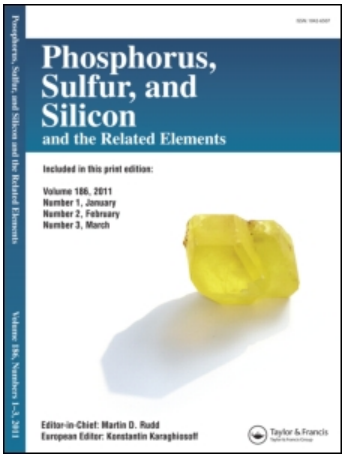

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ORGANOPHOSPHORUS CHEMISTRY 31[1]

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ORGANOPHOSPHORUS CHEMISTRY 31[1]

On the Reaction of 3-(Aryliminomethyl)Chromones with Alkyl Phosphites and Methylenetriphenylphosphoranes (Wittig Reagents)*

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3-(Aryliminomethyl)chromones (**5a,b**) produce the respective phosphonates (**8a-f**) upon reaction with the appropriate dialkyl phosphite (**2a-c**) and/or trialkyl phosphhite (**3a-c**). New complex ylidenetriphenyl-phosphoranes (**13a,b**) were obtained directly and in good yield *via* condensing arylimines **5a,b** with the resonance stabilized methylenetriphenylphosphoranes (**4a,b**) in boiling toluene. The reaction mechanism of **5a,b** with trialkyl phosphites (**3a-c**) was discussed. Compatible elementary and spectroscopic measurements were recorded for the new products.

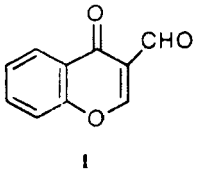
Keywords: 3-(Aryliminomethyl)chromones; alkyl phosphites; Wittig reagents; phosphonates; complex P-ylides

INTRODUCTION

Recently,[2] we have reported on the reaction of 3-formylchromone (**1**) with dialkyl phosphites (**2**), trialkyl phosphites (**3**) (Scheme 1) and resonance-stabilized ylidenetriphenylphosphoranes (**4**). This together with our growing interest in the organo-phosphorus chemistry of arylimines derived from polycarbonyl compounds[3–6] has prompted us to study the behavior of arylimines of **1** toward the same phosphorus reagents.

* Dedicated to Professor Mahmoud Sidky on the occasion of his 69th birthday.

† Corresponding Author.



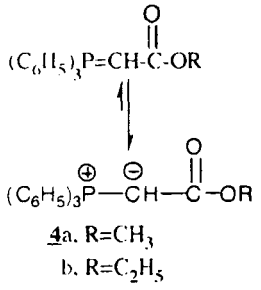
1

$(RO)_2P(O)H$

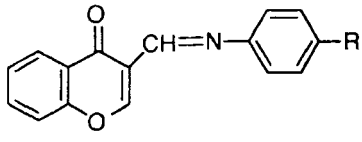
2a, R=CH_3, DMP
b, R=C_2H_5, DEP
c, R=C_3H_7-i, DIP

$(RO)_3P$:

