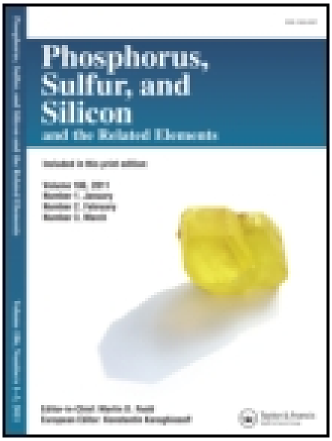

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Studies on Organophosphorus Compounds XI: The Reaction of Phosphorus Reagents With Hydrazonoyl Halides, Hydrazonoyl Azides, and Shiff's Bases

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To cite this article: Nadia R. Mohamed (2006) Studies on Organophosphorus Compounds XI: The Reaction of Phosphorus Reagents With Hydrazonoyl Halides, Hydrazonoyl Azides, and Shiff's Bases, Phosphorus, Sulfur, and Silicon and the Related Elements, 181:3, 683-691, DOI: 10.1080/10426500500269968

To link to this article: http://dx.doi.org/10.1080/10426500500269968

Phosphorus, Sulfur, and Silicon, 181:683–691, 2006
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500269968

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Studies on Organophosphorus Compounds XI:* The Reaction of Phosphorus Reagents With Hydrazonoyl Halides, Hydrazonoyl Azides, and Shiff's Bases

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*N-(chloro-furan-2-yl)methylene-N′-(4-nitrophenyl)hydrazone (**I**) reacted with triethylphosphite to produce the phosphonate derivative **III**. The tetrazine derivative **VI** was produced by the interaction of **I** with diethyl-phosphite. Hydrazonoyl azide derivatives **VIIIa–c** reacted with triphenyl phosphine to form the iminophosphorane derivatives **Xa–c**. On the other hand, the azide derivative **VIIIc** reacted with the phosphonium ylide **XI** to form the 1,2,3-triazole adduct **XIII**. The reaction of triethyl phosphite with Shiff's bases **XIVa–c** yielded the corresponding phosphonates **XVa–c**. The structures of the newly prepared compounds were confirmed with the analytical and spectroscopic evidences.*

Keywords Azides; hydrazonoyl halides; phosphines; phosphites; phosphonium ylides; Shiff's bases

INTRODUCTION

Hydrazonoyl halides have been extensively studied and have been known as useful synthones for heterocyclic compounds.[1–4] In a previous work, we have examined the reactions of these halides with different phosphorus reagents.[5–8] This communication describes the behavior of hydrazonoyl halides towards phosphites, phosphines, and phosphonium ylides. The work is extended also to include the reaction of some of Shiff's bases with triethyl phosphite.

DISCUSSION

We have found that the reaction of an equalmolar ratio of *N*-(chloro-furan-2-yl)methylene-N′-(4-nitrophenyl)hydrazones (**I**) and triethyl phosphite (**II**) in toluene proceeded under the condition of the

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[*] C.f. Reference 20.

Received January 31, 2005; accepted April 15, 2005.

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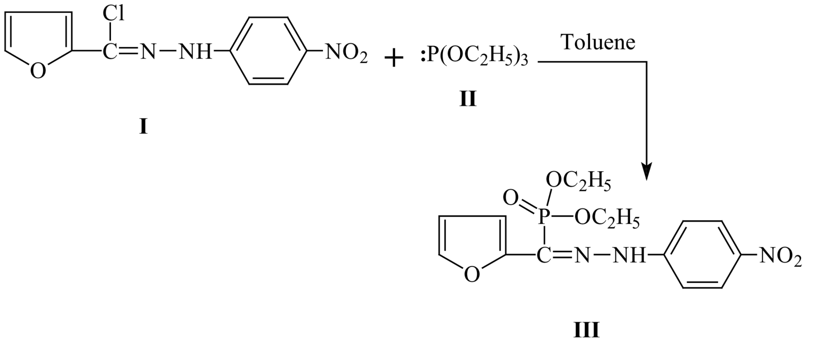
Arbusov reaction[9] via the loss of ethyl chloride to yield the phosphonate derivative **III** (Scheme 1).

