^{1}J_{CP} = 115.3$ Hz), 132.5 (d, 2C—C—P, $^{2}J_{CP} = 22.0$ Hz), 113.97 (d, 2C—C—C—P, $^{3}J_{CP} = 15.7$ Hz), and 161.86 (C—$OCH_3$), corresponding to the carbon atoms of the methoxy phenyl ring attached to the phosphorous, 143.9 (C=N) and 195.821 ($2H_3C$—C=O).[21] Compound **13** is formed by the addition of oxime **1a** to the monomer of LR followed by migration of a proton to the sulfur anion.[22,23] The reaction of **1a** with Japanese reagent **5b** was also investigated. We have found that reaction with Japanese reagent **5b** affect thionation of **1a** to form 3-(hydroxyimino)pentane-2,4-dithione




**Scheme 5**




**Scheme 6**

(**14**) as a the sole reaction product (Scheme 5). The spectroscopic data of product **14** were in good agreement with the proposed structure (*cf. Experimental*).

Furthermore, this study has been extended to include the reaction of 3-(phenylimino)pentane-2,4-dione (**1b**) with phosphonium ylide **2a**, *Wittig–Horner* reagent **3a**, and trialkyl phosphite **4a** to establish whether they would behave in a similar manner. We have found that 3-(phenylimino)pentan-2,4-dione (**1b**) reacts with one mol equivalent of **2a** in refluxing toluene to give diehyl-3,5-dimethyl-4-(phenylimino)hepta-2,5-dienedioate (**15**) in 40% yield. Triphenylphosphane oxide was also isolated and identified (Scheme 6). When **1b** was treated with 2 mol equivalents of **2a** in refluxing toluene, the new olefinic **15** was isolated in a good yield together with triphenylphosphane oxide. The elemental analysis, IR, $^{1}$H, $^{13}$C NMR, spectra and molecular weight determination (MS) were in good agreement with structure **15** (*cf. Experimental*).

Moreover, the reaction product of **1b** with triethylphosphonoacetate **3a** in the presence of alcoholic sodium ethoxide solution at reflux temperature for 4 h afforded compound **16** on the basis of spectroscopic evidences (Scheme 6, *cf. Experimental*). Moreover, trimethyl phosphite **4a** reacted with **1b** in refluxing toluene to give dimethyl-(4-oxo-3(phenylamino) pent-2-en-2-yl) phosphate **(17)** (Scheme 6). The structure of **17** was assigned on the basis of IR, $^{1}$H, $^{13}$C, $^{31}$P NMR, and MS data (*cf. Experimental*).



## CONCLUSION

From the results of the present investigation, it could be concluded that the reaction of 3-(hydroxyimino)pentane-2,4-dione **1a** and 3-(phenylimino)pentane-2,4-dione **1b** with phosphonium ylide **2a–c** proceeds according to the *Wittig* reaction to give the olefinic products **6**, **8**, **9**, **15**. Moreover, the reaction of 3-substituted-2,4-pentanediones **1a**, **b** with *Wittig–Horner* reagents **3** led to different products **10a–b**, **11**, **16** depending on the nature of the phosphonate anion used as well as the stability of the addition products. In the reaction of **1a**, **1b** with trialkyl phosphites **4a–b**, the dialkyl phosphate adducts **12a–b**, **17** were the sole reaction products. The reaction of LR **5a** with **1a** represents an interesting approach to the construction of new bioactive compound containing phosphorus and sulfur as 2,4-dioxopentan-3-ylidene)aminooxy)4-methoxyphenyl)phosphinodithioic acid (**13**). This finding clearly indicated that Lawesson's reagent preferentially attacked the =NOH rather than the carbonyl carbon. On the other hand, Japanese reagent **5b** reacted with **1a** to give the dithione product **14** through thionation reaction. These processes can be considered as new and simple routes for the preparation of different organophosphorus and cyclic compounds that cannot be obtained by other conventional methods.

## BIOLOGICAL EVALUATION OF THE TESTED COMPOUNDS

### Biological Screening

The antibacterial and antifungal activities were carried out in the Microbial Chemistry Department, National Research Centre, using the diffusion plate method.[24–27]

### Antibacterial and Antifungal Activities

**Evaluation.** [The antimicrobial activity of the tested compounds were examined against Gram positive bacteria *Bacillus subtilis*, *Bacillus cereus*, and *Staphylococcus aureus*and Gram negative bacteria *Escherichia coli*, *Pseudomonas aeruginose*and fungus

*Candida albicans.* The obtained results are compared with reference antibiotics[24–27] that were purchased from Egyptian markets].

**Conclusion.** All the biologically active compounds exceeds the values of the starting material **1a** which means that improvement of compounds takes places raising their medical value.

