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Synthesis and Reactions of Phosphino- and Phosphono Substituted-Coumarins

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Abstract: Aminophosphine-ylides **4a** and **4b** were prepared in high yields by treating 3-acetyl coumarins **1a** and **1b** with trisdimethylaminophosphine **2**. Chemical degradation reactions for the ylides **4a,b** (e.g., formation of the phosphonium salt, Wittig reaction, hydrolysis) were suggested and illustrated. Reaction of trialkyl phosphites with 3-acetyl coumarins **1a** and **1b** yields the respective dialkyl phosphonates (1:4 addition) **12a,b.** Conversely, dialkyl phosphonates react with the same species **1a,b** to give the tautomeric monophosphonates **17A** $\rightleftharpoons$ **17B** *via* both 1,4- and 1,2 additions, in contrast to earlier reports.

Key words: 3-Acetyl coumarins-trialkyl phosphites-trisdimethylaminophosphine-aminophosphine-ylides.

INTRODUCTION

Research into new phosphino- and phosphono- heterocyclic compounds has received close scrutiny over the past two decades because of its possible relevance to the mechanisms of certain enzymatic events.[1-4] It is less well known that a number of modified phosphino- and phosphono substituted-heterocycles have been synthesized and applied in mechanistic and enzymatic studies.[1,5] Due to this fact, our interest has been recently directed towards the synthesis of these compounds.[6-11] Phosphino- and phosphono substituted-coumarins should be important as a considerable number of naturally occuring coumarins such as *murralongin*,[12] *osthol* and *2,3-auraptin*[12,13] were found to have strong antimicrobial and anticancer activities. Also it is reported that coumarin derivatives are known to possess fungicidal and bactericidal properties.[14,15]

In a previous communication[16] we reported syntheses of different coumarinyl [2,1-*b*] fused cyclic derivatives by treating 2-acetyl (3H)naphtho[2,1-*b*]pyran-3-one **1a** (also known as 3-acetyl 5,6-benzocoumarin) with different types of phosphorus ylides. In this article we encountered efficient synthetic routes to a number of phosphino- and phosphono substituted-coumarins. and a comment on related papers[17,18] in this area.

RESULTS AND DISCUSSION

I. *Reaction of* 1a,b *with Trisdimethylaminophosphine* 2.

The reaction of triaminophosphine **2** with 3-acetyl 5,6-benzocoumarin **1a** was rapid and exothermic in

