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Organophosphorus Chemistry 23 [1], The Reaction of α,β-Unsaturated Nitriles with Alkyl Phosphites and Phosphorus Ylides

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ABSTRACT

Wittig reagents **2** *react with furfurylidenemalonitrile* (**1a**) *and thienylidenemalonitrile* (**1b**) *to give a mixture of products* (**6** *and* **7**). *Compound* **1b** *reacts with dialkyl phosphites* (**3**) *and trialkyl phosphites* (**4**) *to give the phosphonate 1:1 adducts* **9** *and* **12**, *respectively. Structures of the new products were confirmed on the basis of elemental analyses and spectral studies.*

INTRODUCTION

The chemistry of α,β-unsaturated nitriles has received a tremendous amount of interest both from theoretical and synthetic viewpoints [2, 3]. Although the reactivity of this class of compounds has been tested with a variety of reagents [3], no attention has been paid to its potentialities with respect to phosphorus ylides. In response to our growing interest in organophosphorus syntheses utilizing α,β-unsaturated nitriles [4–7], we present now a study on the reaction of furfurylidenemalonitrile (**1a**) (also known as 1,1-dicyano-2-(2-furyl) ethylene and 2-furanylmethylenepropane dinitrile) and its sulfur analogue (**1b**) with resonance-stabilized ylide phosphoranes (**2a–c**). A comparative study of the behavior of **1b** toward dialkyl phosphites (**3a–c**) and trialkyl phosphites (**4a–c**) is also reported.

RESULTS AND DISCUSSION

Furfurylidenemalonitrile (**1a**) was found to react with carbethoxymethylenetriphenylphosphorane (**2b**) in toluene at reflux for 12 h to give a mixture of two main products (A + B), which could be separated by column chromatography. Triphenylphosphine was also isolated and identified.

The first product (**A**, 53%) was assigned structure **6b** because its ^{31}P-NMR spectrum (in $CDCl_3$) showed a signal at δ 24.6 that agrees with an ylide structure [8], and it excludes an alternative betaine structure such as **5** ($Y = 0$, $R = COOC_2H_5$). Moreover, the ^{1}H-NMR spectrum of **6b** (in $CDCl_3$) showed two signals due to the exocyclic methine protons at δ 3.15 (d of d, H(d), $^3J_{HP}$ = 10.5 Hz) and δ 3.63 (d of d, H(e), $^4J_{HP}$ = 6.2 Hz). The main features of the IR spectrum of **6b** (in KBr, expressed in cm^{-1}) were the presence of absorption bands at 2215 (–CN) and 1730 (C=O, ester). It also revealed the presence of strong bands around 1680 and 1510 cm^{-1}, characteristic of the C=P group absorption [9], and around 1430 and 990 for the P–C (phenyl) absorption. The second product (B, ~14%) has been found to be devoid of phosphorus, as is inferred from its elemental analyses and ^{31}P-NMR measurements. It was identified as 1,1-dicyano 2-(2-furyl)-2-(carbethoxymethyl)ethylene (**7b**) for the following reasons: (a) Its elemental analysis and molecular weight determination (MS) agreed with the molecular formula, $C_{12}H_{10}N_2O_3$; (b) The IR spectrum of **7b** (KBr, cm^{-1}) showed a strong band due to the exocyclic C=C group at 1645 cm^{-1} (recorded with **1a** at 1640 cm^{-1}). Bands were also present at 2230 (–CN), 1715 (C=O, ester) and 1605 (C=C, furan) [10]; (c) The ^{1}H-NMR spectrum of **7b** (in $CDCl_3$, δ) showed sig-

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Dedicated to Professor M. Sidky on the occasion of his sixty-second birthday.