3a, R=CH_3, TMP
b, R=C_2H_5, TEP
c, R=C_3H_7-i, TIP



4a, R=CH_3
b, R=C_2H_5

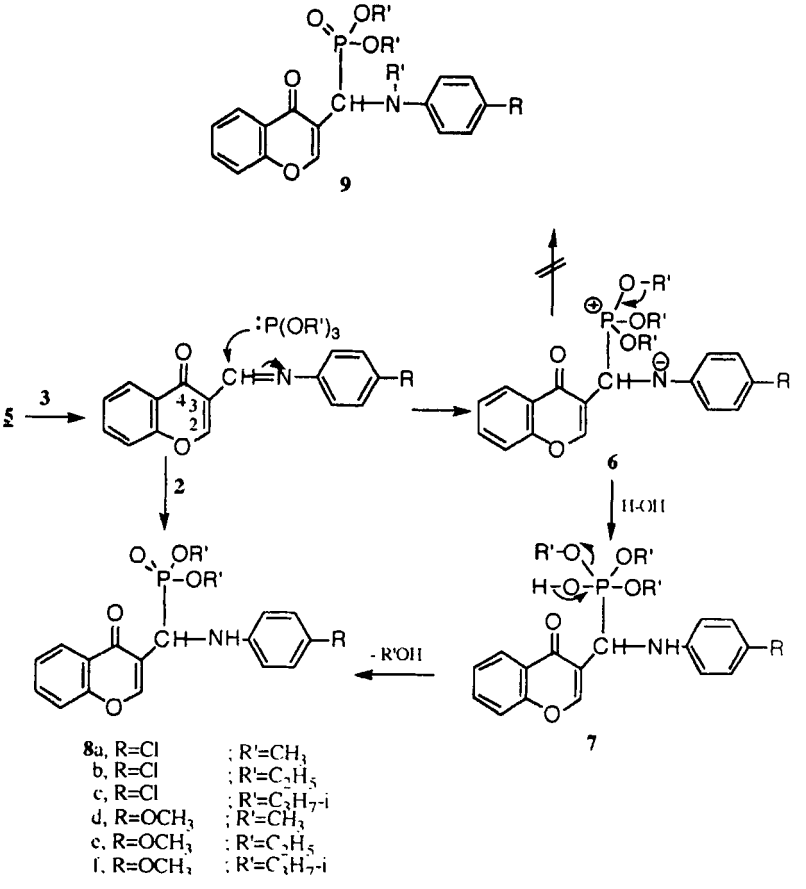


5a, R=Cl
b, R=OCH_3

Arylimines in the present study, namely 3-(p-chlorophenyl-iminomethyl)chromone (**5a**) and 3-(p-anisyliminomethyl)chromone (**5b**) were prepared by condensing **1** with p-chloroaniline and p-anisidine, respectively in the presence of p-toluene sulfonic acid (Experimental).

RESULTS AND DISCUSSION

We have found that arylimine **5a** reacts with trimethyl phosphite (**3a**, TMP) at 100 °C in absence of solvent to give a colorless crystalline substance for which structure **8a** was assigned for the following reasons : (a) elementary analyses and molecular weight determinations (MS) corresponded to $C_{18}H_{17}ClNO_5P$; (b) positive chemical shift at δ=20.1 in the ^{31}P-NMR spectrum (*vs.* 85% H_3PO_4) confirming the presence of a *phosphorus -to-carbon* linkage (phosphonate group)[7] in the structure; (c) IR spectrum of **8a** (KBr, cm^{-1}) revealed the presence of strong absorption bands at 3320 (NH, free), 1640 (C=O), 1600, 1560 (C=C, aromatic), 1225 ($\rightarrow$P=O , free)[8] and at 1030 (P-OCH_3)[8]. The strong $\diagdown$C=N- band



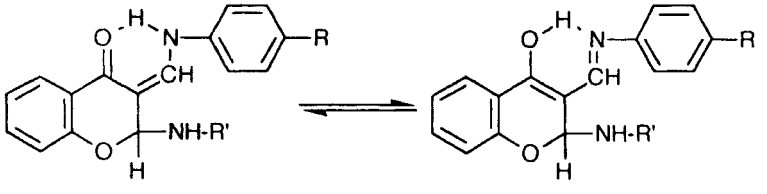
SCHEME 1

present in the spectrum of **5a** at 1590 was absent in the IR spectrum of **7a**: (d) the ^{1}H-NMR spectrun of **8a** ($CDCl_3$, δppm) showed protons of the OCH_3 groups attached to phosphorus as two doublets (each with J_{HP}=12 Hz) at 3.70 and 3.60. Apparently, the asymmetry of the molecule due to the presence of a stereo-center, would render the two methoxyl groups diastereotropic and hence anisochronous, resulting in the observed splitting pattern.[9,10] The spectrum also showed two doublets (each with J_{HP}= 9 Hz) due to protons of the -N-C_6H_4-Cl moiety (4H) at 7.05 and 7.25. The remaining aromatics (5H) appeared as a multiplet in the 8.30–7.35 ppm