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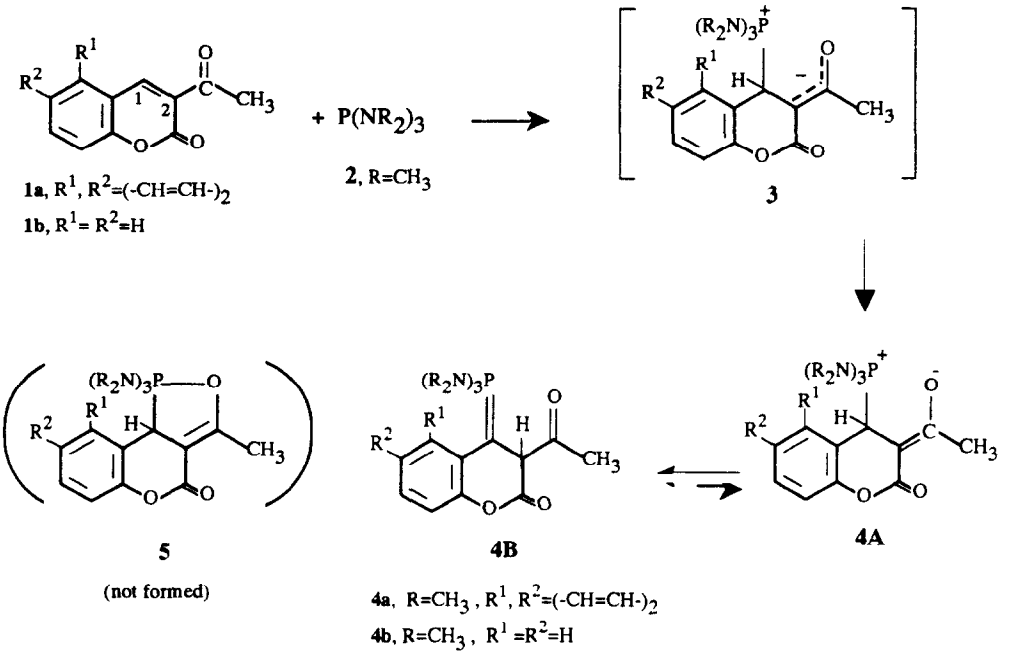
methylene chloride at 5 °C. The resulting 1:1 adduct is formulated as trisdimethylamino 2-acetyl (3H)naphtho[2,1-*b*][1H-3-oxo-pyran-1-yl] phosphorane **4Aa** ⇌ **4Ba** (82%) (Scheme 1) from the spectral and chemical data presented below. Likewise, the reaction product of trisdimethylaminophosphine **2** with 2-acetyl (3H)benzo[*b*]pyran-3-one **1b** (also known as 3-acetyl coumarin) is assigned an analogous structure **4Ab** ⇌ **4Bb** (82%, crude) on the basis of comparable spectroscopic arguments. No metastable precursor of **4** could be detected in a spectral investigation of the course of the reaction. Evidently, the α,β-unsaturated ketone system **1** underwent a 1,4 addition, as usual, at the β-carbon atom; but the resulting C-phosphonium betaine **3** rearranged to the more stable ylidic forms **4A** ⇌ **4B**. The situation is somewhat analogous to that encountered in the addition of triaminophosphines to activated double bonds.[19,20] Obviously, the very weak basicity of the ylides shows the stability which is conferred to a molecule by the presence of a phosphonium ion and a highly delocalized negative charge. Part of this stability is undoubtedly due to some phosphorane contribution to the resonance hybride. A point worth mentioning is that the phosphorus of trisdialkylaminophosphines add to the oxygen atom of phenanthraquinone, of diphenylpropanetrione and of diethyloxamalonate. The central carbonyl-oxygen is attacked in the last two compounds. The 1:1 adducts thus formed have open dipolar structures with positive ^{31}P-NMR shifts.[21]

Scheme 1



1a, R^1, R^2=(-CH=CH-)$_2$
1b, R^1= R^2=H

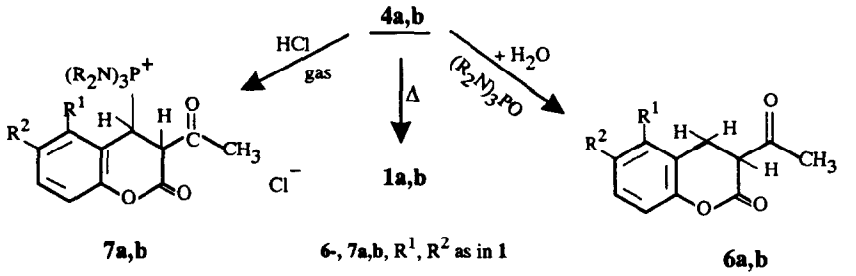
4a, R=CH_3, R^1, R^2=(-CH=CH-)$_2$
4b, R=CH_3, R^1 =R^2=H

Compounds **4** are obtained as water-sensitive, yellow crystals, quite stable for two weeks in a dissicator. The ^{31}P-NMR ($CDCl_3$) spectrum of **4a** (for example) has two chemical shifts at δp 58.4 and 64.6 ppm (1:3 *ratio*) assigned to **4Aa** and **4Ba**, respectively. These high-field resonances are inconsistent with oxaphospholenes **5**. The ^{1}H-NMR spectrum of **4a** showed the C-1-proton (**4Aa**) as a doublet at 4.13 with a