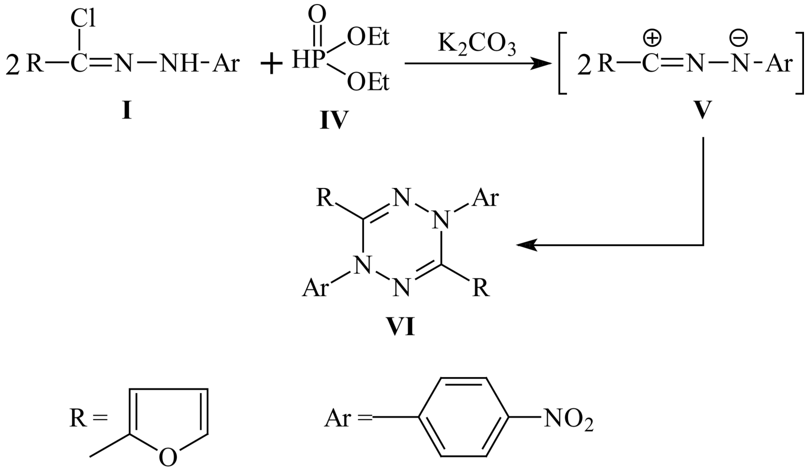


SCHEME 1

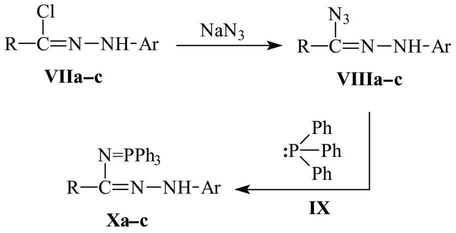
Structure **III** is given to this product according to the analytical and spectroscopic evidence. The Ms of compound **III** showed ion peaks at m/z = 367 [M^+], 338 [M^+—C_2H_5], and at 230 [M^+-O=P(OC_2H_5)$_2$]. Its IR spectrum revealed the presence of strong bands at 1260 cm^{-1} (P=O), 1030 [P—O-alkyl], and 3400 (NH). Moreover, the ^1H NMR spectrum of this compound disclosed the presence of the characteristic triplet quintet pattern for the ethoxy group attached to phosphorus: a triplet at $\delta = 1.29$ ppm (6H) and a quintet at $\delta = 4.23$ ppm (4H). The furanyl protons appeared as a triplet at $\delta = 6.7865$ ppm (1H), two doublets at $\delta = 6.65$ ppm (1H), and at $\delta = 7.11$ ppm (1H). The four aromatic protons appeared as two doublets centered at $\delta = 7.50$ ppm and at $\delta = 8.25$ ppm (AB system). The NH proton appeared as singlet at $\delta = 11.16$ ppm.

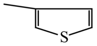
The tetrazine **VI** was produced when diethyl phosphite **IV** and was allowed to react with **I** under the same experimental conditions quantitatively. It was probably formed via a head-to-tail dimerization of the corresponding nitrilimine **V**. The nitrilimine was firstly formed by the action of **I** with dialkyl hydrogen phosphite in the presence of K_2CO_3. Tetrazine derivatives were previously reported to be formed when compound **I** in toluene was heated in the presence of triethylamine by a similar head-to-tail dimerization[10] (Scheme 2). The formation of these derivatives could be explained also in terms of the Hard-Soft, Acid Base principle.[11–14] The structure of the tetrazine derivative **V** was supported by analytical and spectral evidences (c.f. Experimental section).

1-azido-1-(phenylhydrazone)propane-2-one, ethyl-1-azido-1-(phenylhydrazone)acetate and N-(azido-thiophene-2-yl)methylene-N′(4-nitrophenyl)hydrazine **VIIIa–c** were prepared by the action of sodium azide on the respective hydrazonoyl halides **VIIa–c** (c.f. Scheme 3).



