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### THE REACTION OF ALKYL PHOSPHITES WITH $\alpha,\beta$ -UNSATURATED NITRILES, ANILS AND OXIMES DERIVED FROM AROMATIC ALDEHYDES

Mohamed Refat H. Mahran<sup>a</sup>; Taghrid S. Hafez<sup>a</sup>; Maged Mories Henary<sup>a</sup>

<sup>a</sup> Dept. of Pesticide Chemistry, National Research Centre, Cairo, Egypt

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## THE REACTION OF ALKYL PHOSPHITES WITH $\alpha,\beta$ -UNSATURATED NITRILES, ANILS AND OXIMES DERIVED FROM AROMATIC ALDEHYDES

MOHAMED REFAT H. MAHRAN<sup>1</sup>, TAGHRID S. HAFEZ and  
MAGED MORIES HENARY

*Dept. of Pesticide Chemistry, National Research Centre, Cairo, Egypt*

*(Received 21 January, 1996; Revised 8 April, 1997)*

*Dedicated to Professor M.M. Sidky on the occasion of his 67th Birthday*

Reactions of dialkyl phosphites (**DAP**, **1a,b**) and trialkyl phosphites (**TAP**, **2a,b**) with the  $\alpha,\beta$ -unsaturated nitriles (**3a,b** and **4a,b**) as well as with anils (**5a** and **6**) derived from aromatic aldehydes (vanillin and/or piperonal) are reported. Structures of the new phosphonate products (cf. **7,8,15,16** and **17**) were based upon compatible elementary and spectroscopic results. Tervalent phosphites (**TAP**, **2a,b**) and triphenylphosphine convert vanillin-oxime (**5b**) into 4-hydroxy-3-methoxybenzonitrile (**19**). Possible reaction mechanisms to account for formation of compounds **7a-d**, **8a,b** and **19** were also postulated.

**Keywords:** Alkyl phosphites; vanillin, piperonal;  $\alpha,\beta$ -unsaturated nitriles; imines; oximes

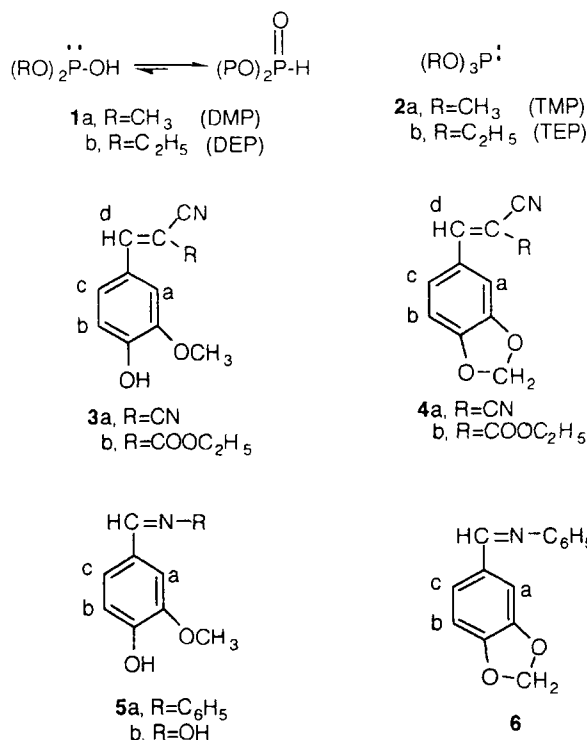
### INTRODUCTION

The first report on the behaviour of  $\alpha,\beta$ -unsaturated nitriles toward alkyl phosphites has appeared from this laboratory.<sup>2</sup> It explored a new type of attack by tervalent phosphite esters on these systems. In the line with our growing interest in this area,<sup>3-8</sup> we have now studied the reaction of dialkyl phosphites (**1a,b**) and trialkyl phosphites (**2a,b**) with the  $\alpha,\beta$ -unsaturated nitriles **3a,b** and **4a,b**. The latter substrates are accessible through interacting vanillin or piperonal with the appropriate active methylene derivative. A comparative study on the reactivity of anils (**5a**, **6**) and oxime **5b** of the same aldehydes toward the phosphite reagents, is also undertaken.