## EXPERIMENTAL

Melting points were measured by means of an electrothermal melting points apparatus. Starting materials **1a**, **b** were prepared according to reference,[28,29] respectively. The IR spectra were measured in KBr pellets with a Perkin–Elmer Infrared Spectrometer Model 157. The $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ or DMSO on a Jeol spectrometer at 500 and 125 MHz respectively and the chemical shifts were recorded in $\delta$ values relative to tetramethylsilane (TMS) as internal reference. The $^{31}P$ NMR (200 MHz) spectra were recorded in $CDCl_3$ or DMSO on a Jeol-500 spectrometer, too. The MS were recorded at 70 eV with a kratosMS equipment or Varian MAT311A Spectrometer. Elemental analyses were performed using the Elementarvaru EL-Germany Instrument. Their values agreed favorably with the calculated ones. The using reported yields are of pure isolated materials obtained by column chromatography silica gel 60 (Merk).



### Reaction of Phosphonium Ylide (2a) with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A mixture of 1.36 g **2a** (4 mmol) and 0.26 g (2 mmol) of **1a** in dry toluene (30 mL) was refluxed for 2 h. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography to give product **6a** [ethyl-4-(hydroxyimino)-3-methyl-5-oxohex-2-enoate] (**6a**, $C_9H_{13}NO_4$) and product **7** [3-acetyl-4-methyl-6*H*-1,2-oxazin-6-one] (**7**, $C_7H_7NO_3$). Triphenylphosphane oxide was also isolated and identified.

**6a:** Eluent: petroleum ether (60–80 °C)/ethyl acetate (90/10, v/v), product **6a** was separated as pale yellow crystals, yield 25%, m.p. 99–101 °C. IR [$\nu$,KBr, $cm^{-1}$]: 1653 (C=N), 1672 ($COCH_3$), 1720 (CO, ester), 3520 (OH).$^{1}H$ NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 1.27 (t, 3H, $CH_3$ ethyl), 2.23 (s, 3H, $CH_3$−C=CH), 2.39 (s, 3H, $CH_3$−C=O), 4.17 (q, 2H, $CH_2$ ethyl), 5.64 (s, 1H, CH), 8.56 (s, 1H, OH). $^{13}C$ NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 14.1 ($CH_3$−C=CH), 17.5 ($CH_3$, ethyl), 25.9 ($\underline{C}H_3$−C=O), 60.4 ($CH_2$, ethyl), 121.6 (CH), 145.9 (C=N), 158.8 (C=C), 165.7 (C=O, ester), 195.4 ($CH_3$−$\underline{C}$=O). MS *m/z* (%) 199 [$M^+$] (100), 154 [$M^+$-$OC_2H_5$] (30), 126 [$M^+$-$COOC_2H_5$] (40). Anal. Calcd for $C_9H_{13}NO_4$ (199.2): C, 54.26; H, 6.58; N, 7.03. Found: C, 54.66; H, 6.56; N, 7.2.

**7:** Eluent: petroleum ether (60–80 °C)/ethyl acetate (95/5, v/v), product **7** was separated as pale yellow crystals, yield 65% and m.p. 85–86 °C. IR [$\nu$, KBr, $cm^{-1}$]: 1658 (C=N), 1680 (CO), 1737(CO, lactone). $^{1}H$ NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.38 (s, 3H, $CH_3$−C=CH) 2.60 (s, 3H, $CH_3$−C=O), 6.47 (s, 1H, CH). $^{13}C$ NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 14.8 (CH3), 29.77 ($\underline{C}H_3$−C=O), 122.7(C=C), 147.4 (C=N), 166.3 ($\underline{C}$−$CH_3$), 169.9 (C=O, lactone), 195.3 ($\underline{C}$=O). MS *m/z* (%) 153 [$M^+$] (100), 110 [$M^+$-$\underline{C}OCH_3$] (40). Anal. Calcd for $C_7H_7NO_3$ (153.14): C, 54.90; H, 4.61; N, 9.15. Found: C, 54.63; H, 4.31; N, 9.33.

### Reaction of Phosphonium Ylide 2b with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A mixture of 1.32 g **2b** (4 mmol) and 0.26 g (2 mmol) of **1a** in dry toluene (30 mL) was refluxed for 4 h. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography to give product **6b** methyl-4-(hydroxyimino)-3-methyl-5-oxohex-2-enoate (**6b**, $C_8H_{11}NO_4$) (elution of the column with petroleum ether (60–80 °C)/ethyl acetate (90/10, v/v) and product **7** 3-acetyl-4-methyl-6*H*-1,2- oxazin-6-one (**7**, $C_7H_7NO_3$) (elution of the column with petroleum ether (60–80 °C)/ethyl acetate (95/5, v/v), (mixed melting points and comparative IR spectra with authentic samples previously obtained). Triphenylphosphane oxide was also isolated and identified. When compound **6a** or **6b** were heated in refluxing xylene for 4 h, compound **7** was obtained in good yield via expulsion of alcohol.