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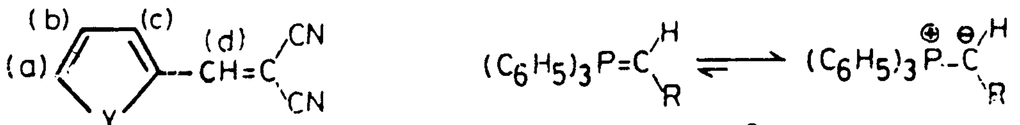


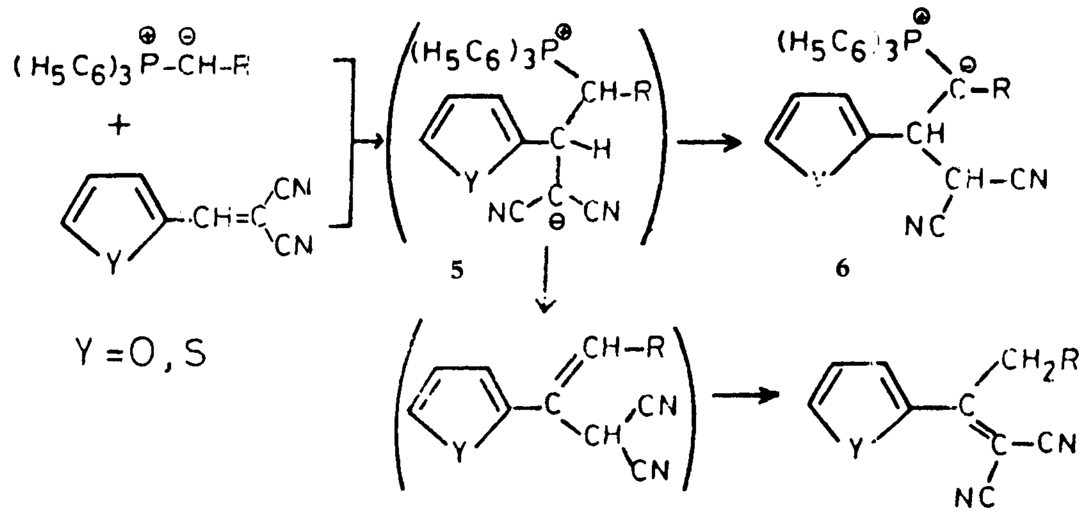
1a, Y = O
b, Y = S

2

$(RO)_2\ddot{P}OH \rightleftharpoons RO_2P(O)H$ **3**

$(RO)_3P$ **4**

Cpd.	R	Cpd.	R
2a	$COOCH_3$	**3,4 a**	CH_3
b	$COOC_2H_5$	**b**	C_2H_5
c	COC_6H_5	**c**	C_3H_7-i



8 (not detected)

7

Cpd.	Y	R	Cpd.	Y	R
a	O	$COOCH_3$	**d**	S	$COOCH_3$
b	O	$COOC_2H_5$	**e**	S	$COOC_2H_5$
c	O	COC_6H_5	**f**	S	COC_6H_5

SCHEME 1

nals at 1.25 (t, 3H, ethoxy-CH_3), and 2.65 (s, 2H, CH_2), and at 4.35 (q, 2H, OCH_2) [10]. The familiar pattern of the furan ring protons was represented by signals at δ 6.42 (H(a), d, J_{HH} = 2.5 Hz), 6.59 (H(b), d of d, J_{HH} = 3 Hz) and 7.46 (H(c), d, J_{HH} = 2.5 Hz). Evidence against an alternative structure such as **8** ($R = COOC_2H_5$) is the absence of absorption of olefinic nature (other than the furans) in the region δ 5.0–8 as well as the absence of a signal (singlet) due to the $CH(CN)_2$ group proton in the region of δ 3–5 [10].

The reaction products of **1a** with **2a,c** (and of **1b** with **2a–c**) were assigned analogous structures (see **6a–f** and **7a–f**) on the basis of comparable spectroscopic arguments (see Tables **1** and **2**).

Apparently, the initial step involves nucleophilic attack by the anionic center in **2** on the more electrophilic site of the exocyclic ethylenic linkage in **1** to give the resonance hybrid **5**. The R-moiety in **5**, which is electron-withdrawing in nature, would stabilize formation of the phosphorus ylide structure **6** (major) via the migration of the proton α to the positive phosphorus atom to the electron rich carbanionic center of the initially formed intermediate. On the other hand, the dipolar form **5** undergoes an elimination reaction [11] with ejection of TPP to produce **7** as a minor reaction product (Scheme 1).