region. The NH proton gave a D_2O-exchangeable singlet at 11.90 and the exocyclic methine proton appeared as a doublet ($^2J_{HP}$=18 Hz) due to coupling with the phosphorus atom at 5.30 ppm. These data rule out an alternative structure like **9** (R′=CH_3). (d) Finally, compound **8a** was unequivocally prepared and identified (m.p., mixed m.p. and comparative IR spectra) by allowing **5a** to react with dimethyl phosphite (**2a**) at 100 °C in absence of solvent.

Upon thermolysis under reduced pressure, compound **8a** regenerated the starting materials, namely 3-[(4-chlorophenyl)imino]-methyl]-4H-1-benzopyran-4-one (**5a**) and DMP (**2a**). In the same sense, phosphonates **8b-f** were obtained by allowing **5a** (or **5b**) to react with the appropriate alkyl phosphite (**2** and/or **3**). Reactions of arylimines **5a,b** with trialkyl phosphites, however, were accelerated when a few drops of water were added to the reactants (Experimental).

A mechanism for the formation of compounds **8** *via* reacting **5a,b** with trialkyl phosphites (TAP, **3a-c**) is outlined in "*Scheme 1*". This involves *C*-attack on **5a,b** by the nucleophilic phosphorus atom to give an intermediate dipolar species of type **6**, which can be solvated by water unavoidably present in the reaction medium to give a transient like **7**. The latter decomposes *via* removal of an alcohol molecule to afford the final products (**8a-f**).



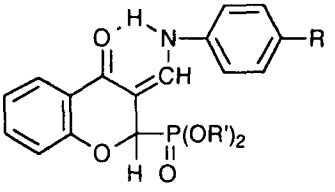
10 **11**

R as in **5**;

R' = aryl

The reaction of alkyl phosphites (**2** and **3**) with **5a,b** to give phosphonates **8** is in complete variance with the unusual ring addition of *N*-nucleophiles[11], namely, aromatic amines to arylimines **5** which produce 1:1 adducts of type **10** due to formation of stable hydrogen-bonded systems

(*cf.* **10** ⇌ **11**).[11] This difference in behaviour may be attributed to the nucleophilicity power of the reagents and their ability to remove the hydrogen-bonded system.[11] In terms of the Hard-Soft-Acid-Base (HSAB)-principle,[12–15] the phosphite reagents (**2** and **3**) are more nucleophilic than aromatic amines. Therefore, these *P*-nucleophiles by virtu of being soft (strong) bases can induce attack at the azomethine-carbon atom in **5** to yield **8**. Formation of a hydrogen-bonded system (*cf.* **12**) in these interactions is thus prohibited.



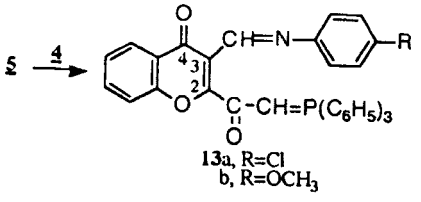
12. R as in **5**;
R' as in **2** and **3**