**6b:** Eluent: petroleum ether (60–80 °C)/ethyl acetate (90/10, v/v), product **6b** was separated as pale yellow crystals, yield 30%, m.p. 147–149 °C. IR [$\nu$, KBr, $cm^{-1}$]: 1678 ($COCH_3$), 1728 (CO, ester), 3527 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 1.60 (s, 3H, $CH_3C{=}C$), 2.40 (s, 3H, $CH_3{-}C{=}O$), 3.72 (s, 3H, $OCH_3$), 5.63 (s, 1H, CH), 8.58 (s, 1H, OH). $^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 14.8 ($CH_3{-}C{=}CH$), 26.9 ($\underline{C}H_3{-}C{=}O$), 52.6 ($OCH_3$), 122.0 (CH), 145.4b (C=N), 159.0 (C=C), 166.5 (C=O, ester), 195.3 ($CH_3{-}\underline{C}{=}O$). MS *m/z* (%) 185 [$M^+$] (100), 154 [$M^+$-$OCH_3$] (35), 126 [$M^+$-$COOCH_3$] (53). Anal. Calcd for $C_8H_{11}NO_4$ (185.18): C, 51.89; H, 5.99; N, 7.56. Found: C, 51.99; H, 5.63; N, 7.27.

### Reaction of Acetylmethylenetriphenylphosphorane (2c) with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A mixture of 0.6 g **2c** (2 mmol) and 0.26 g (2 mmol) of **1a** in dry toluene (30 mL) was refluxed for 8 h. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography to give product **8** [5-(hydroxyimino)-4-methylhept-3-ene-2,6-dione] (**8**, $C_8H_{11}NO_3$). Triphenylphosphane oxide was also isolated and identified.

Eluent: petroleum ether (60–80 °C)/ethyl acetate (90/10, v/v), product **8** was separated as colorless crystals, yield 85%, m.p. 110–111 °C. IR [$\nu$, KBr, $cm^{-1}$]: 1653 (C=N), 1681 (COC=C), 1684 (CO−C=N), 3518 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.19 (s, 3H, $C\underline{H}_3COCH$), 2.26 (s, 3H, $C\underline{H}_3{-}C{=}CH$), 2.39 (s, 3H, $C\underline{H}_3COCN$), 6.00 (s, 1H, CH), 8.22 (s, 1H, OH). $^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 17.8 ($\underline{C}H_3{-}C{=}C$), 26.0 (CH3−C=O), 32.2 ($CH_3\underline{C}OCN$), 128.0 (CH), 143.7 (C=N), 159.0 (C=C), 195.3($\underline{C}{=}OCH_3$), 198.4 ($\underline{C}OC{=}C$). MS *m/z* (%) 169 [$M^+$] (100), 127 [$M^+$-$COCH_3$] (32).Anal. Calcd for $C_8H_{11}NO_3$ (169.18): C, 56.80; H, 6.55; N, 8.28. Found: C, 56.62; H, 6.22; N, 8.43.

### Reaction of N-(Triphenylphosphoranylidene) Aniline (2d) with 3-(Hydroxyimino)-Pentane-2,4-Dione (1a)

A mixture of 0.7 g (2 mmol) of **2d** and 0.26 g (2 mmol) of **1a** was refluxed 3 h in 30 mL dry toluene. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography to give product **9** [3-(hydroxyimino)-4-(phenylimino)pentan-2-one] (**9**, $C_{11}H_{12}N_2O_2$). Triphenylphosphane oxide was also isolated and identified.

Eluent: petroleum ether (60–80 °C)/ethyl acetate (90/10,v/v), product **9** was separated as colorless crystals yield, 87%, m.p. 219–221 °C. IR [$\nu$, KBr, $cm^{-1}$]: 1655 (2C=N),

1680 ($COCH_3$), 3523 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.43 (s, 3H, $CH_3CNPh$), 2.45 (s, 3H, $CH_3CO$), 7.61(m, 5H, aromatic), 8.60 (s, 1H, OH).$^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 26.1 ($\underline{C}H_3-C=N$), 31.4($CH_3C=O$), 118,122,124,128,129 (aromatic carbon), 140.2 (C=NOH), 153.1 (C=N−Ph), 192.0 ($C=OCH_3$). MS *m/z* (%) 204 [$M^+$] (100), 127 [$M^+$-Ph] (30). Anal. Calcd for $C_{11}H_{12}N_2O_2$ (204.23): C, 64.69; H, 5.92; N, 13.72. Found: C, 64.99; H, 5.73; N, 14.02.

### Reaction of Triethoxyphosphonate (3a) with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A solution of sodium ethoxide (0.136 g, 2 mmol) in absolute ethanol (30 mL) was treated with an equimolar amount of triethoxyphosphonate **(3a)** (0.44 g, 2 mmol) then 1 mol of **1a** (0.26 g, 2 mmol) was added and the resulting reaction mixture was refluxed for 2 h (TLC). Then, poured on a small amount of water, extracted with ethyl acetate, dried and the extracts were evaporated under reduced pressure. The residue was applied to silica gel column chromatography to give product **10a** [methyl 2-(diethoxyphosphoryl)-3-hydroxy-4-(ethoxyimino)3-methyl-5-oxo-hexanoate] (**10a**, $C_{15}H_{28}NO_8P$).