Thienylidenemalonitrile (**1b**, also known as 2-thienylmethylenepropanedinitrile) has been found to react with dimethyl-, diethyl-, and/or diisopropyl phosphites (**3a–c**) at 100°C in absence of solvent to give 1:1 adducts for which structures **9a–c** were assigned (Scheme 2) for the following reasons: (a) Satisfactory elementary analyses and molecular weight determinations (MS) were recorded for all products; (b) Adducts **9** showed positive chemical shifts around δ 23 (vs. 85% H_3PO_4) in their ^{31}P-NMR spectra, which indicates the presence of a P–C linkage in their molecules [8]; (c) Upon heating adducts **9a–c** above their melting points under reduced pressure, they regenerated the starting materials

TABLE 1 Analytical Data and Physical Properties of the Products **6** and **7**

				Anal. Found/(Calcd.)%					
Compound[a]	*Yield*[b] *in %*	*mp °C*	*Mol. Form. (M.Wt)*	*C*	*H*	*N*	*P*	*S*	*M⁺ m/z%*
6a	50	130–131[c]	$C_{29}H_{23}N_2O_3P$	72.77	4.83	5.74	6.29	—	478
			(478.48)	(72.79)	(4.84)	(5.85)	(6.47)	—	28
6b	53	167–170[d]	$C_{30}H_{25}N_2O_3P$	73.09	5.10	5.65	6.07	—	492
			(492.51)	(73.16)	(5.11)	(5.68)	(6.28)	—	22
6c	62	182–184[d]	$C_{34}H_{25}N_2O_2P$	77.76	4.82	5.31	5.87	—	524
			(524.55)	(77.85)	(4.80)	(5.33)	(5.90)	—	33
6d	40	137–139[c]	$C_{29}H_{23}N_2O_2PS$	70.33	4.62	5.58	6.09	6.37	494
			(494.55)	(70.43)	(4.68)	(5.66)	(6.26)	(6.48)	31
6e	46	144–145[d]	$C_{30}H_{25}N_2O_2PS$	70.78	4.92	5.55	6.17	6.26	508
			(508.59)	(70.85)	(4.95)	(5.50)	(6.09)	(6.30)	18
6f	58	156–157[d]	$C_{34}H_{25}N_2OPS$	75.47	4.64	5.09	5.66	5.90	540
			(540.62)	(75.53)	(4.66)	(5.18)	(5.72)	(5.93)	22
7a	10	74–75[e]	$C_{11}H_8N_2O_3$	60.80	3.67	12.87	—	—	216
			(216.19)	(61.11)	(3.72)	(12.95)	—	—	48
7b	14	66–67[e]	$C_{12}H_{10}N_2O_3$	62.56	4.33	12.05	—	—	230
			(230.22)	(62.60)	(4.38)	(12.17)	—	—	55
7c	17	91–93[d]	$C_{16}H_{10}N_2O_2$	73.21	3.67	10.57	—	—	262
			(262.27)	(73.27)	(3.84)	(10.68)	—	—	60
7d	8	61–63[e]	$C_{11}H_8N_2O_2S$	56.46	3.43	11.79	—	13.67	232
			(232.26)	(56.88)	(3.47)	(12.06)	—	(13.80)	42
7e	10	56–57[e]	$C_{12}H_{10}N_2O_2S$	58.22	4.14	11.18	—	13.88	246
			(246.28)	(58.52)	(4.09)	(11.37)	—	(13.01)	55
7f	20	80–81[f]	$C_{16}H_{10}N_2OS$	69.01	3.60	10.23	—	11.26	278
			(278.33)	(69.04)	(3.62)	(10.06)	—	(11.52)	68

[a] IR spectra of compounds **6** and **7** also showed bands around 2220 (CN) and around 1610 ($>C=C<$, furan or thiophene). Compounds **6a–f** have signals ~1700 (C=O), 1650, 1540 (C=P), and at 1450 cm^{-1} (*P*-phenyl) in their IR spectra, while compounds **7a–f** have absorption bands at ~1710 (C=O) and at ~1650 (C=C) in their IR spectra.

[b] Yields are approximate.

solvent of cryst:

[c] Benzene.

[d] Chlorform.

[e] Pentane.

