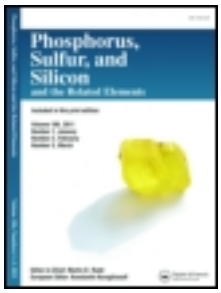

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorylation and Amine-induced Dephosphorylation of 4-Chlorocoumarin-3-carboxaldehyde and 4-Chloro-3-(β,β-dicyanoethenylidene)coumarin

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PHOSPHORYLATION AND AMINE-INDUCED DEPHOSPHORYLATION OF 4-CHLOROCOUMARIN-3-CARBOXALDEHYDE AND 4-CHLORO-3-(β, β-DICYANOETHENYLIDENE)COUMARIN

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4-Chlorocoumarin-3-carboxaldehyde ***(1)*** *and 4-chloro-3-(β,β-dicyanoethenylidene)coumarin* ***(2)*** *produce their respective 1:1 phosphonate adducts* ***(5a–c)*** *and* ***(6a–c)*** *upon reaction with the appropriate dialkylphosphonates* ***(3a–c).*** *Compounds* ***5*** *undergo dechlorination and dephosphorylation upon reaction with certain primary aliphatic amines to yield* ***9*** *(or* ***10****) according to the nature of the amine used. Compounds* ***1*** *and* ***2*** *undergo dechlorination through reaction with hexamethyl-phosphorustriamide* ***4*** *to give the respective 4-dimethylamino-derivatives (****11a*** *and* ***11b****). Structural reasonings for the new compounds are based on compatible analytical and spectroscopic measurements. The mechanism for formation of compounds* ***11*** *also is discussed.*

Keywords: Amine-induced dephosphorylation; coumarins; dialkylphosphonates; hexamethylphosphorustriamide; phosphonates; reaction mechanism

It is widely realized that the activity of certain natural products, drugs and pesticides owes much to presence of a coumarin nucleus in their molecules.[1,2] Various widely used oral anticoagulants and rodenticides[3] also incorporate the same nucleus. Therefore, it appeared of interest to study the reaction of 4-chloro coumarin-3-carboxaldehyde **(1)** and 4-chloro-3-(β,β-dicyanoethenylidene)coumarin **(2)** with dialkylphosphites **(3a–c)** and hexamethylphosphorustriamide **(4)**. Compound **2** is now prepared for the first time by reacting **1** with malononitrile in ethanol. Phosphorylation of compounds **1** and **2** may endow interesting

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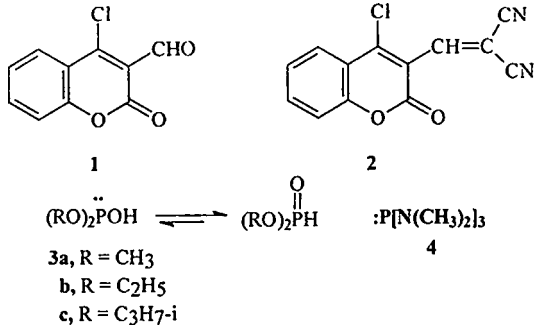
biocidal potentialities to the new products. The present study runs thus in the line with our growing interest that searchs for new organophosphorus compounds derived from heterocycles[4–6] for evaluating their biological activities.



RESULTS AND DISCUSSION

It has been now found that 4-chlorocoumarin-3-carboxaldehyde **(1)*** reacts with dialkyl phosphites **(3a–c)** at 100°C in absence of solvent to give colorless phosphonate 1:1 adducts for which structures **5a–c** are respectively assigned.

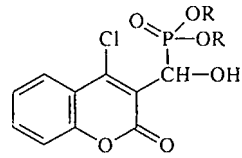
Structural reasoning for **5** are: Compatible elementary and molecular weight determinations (MS) were gained for **5a–c**. Positive chemical shifts were recorded for **5a** ($\delta = 20.80$ ppm) [^{31}P-NMR spectrum (vs 85% H_3PO_4], confirming the presence of phosphorus-to-carbon linkage (phosphonate group).[7]

The IR spectrum (KBr, cm^{-1}) of 4-chloro-3-[(α-dimethoxyphosphoryl-α-hydroxy)methyl]coumarin (**5a**), taken as a representative example, showed absorption bands at 3250 (OH), 1685 (C=O, lactone), 1520 (C=C, aromatic), 1220 (P=O)[8], 1050 (P—O—CH_3)[8] and at 860 (—C—Cl). The latter band appeared in the IR spectrum of **1** at 780.