Eluent: petroleum ether (60–80 °C) : ethyl acetate (60/40, v/v), product **10a** was separated as pale yellow crystals, yield (71%), m.p. 212–214 °C. IR ($\nu$, KBr, $cm^{-1}$): 1129 ($P-O-C_2H_5$), 1252 (P=O),[14] 1683 ($COCH_3$), 1739 (C=O, ester), 3498(OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 1.03 (t, 3H, $NOCH_2\underline{CH_3}$), 1.04, 1.05 (2t, 6H, $PO(OCH_2\underline{CH_3})_2$, $J_{HP} = 11.0$ Hz), 1.10 (t, 3H, $COOCH_2\underline{CH_3}$), 2.68 (s, 3H, $\underline{CH_3}C-OH$), 2.72 (s, 3H, $CH_3\underline{C}O$), 3.40 (s, 1H, OH, exchangeable with $D_2O$), 3.35 (q, 2H, $CH_2$, $NO\underline{CH_2}CH_3$),3.47 (d, 1H, CH, $^2J_{HP} = 18.0$ Hz), 3.85, 3.87 (2q, $2CH_2$, $P=O(O\underline{CH_2}CH_3)_2$), 3.88 (q, 2H, $COO\underline{CH_2}CH_3$). $^{13}$C NMR (125 Hz, $\delta$ ppm,$CDCl_3$): 14.4 (s, $\underline{C}H_3CH_2ON$), 15.3 (s,$\underline{C}H_3CH_2COO$), 16.1, 16.3 (d, $^3J_{CP} = 11.0$ Hz$(CH_3CH_2O)_2P=O$), 22.3 (d, $^3J_{CP} = 10.0$ Hz, $\underline{C}H_3COH$), 33.7 ($\underline{C}H_3CO$), 51.2(C−OH, d, $^2J_{CP} = 23.0$ Hz), 52.3 (CHPO, $^1J_{CP} = 105.0$ Hz), 61.7($COO\underline{C}H_2CH_3$), 62.6, 62.6 ($(CH_3\underline{C}H_2O)_2PO$), 63.4 ($C=NO\underline{C}H_2CH_3$), 148.2 (CN), 167.5 (C=O, ester) 195.0 ($\underline{C}OCH_3$). $^{31}$P NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 20.2. MS *m/z* (%): 381 [$M^+$] (100). Anal. Calcd for $C_{15}H_{28}NO_8P$ (381.36): C, 47.24; H, 7.40; N, 3.67; P, 8.12, Found: C, 46.98; H, 7.73; N; 4.00; P, 8.33.

### Reaction of Trimethoxyphosphonate 3b with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A solution of sodium methoxide (0.108 g, 2 mmol) in absolute methanol (30 mL) was treated with an equimolar amount of trimethyoxyphosphonate **(3b)** (0.36 g, 2 mmol) then 1 mol of **1a** (0.26 g, 2 mmol) was added and the resulting reaction mixture was refluxed for 3 h (TLC). Then, poured on a small amount of water, extracted with ethyl acetate, dried, and the extracts were evaporated under reduced pressure. The residue was applied to silica gel column chromatography to give product **10b** [methyl 2-(dimethoxyphosphoryl)-3-hydroxy-4-(methoxyimino) 3-methyl-5-oxohexanoate] (**10b**, $C_{11}H_{20}NO_8P$).

Eluent: petroleum ether (60–80 °C): ethyl acetate (60:40, v:v), product **10b** was separated as pale yellow crystals, yield (75%), m.p. 205–206 °C. IR ($\nu$, KBr, $cm^{-1}$): 1129 ($P-O-CH_3$), 1252 (P=O),[14] 1688 ($COCH_3$), 1742(C=O, ester), 3502 (OH). $^1$H NMR (500 MHz, $\delta$ ppm,$CDCl_3$): 2.33 (s, 3H, $\underline{CH_3}C-OH$), 2.96 (s, 3H, $CH_3CO$), 3.00 (s, 1H, OH, exchangeable with $D_2O$), 3.70 (s, 3H, $CH_3COO$), 3.73 (s, 3H, $NOCH_3$), 3.78 (d, 1H,

CH, $^2J_{HP}$ = 18.0 Hz), 3.80, 3.85 (2d, 6H, $J_{HP}$ = 11.0 Hz, P=O(OC$\underline{H}_3$)$_2$). $^{13}$C NMR (125 Hz, $\delta$ ppm, $CDCl_3$): 14.7 ($\underline{C}H_3COH$), 26.7 ($CH_3CO$), 51.7 (s, $\underline{C}H_3ON$), 51.2 (C−OH, d, $^2J_{CP}$ = 23.0 Hz), 52.3 (CHP=O, $^1J_{CP}$ = 102.0 Hz), 52.86, 52.9 ($(CH_3O)_2PO$, $^2J_{CP}$ = 22.3 Hz), 150.6 (C=N), 166.1 ($\underline{C}$=O, ester), 196.3 ($\underline{C}OCH_3$); $^{31}$P NMR (125 Hz, $\delta$ ppm, $CDCl_3$): 20.2. MS *m/z* (%) 325 [$M^+$] (100). Anal. Calcd for $C_{11}H_{20}NO_8P$ (325.25): C, 40.62; H, 6.20; N, 4.31; P, 9.52, Found: C, 40.22; H, 6.25; N; 3.98; P, 9.19.