[f] Cyclohexane.

TABLE 2 ^{1}H and ^{31}P NMR data[a] for Compounds **6** and **7**

	$^1H(\delta, ppm)^{b,c}$				
Compound	*C–CH$_3$*	*–CH(d)*	*–CH(e)*	*OCH$_3$, OCH$_2$*	*(δ^{31P}, ppm)*
6a		3.15 (dd, 1H) $^3J_{HP}$ = 9.2 J_{HH} = 18.1	3.63 (dd, 1H) $^4J_{HP}$ = 6.5 J_{HH} = 18.1	3.80 (s, 3H)	21.7
6b	1.3 (t, 3H) J_{HH} = 6.4	3.15 (dd, 1H) $^3J_{HP}$ = 10.58 J_{HH} = 18.03	3.63 (dd, 1H) J_{HP} = 6.2 J_{HH} = 18.03	4.26 (q, 2H) J_{HH} = 6.06	24.6
6c		3.2 (dd, 1H) $^3J_{HP}$ = 11.5 J_{HH} = 16.14	3.54 (dd, 1H) J_{HP} = 6.5 J_{HH} = 16.14		20.3
6d		2.95 (dd, 1H) $^3J_{HP}$ = 10.50 J_{HH} = 18.55	3.55 (dd, 1H) $^4J_{HP}$ = 4.5 J_{HH} = 18.55	4.24 (s, 3H)	24.6
6e	1.21 (t, 3H) J_{HH} = 6.06	3.4 (dd, 1H) $^3J_{HP}$ = 13.51 J_{HH} = 18.0	3.72 (dd, 1H) $^4J_{HP}$ = 4.5 J_{HH} = 18.0	4.16 (q, 2H) J_{HH} = 6.07	20.3
6f		3.1 (dd, 1H) $^3J_{HP}$ = 10.52 J_{HH} = 16.55	3.5 (dd, 1H) $^4J_{HP}$ = 4.5 J_{HH} = 16.55		22.7
7a		2.7 (s, 2H)		3.88 (s, 3H)	—
7b	1.25 (t, *J*6.3, 3H)	2.65 (s, 2H)		4.35 (q, *J*7.4, 2H)	—
7c		3.21 (s, 2H)			
7d		2.48 (s, 2H)		3.85 (s, 3H)	
7e	1.61 (t, *J*7.2, 3H)	2.53 (s, 2H)		3.94 (q, *J*7.08, 2H)	
7f		2.88 (s, 2H)			

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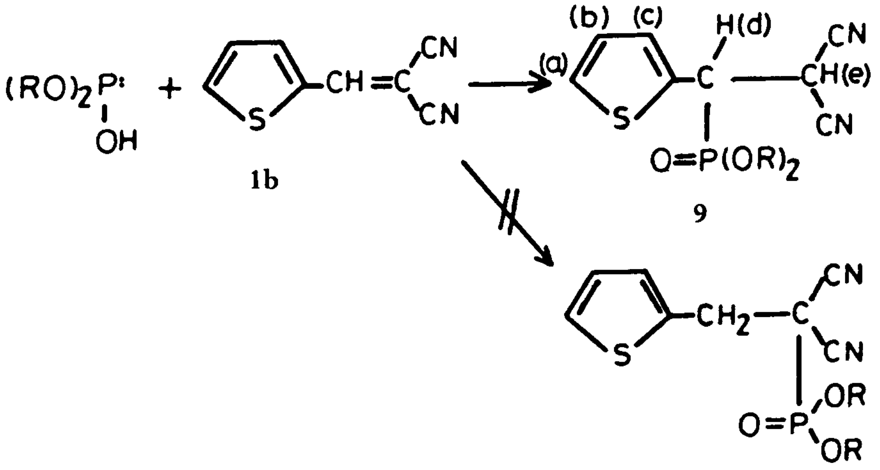
[a] See experimental for details for NMR experiments.
[b] Coupling constant is recorded in Hertz.
[c] Furan, thiophene and aromatic hydrogen protons lie in δ 6.4–8.4 region.