The ^{1}H NMR spectrum of **5a** ($CDCl_3$, δ ppm) showed protons of the OCH_3 groups attached to phosphorus as two doublets (each with $^3J_{HP} =$ 12 Hz) at 3.95 and 3.75. Apparently, the asymmetry of the molecule

*Also known as 4-chloro-3-formylcoumarin and 4-chloro-2-oxo-2H-chromene-3-carbaldehyde.

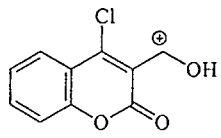
due to the presence of a stereo-center would render the two methoxyl groups diastereotropic and hence anisochronous; resulting thus in the observed splitting pattern.[9] The spectrum revealed the P-**CH** proton as a doublet ($^2J_{HP} = 22$ Hz) at 5.50. The spectrum also showed a multiplet in the region 8.00–7.40 (4H, aromatics) and a broad singlet at 4.25 (OH, exchangeable with D_2O).



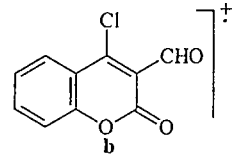
5a, R = CH_3
b, R = C_2H_5
c, R = C_3H_7-i

The mass spectrum of **5a** showed the molecular ion peak at m/z 318 (320) which corresponded to $C_{12}H_{12}ClO_6P$. Loss of $\cdot P(O)(OCH_3)_2$ radical from M^+ afforded the base peak (cation **a**) at m/z 209 (211). Meanwhile, loss of $H(O)P(OCH_3)_2$ molecule from M^+ afforded cation **b** at m/z 208 (210) which corresponded to the molecular ion peak of compound **1** itself [MS: m/z 208 (210), $C_{10}H_5ClO_3$]. This behavior of **5a** under electron impact recalls its thermolysis upon heating under reduced pressure which yields compound **1** and dimethyl phosphite **3a** (see Experimental).

The ^{13}C-NMR of **5a** showed signals at 53.69 (**C**—OH), 67.24 (O**C**H_3), 68.54 (O**C**H_3), 116.88, 118.16, 120.97, 125.43, 126.28, 133.47, 151.70, 159.96, coumarin ring carbon atoms and at 211.40 (**C**=O).

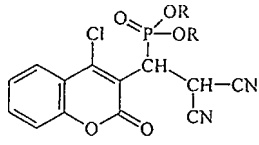


a
m/z = 209 (211)



b
m/z = 208 (210)

In the same sense, 4-chloro-3-(β,β-dicyanoethenylidene)coumarin **(2)** reacted with dialkylphosphonates (**3a–c**) to give colorless phosphonate 1:1 adducts for which structure **6a**–c were assigned respectively.

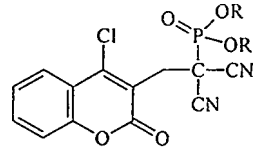


6a, R = CH_3
b, R = C_2H_5
c, R = C_3H_7-i

Compatible elementary and molecular weight determinations (MS) were gained for all adducts. They showed positive chemical shifts in the region 15–20 ppm (vs. H_3PO_4) in their ^{31}P NMR spectra; indicating that they are phosphonate in nature.[7]

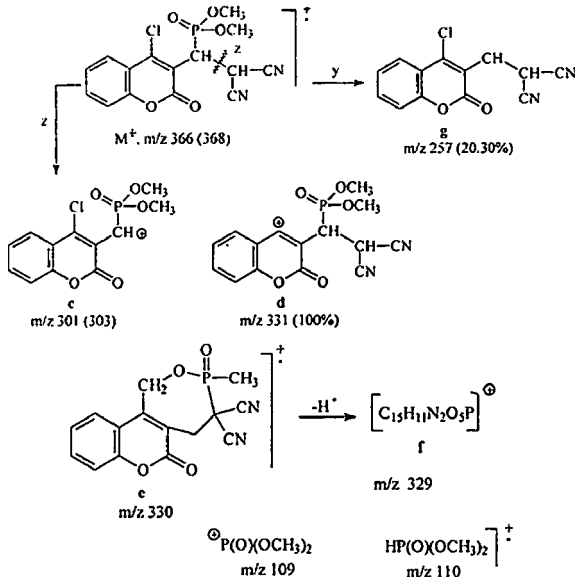
The IR spectrum (KBr, cm^{-1}) of **6a** taken as example, revealed the presence of absorption bands at 2220 (CN), 1260 (P═O, free), 1050 (P—O—CH_3) and 765 (C—Cl). The latter band appeared in the spectrum of **2** at 760 cm^{-1}.