## Reaction of Diethyl (Cyanomethylene)Phosphonate (3c) with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A solution of sodium ethoxide (0.136 g, 2 mmol) in absolute ethanol (30 mL) was treated with an equimolar amount of diethyl(cyanomethylene)phosphonate (**3c**) (0.35 g, 2 mmol) then **1a** (0.13 g, 1 mmol) was added and the resulting reaction mixture was refluxed for 5 h at 60–70 °C (TLC). Then, poured on a small amount of water, extracted with ethyl acetate, dried, and concentrated under reduced pressure. The precipitate was filtered off and recrystallized from benzene to afford product **11** [4-(hydroxyimino)-3,5-dimethyl-hepta-2,5-dienedinitrile] (**11**,$C_9H_9N_3O$).

Crystallized from benzene, **11** as colorless crystals, yield 85%, m.p. 145–147 °C. IR [*v*, KBr, $cm^{-1}$]: 2228 (C≡N), 3502 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.31 (s, 6H, $2CH_3$), 5.85 (s, 2H, 2CH), 6.21 (s, 1H, OH).$^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 22.4 ($2CH_3$), 112.4 (2CH), 123.04 (2C≡N), 158.2 (2C=C), 170.0 (C=N). MS *m/z* (%) 174 [$M^+$] (100), 149 [$M^+$-CN] (32), 122 [$M^+$-2C≡ N). Anal. Calcd for $C_9H_9N_3O$ (175.19): C, 61.7; H, 5.18; N, 23.99. Found: C, 62.01; H, 5.37; N, 23.83.

## General Procedure for the Reaction of Trialkyl Phosphites 4a–b with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

Trimethyl phosphite **4a** (0.24 g, 2 mmol) and/or triethyl phosphite **4b** was added dropwise to a solution of compound **1a** (0.26 g, 2 mmol) in dry benzene (30 mL), and the reaction mixture was refluxed for 12 h. After evaporation of the volatile material under reduced pressure, the residue was applied to silica gel column chromatography. Elution of the column with petroleum ether (60–80 °C) : ethyl acetate (50: 50, v:v) afforded **12a** [dimethyl(3-(hydroxy(methyl)amino)-4-oxopent-2-en-2-yl) phosphate] (**12a**, $C_8H_{16}NO_6P$) and/or **12b** [diethyl (3-(hydroxy (ethyl)amino)-4-oxopent-2-en-2-yl) phosphate] (**12b**, $C_8H_{16}NO_6P$).

**12a:** pale yellow crystals, yield 62%, m.p. 162–164 °C, IR [*v*, KBr, $cm^{-1}$]: 1118 (P−O−$CH_3$), 1260 (P=O), 1675 (C=O), 3492 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.56 (s, 3H, N−$CH_3$), 2.79 (s, 1H, OH, exchangeable with $D_2O$), 2.83,2.85 (2s, 6H, $2CH_3$), 3.74, 3.87 (2d, 6H, $^3J_{HP}$ = 11.5 Hz, P($OCH_3$)$_2$)). $^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 22.5 (s, $\underline{C}H_3C$−O), 31.1 (s, $\underline{C}H_3C$=O), 54.3, 54.5 (2d, $^2J_{CP}$ = 29.30 Hz, P ($OCH_3$)$_2$), 113.0 (C−N), 190.3 (C−O), 194.0 (C=O). $^{31}$P NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 2.1. MS m/z (%): 253 [$M^+$] (100). Anal. Calcd for $C_8H_{16}NO_6P$ (253.19): C, 37.95; H, 6.37; N, 5.53; P, 12.23. Found: C, 37.88; H, 6.21; N, 5.82; P, 12.35.

**12b:** Pale yellow crystals, yield 60%, m.p. 170–172 °C, IR [*v*, KBr, $cm^{-1}$]: 1123 (P−O−$C_2H_5$), 1263 (P=O), 1669 (C=O), 3494 (OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 1.27 (t, 3H, $NCH_2C\underline{H}_3$), 1.30, 1.33 (2t, 6H, $PO(OCH_2C\underline{H}_3)_2$), 2.35 (s, 1H, OH, exchangeable with $D_2O$), 2.51, 2.63 (2s, 6H, $2CH_3$), 2.69 (q, 2H,$NC\underline{H}_2CH_3$), 4.10, 4.18 (2q, 4H, $^3J_{HP}$ = 10.5 Hz,$PO(OC\underline{H}_2CH_3)_2$). $^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 14.2

(N−$\underline{C}H_3$−$CH_2$), 16.2, 16.5 (2$\underline{C}H_3CH_2O$), 22.8 (s, $\underline{C}H_3C$−O), 30.1 (s, $\underline{C}H_3C$=O), 52.6 (N−$\underline{C}H_3$−$\underline{C}H_2$), 64.3, 64.4 (2d, $^2J_{cp}$ = 28.5 Hz, P−O−$\underline{C}H_2$), 113.2 (C−N), 190.3 (C−O), 193.4 (C=O). $^{31}$P NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 2.15. MS m/z (%) 295 [$M^+$] (100). Anal. Calcd for $C_{11}H_{22}NO_6P$ (295.27): C, 44.74; H, 7.51; N, 4.74; P, 10.49. Found: C, 44.71; H, 7.82; N, 4.70; P, 10.21.