1b

9

10 (not formed)

SCHEME 2

(**1b** + DAP); (d) The IR spectrum (KBr, cm^{-1}) of **9a**, taken as an example, revealed the presence of absorption bands at 2230 (CN), 1610 (C=C, thiophene), 1260 (P=O, free), and at 1050 (P–O–CH_3) [10]; (e) The ^1H-NMR spectrum of **9a** ($CDCl_3$, δ) showed the thiophene ring-protons as a multiplet centered at 7.4 (3H). The two methoxyl groups appeared as a doublet (6H, $^3J_{HP}$ = 12 Hz) at δ 3.77. On the other hand, the exocyclic ethylenic proton (d) present in the ^1H-NMR spectrum of **1b** at δ 7.45 was absent in the spectrum of **9a**. Instead, each of the exocyclic methine protons (2H) in **9a** appeared as a doublet of doublets. That of proton (**d**) was centered at 4.0 with $^2J_{HP}$ = 22.6 Hz, while the other proton [*H*(e), C*H*$(CN)_2$] was centered at 4.54 with $^3J_{HP}$ = 12 Hz. The presence of the AB system, H(d)–H(e), and lack of a signal resulting from a methylene group (see **10**) in the ^1H-NMR spectrum of **9a** confirm the assigned structure **9** and rule out the other alternative structure **10** from further consideration.

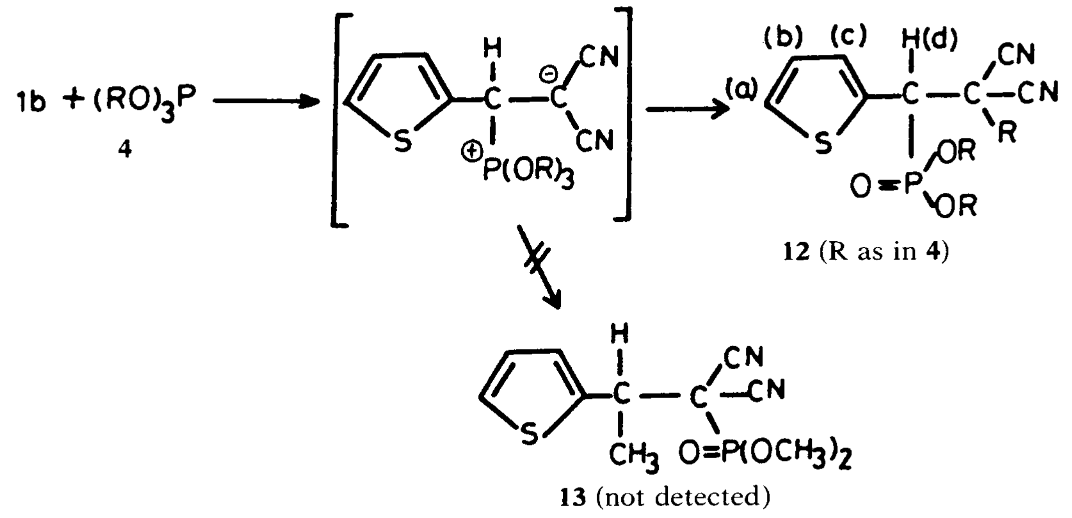
The reaction of **1b** with trimethyl-, triethyl-, and triisopropyl phosphites (**4a–c**) was completed by heating the reactants at 100°C in the absence of solvent for 6 h to give colorless crystalline adducts for which structures **12a–c** were assigned (Scheme 3). Evidence for structure **12** are: (a) The ^{31}P-NMR spectra of **12** showed chemical shifts at δ 19 indicating that they are phosphonates; (b) Elemental analysis and MS for **12a**, taken as example, corresponded to $C_{11}H_{13}N_2O_3PS$; (c) The IR spectrum of **12a** (KBr, cm^{-1}) disclosed strong absorption bands at 1275 (P=O, free) and at 1030 cm^{-1} (P–O–CH_3); (d) The ^1H-NMR spectrum of **12a** ($CDCl_3$, δ) showed protons of the $P(O)(OCH_3)_2$ groups (6H) as a doublet ($^3J_{HP}$ = 12 Hz) at δ 3.63. It also showed a doublet (3H, $^4J_{HP}$ = 4.5) at δ 1.90. This value is in accordance with a chemical shift expected for a methyl group on an sp^3-carbon atom containing two electron-withdrawing groups [10]. The exocyclic methine proton (**d**) appeared as a doublet at δ 4.37 ($^2J_{HP}$ = 24.5 Hz). The data recorded for proton (d) can positively confirm the assigned structure **12** and exclude structure **13**, which would predict a quintet for the exocyclic methine proton and a doublet of doublets resulting from the CH_3-protons.