## RESULTS AND DISCUSSION

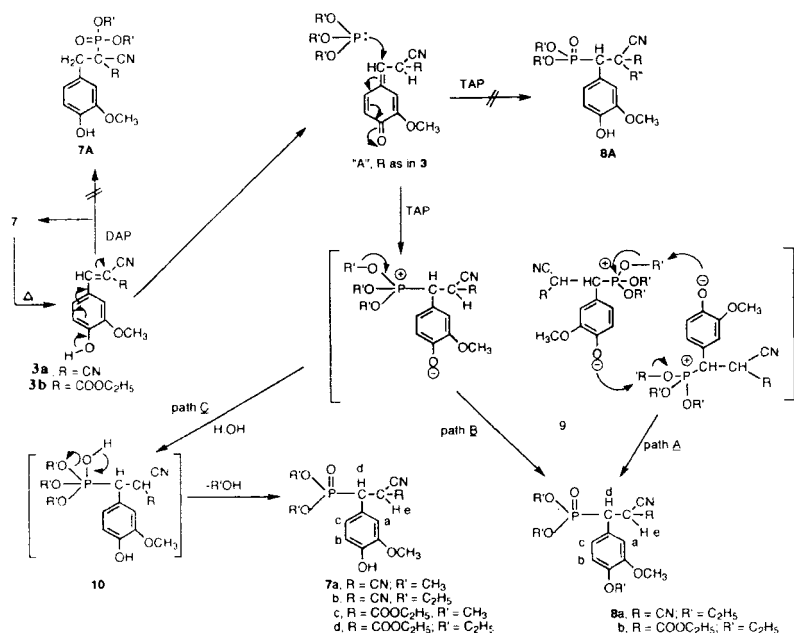
We have found that  $\alpha,\alpha$ -dicyano-(4-hydroxy-3-methoxy)styrene (**3a**) reacts with trimethyl phosphite (*TMP*, **2a**) at 100 °C in absence of solvent to give a yellow crystalline product for which structure **7a** was assigned for the following reasons : (a) Its elementary analyses and molecular weight determination (MS) corresponded to  $C_{13}H_{15}N_2O_5P$ , (b) It recorded a positive chemical shift at  $\delta$  21.86 in its  $^{31}P$ -NMR spectrum (vs 85%  $H_3PO_4$ ) confirming its phosphonate structure.<sup>9</sup> (c) The IR spectrum of  $\alpha,\alpha$ -dicyano- $\beta$ -dimethylphosphinyl- $\beta$ -(4-hydroxy-3-methoxyphenyl) ethane (**7a**) revealed the presence of strong absorption bands at 3310 (OH), 2235 (CN), 1590, 1490 (C=C, aromatic), 1160 (P=O, free)<sup>10</sup> and at 1060  $cm^{-1}$  (POCH<sub>3</sub>).<sup>10</sup> Moreover, it lacked the strong ethylenic C=C band which is present in the IR spectrum of **3a** at 1620  $cm^{-1}$ , (d) the  $^1H$ -NMR spectrum of **7a** (in DMSO,  $\delta$ ppm) showed protons of the OCH<sub>3</sub> groups attached to phosphorus as two doublets (each with  $^3J_{HP}$ =12 Hz) at 3.75 and 3.45. Apparently, the asymmetry of the molecule due to presence of a stereo-centre, would render the two methoxyl groups diastereotropic and hence anisochronous, resulting thus in the observed splitting pattern.<sup>11</sup> On the other hand, the exocyclic ethylenic proton Hd (-CH=C) present in the  $^1H$ -NMR spectrum of **3a** as a singlet at 7.66 ppm was absent in the spectrum of **7a**. Instead, two doublets were shown in the spectrum of **7a** due to the exocyclic methine protons (2H). That of proton d(P-CH-) was centred at 4.30 with  $^2J_{HP}$ =20 Hz while the other proton He[-CH(CN)<sub>2</sub>] was centred at 5.5 ppm with  $^3J_{HP}$ =12 Hz. These data rule out an alternative structure like **7A** (R=CN, R'=CH<sub>3</sub>; R'=H). Compound **7a** was also unequivocally prepared and identified (m.p., mixed m.p. and comparative IR spectra) by allowing **3a** to react with DMP, (**1a**) at 100 °C in absence of solvent.

Upon reacting **3a** with triethyl phosphite (**2b**) on the other hand, a mixture of two products (**A+B**) was obtained. The first product (**A**, 65%) was identified as  $\alpha,\alpha$ -dicyano- $\beta$ -diethylphosphinyl- $\beta$ -(4-hydroxy-3-methoxyphenyl)ethane (**7b**) by comparing its physical and spectral properties with those of an authentic sample unequivocally prepared by reacting **3a** with diethyl phosphite (DEP, **1b**). The second product (**B**, 35%) was formulated as  $\alpha,\alpha$ -dicyano- $\beta$ -diethylphosphinyl- $\beta$ -(4-ethoxy-3-methoxy-phenyl) ethane (**8a**) for the following reasons : (a) Its elementary analyses and molecular weight determination (MS) corresponded to  $C_{17}H_{23}N_2O_5P$ , (b) The



<sup>31</sup>P-NMR measurement (in CDCl<sub>3</sub>) for **8a** showed a positive chemical shift (*vs* 85% H<sub>3</sub>PO<sub>4</sub>) at δ 19.90 ppm which coincides with a phosphonate structure,<sup>9</sup> (c) Its IR spectrum (in KBr, cm<sup>-1</sup>) revealed the absence of (OH)-absorption bands in the 3500–3200 region. On the other hand, the spectrum showed strong bands at 2230 (CN), 1520 (C=C, aromatic), 1220 (P=O, free) and at 1050 (P-O-CH<sub>2</sub>CH<sub>3</sub>), (d) The upfield region in the <sup>1</sup>H-NMR spectrum of **8a** (in CDCl<sub>3</sub>, δppm) showed a triplet due to protons of the ethoxy-CH<sub>3</sub> group at 1.10 and two triplets due to protons of P(O)(OCH<sub>2</sub>-CH<sub>3</sub>) groups at 1.45 and 1.35. The spectrum also showed signals at 4.15 (2H, ethoxy-CH<sub>2</sub>, quartet), 4.00, 3.75 [4H, P(O)-CH<sub>2</sub>-CH<sub>3</sub>, 2 quintets] and 3.90 (3H, OCH<sub>3</sub>, s). The exocyclic methine protons (**2H**) appeared as doublet of doublets. Those of proton *d* (P-CHb) were centred at 3.5 with <sup>2</sup>J<sub>HP</sub>=20 Hz while those of proton *e* [-CH(CN)<sub>2</sub>] were centred at 4.45 ppm with <sup>3</sup>J<sub>HP</sub>=12 Hz. These data rule out an alternative structure