When an equimolecular mixture of arylimine **5a** and carbmethoxy-methylenetriphenylphosphorane (**4a**) was refluxed in dry toluene for 4 hrs, a colorless crystalline product (A) was obtained. The same compound (A) was isolated and identified (m.p., mixed m.p. and comparative MS spectra) when **5a** was allowed to react with the phosphorus ylide **4b** under the same conditions. Triphenylphosphine oxide [$(C_6H_5)_3P{=}O$, TPPO] was neither isolated nor identified (TLC) in both reactions. Product (A) was therefore assigned the complex ylidenetriphenylphosphorane structure **13a**. Similarly, the reaction of **5b** with phosphoranes **4a** and/or **4b** yielded one and the same product (**13b**) in both reactions. The following measurements were in support of the postulated structure **13** : (a) Correct analytical and molecular weight determinations (MS) for **13a** and **13b** corresponded to $C_{36}H_{25}ClNO_3P$ and $C_{37}H_{28}NO_4P$, respectively; (b) Both compounds showed positive chemical shifts around 20 ppm in their ^{31}P-NMR spectra; (c) The singlet due to the H-2 proton present at 7.30 in the ^{1}H-NMR spectrum of **5a** and at 7.15 in the spectrum of **5b**; was not recorded in the spectra of compounds **13a,b**. Meanwhile, the ^{1}H-NMR spectrum of **13b** ($CDCl_3$, δppm) showed the azomethine proton (1H) as a singlet at 7.90. Moreover, a proton-ratio-value of 3 : 25 was recorded for signals due to OCH_3 : aromatics. The singlet due to the OCH_3 protons appeared at

δ=3.80 while the multiplet due to the aromatics was extended in the δ6.80–7.60 ppm region; (d) A prominent ion peak was observed in the mass spectra of **13a,b** at m/z 262 due to cation **a** of triphenylphosphine.

$(C_6H_5)_3P^+$

a



13a, R=Cl
b, R=OCH_3

CONCLUSION

The present study offers a new group of phosphonates (*cf.* **8a-f**) derived from heterocycles to which belong many biologically active principles frequently used as pesticides.[16,17] Also, it explores a new approach for preparing new models of complex ylidenetriphenylphosphoranes (Wittig reagents, **13a,b**) which are of significance both from synthetic and preparative view points.[13] This was achieved in a one-step process by allowing aryliamines **5a,b** to condense with the phosphorus-ylides (**4a,b**). This study shows clearly that the γ-pyrone carbonyl group in **5a,b** shows marked stability toward attack by the examined phosphorus reagents at least under the prevailing experimental conditions.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded by using Unicam SP 1100 or PU 7912 infracords. The ^{1}H-NMR spectra were recorded on Jeol GLMEX 270 MHz spectrometer (super conducting magnet) in $CDCl_3$ using TMS as an internal standard. ^{31}P-NMR spectra were recorded with Jeol GLMEX 270 MHz spectrometer in $CDCl_3$ (vs 85% H_3PO_4). The Mass spectra were obtained with Finnigan MAT-SSQ 7000 spectrometer (70 eV). Monoanils **5a**,[18] **5b**[18] and phosphorus-ylides **4a**[19] and **4b**[19] were prepared by known procedures. Phosphites **2a-c** and **3a-c** were available from Aldrich Co., and freshly distilled before use.

Reaction of 3-[4-chlorophenyl)imino]methyl]-4H-1-benzopyran-4-one (5a) and 3-[(4-methoxyphenyl)imino]methyl]-4H- 1-benzopyran-4-one (5b) with trialkyl phosphites (3a-c)

General procedure

In presence of a protonating agent

A mixture of **5a** or **5b** (0.005 mol) and trialkyl phosphite (trimethyl, triethyl and triisopropyl)phosphites (0.05 mol) was heated at 100 °C for 10–12 h (cf. Table I) in presence of H_2O (1 ml). After evaporation of the volatile materials *in vacuo*, the residual substance was treated with cyclohexane (5 ml). The solid material was collected and recrystallized from the appropriate solvent (cf. Table II) to give adducts (**8a-f**).

Reaction of 3-[[4-chlorophenyl)imino]methyl]-4H-1-benzopyran-4-one (5a) and 3-[(4-methoxyphenyl)imino]methyl]-4H-1 -benzopyran-4-one (5b) with dialkyl phosphites (2a-c)

General procedure

A mixture of **5a** or **5b** (0.01 mol) and dialkyl phosphite (dimethyl, diethyl or diisopropyl phosphite) (5 ml) was heated in the absence of solvent at 100 °C for 4 h. After removing the volatile materials *in vacuo*, the residue was triturated with light petroleum and left to cool. The solid so formed was collected and recrystallized from a suitable solvent to give compounds **8a-f** Physical and analytical data for compounds **8a-f** are presented in Table I, Table II.