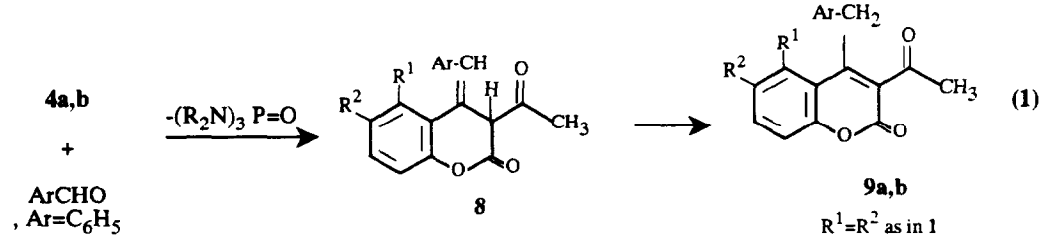
rather large coupling constant ($^2J_{HP}$= 24.4 Hz), while the C-2-proton (**4Ba**) appeared as a doublet ($^3J_{HP}$= 11.8 Hz) at 4.55 ppm. The six methyl groups attached to nitrogen gave two doublets (**4Aa** & **4Ba**) (J_{HP}= 10.7 Hz) at 2.61 and 2.64, indicating that the three dimethylamino groups are magnetically equivalent. However, attempts at resolving **4** into **4A** and **4B** have been unsuccessful so far, although this has been achieved on similar occasions.[20,21a]

Exposure of **4** to air or quenching the crude reaction product with water resulted in its conversion to the reduced form **6**. Hexamethylphosphorustriamide was also identified in the product mixture, ^{31}P-NMR, δ= 24.3 ppm (Scheme 2). On heating amino-ylides **4** above their melting points under reduced pressure, they regenerated the respective starting material **1a** or **1b**, respectively. Moreover, amino-ylides **4** could be converted into stable phosphonium salts **7** by anhydrous hydrogen chloride in CH_2Cl_2 solution. The elemental analyses of **7** showed that one mole of HCl had combined with one mole of **4**. The ^{31}P-NMR shifts of **7** (δp= ~52 ppm) is consistent with the fact[19a] that ^{31}P-NMR resonances of triaminophosphine ylides occur, in

Scheme 2



contrast to triphenylphosphine ylides, at higher magnetic fields than the resonance of corresponding phosphonium betaines or phosphonium salts. Finally, we have also investigated whether the amino-ylides **4** can undergo reactions with aromatic aldehydes in the Wittig reaction. Such a reaction would be expected to lead to the formation of hexamethylphosphorustriamide and an alkene. When a mixture of **4a** (or **4b**) and benzaldehyde was heated under reflux in toluene for 5 h, ^{31}P-NMR spectroscopy indicated the formation of $(R_2N)_3P{=}O$, δp= 24.5 ppm) and the coumarin derivatives **9a,b** (eqn. 1), on the basis of their elemental analyses and spectral properties. Obviously, the initial Wittig product **8** underwent a rapid proton shift to give 1-benzyl substituted-coumarin **9a** or **9b**.

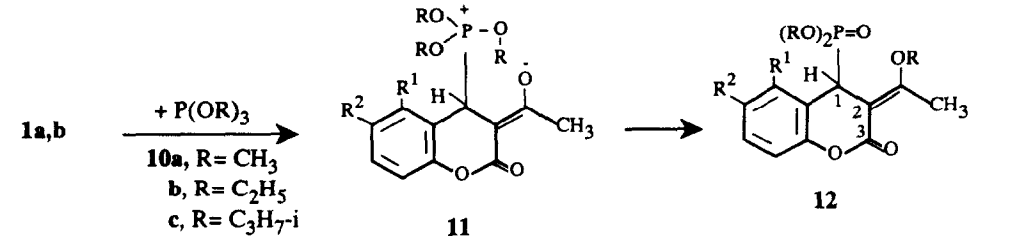


(1)