SCHEME 2



VII, VIII, X	R	Ar
a,	$COCH_3$	C_6H_5
b,	$COOC_2H_5$	C_6H_5
c,		C_6H_4-NO_2(p)

SCHEME 3

We have found that the reaction of triphenyl phosphine **IX** with the azide derivative **VIIIa** in dry benzene yielded a chromatographically pure adduct formulated as **Xa**. The structure elucidation of this compound was verified by the following evidences:

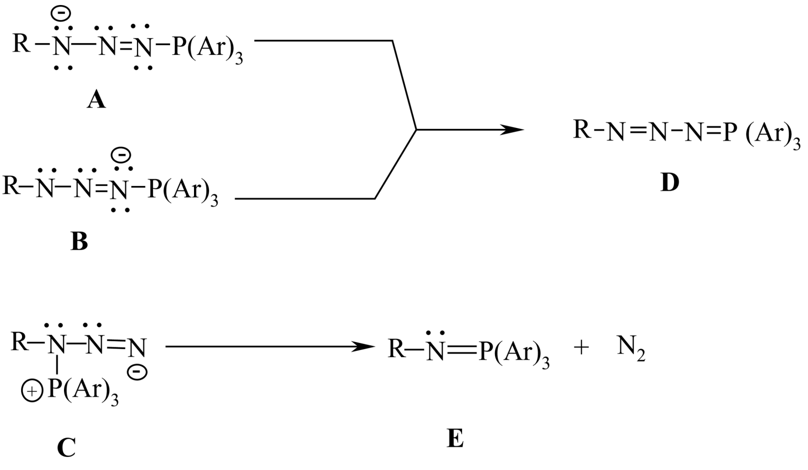
1. Correct analytical values corresponded to $C_{27}H_{24}N_3OP$.
2. The Ms showed ion peaks at m/z = 437 [M^+], 394 [M^+-$COCH_3$], 276 [N =P $(C_6H_5)_3$], 303 [M^+-C_6H_5N], and at 288 [M^+-C_6H_5-N-NH].
3. The IR spectrum of compound **Xa** revealed the absence of the azide absorption, which appeared as a strong band at $\nu = 2136$ cm^{-1} in the spectrum of the starting azide **VIIIa**. The spectrum showed

absorption bands at 1438 cm^{-1} (P-Ph), 1365 cm^{-1} ($N = P$), and 3250 cm^{-1} (NH).

4. The ^1H NMR spectrum of this compound revealed the presence of signals at $\delta = 2.25$ ppm (3H, acetyl CH_3, s), $\delta = 7.26$–7.78 ppm (20H, aromatic protons, m), and $\delta = 9.28$ ppm (1H, NH, s).
5. The ^{31}P NMR spectrum of this compound has one signal at $\delta = 20.10$ ppm (iminophosphorane).

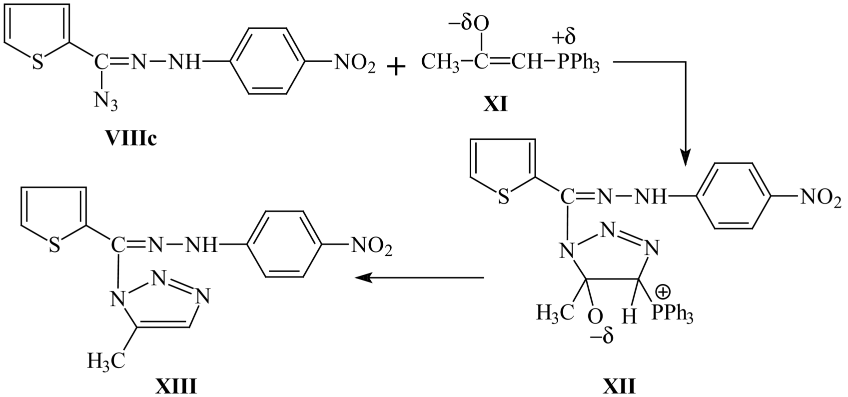
In a similar manner, the reaction of triphenylphosphine with azides **VIIIb**, **c** proceeded under the same conditions to yield compounds bearing the iminophosphorane structures **Xb**, **c**, respectively. This is based on analytical and spectroscopic data (c. f. Experimental section).