Action of heat on phosphonate 8a

Compound **8a** (0.5 g) was heated in a cold finger-sublimator at 230 °C (bath temperature) under reduced presure (5 mm/Hg) for 30 minutes. The compound that sublimed was collected (55%), recrystallized from ethyl acetate to give yellow crystals, proven to be 3-[[(4-chlorophenyl)imino]methyl]4H-1-benzopyran-4-one (**5a**) (m.p., mixed m.p. 151 °C and comparative i.r spectra).

Dimethyl phosphite was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali.[20]

TABLE I Physical, analytical and IR Spectral Data of Compounds 8a-f and 13a,b

*Compd***.	*Yield** *(%)*	*m.p.* *°C*	*Mol. Form* *(M. wt)*	*Anal. (calcd./Found)*					*M^+* *m/z (%)*	*IR cm^{-1}*			
				C	*H*	*Cl*	*N*	*P*		*-NH*	*>C=O*	*>P=O*	*P-O-C*
8a	75	151	$C_{18}H_{17}ClNO_5P$ (393.76)	54.90	4.35	9.00	3.55	7.86	393	3260	1640	1220	1030
				54.73	4.76	8.82	3.41	7.51	(<5)				
8b	80	128	$C_{20}H_{20}ClNO_5P$ (421.81)	56.94	5.01	8.40	3.32	7.34	421	3240	1640	1220	1020
				56.81	4.94	4.64	3.71	7.53	(<5)				
8c	85	135	$C_{22}H_{25}ClNO_5P$ (449.87)	58.73	5.60	7.88	3.11	6.88	449	3200	1640	1240	1000
				58.63	5.31	7.48	3.35	7.13	(8.59)				
8d	80	98	$C_{19}H_{20}NO_6P$ (389.34)	58.61	5.17	-	3.59	7.95	389	3100	1640	1280	1020
				58.25	4.92	-	3.95	7.53	(<5)				
8e	85	106	$C_{21}H_{24}NO_6P$ (417.39)	60.42	5.79	-	3.35	7.42	417	3260	1640	1220	1020
				60.32	5.31	-	3.59	7.15	(10.12)				
8f	88	140	$C_{23}H_{28}NO_6P$ (445.45)	62.0 1	6.33	-	3.14	6.95	445	3000	1640	1220	1040
				62.42	6.31	-	3.50	7.21	(41.30)				
										CH=N	**CH=CH**	**C=O**	**P-Ph**
13a	80	265	$C_{36}H_{25}ClNO_3P$ (586.02)	73.78	4.30	6.04	2.39	5.28	586	1610	1550	1540	1200
				73.52	3.94	5.83	2.79	5.13	(20.4)				
13b	80	250	$C_{37}H_{28}NO_4P$ (581.60)	76.41	4.85	-	2.40	5.3 2	581	1610	1600, 1540	1540	1200
				76.25	4.52	-	2.81	5.71	(100)				

*Approximated

**Solvent of crystalliztion is (8a) ethyl acetate, (b) ether, (c) chloroform, (d), (e) acctone, (f) ethanol/ether; 13(a) acetone,(b) chloroform.

The reaction times were 10hrs in the case of **5a** and 6–8 hrs in the case of **5b**.