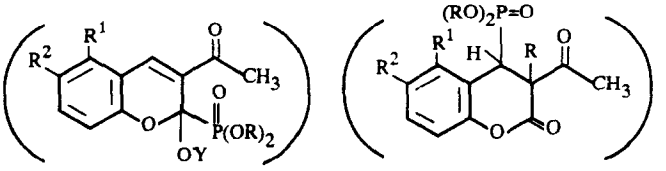
II. *Reaction of 3-Acetyl 5,6-Benzocoumarin* 1a *with Trialkyl Phosphites*.

When equimolar amounts of 3-acetyl 5,6-benzocoumarin **1a** and trimethyl phosphite (TMP, **10a**) in toluene were allowed to react at reflux, a crystalline 1:1 adduct was formed in 72% yield, the structure of which is established to be **12a** rather than **13** or **14** (Scheme 3) based upon spectral data interpretation.

Scheme 3



12-14	R	R^1, R^2
a	CH_3	$(-CH=CH-)_2$
b	C_2H_5	$(-CH=CH-)_2$
c	C_3H_7-i	$(-CH=CH-)_2$
d	CH_3	$R^1=R^2=H$
e	C_2H_5	$R^1=R^2=H$
f	C_3H_7-i	$R^1=R^2=H$



The ^{31}P-NMR spectrum (d_6-DMSO) of dimethyl 2-ethyl-1-ene-l-methylether (3H)naphtho[2,1-*b*]-(1H-3-oxo-pyran-1-yl)phosphonate **12a** recorded a positive shift at δ 22.29 ppm. Presence of the lactone carbonyl function **12a** was inferred from a strong band at 1711 in its IR-spectrum, and a signal at δc 169.5 ppm. On the other hand, the strong acetyl carbonyl band present in the IR spectrum of **1a** at 1688 cm^{-1} was absent in the IR spectrum of **12a**. Presence of the methylether group (C-O-CH_3) in **12a** was strongly supported by a singlet at δ_H 3.88 and at δc 53.5 ppm. The two methoxyl groups attached to the phosphorus atom appeared as two doublets (6H, each with $^3J_{HP}$ = 11.9 Hz) at δ_H 3.55 and 3.75 ppm. This splitting is due to the asymmetric center of the molecule.[22] Furthermore, the C-1-proton present in the ^{1}H-NMR spectrum of **1a** at 6.45 was absent in the spectrum of **12a**. Instead, the C-1-proton in **12a** appeared as a doublet ($^2J_{HP}$= 24.5 Hz) at δ_H 4.75 and as a doublet ($^1J_{cp}$ = 143.3 Hz) at δc 33.8. The presence of CH-P and C-O-CH_3 signals and the lack of signals due to C-2-CH_3 (*cf.* **13**) nor C-OH (*cf.* **14**) in the NMR of **12a**, as well as the absence of an acetyl carbonyl band (*cf.* **13** or **14**) in the IR- or ^{13}C-NMR spectra confirm the assigned structure **12** and rule out other alternative structures like **13** or **14**.

In a similar way, the reaction product of **1a** with triethyl phosphite (TEP, **10b**) was assigned an analogous structure **12b** (78%). Conversely, treatment of **1a** with triisopropyl phosphite **10c** afforded a

mixture of the expected analogue **12c** together with the vinyl phosphonate **17c** (Scheme 4). This behaviour is not unexpected since the bulky isopropyl group could impede the Arbusov reaction, whereas a partial hydrolysis at the dipolar intermediate **11c** has occured to give the final products **12c** along with **17c** *via* the intermediate **16c**.