The ^1H NMR spectrum of **6a** ($CDCl_3$, δ ppm) showed protons of the two methoxyl groups attached to phosphorus (6H) as two doublets (each with $^3J_{HP} = 12$ Hz) at 3.95 and 3.80. The exocyclic methine protons (2H) appeared in doublet patterns. That of the C**H**—P group appeared at 4.50 (2d, $^2J_{HP} = 18$ Hz) while that of the P—C—CH grouping appeared at 5.2 (2d, $^3J_{HP} = 12$ Hz). The multiplet (4H) due to the aromatic protons appeared in the region 8.00–7.35 ppm. Presence of an AB-system due to protons of the P—CH—CH-grouping and lack of a signal due to protons of a methylene group (—CH_2—C—P) rules out an alternative structure like **7**.



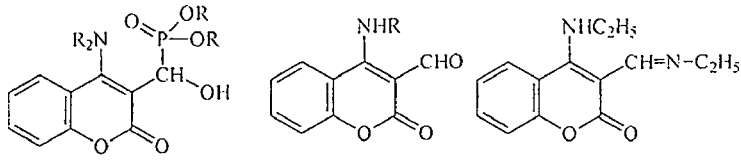
7
(not formed)

The mass spectrum of **6a** showed the molecular ion peak at m/z 366 (368); corresponding to $C_{15}H_{12}ClN_2O_5P$. Loss of $CH(CN)_2$ radical from M^+ yields cation **c** at m/z 301 (303). Meanwhile, loss of Cl radical from M^+ affords cation **d** at m/z 331 (base peak). The molecular ion peak of **6a** can also eject a neutral HCl molecule to give a radical cation of type **e** (m/z 330). Cation **g** at m/z 257 is most probably formed via expulsion of $P(O)(OCH_3)_2$ radical from M^+. The same process also can afford cations **h**, m/z 109 and **i**, m/z 110 respectively.



Compounds **6** regenerate the appropriate starting materials (**2** + **3**) upon thermolysis under reduced pressure. ^{13}C NMR spectrum of **6a** showed signals at 39.98 (—CH), 42.30 (—CH), 53.68 (OCH_3), 55.11 (OCH_3), 110.76, 111.29, 117.70 (125.65), 126.81, 134.20, 152.11, 158.85 coumarin ring carbon atoms, 117.07, 117.94 $(CN)_2$ and 201 (C=O).

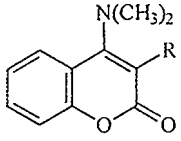
In an attempt to obtain new structures incorporating both P and N moieties as in the case of a variety of broadly used biocides,[10–12] we have investigated the reaction of certain amines with compounds **5**. The beseeched products **8**, however, could not be formed. Instead, compounds **5** underwent amine-induced dephosphorylation yielding aminated products of type **9**.