TABLE II ^{1}H-NMR Spectral Data of Compounds 8b-f and 13a,b

Compd.	*^{31}P-NMR*	*^{1}H-NMR*
8b	22.40	1.15 and 1.35 (d of t, 6H, $^{3}J_{HP}$=9 Hz, P-O-C-C$\underline{H}_3$), 4.25 (d of q, 4H. J_{HP}=9 Hz, P-O-C$\underline{H}_2$), 5.3 (d, 1H, $^{2}J_{HP}$=27 Hz, C$\underline{H}$-P, 6.6, 7.1 (2d, 4H, J_{HH}=13.5 Hz, N-C$_6\underline{H}_4$-Cl), 7.4–8.3 (m,5$\underline{H}$ aromatics).
c		1.25 (d of d, 12H, J_{HP}=10.3 Hz, P-O-C-C$\underline{H}_3$), 4.7 (d of sept, 2H, $^{3}J_{HP}$=10.3 Hz, P-O-C*H*), 5.2 (d, 1H, $^{2}J_{HP}$=15.45 Hz, C$\underline{H}$-P, 6.8, 7.0 (2d 4H,J_{HH}= 10.3 Hz, N-C$_6\underline{H}_4$-Cl),7.2–7.85 (m, 5H aromatic),11.9 (s,N$\underline{H}$).
d	23.50	3.4 (s, 3H, -OC$\underline{H}_3$), 3.7, 3.85 (2d, 6H, J_{HP}=12 Hz, P-O-C$\underline{H}_3$), 4.2 (s, N$\underline{H}$), 5.3 (d, 1H, $^{2}J_{HP}$=25.2 Hz, -C$\underline{H}$-P), 6.7, 7.05 2d 4H, J_{HH}= 12.6 Hz,N-C$_6\underline{H}_4$-Cl), 7.4–8.3 m, 5H aromatics).
e		1.2, 1.3 (d of t, 6H, J_{HP}=8.7 Hz, P-O-C-C$\underline{H}_3$), 3.6 (s, 3H, -OC$\underline{H}_3$), 3.85 (s, N$\underline{H}$), 4.1, 4.25 (d of q, 4H, $^{3}J_{HP}$=8.7 Hz, P-O-C$\underline{H}_2$), 5.25 (d 1H, $^{2}J_{HP}$=26 Hz, -CH-P), 6.6, 6.7 (2d, 4H, J_{HH}=26 Hz, N-C$_6\underline{H}_4$-OCH$_3$), 7.39, 8.3 (m, 5H, aromatics).
f		1.05, 1.4 (2d, 12H, $^{3}J_{HP}$=9 Hz, P-O-C-C$\underline{H}_3$), 3.75 (s, 3H, C$_6$H$_5$-OC$\underline{H}_3$), 4.6 (d of sept, 2H, $^{3}J_{HP}$=9 Hz, P-O-C$\underline{H}$), 5.15 (d, 1H, $^{2}J_{HP}$=13.5 Hz, -C$\underline{H}$-P 6.85, 7.05 (2d, 4H, J_{HH}=9 Hz, N-C$_6\underline{H}_4$-OCH$_3$), 7.4–7.85 m, 5H, aromatics)
13a		6.6–7.9 (m, 25H, aromatics).
13b	19.85	3.8 (s,3H,-OC$\underline{H}_3$), 6.75–7.85 (m, 25H, aromatics).

Reaction of 5a with Wittig reagents 4a,b

General procedure

A mixture of 5a (2.83 g, 0.01 mol) and ylide 4a (0.01 mol) in toluene (100 ml) was refluxed for 3 h. The solid formed was collected and recrystallized from acetone to give **13a**.

Similarly, **13a** was isolated and identified (mixed m.p. and comparative IR spectra) upon reacting **5a** with **4b** (yield 85%).

Reaction of 5b with Wittig reagents 4a,b

General procedure

A mixture of **5b** (2.79 g, 0.01 mol) and ylide **4a** (0.01 mol) in toluene (100 ml) was refluxed for 5 h. The colorless solid product was collected and recrystallized from acetone to give **13b**.

Similarly, **13b** was isolated and identified (mixed m.p. and comparative IR spectra) upon reacting **5b** with **4b** (yield 85%), (*cf.* Tables I and II).

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