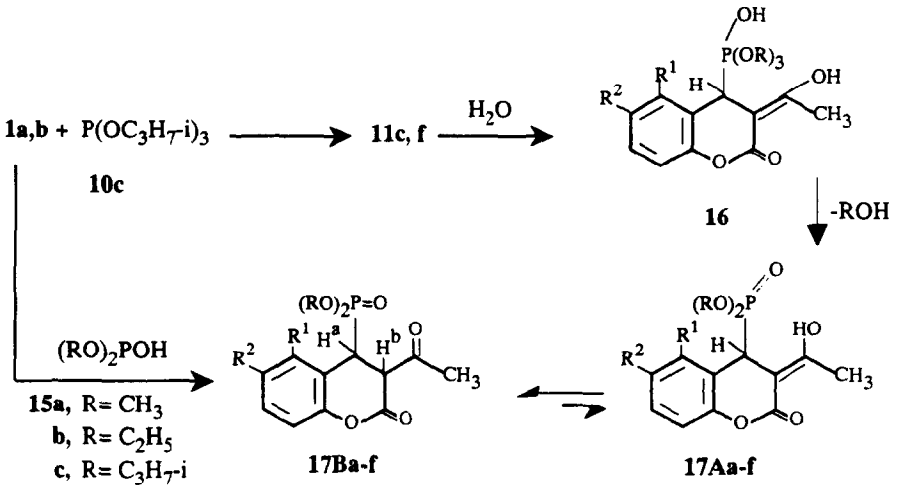
The formation of monophosphonates **12** could be rationalized in terms of a nucleophilic attack by the phosphite-phosphorus on the β-carbon atom (C-1) of the α,β-unsaturated carbonyl system in **1a** to give the dipolar form **11** (Scheme 3), which occurs *via* 1,4 addition. Stabilization of **11** was attained by formation of the P=O and the intramolecular alkyl group transfer to the more stable phosphonate product (with **10a,b**, Scheme 3) or underwent partial hydrolysis (with **10c**) to give **12c** and **17c** (Scheme 4).

III. *Reaction of 3-Acetyl 5,6-Benzocoumarin* **1a** *with Dialkyl Phosphonates. :*

The behaviour of **1a** towards dialkyl phosphonates **15a-c** was next studied and the products obtained are detected in Scheme 4.

Treatment of **1a** with dimethyl phosphonate **15a** under the conditions previously described with **10**, led to the formation of noncrystalline material which was assigned dimethyl 2-ethyl-1-en-1-ole (3H)naphtho-[2,1-b](1H-3-oxo-pyran-1-yl) phosphonate **17a**. The ^{31}P-NMR spectrum of **17a**, however, showed two resonances at δp 21.5, 22.88 ppm (1:2.5 *ratio*), indicating that **17a** is present in two different tautomeric structures **17Aa** and **17Ba**. Evidently, the initial vinyl phosphonate **17Aa** showed some tendency to rearrange to the more stable tautomer **17Ba**. Similar 1,2-addition has been encountered in the reaction of dialkyl phosphonates with 1-dicyanomethylene acenaphthen-2-one and others.[23] Structural assignment for **17a-c** is based upon correct analytical values and molecular weight measurements (MS) for all new compounds. Adducts **17** regenerate the starting material **1a** upon heating above their melting points under reduced pressure and yield the corresponding monomethyl ether **12a** upon treatment with CH_3I and K_2CO_3 in acetone solution.

Scheme 4



17a-f. R. R^1, R^2 as in **12**

On the other hand, the presence of the two tautomeric structures **17A**⇌**17B** in solution could be detected by NMR spectroscopy. In the ^{1}H-NMR (d_6-DMSO) spectrum of **17a**, C-1-H**a** and C-2-H**b** protons (**17Ba**) appeared as two doublets (*AB* system). That of proton **a** was centered at 4.45 with $^2J_{HP}$= 8.5 Hz along with the OH proton (**17Aa**) at 12.83 ppm. The presence of the *AB* system in **17Ba** was also attested by a doublet ($^1J_{cp}$ = 143.7 Hz) at δc 35.8 (HC-1-P) and a doublet ($^2J_{cp}$ = 10.2 Hz) at δc 84.7 ppm (HC-P-C-2H). These values coincide with expected shifts for deshielded methine carbons due to the electron withdrawing phosphono- and carbonyl groups, respectively. However the weak signals for the OH in the ^{1}H-NMR and IR spectra as well as its melting point being lower than its methylether **12a** indicate **17B** as the main tautomer.