It has been established[15–17] that a nucleophilic attack by phosphorus on azides gives rise to 3 dipolar ion structures A, B, C. Forms A and B are resonance forms for D. However, form C decomposes to afford E (Scheme 4). According to this assumption, a possible explanation for the reaction of azides **VIIIa–c** is postulated. This involves an initial attack of phosphorus on the azide nitrogen attached to the carbon atom (form C) to give the iminophosphoranes (**Xa–c**).[15]



SCHEME 4

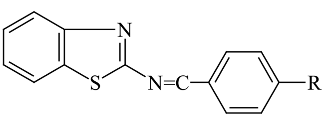
On the other hand, when azide **VIIIc** was allowed to react with acetylmethylenetriphenylphosphorane **XI**, the 1,2,3-triazole adduct **XIII** was produced in a quantitative yield. A mechanism that accounts for the formation of this compound is depicted in Scheme 5. This involves a 1,3 dipolar cycloaddition of azide **VIIIc** to the C=C bond of the ylide **XI** followed by the loss of triphenylphosphine oxide from the cyclic intermediate **XII** to yield **XIII** (Scheme 5).



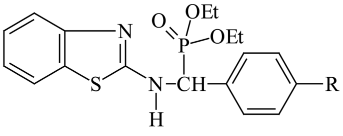
SCHEME 5

Structure elucidation of compound **XIII** was accomplished with the following evidences: (a) correct analytical values correspond to $C_{14}H_{11}N_6O_2S$; (b) the Ms of **XIII** showed ion peaks at m/z = 327 [M^+], 39.15%, and m/z = 300 [M^+-N_2] and 27.09%, m/z = 109 [furyl-C=N]; and 41.31; and (c) the IR spectrum of **XIII** revealed the presence of the triazole absorption band at 1180 cm^{-1} and NH absorption at 3180 cm^{-1} and (d) the ^{1}H NMR spectrum showed signals at $\delta = 2.20$ (d, 3H, CH_3), 6.43 (d, 1H), 7.06 (t, 1H), 7.69 (d, 1H), for the thiophene protons. This is beside two singlet signals at 7.98 and 10.72 for the triazole proton and the NH, respectively.

A similar behavior of azide **VIIIc** towards ylide **XI** was previously noticed when 3-azidotriazines reacted with the same ylide to produce 1-triazino-1,2,3-triazoles.[18]



XIV



XV

XIV,XV	R
a,	H
b,	NO_2
c,	Cl

SCHEME 6

Next, the reaction of triethylphosphite **II** with the Shiff's bases benzothiazo(2,l)-arylidine amine derivatives **XIVa–c** was investigated.[19] The reaction proceeded in toluene with stirring at r.t. overnight, whereby the reactants disappeared (TLC) and the corresponding phosphonates **XVa–c** were produced and identified (Scheme 6). This is based on analytical and spectroscopic evidences. (c.f. Experimental section).

EXPERIMENTAL

All melting points were uncorrected. Solvents used were distilled and dried over sodium sulfate. Microanalysis experiments were carried out in the analytical lab unit at the National Research Centre, Dokki, Egypt. IR spectra were taken in KBr on a OK 9712 IR spectrometer with DMSO-D_6 as a solvent and TMS as an internal reference. Chemical shifts are expressed as δ units (ppm). The mass spectra were recorded on Kratos (75 ev) Ms equipment.

N-(DIETHYLPHOSPHONATE-FURAN-2-YL)METHYLENE-N′-(4-NITROPHENYL)HYDRAZONE III

To a solution of hydrazonoyl halide **I** (2.66 g, 0.01 mol) in benzene, 30 mL containing 0.5 gm of K_2CO_3, and triethylphosphite **II** (0.01 mol) was added. The reaction mixture was stirred at r.t. for 3 h. The inorganic salt filtered and the filterate was evaporated under vacuum. The remaining residue triturated with n-hexane.