CONCLUSIONS

The reaction of **1a,b** with stabilized ylide–phosphoranes (**2**) to give products of type **7** represents a novel process for alkylating α,β-unsaturated nitriles. This new finding supplements the wide aspects for utilization of Wittig reagents in preparative work [11, 12]. In addition, the reaction of **1b** with **4a–c** to give **12** adds a new dimension to the line we have recently explored [4–7] for C-alkylation of α-β-unsaturated nitriles by trialkyl phosphites. It is also important to note that C-alkylation of the α-β-unsaturated system in **1** by phosphorus–ylides and TAP is regiospecific.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin Elmer Infracord Spectrometer Model 197 (Grating) in KBr. The ^1H-NMR spectra are recorded with a Bruker Spectrometer Model WH-90 and the chemical shifts are recorded in δ relative to TMS. The ^{31}P-NMR spectra were taken on a Varian CFT20 (vs. external 85% H_3PO_4). The mass spectra were done at 70 eV with MS-50 Kratos (A.E.I.) Spectrometer provided with data system. Elemental analyses were carried out at the "Microanalysis Laboratory, National Research Centre, Cairo."



12 (R as in 4)

13 (not detected)

SCHEME 3

Reaction of α,β-Unsaturated Nitriles (**1a,b**) *with Phosphorus Ylides* (**2a–c**): *General Procedure*

To a suspension of nitrile **1a** [13] or **1b** [14] (0.01 mol) in dry toluene (30 mL) was added a solution of ylide **2a** [15], **2b** [15], and/or **2c** [16] (0.011 mol) in the same solvent (20 mL), and the reaction mixture was refluxed for 10–15 h (TLC). The reaction mixture was then evaporated at 60°C under reduced pressure. The solid product was redissolved in methanol (100 mL) and evaporated to dryness in the presence of silica gel (5 g). The mixture was then added to a column previously charged with silica gel in petroleum ether. The column was developed with petroleum ether followed by petroleum ether containing increasing amounts of ethyl acetate. A fraction from 100% petroleum ether afforded colorless needles, mp 80°C (ca. 70% yield) of triphenylphosphine (mp, mixed mps, and comparative IR spectra) [17].

The next fraction (up to 4:1 v/v petroleum ether/ethyl acetate) eluted a yellow substance that was recrystallized from the suitable solvent to give **7a–f**. For yields, mps, physical, and analytical data see Tables **1** and **2**.

The next fraction (up to 5:5 v/v petroleum ether/ethyl acetate) yielded a brown substance, recrystallized to give **6a–f** (see Tables **1** and **2**).

Reaction of Thienylidenemalonitrile (**1b**) *with Dialkyl Phosphonates* (**3a–c**): *General Procedure*

A mixture of **1b** (0.01 mol) and dialkyl phosphites (dimethyl-, diethyl-, or diisopropyl phosphite) (6 mL) was heated in the absence of solvent at 100°C for 10 h. After the reaction had been completed (TLC), the volatile materials were evaporated, *in vacuo*, and the residual substance was collected and recrystallized from the appropriate solvent (see Table 3) to give compounds **9a–c**. Percentage yields, physical, and analytical data for compounds **9** are given in Tables **3** and **4**.

Action of Heat on **9**

The phosphonate adduct **9a** (0.5 g), taken as example, was heated (bath temperature, 230°C) for 1 h under reduced pressure (5 mm Hg) in a cold finger sublimator. The reaction vessel was left to cool and ethyl alcohol (5 mL) was added. The crystals that separated were recrystallized from ethanol to give the nitrile **1b** (identified by mp, mixed mps and comparative IR, PMR, and MS spectra [14]. Dimethyl phosphonate was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali [18].