a, R = $-(CH_2)_2-CH_3$
b, R = $-(CH_2)_3-CH_3$
c, R = $-(CH_2)_2OCH_3$

The Schiff base **10** was formed only when ethylamine was used in the transamination reaction. Compatible elementary and spectroscopic data were obtained for compounds **9a–c** and **10**. Elementary analyses and molecular weight determination (MS) of **9c**, taken as a representative example, corresponded to $C_{13}H_{13}NO_4$. Its IR spectrum (KBr, cm^{-1}) showed bands at 3400 (NH), 1680 (C=O), 1610, 1550 (C=C) and 1260 (C–O, stretching). The ^1H NMR of **9c** ($CDCl_3$, δ ppm) showed signals at 12.15 (NH, s), 8.05–7.30 (4H, aromatics, m), 10.20 (C=C<u>H</u>, s), 4.10 (C<u>H</u>$_2$, d, $J_{HH} = 9$ Hz), 3.80 (CH_2, d, $J_{HH} = 9$ Hz), 3.50 (3H, OC<u>H</u>$_3$, s), and 3.35 (2H, C<u>H</u>$_2$, d, $J_{HH} = 9$ Hz). Its ^{13}CNMR spectrum showed signals due to the C=O groups at 211.82 (C=O, pyrone) and at 191.84 ppm (<u>C</u>–O, aldehyde). The coumarin-ring carbon atoms appeared as a cascade of signals at 106.76, 114.12, 118.89, 123.63, 127.37, 134.45, 155.46, and 159.73 ppm. The spectrum also showed signals at 70.40 (<u>C</u>H$_2$), 59.40 (O<u>C</u>H$_3$), 47.52 (<u>C</u>H$_2$). This conclusion is also confirmed by Distortion less Enhancement by Polarization Transfer (DEPT) measurement

The behavior of compounds **1** and **2** toward hexamethylphosphorustriamide **4** also was investigated. The reactions proceeded in tetrahydrofuran at ambient temperature to give products devoid of phosphorus (**11a** and **11b** respectively).



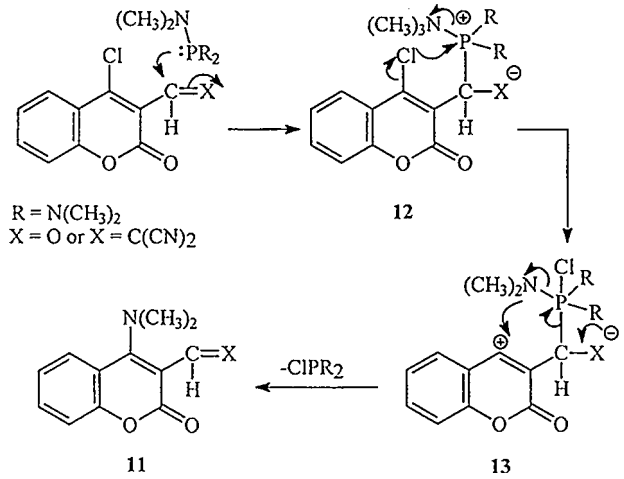
11

a, R = CHO
b, R = -CH=C(CN)2

Compounds **11a** and **11b** were unequivocally prepared and identified (m.p., mixed m.p. and comparative IR and MS spectra) upon reacting **1** and **2**, respectively with dimethylamine in tetrahydrofuran.

The reaction mechanism is depicted in Scheme 1. Initial nucleophilic attack by the phosphine-phosphorus atom on **1** (or **2**) would produce a betaine of structure like **12**.[13b] By virtue of the great affinity of phosphonium ions to halides,[13a] would facilitate formation of a transient betaine of type **13**. The latter in which phosphorus can act as a good leaving group due to its bulkiness[13a] decomposes then to afford **11**.

Analytic and spectroscopic data recorded for compound **11** afford strong support for the postulated mechanism.



SCHEME 1

CONCLUSION

Apparently, 4-chloro-3-coumarincarboxaldehyde **(1)** and 4-chloro-(β,β-dicyanoethenylidene)coumarin **(2)** undergo preferential attack by dialkylphosphonates **(3a–c)** at position-3 to give phosphonate 1:1 adducts of types **5** and **6** respectively. Adducts **5** undergo amine-induced dephosphorylation and dechlorination upon reaction with aliphatic primary amines. In terms of the Hard-Soft-Acid-Base (HSAB) principle,[14,15] the reacting amines may be considered as softer (stronger) bases, than dialkyl phosphonates **(3)**.

Hexamethylphosphorustriamide **4** induces chlorine displacement in **1** and **2** to yield the respective 4-(dimethylamino)- derivatives **11**. To the best of our knowledge, this represents a new era for utilising **4** as an aminating agent.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded in KBr 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 at 70 eV.