### Reaction of Lawesson's Reagent 5a with 3-(Hydroxyimino)-2,4-Pentanedione (1a)

A mixture of 0.8 g (2 mmol) of **5a** and 0.26 g (2 mmol) of **1a** was stirred for 1 h in dry benzene. The volatile material was evaporated under reduced pressure. The precipitate was filtered off and washed with cyclohexane then recrystallized from methanol to afford product **13** (((2,4-dioxopentan-3-ylidene)amino)oxy)(4-ethoxyphenyl)phosphinodithioic-acid (**13**, $C_{12}H_{14}NO_4PS_2$).

Crystallized from methanol, **13** as buff crystals, yield 85%, m.p. 170–172 °C. IR [*v*, KB, $cm^{-1}$]: 625 (P=S), 1654 (C=N), 1673 ($CH_3CO$), 2320 (SH). $^1$H NMR (500 MHz, $\delta$ ppm, DMSO): 2.05 (s, 6H, 2$CH_3$), 3.30 (s, 1H, SH, exchangeable with $D_2O$), 3.75 (s, 3H, $OCH_3$), 7.11 (m, 4H, aromatic). $^{13}$C NMR (125 MHz, $\delta$ ppm, DMSO): 30.2 (2$CH_3$), 55.7 ($OCH_3$), 114.0 (d, 2$\underline{C}$−C−C−P, $^3J_{CP}$ = 15.7 Hz), 121.5 (d, P−C−Ph, $^1J_{CP}$ = 115.3 Hz), 132.5 (d, 2$\underline{C}$−C−P, $^2J_{CP}$ = 22.0 Hz), 143.9 (C=N), 195.8 (2C=O). $^{31}$P NMR (125 MHz, $\delta$ ppm, DMSO): 18.7. MS *m/z* (%) 331 [$M^+$] (100), 300 [$M^+$-$OCH_3$] (47). Anal. Calcd for $C_{12}H_{14}NO_4PS_2$ (331.35): C, 43.50; H, 4.26; N, 4.23;P, 9.35; S, 19.35. Found: C, 43.82; H, 4.37; N, 4.52; P, 9.01 S, 19.0.

### Reaction of Japanese Reagent 5b with 3-(Hydroxyimino)Pentane-2,4-Dione (1a)

A mixture of 0.8 g (2 mmol) of **5b** and 0.26 g (2 mmol) of **1a** was stirred for 1 h in dry benzene. The volatile material was evaporated under reduced pressure. The precipitate was filtered off and washed with benzene then recrystallized from methanol to afford product **14** [3-(hydroxyimino) pentane-2.4-dithione] (**14**, $C_5H_7NOS_2$).

Crystallized from methanol, **14** as colorless crystals, yield, 75%, m.p. 172–174 °C. IR [*v*, KBr, $cm^{-1}$]: 1255 (C=S), 1652 (C=N), 3511(OH). $^1$H NMR (500 MHz, $\delta$ ppm, DMSO): 1.01 (s, 6H, 2$CH_3$), 8.021 (s, 1H, OH, exchangeable with $D_2O$). $^{13}$C NMR (125 MHz, $\delta$ ppm, DMSO): 28.1 (2$CH_3$), 143.5 (C=N), 205.2 (2C=S). MS *m/z* (%) 161 [$M^+$] (45). Anal. Calcd for $C_5H_7NOS_2$ (161.25): C, 37.24; H, 4.38; N, 8.69; S, 39.77. Found: C, 37.01; H, 4.72; N, 8.52; S, 40.00.

### Reaction of Phosphonium Ylide 2a with 3-(Phenylimino)Pentane-2,4-Dione (1b)

A mixture of 0.68 g **2a** (2 mmol) and 0.38 g (2 mmol) of **1b** in dry toluene (30 mL) was refluxed for 4 h. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography to give **15** [diehyl-3,5-dimethyl-4-(phenylimino)hepta-2,5-dienedioate] (**15**,$C_{19}H_{23}NO_4$). Triphenylphosphane oxide was also isolated and identified. When compound **1b** was treated with two mol equivalents of **2a** in refluxing toluene, compound **15** was obtained in good yield and triphenylphosphane oxide was also isolated.

Eluent: petroleum ether (60–80 °C)/ethyl acetate (90/10, v/v), compound **15** was separated as pale yellow crystals, yield 40%, m.p. 135-137 °C, IR [*ν*, KBr, $cm^{-1}$]: 1735 (CO, ester). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 1.24-1.25 (2t, 6H, $2CH_3$ ethyl), 2.01, 2.438 (2s, 6H, $2CH_3$), 4.17,4.35 (2q, 4H, $2CH_2$, ethyl), 6.19, 6.24 (2s, 2H, 2CH), 6.95 (m, 5H, aromatic). $^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 14.2, 14.4 ($2CH_3$), 19.1, 29.4 ($2CH_3$, ethyl), 60.3, 60.6 ($2CH_2$, ethyl), 126.1, 126.8, (2CH), 119.1–150.3 (aromatic carbon), 151.1, 151.3 (2C=CH), 165.9 (C=N), 166.43, 168.42 (2C=O, ester). MS m/z (%) 329 [$M^+$] (100). Anal. Calcd for $C_{19}H_{23}NO_4$ (329.39): C, 69.28; H, 7.04; N, 4.25. Found: C, 69.5; H, 7.22; N, 4.01.