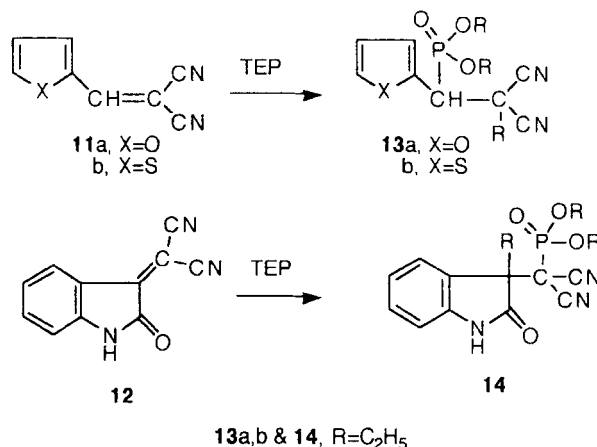
like **8a** ( $R=CN$ ,  $R'=R''=C_2H_5$ ), (e) Compound **8a** could be prepared and identified by reacting phosphonate **7b** with ethyl iodide in dry acetone in presence of anhydrous  $K_2CO_3$ . Similarly, phosphite **8b** was obtained by reacting compound **3b** with TEP (**2b**) as well as by the ethylation of phosphonate **7d** with ethyl iodide in presence of an alkali. The latter compound (**7d**) is obtained when **3b** is allowed to react with DEP (**1b**) at  $100^\circ C$  in absence of a solvent.



SCHEME 1

A mechanism for formation of adducts **7** and **8** from the reaction of TAP (**2a,b**) with **3a,b** is depicted in Scheme 1. This involves C-attack by the nucleophilic phosphite-phosphorus atom on **3a,b** which are best represented by the quinoid form "A" to give an intermediate dipolar species of type **9**. The latter ( $R'=C_2H_5$ ) undergoes ethyl-group translocation<sup>12-14</sup> either intermolecularly (path A) or intramolecularly (path B) to yield adducts **8a,b**. Concurrent with this process, the phospho-betaine **9** can be solvated by water unavoidably present in the reaction medium to yield transient **10** ( $R'=CH_3$  or  $C_2H_5$ ) which yields phosphonates **7a,b** via expul-

sion of an alcohol. The susceptibility of betaine **9** ( $R'=\text{CH}_3$ ) to the action of water recalls the facile hydrolysis of TMP as compared to the relative stability of its ethyl analogue.<sup>13</sup> It is worthwhile to state that the behaviour of compounds **3a,b** toward TAP is in complete variance with the behaviour of other  $\alpha,\beta$ -unsaturated nitriles derived from heterocyclic aldehydes<sup>5,8</sup>, e.g. furfurylidene malononitrile (**11a**) and thienylidene malononitrile (**11b**) and also from those derived from  $\alpha$ -diketones,<sup>2,3</sup> e.g. 3-dicyanomethylene-oxindole (**12**). Thus, compounds **3a,b** behave as *p*-quinone methides<sup>13,15</sup> towards TEP yielding structures **8a,b** via 1 : 6 addition. On the other hand, a mechanism of 1 : 2 addition is recorded in the reaction of **11a,b** and **12** with the same phosphite ester resulting in formation of structures **13a,b** and **14**, respectively (Scheme 2).

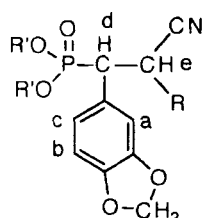


SCHEME 2

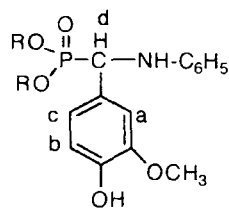
The reaction of  $\alpha,\alpha$ -dicyano-(3,4-methylenedioxy)styrene (**4a**) and ethyl  $\alpha$ -cyano- $\beta$ -(3,4-methylenedioxyphenyl)acrylate (**4b**) with DAP (**1a,b**) proceeded at 100 °C in absence of solvent to give the respective phosphonates **15a-d**. The same adducts were isolated and identified when the reaction of **4a** (or **4b**) with the appropriate TAP (**2a,b**) was conducted at 100 °C only in presence of a few drops of water. Structural reasonings for **15a-d** are : (a) Correct elementary analyses and molecular weight determination (MS) were obtained for all adducts and they also recorded positive chemical shifts around  $\delta$  21 ppm in their <sup>31</sup>P-NMR spectra (*vs* 85% H<sub>3</sub>PO<sub>4</sub>). (b) Upon thermolysis under reduced pressure, compounds

**15a-d** regenerated the starting materials [**4a** or (**4b**) and DAP], (c) The IR spectrum of **15a** (in KBr,  $\text{cm}^{-1}$ ), taken as representative example, disclosed the presence of strong absorption bands at 2840, 2820 (CH-aliphatic), 2250 (CN), 1610, 1510, 1490 (C=C, aromatic), 1250 (P=O, free) and at 1050 ( $\text{POCH}_3$ ), (e) The  $^1\text{H}$ -NMR spectrum of **15a** (in  $\text{CDCl}_3$ ,  $\delta\text{ppm}$ ) showed protons of the methoxyl groups attached to the phosphorus atom as two doublets (each with  $^3J_{\text{HP}}=12\text{ Hz}$ ) at 3.80 and 3.55. Protons of the methylenedioxy group gave a singlet at 6.05. The aromatics (3H) appeared in the spectrum of **15a** at 7.30 (Ha, s), 6.9 (Hb, d) and 7.10 (Hc, dd). The spectrum also disclosed the presence of two signals due to the exocyclic methine protons. That due to Hd appeared as dd ( $^2J_{\text{HP}}=20\text{ Hz}$ ) at 4.15 ppm and that due to He appeared as dd ( $^3J_{\text{HP}}=12\text{ Hz}$ ) at 5.15 ppm. For analytical, physical and spectroscopic analyses of **15a-d**, cf. Tables I and II.