Reaction of Thienylidenemalonitrile (**1b**) *with Trialkyl Phosphites* (**4a–c**): *General Procedure*

A mixture of **1b** (0.01 mol) and trialkyl phosphites (trimethyl-, triethyl-, or triisopropyl phosphite) (5 mL) was heated in the absence of solvent at 100°C for 6 h. After removal of the volatile materials, *in vacuo*, the residue was triturated with light petroleum ether and left to cool. The solid was collected, and recrystallized from a suitable solvent to give

TABLE 3 Analytical Data and Physical Properties of the Products **9** and **12**

Compound[a]	*Yield in %*	*mp °C*	*Mol. Form. (M.Wt)*	*Anal. Found/(Calcd.), %* C	H	N	P	S	*M⁺ m/z%*
9a	76	114–116[b]	$C_{10}H_{11}N_2O_3PS$	45.02	4.14	10.33	11.22	11.62	270
			(270.24)	(44.49)	(4.10)	(10.36)	(11.46)	(11.86)	100
9b	68	106–107[c]	$C_{12}H_{15}N_2O_3PS$	48.27	5.01	9.27	10.09	10.84	298
			(298.25)	(48.32)	(5.06)	(9.39)	(10.38)	(10.72)	100
9c	70	146–148[d]	$C_{14}H_{19}N_2O_3PS$	51.35	5.55	8.53	9.18	9.77	326
			(326.35)	(51.53)	(5.87)	(8.58)	(9.49)	(9.82)	100
12a	75	107–109[e]	$C_{11}H_{13}N_2O_3PS$	46.27	4.57	9.86	10.94	11.06	284
			(284.27)	(46.47)	(4.60)	(9.85)	(10.89)	(11.28)	68
12b	82	87–90[c]	$C_{14}H_{19}N_2O_3PS$	51.50	5.48	8.09	9.44	9.99	326
			(326.35)	(51.52)	(5.86)	(8.58)	(9.49)	(9.82)	75
12c	60	120–121[f]	$C_{17}H_{25}N_2O_3PS$	55.71	6.73	7.56	8.48	8.27	368
			(368.43)	(55.42)	(6.84)	(7.60)	(8.41)	(8.70)	83

[a] IR spectra of the products **6** and **7** also showed bands around 2220 (CN) and around 1610 ($>C=C<$, furan or thiophene). Compounds **9a–c** and **12a–c** gave absorption bands at ~1250 (P=O) and at ~1035 cm^{-1} (P–O–C) in their IR spectra.

[b] Benzene/pet. ether (b.r. 40–60°C).

[c] Cyclohexane.

[d] Ether.

[e] Pentane.

[f] Acetone.

TABLE 4 ^1H and ^{31}P NMR data[a] for the adducts **9** and **12**

	$^1H(\delta, ppm)$[b,c]					
Compound	C–CH$_3$	C–CH$_2$, C–CH	OCH$_3$, OCH$_2$, OCH	HC–P	C–CH	($\delta^{31}P$, ppm)
9a			3.65, 3.83 (2d)[d] $^3J_{HP} = 12.0$ 6H	4.0 (d of d) $^2J_{HP} = 22.6$ $J_{HH} = 15.4$ 1H	4.54 (d of d) $^3J_{HP} = 12.0$ $J_{HH} = 15.4$ 1H	23.0
9b	1.22 (2dt) $^3J_{HP} = 12.0$ $J_{HH} = 4.3$ 6H		4.08 (2 qt)[e] $J_{HP} = 12.05$ $J_{HH} = 4.3$ 4H	4.2 (d of d) $^2J_{HP} = 21.8$ $J_{HH} = 15.6$ 1H	4.6 (d of d) $^3J_{HP} = 12.05$ $J_{HH} = 15.6$ 1H	23.2
9c	1.31 (2 dd) $^3J_{HP} = 11.5$ $J_{HH} = 4.0$ 12H		4.2, 4.62 (2m)[f] 4H			22.6
12a	1.93 (dd) $^4J_{HP} = 4.5$ $J_{HH} = 6.2$ 3H		3.5, 3.7 (2d) $^3J_{HP} = 13.5$ 6H	4.37 (dd) $^2J_{HP} = 24.5$ $J_{HH} = 6.2$ 1H		19.9
12b	1.28 (m) 9H	2.13 (q) $J_{HH} = 6.2$ $J_{HP} = 4.5$ 2H	4.19 (2 qt) $J_{HH} = 6.2$ $J_{HP} = 11.5$ 4H	4.4 (dd) $^2J_{HP} = 24.0$ $J_{HH} = 5.5$ 1H		19.9
12c	1.25 (m) 18H	2.84 (sept.) $J_{HH} = 6.4$ $J_{HP} = 4.5$ 1H	4.55 (2 sept.) $J_{HH} = 6.4$ $J_{HP} = 11.5$ 2H	4.68 (dd) $^2J_{HP} = 24.5$ $J_{HH} = 5.8$ 1H		18.9