### Reaction of Triethoxyphosphonate 3a with 3-(Phenylimino)Pentane-2,4-Dione (1b)

A solution of sodium ethoxide (0.136 g, 2 mmol) in absolute ethanol (30 mL) was treated with an equimolar amount of triethoxyphosphonoacetate **(3a)** (0.44 g, 2 mmol) then **1b** (0.38 g, 2 mmol) was added and the resulting reaction mixture was refluxed for 4 h (TLC). Then, poured on a small amount of water, extracted with ethyl acetate, dried, and the extracts were evaporated under reduced pressure. The residue was applied to silica gel column chromatography to give product **16** [ethyl2-(diethoxyphosphoryl)-3-hydroxy-3-methyl-5-oxo-4-(phenylimino)hexanoate] (**16**,$C_{19}H_{28}NO_7P$).

Eluent: petroleum ether (60–80 °C)/ethyl acetate (50/45, v/v), **16** was separated as yellow crystals, yield (60%), m.p. 193–194 °C, IR (*ν*, KBr, $cm^{-1}$): 1132 (P−O−$C_2H_5$), 1256 (P=O),[14] 1682 ($COCH_3$), 1754 (C=O, ester), 3418(OH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$):1.24, 1.39 (2t, 6H, $PO(OCH_2\underline{C}H_3)_2$, $J_{HP} = 10.83$ Hz), 1.59 (t, 3H, $COOCH_2\underline{C}H_3$), 2.17 (s, 3H, $\underline{C}H_3C$−OH), 2.22 (s, 3H, $\underline{C}H_3CO$), 3.00, 3.01 (2q, 4H, $2CH_2$, $^3J_{HP} = 11.00$ Hz, $P{=}O(\underline{C}H_2CH_3)_2$), 3.72 (d, 1H, CH, $^2J_{HP} = 20.2$ Hz), 3.82 (s, 1H, OH, exchangeable with $D_2O$), 3.88 (q, 2H, $COO\underline{C}H_2CH_3$), 7.03 (m, 5H, aromatic). $^{13}$C NMR (125 Hz, $CDCl_3$, $\delta$ ppm): 13.2 (s, $\underline{C}H_3CH_2COO$), 14.3,19.9 (d, $(\underline{C}H_3CH_2)_2PO$), 29.8 ($\underline{C}H_3COH$), 30.4 ($\underline{C}H_3CO$), 45.7 (COH, d, $^2J_{CP} = 22.0$ Hz), 52.7(CHPO, $^1J_{CP} = 114.0$), 64.2 ($COO\underline{C}H_2CH_3$), 65.0, 66.4 (($CH_3\underline{C}H_2O)_2PO$), 65.2 ($\underline{C}$−OH, $^2J_{CP} = 36.9$ Hz), 113.8–129.5 (aromatic carbon), 164.2 (CN), 174.0 (C=O), 195.00 ($\underline{C}OCH_3$). $^{31}$P NMR (125Hz, $\delta$ ppm, $CDCl_3$): 18.7. MS *m/z* (%) 413[$M^+$] (100). Anal. Calcd for $C_{19}H_{28}NO_7P$ (413.40): C, 55.20; H, 6.83; N, 3.39; P, 7.49. Found: C, 55.58; H, 7.02; N; 3.33; P, 7.83.

### Reaction of Trimethyl Phosphite (4a) with 3-(Phenylimino)Pentane-2,4-Dione (1b)

Trimethyl phosphite **(4a)** (0.24 g, 2 mmol) was added dropwise to a solution of compound **1b** (0.38 g, 2 mmol) in dry toluene (30 mL), and the reaction mixture was refluxed for 6 h. After evaporation of the volatile material under reduced pressure, the residue was applied to silica gel column chromatographyto afford **17** [dimethyl (4-oxo-3-(phenylamino)pent-2-en-2-yl) phosphate (**17**, $C_{13}H_{18}NO_5P$).

Eluent: petroleum ether (60–80 °C) : ethyl acetate (30 : 70, v:v), **17** was separated as yellow crystals, yield 62%, m.p. 162–164 °C. IR [*ν*, KBr, $cm^{-1}$]: 1118 (P−O−$CH_3$), 1264 (P=O),[14] 1677 (C=O), 3500 (NH). $^1$H NMR (500 MHz, $\delta$ ppm, $CDCl_3$): 2.10, 2.23 (2s, 6H, $2CH_3$), 3 (s, 1H, NH, exchangeable with $D_2O$), 3.75, 3.77 (2d, 6H, $^3J_{HP} = 11.00$ Hz, $PO(OCH_3)_2$)), 7.16(m, 5H, aromatic).$^{13}$C NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 22.5 (s, $\underline{C}H_3C$−O), 30.3 (s, $\underline{C}H_3C{=}O$), 54.2, 54.3(2d, $^2J_{CP} = 29.0$ Hz, $PO(OCH_3)_2$), 116.5 (C−N),

119.00–142.9 (aromatic carbon), 192.2 (C—O), 193.4 (C═O).$^{31}$P NMR (125 MHz, $\delta$ ppm, $CDCl_3$): 5.8.MS *m/z* (%)299[$M^+$] (100). Anal. Calcd for $C_{13}H_{18}NO_5P$ (299.26): C, 52.18; H, 6.06; N, 4.68; P, 10.35. Found: C, 52.08; H, 6.21; N, 5.75; P, 10.15.