Compound **III**: yellow crystals, m.p. 88–89°C cryst., solvent: benzene, yield = 2.38 g, (65%) IR ν: 3400 (NH), 1260 (P=O), 1030 (P-O-alkyl) cm^{-1}; ^1H NMR (DMSO-D_6) = δ 1.29 (t, 6H, $2CH_3$), 4.23 (quintet, 4H, $2CH_2$), 6.78 (t, 1H, furan protons), 6.65, 7.11 (2d, 2H, furan protons), 7.50, 8.25 (2d, 4H, aromatic protons), 11.16 (s, 1H, NH); MS: m/z = 376 (M^+); 338 (M^+-C_2H_5); 230 (M^+-O=PO$(C_2H_5)_2$). Anal. found C: 48.89; H: 4.71; N: 11.11; P: 8.14. Calcd. for $C_{15}H_{18}N_3O_6P$ (367.30): C: 49.05; H: 4. 93; N: 11.44; P: 8.43.

REACTION OF HYDRAZONOYL HALIDE I WITH DIETHYLPHOSPHITE

To a solution hydrazonoyl halide **I** (2.66 g, 0.01 mol) in benzene, 25 mL containing 0.5 gm of K_2CO_3 and diethyl phosphite (0.01 mol) was added. The reaction mixture was stirred for 3 h and then heated under reflux for 3 h. The formed inorganic salt was isolated by filtration; the residual material formed after evaporation of the solvent under vacuum was treated with cyclohexane.

Compound **VI**: Pale yellow crystals, m.p. 164°C cryst., solvent: cyclohexane; yield = 2.57 g, (68%) IR ν: 1560 aromatic C=C; ^{1}H NMR (DMSO-D$_6$) = δ 6.56 (m, 2H, furanyl protons), 7.01–7.13 (2d, 2H, furanyl protons), 7.47, 7.58 (2d, 2H, furanyl protons) 7.73 and 8.39 (m, 8H, aromatic protons). Ms: m/z = 458 [M$^+$]; 221 [nitrile imine]. Anal. found: C: 57.55; H: 3.68; N: 18.01. Calcd. for $C_{22}H_{14}N_6O_6$ (458.39): C: 57.64; H: 3.78; N: 18.33.

REACTION OF 1-AZIDOHYDRAZONOYL DERIVATIVES VIIIa–c WITH TRIPHENYL PHOSPHINE

To a solution of azidohydrazonoyl derivatives **VIIIa–c** (0.01 mol) in toluene, 25 mL of triphenyl phosphine (2.62 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 3 h. The residual material remained after evaporation, and the solvent under vacuum was treated with pet-ether at 80–100°C.

Iminophosphorane **Xa**: Yellow crystals, m.p. 166°C cryst., solvent: benzene/n-hexane; yield = 1.45 g, (72%); IR ν: 3250 (NH), 1438 (P-Ph), 1365 (N=P)cm^{-1}; ^{1}H NMR = δ 2.25 (s, 3H, CH$_3$), 7.26–7.78 (m, 20H, aromatic protons), 9.28 (s, 1H, NH) ppm. ^{31}P NMR δ = 20.10 ppm (imino phosphorane); MS: m/z = 437 (M$^+$); 394 (M$^+$-COCH$_3$); 276 [N=P(Ph)$_3$] 303 (M$^+$-NPh)] and 288 [M$^+$-Ph-N-NH]. Anal. found: C: 74.10; H: 5.40; N: 9.48; P: 6.97. Calcd. for $C_{27}H_{24}N_3OP$ (437.48): C: 74.12; H: 5.52; N: 9.60; P: 7.08.

Iminophosphorane **Xb**: Pale yellow crystals, m.p. 149–150°C cryst., solvent: benzene, yield = 3.27 g, (70%); IR ν: 3300 (NH), 1440 (P-Ph), 1360 (N=P)cm^{-1}; ^{1}H NMR (DMSO-d$_6$) = δ 1.01 (t, 3H, CH$_3$), 3.88 (q, 2H, CH$_2$), 6.74–7.52 (m, 10H, aromatic protons), 7.57–7.80 (m, 10, aromatic protons), 9.01 (s, 1H, NH); MS: m/z = 467 [M$^+$]. Anal. found: C: 71.63; H: 5.49; N: 8.87; P: 6.50. Calcd. for $C_{28}H_{26}N_3O_2P$ (467.51): C: 71.93; H: 5.60; N: 8.98; P: 6.62.