4-Chloro-2-oxo-2H-chromene-3-carboxaldehyde was prepared by a known procedure.[17] The phosphorus reagents and amines were available from Aldrich Co. The phosphites were freshly distilled before use.

Physical and spectral data of the new compounds are compiled in Tables I and II.

Preparation of 4-Chloro-3-(β,β-dicyanoethenylidene)-coumarin (2)

A mixture of **1** (2.08 g, 0.01 mmol) and malononitrile (0.66 g, 0.01 mmol) in 50 ml absolute ethanol was stirred at room temperature for 4 h. The solid formed was collected then recrystallized from cyclohexane to give **2** as yellow crystals, yield 79%. Physical and analytical data of compound **2** are presented in Table I. The ^{1}H NMR spectrum showed a multiplet due to the aromatic protons in the δ 8.00–7.30 region wherein emerged a singlet (1H) at δ 7.80 due to the exocyclic ethylenic proton.

Reaction of 4-Chlorocoumarin-3-carboxaldehyde (1) and 4-chloro-3-(β,β-dicyanoethenylidene)coumarin (2) with Dialkyl Phosphites (3a–c)

General Procedure

A mixture of **1** (0.01 mmol) and dialkyl phosphite (dimethyl-, diethyl-, and diisopropyl phosphites, 5 ml) was heated in the absence of solvent at 100°C for 2–4 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 **5a–c**.

Similarly compounds **6a–c** were isolated upon reacting **2** with **3a–c** (yield 80%). Physical, analytical and spectral data for compounds **5a–c** and **6a–c** are presented in Tables I and II.

Action of Heat on Phosphonate 5a

Compound **5a** (0.05 g) was heated in a cold finger sublimator at 230°C (bath temperature) under reduced pressure (5 mm/Hg) for 30 min. The compound that sublimed was collected (85%), recrystallized from ethyl alcohol to give yellow crystals, proved to be 4-chlorocoumarin-3-carboxaldehyde **(1)** (m.p., mixed m.ps. 123°C, and comparative IR spectra). Dimethyl phosphite was detected in receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of alkali.[16]

TABLE I Physical, Analytical, IR, and MS Spectral Data of Compounds **2**, **5a–c**, **6a–c**, **9a–c**, **10**, and **11a**,**b**

Comp.	Yield[a] (%)	m.p. (°C)	Mol. form (m. wt.)	Anal. (Calcd./Found) C	H	Cl	N	P	M + M/z %	IR cm^{-1} C=O	C=C	CN
2	79	198–200	$C_{13}H_5ClN_2O_2$	60.83	1.96	13.81	10.91		256	1750	1600	2210
			(256.64)	60.56	2.10	14.00	11.15		(100)			
										P=O	P–O–C	OH
5a	80	151–153	$C_{12}H_{12}ClO_6P$	45.23	3.79	11.12	—	9.72	318	1220	1050	3250
			(318.64)	45.00	4.00	10.94		10.01	(8.40)			
5b	75	106–108	$C_{14}H_{16}ClO_6P$	48.50	4.65	10.22	—	8.93	346	1200	1050	3300
			(346.70)	48.82	4.94	10.58		8.64	(100)			
5c	85	95–98	$C_{16}H_{20}ClO_6P$	51.28	5.37	9.46	—	8.26	374	1220	1000	3440
			(374.75)	50.98	4.97	9.63		7.89	(100)			
										P=O	P–O–C	CN
6a	60	160–162	$C_{15}H_{12}ClN_2O_5P$	49.13	3.29	9.66	7.63	8.44	366	1260	1050	2220
			(366.69)	49.45	3.50	9.83	7.92	8.50	(10.35)			
6b	65	125–127	$C_{17}H_{16}ClN_2O_5P$	51.72	4.08	8.98	7.09	7.84	394	1253	1049	2260
			(394.72)	52.00	4.34	9.11	6.85	7.50	(16.99)			
6c	70	105–107	$C_{19}H_{20}ClN_2O_5P$	53.97	4.76	8.38	6.62	7.32	422	1263	1096	2200
			(422.80)	54.24	5.01	8.55	6.93	7.54	(30.15)			
										HC=O	NH	C=C
9a	70	185–187	$C_{13}H_{13}NO_3$	67.52	5.66	—	6.06	—	231	1700	3400	1600
			231.25	67.88	5.95		5.86		(50.18)			
9b	60	158–160	$C_{14}H_{15}NO_3$	68.55	6.16	—	5.71	—	245	1705	3420	1605
			245.27	68.90	6.45		5.95		(66.55)			
9c	65	125–127	$C_{13}H_{13}NO_4$	63.15	5.29	—	5.66	—	247	1710	3400	1605
			247.24	63.50	4.95		6.00		(30.45)			
10	75	102–104	$C_{14}H_{16}N_2O_2$	68.83	6.60	—	11.46	—	244	C=O	NH	CH=N
			244.29	69.02	6.35		11.85		(30.68)	1700	3400	1640
11a	75	130–132	$C_{12}H_{11}NO_3$	66.35	5.10	—	6.44	—	217	HC=O	$-N-(CH_3)_3$	C=C
			217.22	66.00	4.95		6.21		(100)	1702	2942	1567
11b	80	75–77	$C_{15}H_{11}N_3O_2$	67.91	4.17	—	15.84	—	265	C=O	$-N-(CH_3)_3$	CN
			265.27	68.23	4.45		16.03		(100)	1704	2930	2209