## REFERENCES


1. Abdou, W. M.; Ganoub, N. A. F.; Shaddy, A. M. *Phosphorus Sulfur Silicon Relat. Elem.* **2000,** 165, 171-189.
2. Soliman, F. M.; Said, M. M.; Maigali, S. S. *Heteroatom Chem.* **2005,** 16, 476-483.
3. Abdou, W. M.; Sediek, A. A.; Khidre, M. D. *Monatsh. Chem.* **2008,** 139, 617-623.
4. Arsanious, M. H. N.; Maigali, S. S.; Boulos, L. S. *Phosphorus Sulfur Silicon Relat. Elem.* **2010,** 185, 57-64.
5. Boulos, L. S.; Arsanious, M. H. N.; Ewies, E. F. *Phosphorus Sulfur Silicon Relat. Elem.* **2009,** 184(2), 275-290.
6. Arsanious, M. H. N.; Nahed, K. El-Din; Boulos, L. S. *Phosphorus Sulfur Silicon Relat. Elem.* **2009,** 184(11), 2813-2826.
7. Boulos, L. S.; Arsanious, M. H. N.; Yakout, El-Sayed, M. A. *Monatsh. Chem.* **2007,** 138, 979-984.
8. Arsanious, M. H. N.; Boulos, L. S. *Monatsh. Chem.* **2006,** 137, 1177-1184.
9. Boulos, L. S.; Abd El-Malek, H. A. *Phosphorus Sulfur Silicon Relat. Elem.* **2004,** 179, 97-105.
10. Boulos, L. S.; Arsanious, M. H. N. *Synth. Commun.* **2002,** 32, 2779-2790.
11. Boulos, L. S.; Arsanious, M. H. N. *Monatsh. Chem.* **2001,** 12, 511-518.
12. Boulos, L. S.; Shabana, R.; Shaker, Y. M. *Heteroatom Chem.* **2000,** 11, 57-64.
13. Albrecht, A.; Kedzia, J.; Koszuk, J. F.; Warzcha, E.; Janeckic, T. *Tetrahedron Lett*. **2006,** 47, 2353.
14. William, D. H.; Fleming, I. In: *Spectroscopic Methods in Organic Chemistry*; Mc Graw–Hill: Maidenhead, U.K., 1987; p. 55.
15. Berger, S.; Braun S.; Kalinowski, H. O. *NMR-Spektroskopie von Nichtmetallen, vol. 3, $^{31}$P-NMR-Spektroskopie*; Thieme, Stuttgart/New York, 1993, pp. 135-140.
16. Johnson, A. W. *Ylides and Imine of Phosphorus*; John Wiley and Sons, Inc.: New York, 1993.
17. Grim, S. O.; Farlane, W. Mc.; Mark, T. J. *J. Chem. Commun.* **1967,** 12, 1191-1192.
18. Ramirez, F.; Bhatia, S. B.; Patwardhan, A. V.; Chen, E. H.; Smith, C. P. J. *Org. Chem.* **1968,** 33, 20-26.
19. Ramirez, F.; Chen, E. H.; Dershowitz, S. *J. Am. Chem. Soc.* **1959,** 81, 4338-4342.
20. Erker, G.; Aust, N. C. *J. Am. Chem. Soc.* **1998,** 120, 4863-4864.
21. Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Thieme: Stuttgart; 1991; pp. 130-131.
22. Shabana, R.; EL–Barbary, A. A.; Ghattas, A. B. A. G.; Lawesson, S. O.; Romming, C. *Sulfur Lett.* **1984,** 2, 224-239.
23. Maigali, S. S.; Shabana, R.; EL-Hussieny, M.; Soliman, F. M. *Phosphorus Sulfur Silicon Relat. Elem.* **2009,** 184, 2408-2426.
24. Grayer R. J.; Harborne, B. J. *Phytochem.* **1994,** 37, 19-41.
25. Irobi, O. N.; Moo-Young, M.; Anderson, W.A. *Int. J. Pharmacog.* **1996,** 34, 87-90.
26. Jawetz, E.; Melnick, J. L.; Adelberg, E.A. *Review of Medical Microbiology*, 5th ed.; Lang Medical Publication: Los Altos, CA, 1974, 57, 399-401.
27. Muanza, D. N.; Kim, B. W.; Euler, K. L.; Williams, L. *Int. J. Pharmacog.* **1994,** 32, 337-345.
28. De Neufvillo, R.; Pechmann, H. V. *Chem. Ber.* **1890,** 23, 3375-3387.
29. Mirek, J.; Moskal, J.; Moskal, A. *Tetrahedron* **1975,** 31, 2145-2149.