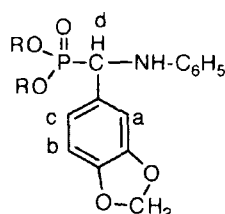
Whereas no reaction occurred between vanillin-anil (4-hydroxy-3methoxybenzylidene aniline, **5a**) and TMP (**2a**) or TEP(**2b**) even at  $100^\circ\text{C}$  for 12 hr, pale yellow to buff crystalline products assigned structures **16a** and **16b** were respectively obtained only when a few drops of water were introduced in the reaction medium. The same phosphonate products were equally produced and identified upon heating anil **5a** with DMP (**1a**) and DEP (**1b**), respectively.



- 15a**, R=CN ; R'=CH<sub>3</sub>  
 b, R=CN ; R'=C<sub>2</sub>H<sub>5</sub>  
 c, R=COOC<sub>2</sub>H<sub>5</sub> ; R'=CH<sub>3</sub>  
 d, R=COOC<sub>2</sub>H<sub>5</sub> ; R'=C<sub>2</sub>H<sub>5</sub>



- 16a**, R=CH<sub>3</sub>  
 b, R=C<sub>2</sub>H<sub>5</sub>



- 17a**, R=CH<sub>3</sub>  
 b, R=C<sub>2</sub>H<sub>5</sub>

## ALKYL PHOSPHITES

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TABLE I Physical, Analytical and IR Spectral Data of 7a-d and 8a,b

Compound (crystal's colour)	m. p. °C	Yield* %	Reaction time (hour)	Molecular formula (Mol. wt.)	Analysis Found / (Calcd.) %				M <sup>+</sup> (%) m/z	IR <sup>***</sup> (KBr, cm <sup>-1</sup> )				
					C	H	N	P		OH	CN	P=O	P-O-C	
<b>7a</b> (yellow)	158–160 <sup>a</sup>	90	(12)	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> P (310.5)	50.34 50.33	4.81 4.87	9.20 9.03	9.95 9.98	310 (25)	3310	2235	1250	1060	
<b>7b</b> (pale yellow)	95–97 <sup>a</sup>	85	(8)	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> P (338.3)	53.20 53.25	5.70 5.66	8.31 8.28	9.17 9.15	338 (60)	3200	2220	1250	1020	
<b>7c</b> (colourless)	127–129 <sup>a</sup>	90	(24)	C <sub>13</sub> H <sub>20</sub> NO <sub>7</sub> P (357.3)	50.35 50.43	5.64 5.64	3.93 3.92	8.88 8.67	357 (60)	3250	2220	1240	1030	
<b>7d</b> (colourless)	53–54 <sup>b</sup>	90	(12)	C <sub>17</sub> H <sub>24</sub> NO <sub>7</sub> P (385.4)	53.00 52.98	6.26 6.28	3.62 3.63	8.02 8.04	385 (100)	3370	2250	1230	1050	
<b>8a</b> (colourless)	107–109 <sup>b</sup>	35*	(8)	C <sub>17</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> P (366.4)	55.80 55.73	6.34 6.32	7.60 7.65	8.36 8.46	366 (30)	-	2230	1230	1050	
<b>8b</b> (yellow)	88–90 <sup>c</sup>	40**	(30)	C <sub>19</sub> H <sub>28</sub> NO <sub>7</sub> P (413.4)	55.10 55.20	6.84 6.82	3.40 3.39	7.58 7.49	414 (100)	-	2220	1235	1060	

\*) Approximated \*\*\*) 7c : a band at 1750 cm<sup>-1</sup> (C=O, ester)\*\*) Based on the reaction of (3b) with TEP 7d : a band at 1750 cm<sup>-1</sup> (C=O, ester)\*) Based on the reaction of (3a) with TEP 8b : a band at 1730 cm<sup>-1</sup> (C=O, ester)

a- Solvent of crystallization is (ethyl acetate)

b- Solvent of crystallization is (pet-ether 60–80 °C)

c- Solvent of crystallization is (cyclohexane)



TABLE I continued :  $^{31}\text{P}$  and  $^1\text{H}$ -NMR Spectral Data of Phosphonates 7a-d and 8a,b