Iminophosphorane **Xc**: Orange crystals, m.p. 184°C cryst., solvent: cyclohexane; yield = 3.81 g, (71%); IR ν: 3305 (NH), 1435 (P-Ph), 1355 (N=P)cm^{-1}; ^{1}H NMR (DMSO-d$_6$) = δ 6.62 (m, 3H, thiophene protons), 7.61 (m, 4H-aromatic protons), 7.71–8.01 (m, 15H, aromatic protons), 9.30 (s, 1H, NH); MS: m/z = 522 [M$^+$]. Anal. found: C: 66.60; H: 4.30; N: 10.48; S: 6.00. Calcd. for $C_{29}H_{23}N_4O_2SP$ (522.57): C: 66.65; H: 4.43; N: 10.72; S: 6.13, P: 5.92.

N-(1,2,3-TRIAZOLO-THIOPHENE-2-YL)METHYLENE-N′-(4-NITROPHENYL) HYDRAZINE XIII

A solution of toluene (30 mL) containing azido hydrazonoyl **VIIIc** (2.88 g, 0.01 mol) and acetylmethylenetriphenylphosphorane **XI**

(3.18 g, 0.01 mol) was heated under reflux for 5 h. The solvent was evaporated under vacuum. The remaining residue was treated with MeOH.

Compound **XIII**: yellow crystals, m.p. 233°C, cryst., solvent: MeOH; yield = 1.79 gm (55%); IR ν: 3180 (NH), 1180 (triazole ab); ^{1}H NMR (DMSO-d$_6$) = δ 2.20 (s, 3H, CH_3), 6.43 (d, 1H, thiophene proton), 7.6 (t, 1H, thiophene proton), 7.69 (d, 1H, thiophene proton), 7.98 (s, 1H, triazole protons), 10.72 (s, 1H, NH); Ms: m/z = 327 [M$^+$]. Anal. found: C: 51.25; H: 3.30; N: 25.55; S: 9.70. Calcd. for $C_{14}H_{11}N_6O_2S$ (327.35): C: 51.36; H: 3.38; N: 25.67; S: 9.79.

REACTION OF SHIFF'S BASES WITH TRIETHYLPHOSPHITE

General Procedure

To a solution of benzene containing one of the Shiff's bases **XIV** (0.01 mol), triethylphosphite (0.01 mol) was added. The reaction mixture was heated under reflux for 6 h. The solvent was evaporated under vacuum and the remaining residue was treated with the proper solvent.

Compound **XVa**: white crystals, m.p. 112°C, cryst., solvent: benzene/n-hexane; yield = 3.00 g (80%); IR ν: 3340 (NH), 1258 (P=O), 1030 (P-O-alkyl) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) = δ 1.08, 1.14 (2t, 6H, 2CH_3), 3.79, 4.04 (2q, 4H, 2CH_2), 5.65 (dd, 1H, CH; J_{HP} = 22.4 Hz, J_{HH} = 9.3 Hz), 7.02–7.38 (m, 5H, aromatic protons), 7.40–7.68 (m, 4H, aromatic protons), 9.07 (dd, 1H, NH, J_{HH} = 9.3 Hz); MS: m/z = 376 [M$^+$]. Anal. found: C: 57.22; H: 5.51; N: 7.30; S: 8.38; P: 8.20. Calcd for $C_{18}H_{21}N_2O_3SP$ (376.42): C: 57.43; H: 5.62; N: 7.44; S: 8.51; P: 8.22.

Compound **XVb**: yellow crystals, m.p. 172°C, cryst., solvent: benzene; yield = 3.28 g (78%); IR ν: 3350 (NH), 1255 (P=O), 1025 (P-O-alkyl) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) = δ 1.05, 1.15 (2t, 6H, 2CH_3), 3.80, 4.15 (2q, 4H, 2CH_2), 5.75 (dd, 1H, CH; J_{HP} = 22.4 Hz, J_{HH} = 9.3 Hz), 6.95–7.32 (m, 4H, aromatic protons), 7.40–7.85 (m, 4H, aromatic protons), 9.25 (dd, 1H, NH, J_{HH} = 9.3 Hz); MS: m/z = 421 [M$^+$] Anal. found: C: 51.20; H: 4.53; N: 9.90; S: 7.46; P: 7.24. Calcd. for $C_{18}H_{20}N_3O_5SP$ (421.41): C: 51.30; H: 4.78; N: 9.97; S: 7.60; P: 7.35.