Solvents of crystallization: **5b**,**c**, **10** cyclohexane, **6b**,**c** pet. ether 60–80°C, **11a**,**b** acetone-pet. ether 40–60°C.
[a]approximated.

TABLE II ^{31}P NMR, ^{1}H NMR, and ^{13}C NMR Spectral Data of Compounds **5b**,**c**, **6b**,**c**, **9a**,**b**, **10** and **11a**,**b**

Comp.	^{31}PNMR	^{1}H NMR[a]	^{13}C NMR
5a	20.80	3.75, 3.95 [2* d, 6H, P–(O–C–C$\underline{H}_3$)$_2$], 4.25 [brs, 1H, O$\underline{H}$], 5.50 [d, 1H, $^{2}J_{HP}$ = 22 Hz, P–C$\underline{H}$], 7.40–8.00 [m, 4H, aromatics].	
5b	19.20	1.25 [d of t, 6H, P–(O–C–C$\underline{H}_3$)$_2$], 4.15 [d of quint, 5H, P–(O–C$\underline{H}_2$–C)$_2$ and O$\underline{H}$], 5.6 [d, 1H, $^{2}J_{HP}$ = 18 Hz, P–CH], 7.4–8.05 [m, 4H, aromatics].	
5c	18.00	1.25 [m, 12H, P–(O–C–C$\underline{H}_3$)], 4.4 [bs, OH], 4.75 [d of sept., 2H, P–(O–C$\underline{H}$–C)$_2$], 7.4–8.00 [m, 4H, aromatics].	
6b	18.00	1.4 [d of t, 6H, P–(O–C–C$\underline{H}_3$)$_2$], 4.25 [d of quint, 4H, P–(O–C$\underline{H}_2$–C)$_2$], 4.5 [2d, 1H, $^{2}J_{HP}$ = 19.8 Hz, P–C$\underline{H}$], 5.25 [2d, 1H, $^{3}J_{HP}$ = 19.8 Hz, CH(CN)$_2$], 7.35–8.05 [m, 4H, aromatics].	
6c	14.79	1.4 [m, 12H, P–(O–C–C$\underline{H}_3$)$_2$], 4.4 [2d, 1H, $^{2}J_{HP}$ = 19 Hz, P–C$\underline{H}$], 4.85 [d of sept. 2H, P–(O–C$\underline{H}$–C)$_2$], 5.2 [2d, 1H, $^{3}J_{HP}$ = 19 Hz, C$\underline{H}$(CN)$_2$], 7.35–8.00 [m, 4H, aromatics].	
9a		1.1 [t, 3H, (–C–C$\underline{H}_3$)], 1.95 [q, 2H, –C$\underline{H}_2$–C], 3.95 [t, 2H, N–C$\underline{H}_2$–C], 7.1–8.05 [m, 4H, aromatics], 10.1 [s, 1H, CHO], 12.05 [s, 1H, N$\underline{H}$].	11.32 (C$\underline{H}_3$), 23.49 (C$\underline{H}_2$), 49.59 (C$\underline{H}_2$), 96.43, 114.23, 118.85, 123.64, 127.64, 134.46, 155.50, 159.55 coumarin ring carbon atoms, 191.87 (C$\underline{H}$O), 211.82 (C$\underline{=}$O).
9b		1.0 [t, 3H, (–C–C$\underline{H}_3$)], 1.9, 4.2 [m, 6H, -(C$\underline{H}_2$)$_3$–C], 7.1–8.0 [m, 4H, aromatics], 10.1 [s, 1H, C$\underline{H}$O], 12.05 [s, 1H, N$\underline{H}$].	
10		1.1 (t, 3H, C–CH$_3$), 1.5 [t, 3H, (–C–C$\underline{H}_3$)], 3.5 (q, 2H, CH$_2$), 4.0 [q, 2H, –(C$\underline{H}_2$–C)], 7.1–8.05 [m, 4H, aromatics], 8.65 [s, 1H, C$\underline{H}$=N].	15.53 (C$\underline{H}_3$), 16.94 (C$\underline{H}_3$), 42.49 (C$\underline{H}_2$), 54.73 (CH$_2$), 92.18, 115.50, 118.31, 123.06, 126.57, 132.32, 154.29, 156.28 (coumarin ring carbon atoms), 160.73 (C$\underline{H}$=N), 201.20 (C$\underline{=}$O).
11a		3.5 [2s, 6H, (–N–C$\underline{H}_3$)$_2$], 7.20–8.10 [m, 4H, aromatics], 8.50 [s, 1H, C$\underline{H}$O].	15.35 (CH$_3$), 20.24 (CH$_3$), 95.01, 115.34, 121.55, 124.22, 126.57, 134.32, 155.30, 163.11 (coumarin ring carbon atoms), 190.28 (C$\underline{H}$O), 201.20 (C$\underline{=}$O).
11b		3.6 [2s, 6H, (–N–C$\underline{H}_3$)$_2$], 7.20–7.80 [m, 4H, aromatics], 8.20 [s, 1H, C$\underline{H}$=C(CN)$_2$].	