Compound	$^{31}\text{P}$ -NMR in ( $\text{CDCl}_3$ )	$^1\text{H}$ -NMR ( $\delta$ ppm)
<b>7a*</b>	+21.86	3.70 (3H, $\text{OCH}_3$ , s), 3.75, 3.45 (6H, $\text{P}(\text{O}-\text{CH}_3)_2$ , 2d <sup>a</sup> ), 4.30 (1H, $\text{P}-\text{CH}-\text{C}$ , dd <sup>b</sup> ), 5.55 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), 6.80 (1H, <i>Hb</i> , aromatic, d), 6.90 (1H, <i>Hc</i> , aromatic, d), 7.05 (1H, <i>Ha</i> , aromatic, s), 9.25 (OH, bs <sup>c</sup> ).
<b>7b**</b>	+22.80	1.35, 1.15 (6H, $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , 2i), 3.95 (3H, $\text{OCH}_3$ , s), 3.55, 3.40 (1H, $\text{P}-\text{CH}-\text{C}$ , 2d <sup>b</sup> ), 4.45 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), 4.05, 3.80 (4H, $\text{P}(\text{OCH}_2-\text{C})_2$ , 2 quintets), 5.80 (OH, bs <sup>c</sup> ), 6.90 (1H, <i>Hb</i> , aromatic, s), 7.05 (1H, <i>Hc</i> , aromatic, s), 7.25 (1H, <i>Ha</i> , aromatic, s).
<b>7c**</b>	-	1.20 (3H, $\text{COO}-\text{C}-\text{CH}_3$ , t), 3.80, 3.70 (6H, $\text{P}(\text{OCH}_3)_2$ , 2d <sup>b</sup> ), 3.90 (3H, $\text{OCH}_3$ , s), 3.75 (1H, $\text{P}-\text{CH}-\text{C}$ , 2d <sup>b</sup> ), 4.15 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), 4.20 (2H, $\text{COOCH}_2-\text{C}$ , quartet), 5.85 (OH, bs <sup>c</sup> ), 6.90 (1H, <i>Hb</i> , aromatic, s), 7.10 (1H, <i>Hc</i> , aromatic, s), 7.25 (1H, <i>Ha</i> , aromatic, s).
<b>7d**</b>	+22.94	A multiplet (9H) in the 1.15–1.40 region for the overlap of the triplets due to $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ and ( $\text{COO}-\text{C}-\text{CH}_3$ ) group protons, 3.80, 3.70 (1H, $\text{P}-\text{CH}-\text{C}$ , d <sup>b</sup> ), 3.90 (3H, $\text{OCH}_3$ , s), 4.20 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), a multiplet (6H) in the 3.95–4.25 region for the overlap of quintets of $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ with quartet of the ( $\text{COO}-\text{CH}_2-\text{C}$ ) group protons, 5.60 (OH, bs <sup>c</sup> ), 6.85 ( <i>Hb</i> , s), 7.15 ( <i>Hc</i> , s), 7.25 ( <i>Hd</i> , s).
<b>8a**</b>	+19.96	1.10, 1.35 (6H, $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , 2i), 1.45 ( $\text{Ar}-\text{O}-\text{C}-\text{CH}_3$ , t), 3.50 (1H, $\text{P}-\text{CH}-\text{C}$ , 2d <sup>b</sup> ), 4.45 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), 3.75, 4.00 (4H, $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ , 2quintets), 4.15 ( $\text{Ar}-\text{O}-\text{CH}_2-\text{C}$ , quartet), 3.90 (3H, $\text{OCH}_3$ , s), 6.85 ( <i>Hb</i> , d), 6.95 (H 7.05 ( <i>Ha</i> , s).
<b>8b**</b>	+22.90	A multiplet (12H) in 1.50–1.15 region for the overlap of the triplets due to $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , ( $\text{COO}-\text{C}-\text{CH}_3$ ) and ( $\text{Ar}-\text{O}-\text{C}-\text{CH}_3$ ) group protons, 3.75, 3.65 (1H, $\text{P}-\text{CH}-\text{C}$ , 2d <sup>b</sup> ), 3.85 (3H, $\text{OCH}_3$ , s), 4.20 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>b</sup> ), a multiplet (8H) in the 4.25–3.90 region for the overlap of quintets of $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ with quartets of ( $\text{COOCH}_2-\text{C}$ ) and ( $\text{Ar}-\text{O}-\text{CH}_2-\text{C}$ ) group protons, 6.60 ( <i>Hb</i> , d), 6.90 ( <i>Hc</i> , d), 7.20 ( <i>Ha</i> , s).

\*) PMR run in DMSO (a)  $^3J_{\text{HP}}=12$  Hz\*\*) PMR run in  $\text{CDCl}_3$  (b)  $^2J_{\text{HP}}=20$  Hz(c)  $\text{D}_2\text{O}$ -exchangeable

## ALKYL PHOSPHITES

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TABLE II Physical, Analytical and IR Spectral data of Phosphonates 15a,b, 16a,b and 17a,b

Compound (crystal colour)	m.p. °C	Molecular formula (Mol. wt.)	Analysis Found / (Calcd.) %				IR * * * (KBr, cm <sup>-1</sup> )				
			C	H	N	P	M+ (%) m/z	CN	-C=O	P=O	P-O-C
15a (white)	116–118 <sup>a</sup>	C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>5</sub> P (308.2)	50.60 50.65	4.20 4.25	9.10 9.09	10.00 10.05	308 (38.3)	2260 -		1250	1050
15b (colourless)	150–152 <sup>b</sup>	C <sub>15</sub> H <sub>17</sub> N <sub>2</sub> O <sub>5</sub> P (336.3)	53.50 53.57	5.00 5.09	8.30 8.33	9.25 9.21	336 (100)	2255 -		1252	1040
15c (pale yellow)	130–132 <sup>c</sup>	C <sub>15</sub> H <sub>18</sub> NO <sub>7</sub> P (355.3)	50.65 50.70	5.00 5.10	3.90 3.94	8.70 8.71	355 (3.47)	2240	1740	1250	1040
15d (yellow)	163–165 <sup>a</sup>	C <sub>17</sub> H <sub>22</sub> NO <sub>7</sub> P (383.3)	53.20 53.26	5.70 5.78	3.60 3.65	8.10 8.08	383 (15.51)	2250	1750	1250	1030
16a (pale yellow)	64–66 <sup>d</sup>	C <sub>16</sub> H <sub>20</sub> NO <sub>5</sub> P (337.3)	56.40 56.97	6.00 5.98	4.00 4.15	9.20 9.18	337 (7.01)	3480	3370	1230	1030
16b (buff)	83–85 <sup>d</sup>	C <sub>18</sub> H <sub>24</sub> NO <sub>5</sub> P (365.4)	58.60 59.17	6.50 6.62	3.80 3.83	8.40 8.48	365 (7.09)	3400	3200	1200	1020
17a (white)	115–116 <sup>d</sup>	C <sub>16</sub> H <sub>18</sub> NO <sub>3</sub> P (335.3)	57.20 57.3	5.00 5.41	4.20 4.17	9.30 9.24	355 - (7.75)		3300	1250	1040
17b (pale yellow)	106–108 <sup>d</sup>	C <sub>18</sub> H <sub>22</sub> NO <sub>3</sub> P (363.3)	59.40 59.49	6.00 6.10	3.70 3.85	8.50 8.53	363 (7.75)		- 3310	1240	1030

a) Solvent of crystallization is (benzene)

b) Solvent of crystallization is (ethyl acetate)

c) Solvent of crystallization is (cyclohexane)