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[a] See experimental for details for NMR experiments.

[b] Coupling constant is recorded in Hertz.

[c] Thiophene hydrogen protons lie in δ 6.4–7.8 ppm region.

[d] The two methoxyl groups attached to the phosphorus atom appeared as two doublets. This splitting is probably the result of the asymmetry of the molecule [7].

[e] qt: quintet.

[f] The signal appears as a complex multiplet wherein the exocyclic methine protons (2H) are obscured by the two septets.

compounds **12a–c**. Physical and analytical data for compounds **12** are presented in Tables **3** and **4**.

REFERENCES

[1] For part 22, see W. M. Abdou, M. D. Khidre, M. R. Mahran, *Phosphorus, Sulfur and Silicon, 61,* 1991, 83.

[2] A. F. Meyer, J. C. Sircar: Addition to the Cyano-group to form Heterocycles, in Z. Rapaport (ed): *The Chemistry of Cyano Group,* John Wiley and Sons, New York, p. 341 (1970).

[3] F. Freeman, *Chem. Revs., 69,* 1969, 591; S. Kambe, A. Sakurai, H. Midorikawa, *Synthesis,* 1981, 531.

[4] M. R. Mahran, W. M. Abdou, N. M. Abdelrahman, M. M. Sidky, *Phosphorus, Sulfur and Silicon, 45,* 1989, 47.

[5] M. R. Mahran, W. M. Abdou, N. A. F. Ganoub, H. A. Abdallah, *Phosphorus, Sulfur and Silicon, 57,* 1991, 217.

[6] W. M. Abdou, N. A. F. Ganoub, M. R. Mahran, *Bull. Chem. Soc. (Japan), 64,* 1991, 747.

[7] W. M. Abdou, M. D. Khidre, M. R. Mahran, *J. Prakt. Chem., 332,* 1990, 1029.

[8] M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark, J. R. van Wazer, in *Topics in Phosphorus Chemistry,* vol. 5, Interscience Publishers, New York, pp. 227–447 (1967).

[9] F. Ramirez, O. P. Madan, C. P. Smith, *J. Org. Chem., 30,* 1965, 2284; F. Ramirez, O. P. Madan, S. R. Heller, *J. Am. Chem. Soc., 87,* 1965, 731.

[10] R. M. Silverstein, G. C. Bassler, T. C. Morril, *Spectroscopic Identification of Organic Compounds,* John Wiley and Sons, Inc., New York, 1981.

[11] I. Gosney, A. G. Rowley, Wittig Reactions, in J. I. G. Cadogan (ed): *Organic Phosphorus Reagents in Organic Synthesis,* Academic Press, London, 1979.

[12] A. Wm. Johnson, *Ylid Chemistry,* Academic Press, New York, 1966.

[13] R. Heuck, *Chem. Ber., 28,* 1985, 2253.

[14] S. W. Schneller, D. R. Moore, *J. Org. Chem., 40,* 1975, 1840.

[15] H. J. Bestmann, O. Kratzer, *Chem. Ber., 95,* 1962, 1894.

[16] F. Ramirez, S. Dershowitz, *J. Org. Chem., 22,* 1957, 41.

[17] A. Michaelis, I. Gleichman, *Chem. Ber., 15,* 1962, 1894.

[18] B. C. Saunders, B. P. Stark, *Tetrahedron, 4,* 1958, 187.