Compound **XVc**: pale yellow crystals, m.p. 195°C, cryst., solvent: benzene; yield = 3.07 g (75%); IR ν: 3400 (NH), 1258 (P=O), 1025 (P-O-alkyl) cm^{-1}; ^{1}H NMR (DMSO-d$_6$) = δ 1.10, 1.25 (2t, 6H, 2CH_3), 3.85, 4.20 (2q, 4H, 2CH_2), 5.55 (dd, 1H, CH; J_{HP} = 22.4 Hz, J_{HH} = 9.3 Hz), 7.05-7.85 (m, 8H, aromatic protons), 9.28 (dd, 1H, NH, J_{HH} = 9.3 Hz); MS: m/z = 410 [M$^+$] Anal. found: C: 52.59; H: 4.85; N: 6.51; S: 7.66; Cl: 8.43; P: 7.51. Calcd. for $C_{18}H_{20}N_2O_3SClP$ (410.86): C: 52.62; H: 4.90; N: 6.81; S: 7.80; Cl: 8.62; P: 7.53.

REFERENCES

[1] H. Ulrich, The Chemistry of Imidoyl Halides (Plenum Press, New York, 1968), p. 173.

[2] H.M. Hassaneen, A. S. Shawali, and N. M. Elwan, *Heterocycles*, **31,** 1041 (1990).

[3] A. O. Abdel-Hamid, H. F. Zohdi, M. M. Sallam, and N. A. Ahmed, *Molecules*, **5,** 967 (2000).

[4] T. A. Abdallah, M. A. Darwish, and H. M. Hassaneen, *Molecules*, **7,** 494 (2002).

[5] N. R. Mohamed, *Heterocyclic Communication*, **5,** 433 (1999).

[6] A. W. Erian, N. R. Mohamed, and M. H. Hassaneen, *Synthetic Communication*, **29,** 1527–1534 (1999).

[7] N. R. Mohamed, M. M. T. Elsaidi, H. M. Hassaneen, and A. W. Erian, *Phosphorus, Sulfur and Silicon*, **179,** 521 (2004).

[8] N. R. Mohamed, M. M. T. Elsaidi, M. S. Ali, K. Pervez, and A. W. Erian, *Egypt. J. Chem.*, **47,** 475 (2004).

[9] R. F. Hudson, Structure and Mechanism in Organic Phosphorus Chemistry (Academic Press, New York, 1965), p. 131–140.

[10] A. S. Shawali, A. A. Abdelkalek, and A. R. Sayed, *J. of Chinese Chem. Soc.*, **46,** 693 (2001).

[11] R. F. Hudson, Structure and Mechanism in Organic Phosphorus Chemistry (Academic Press, New York, 1965), p. 90–91.

[12] R. G. Pearson and J. J. Songstad, *J. Amer. Chem. Soc.*, **89,** 1827 (1927).

[13] R. G. Pearson, *Science*, **151,** 172 (1966).

[14] B. Saville, *Angew. Chem. Intern. Ed. Engl.*, **6,** 928 (1967).

[15] W. L. M. Mosby and M. L. Silva, *J. Chem. Soc.*, **12,** 1003 (1965).

[16] E. F. V. Scriven and K. Turnbull, **88,** 351 (1988).

[17] J. S. Thayer and R. Wort, *Inorg. Chem.*, **3,** 306 (1961).

[18] Y. O. El-Khoshnia, *Heterocyclic Communication*, **5,** 77 (1999).

[19] M. H. N. Arsantous, Y. A. Issac, and L. S. Boulos, *Heteroatom Chem.*, **12,** 594 (2001).

[20] N. R. Mohamed, G. Abdel-Megeed, M. Younis, *Steriodes*, **70,** 131 (2005).