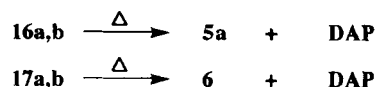
d) Solvent of crystallization is (pet-ether 60–80 °C)

TABLE II continued :  $^{31}\text{P}$  and  $^1\text{H}$ -NMR Spectral Data of Phosphonates 15a-d, 16a,b and 17a,b

Compound	$^{31}\text{P}$ -NMR in ( $\text{CDCl}_3$ )	$^1\text{H}$ -NMR ( $\delta$ ppm)**
15a	+22.25	3.80, 3.55 [6H, $\text{P}(\text{O}-\text{CH}_2)_2$ , 2d <sup>a</sup> ], 4.15 (1H, $\text{P}-\text{CH}_2-\text{C}$ , dd <sup>b</sup> ), 5.15 (1H, $\text{P}-\text{C}-\text{CH}$ , dd <sup>a</sup> ), 6.05 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s), 6.90 (1H, <i>Ha</i> , aromatic, d), 7.15–7.05 (2H, <i>Hb</i> and <i>Hc</i> , aromatics, m).
15b	+21.16	1.25, 1.15 (6H, $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , 2t), 3.5 (1H, $\text{P}-\text{CH}_2-\text{C}$ , dd <sup>b</sup> ), 4.20–3.80 (4H, $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ , m), 4.55 (1H, $\text{P}-\text{C}-\text{CH}-\text{dd}^a$ ), 5.95 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s), 7.00–6.75 (3H, aromatics, m).
15c		1.05 (3H, $\text{COO}-\text{C}-\text{CH}_3$ , t), a multiplet (4H) in the 3.7–3.6 region resulting from overlap of signals due to protons of $\text{COOCH}_2-\text{C}$ , $\text{P}-\text{CH}_2-\text{C}$ and $\text{P}-\text{C}-\text{CH}$ groups, 4.25, 4.00 [(6H, $\text{P}(\text{OCH}_3)_2$ , 2d <sup>a</sup> ], 5.90 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s) and 7.00–6.70 (3H, aromatics, m).
15d		A multiplet (9H) in the 1.25–1.00 region for the overlap of triplets due to $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ and $(\text{COO}-\text{C}-\text{CH}_3)$ group protons, 3.65 (1H, $\text{P}-\text{CH}_2-\text{C}$ , dd <sup>b</sup> ), a multiplet (7H) for the overlap of $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ , $\text{P}-\text{C}-\text{CH}$ and $\text{COO}-\text{CH}_2-\text{C}$ group protons, 5.90 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s) and 6.95–6.65 (3H, aromatics, m).
16a	+25.61	2.80 (NH, bs <sup>*</sup> ), 3.70, 3.45 (6H, $\text{P}(\text{OCH}_3)_2$ , 2d <sup>a</sup> ), 3.85 (3H, $\text{OCH}_3$ , s), 4.65 (1H, $\text{P}-\text{CH}-\text{C}$ , d <sup>b</sup> ), 7.25–6.60 (9H, aromatics + OH <sup>*</sup> , m)
16b	+23.25	1.3, 1.1 (6H, $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , 2t), 3.65 [3H, $\text{P}(\text{O}-\text{CH}_2-\text{C}-\text{NH}^+$ , ml, 4.1 (2H, $\text{P}(\text{O}-\text{CH}_2-\text{C})$ , quintet), 4.65 (1H, $\text{P}-\text{CH}-\text{C}$ , d <sup>b</sup> ), 7.20–6.55 (9H, aromatics + OH <sup>*</sup> , m).
17a	+25.35	3.80, 3.55 (6H, $\text{P}(\text{OCH}_3)_2$ , 2d <sup>a</sup> ), 4.70 (1H, $\text{P}-\text{CH}-\text{C}$ , d <sup>b</sup> ), 5.95 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s), 7.30–6.55 (8H, aromatics, m).
17b	+22.98	1.30, 1.20 [6H, $\text{P}(\text{O}-\text{C}-\text{CH}_3)_2$ , 2t], 3.4 (NH, bs <sup>*</sup> ), 4.10–3.85 [4H, $\text{P}(\text{O}-\text{CH}_2-\text{C})_2$ , m], 4.65 (1H, $\text{P}-\text{CH}-\text{C}$ , d <sup>b</sup> ), 5.95 (2H, $\text{O}-\text{CH}_2-\text{O}$ , s), 7.30–6.60 (8H, aromatics, m).

\*) D<sub>2</sub>O-exchangeable\*\*) Run in  $\text{CDCl}_3$ a)  $^3J_{\text{HP}}=12$  Hzb)  $^2J_{\text{HP}}=20$  Hz

Similarly, phosphonates *17a* and *17b* were obtained by reacting piperonal anil (3,4-methylenedioxybenzylidene aniline, *6*) with the appropriate TAP(**2a,b**) in presence of a few drops of water and/or with the suitable DAP (*1a,b*) at 100 °C in absence of solvent. Adducts **16a,b** and **17a,b** gave positive chemical shifts in the region 6 22–25 ppm in their <sup>31</sup>P-NMR spectra (vs. 85% H<sub>3</sub>PO<sub>4</sub>). Moreover, they regenerated the starting materials upon thermolysis under reduced pressure.



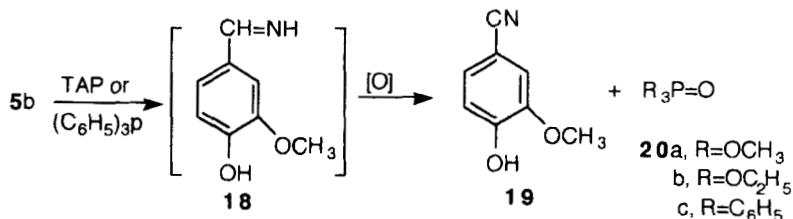
While compounds **17** are alkali-insoluble, compounds **16** dissolve freely in 10% NaOH aq. Correct elementary analyses and compatible spectroscopic data were gained for compounds **16a,b** and **17a,b** (cf. Tables 1 and 2).