[a]NMR measurements run in $CDCl_3$.

Reaction of Phosphonate 5a with Amines

General Procedure

A solution of the amine (propylamine, butylamine methoxy-ethyl amine) (2 mmol) in absolute methanol (20 ml) was added dropwise at 0–5°C to a stirred mixture of **5a** (1 mmol) in the same solvent over a period of 30 min. Upon cooling for 2 h, the crystalline product which separated was collected by filtration, washed successively with methanol, and water then recrystallized from a suitable solvent to give compounds **9a–c**. After concentrating the filtrates under reduced pressure additional products were obtained; for more details see Tables I and II.

Reaction of Phosphonate 5a with Ethylamine

A solution of ethylamine (2 mmol) in absolute ethanol (20 ml) was added dropwise at 0–5°C to a stirred mixture of **5a** (1 mmol) in the same solvent (5 ml) over a period of 10 min. On cooling, the crystalline product which separated was collected by filtration, washed successively with ethanol and water, then recrystallized from cyclohexane. (Tables I and II).

Reaction of 1 and 2 with Hexamethylphosphorustriamide (HMPT) (4)

General Procedure

A mixture of **1** (2.08 g, 0.01 mmol) and HMPT (0.01 mmol) in dry tetrahydrofuran (50 ml) was kept at room temperature for 2 h and the solid formed was collected, then recrystallized from petroleum ether (40–60°C)/ether to give **11a** (yield: 75%). Similarly **11b** was isolated upon reacting **2** with **4** (yield 85%). Physical, analytical and spectral data of compounds **11a**,**b** are presented in Tables I and II.

Reaction of 1 and 2 with Dimethylamine

General Procedure

A mixture of **1** (0.01 mmol) and dimethylamine (0.01 mmol) in dry tetrahydrofuran (50 ml) was refluxed for 4–6 h and the solid formed was collected and proved to be **11a** (m.p., mixed m.p. and comparative IR and MS spectra). Similarly **11b** was isolated upon reacting **2** (0.01 mmol) and diethylamine (0.01 mmol) in dry tetrahydrofuran (50 ml).

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