It is worthy to mention that the reaction of TAP (**2a,b**) with **3a,b**, **4a,b**, **5a** and **6** to give the respective phosphonate derivatives **7a-d**, **15a-d**, **16a,b** and **17a,b** is completed only in presence of water. It is evident that addition of elements of water to the initially formed phospho-betaine (e.g. **9**) yields a transient with penta-covalent phosphours (e.g. **10**). The latter decomposes then via removal of an alcohol to afford the final products. In this respect, water acts as a nucleophile which dealkylates the initially formed zwitterion (e.g. **9**).

When vanillin oxime (4-hydroxy –3-methoxybenzaloxime, **5b**) was allowed to react with TMP (or TEP) in dry toluene or in absence of solvent at room temperature, it was recovered in an almost quantitative yield. On the other hand, when the same reactions were carried out in refluxing toluene or in absence of solvent at 100 °C, one and the same compound was isolated in each case. It was identified as 4-hydroxy –3-methoxybenzonitrile (**19**) upon comparing its m.p., mixed m.p. as well as its IR, <sup>1</sup>H-NMR and mass spectra with those of a reference sample.<sup>16</sup> Meanwhile oxime **5b** was recovered practically unchanged upon heating alone in boiling toluene even for 30 hr. This shows that TAP are assumed to display a role in the transformation : **5b**→ **19**

Apparently, TAP; by virtue of their soft (strong)<sup>17–19</sup> basicity can reduce **5b** to yield an intermediate aldimine (**18**); being themselves oxidized to their respective trialkyl phosphates (**20a** or **20b**). Autoxidation of **18** can

yield **19**. This assumption is supported by the finding that oxime **5b** reacts readily with triphenylphosphine ( $\text{C}_6\text{H}_5)_3\text{P}$  in refluxing toluene to give nitrile **19**. Triphenylphosphine oxide (TPPO, **20c**) was also isolated and identified in the same reaction.



## EXPERIMENTAL

All m.ps are uncorrected. Solvents were purified and dried by usual techniques. The IR spectra (in KBr) were recorded on Philips and/or FT-IR 3000 E infracords. The  $^1\text{H}$ -NMR (in DMSO or  $\text{CDCl}_3$ , ppm) were measured on Jeol JNM-EX 270 MHz FT NMR and  $^{31}\text{P}$ -NMR spectra were recorded on Varian FT-80 spectrometer. The mass spectra were run at 70 eV on Shimadzu GC MS-Q 1000 EX and/or Finnigan SSQ 700 spectrometer. Spectral and Microanalyses were carried out at the National Research Centre and/or Cairo University.

Alkyl phosphites were available from Aldrich Chem. Co. and freshly distilled before use. Compounds **3a**<sup>20</sup>, **3b**<sup>21</sup>, **4a**<sup>22</sup>, **4b**<sup>23</sup>, **5a**<sup>24</sup>, **5b**<sup>25</sup> and **6**<sup>26</sup> were prepared according to known procedures.

Using 2 : 1 molar ratios of phosphite to substrate was to ensure completion of the reaction. Getting-rid of excess phosphite is practically much easier than getting-rid of the unreacted substrates.

Reaction mixtures were resolved into their components by making use of column chromatography on silica gel using the appropriate solvents.

### Reaction of **3a,b** with dialkyl phosphites **1a,b**

#### General Procedure

A mixture of **3a** (or **3b**) (0.005 mol) and DAP **1a** or (**1b**) (0.01 mol) was heated in absence of solvent at 100 °C or in presence of a few drops of pip-

eridine until no more of the reactants could be detected (TLC). After removing the volatile materials *in vacuo*, the residual material was collected and recrystallized from the appropriate solvent to give the respective phosphonates **7a-d**.

Similarly, phosphonates **15a-d** were obtained by reacting **4a** (or **4b**) (0.005 mol) with the appropriate DAP (**1a** or **1b**) (0.01 mol) in absence of solvent at 100 °C.

Similarly, phosphonates **16a,b** and **17a,b** were obtained by reacting vanillin monoanil **5a** (0.005 mol) and piperonal monoanil **6** (0.005 mol) respectively with the appropriate DAP (**1a** or **1b**) (0.01 mol) in absence of solvent at 100 °C.

Column chromatography was used for purification of the products when necessary.

Physical, analytical and spectral data of compounds **7a-d**, **15a-d**, **16a,b** and **17a,b** are presented in Tables I and II.

#### Reaction of **3a,b** with trimethyl phosphite **2a**

A mixture of **3a** (or **3b**) (0.005 mol) and TMP **2a** (0.01 mol) was heated in absence of solvent at 100 °C until no more of the reactants could be detected (TLC). After removing the volatile materials *in vacuo*, the residual substance was collected and recrystallized from the appropriate solvent to give phosphonate **7a** (or **7c**) (m.p., mixed m.p. and comparative IR spectra).

#### Reaction of $\alpha,\alpha$ -dicyano-(4-hydroxy-3-methoxy)styrene **3a** with triethyl phosphite **2b**

A mixture of **3a** (0.005 mol) and triethyl phosphite **2b** (0.01 mol) was heated in absence of solvent at 100 °C until no more of **3a** could be detected (TLC). The reaction mixture was then worked up by column chromatography.

The fraction that eluted by 85 : 15 v/v pet-ether : acetone yielded a substance proved to be **7b** (m.p., mixed m.p. and comparative IR spectra). The fraction eluted with 85 : 15 v/v pet-ether : acetone gave a substance which was collected, recrystallized to give phosphonate **8a** (cf. Table I).

**Reaction of ethyl-  $\alpha$ -cyano- $\beta$ -(4-hydroxy-3-methoxyphenyl)acrylate **3b** with triethyl phosphite **2b****

A mixture of **3b** (0.005 mol) and triethyl phosphite **2b** (0.01 mol) was heated in absence of solvent at 100 °C until no more of **3b** could be detected (TLC). The reaction mixture was then worked up by column chromatography. The fraction that eluted by 95 : 5 v/v pet-ether : acetone yielded phosphonate **7d** (m.p., mixed m.p. and comparative IR spectra). The fraction eluted by 85 : 15 v/v pet-ether : acetone gave a substance which was collected, recrystallized to give phosphonate **8b** (cf. Table I).

Phosphonates **7a-d** dissolve freely in 10% aqueous sodium hydroxide solution, but phosphonates **8a,b** were alkali insoluble. Phosphonates **7a-d** and **8a,b** exhibit no colour reactions with 1% alcoholic ferric chloride solution.

Similarly, phosphonates **15a-d** were obtained by reacting **4a** (or **4b**) (0.005 mol) with the appropriate TAP **2a** (or **2b**) (0.01 mol) at 100 °C in presence of a few drops of water.

Similarly, phosphonates **16a,b** and **17a,b** were obtained by reacting vanillin monoanil **5a** (0.005 mol) and piperonal monoanil **6** (0.005 mol) respectively with the appropriate TAP **2a** (or **2b**) (0.01 mol) in presence of a few drops of water at 100 °C.

Physical, analytical and spectral data of compounds **7a-d**, **8a,b**, **15a-d**, **16a,b** and **17a,b** are presented in Tables I and II.

**$\alpha,\alpha$ -Dicyano- $\beta$ -diethylphosphinyl- $\beta$ -(4-ethoxy-3-methoxyphenyl)ethane (**8a**)**

A mixture of **7b** (0.2g), ethyl iodide (5g) and anhydrous  $K_2CO_3$  (5g) in dry acetone (200 ml) was refluxed for 12hr. The inorganic material was filtered off and washed with a small amount of dry acetone. After evaporation of the filtrate and washings to dryness, the residue was recrystallized from pet-ether (b.r. 60–80 °C) to give colourless crystals (0.2g, 92%), m.p. 107–109 °C proved to be **8a** (m.p., mixed m.p. and comparative IR spectra).

Similarly, compound **8b** was obtained (yield 80%) and identified (m.p., mixed m.p. and comparative IR spectra) upon refluxing a mixture of **7d** (0.2 g), ethyl iodide (5 g) in acetone (200 ml) for 12 hr in presence of anhydrous  $K_2CO_3$  (5 g).

### Thermolysis of phosphonate **7a**

The phosphonate adducts **7a** (0.4g) was heated in a cold finger sublimator at 200 °C (bath temperature) under reduced pressure (1 mm/Hg) for 30 min. The reaction vessel was left to cool and the compound that sublimed was collected and recrystallized from ethyl acetate to give pale yellow crystals, m.p. 131–132 °C proved to be **3a** (m.p., mixed m.p. and comparative IR spectra). Dimethyl phosphite **1a** was detected in the receiver by the development of a violet colour on addition of a solution of 3,5-dinitrobenzoic acid in aqueous NaHCO<sub>3</sub>.<sup>27</sup>

Similarly, adduct **7c** was sublimed to give white crystals, m.p. 116–118 °C proved to be **3b** (m.p., mixed m.p. and comparative IR spectra).

Similarly, phosphonates **15a**, **16a** and **17b** were sublimed to give **4a**, **5a** and **6** respectively (m.p., mixed m.p. and comparative IR spectra) together with the appropriate DAP.

### Reaction of vanillinoxime **5b** with trialkyl phosphites **2a,b**

A mixture of **5b** (0.005 mol) and trialkyl phosphite **2a** (or **2b**)(0.01 mol) was heated either in absence of solvent at 100 °C for 3 hr or in boiling toluene for 12 hr. After removing the volatile materials in vacuo, the residual substance (ca., 95%) was collected, recrystallized from pet-ether (b. r. 60–80 °C) to give colourless crystals proved to be 4-hydroxy-3-methoxybenzonitrile (vanillinonitrile) (**19**)<sup>16</sup> (m.p., mixed m.p. and comparative IR spectra).

### Reaction of vanillinoxime **5b** with triphenylphosphine TPP

To a suspension of **5b** (0.005 mol) in dry toluene (30 ml) was added a solution of TPP (0.005 mol) in the same solvent (20 ml) and the reaction mixture was refluxed, then worked up by column chromatography. The fraction eluted by 90 : 10 v/v pet-ether: ethyl acetate gave a compound which was recrystallized from pet-ether (b.r. 60–80 °C) to give colourless crystals m.p. 87 °C proved to be vanillinonitrile (**19**) (m.p., mixed m.p. and comparative IR spectra). The next fraction up to 70 : 30 v/v pet-ether : ethyl acetate eluted colourless needles (ca, 90%) which were proved to be triphenylphosphine oxide TPPO (m.p. and mixed m.p.).



### Action of heat on vanillin-oxime **5b**

A solution of **5b** (0.4 g) in dry toluene was refluxed for 30 hr. and the reaction mixture was then evaporated under reduced pressure at 60 °C. The solid residue was collected and recrystallized from chloroform to give white crystals m.p. 120–122 °C proved to be unchanged vanillin oxime **5b** (m.p., mixed m.p. and comparative IR spectra).

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