IV. ***Reaction of 3-Acetyl Coumarin*** **1b** ***with*** **10** ***and*** **15.** ***:***

Since 3-acetyl coumarin **1b** has an analogous structure to 3-acetyl 5,6-benzocoumarin **1a**, we presume that the mode of attack by **10** and **15** on **1b** should be along the line we have explained in this investigation for C-1-phosphorylation of **1a** by these phosphorus reagents. Conversely, Hamad *et al*[17] assigned the α-hydroxy phosphonate structure **14** (Scheme 3) to the products formed in the reactions of **1b** either with trialkyl phosphites or with dialkyl phosphonates. These results were, however, not adequately justified. Later on and while this investigation was in progress, the same reactions were reinvestigated by Osman and coworkers[18] and they ascribed the vinyl phosphonate structure **12** to **1b**-TAP adducts and the γ-hydroxy phosphonate structure **17A** to **1b**-DAP products. It has been further claimed that both monophosphonates **12d,e** and **17Ad,e** are formed from the reaction of **1b** with **10a,b**. These contradictory results, however, are inconsistent with our above observations for the adducts obtained from the reaction of **1a** with TAP or DAP. Therefore it seems desirable to summarize at this time the results of our investigation in this field which are at variance with reported proposals.[17,18]

(1) The reaction of trimethyl- or triethyl phosphite **10a,b** with 3-acetyl coumarin **1b** was complete within ~10 h (TLC) whether the reaction was carried out in refluxing toluene or in the absence of solvent[17,18] to produce the corresponding phosphonate **12d** (74%) or **12e** (76%), respectively, as the sole reaction product. The isolated phosphonates **12d,e** are entirely identical in all aspects (m. ps. and spectral data) with that previously described by Osman *et al.*[18] and not with α-hydroxy phosphonates **14**.[17] In constrast to the earlier report,[18] there was no indication of any significant amount of **1b**-DAP adducts, at least under the prevailing experimental conditions.

(2) The reaction of triisopropyl phosphite **10c** with **1b**, which is practically new, afforded (as with **1a**) the corresponding monophosphonates **12f** (31%) and **17f** (21%). The formation of **17f** in the latter reaction was explained, as in the reaction of **1a** with **10c**, by the partial hydrolysis of the initial dipolar intermediate **11f** due to the bulky isopropyl moiety which impede the alkyl transfer (Scheme 4).

(3) Dimethyl-**15a**, diethyl-**15b** and diisopropyl **15c** phosphonates reacted, smoothly, with **1b** in refluxing toluene (or in the absence of solvent) to yield the respective tautomeric phosphonates **17Ad-f**⇌**17Bd-f** (Scheme 4). The presence of the two tautomeric structures **17A** and **17B** could be verified by NMR spectroscopy (see experimental section) and by analogy with **17a-c**. In favour of the tautomeric phosphonate formation is the lower melting points of **1a,b**-DAP products **17a-f** than the corresponding alkyl ethers **12a-f**, indicating **17B** is the major tautomer.

These results allow interesting conclusions to be drawn. Thus, considering the earlier report,[17] the

formation of α-hydroxy phosphonates **14** turned out to be irreproducible. As a consequence, we assume a different reaction course leading to C-1-phosphorylation (Schemes 3 and 4). With respect to the recent work cited,[18] we have been able to isolate the products **12d,e** from the reaction of **1b** with **10a,b**. These phosphonates were, however, obtained almost exclusively and in high yields, whereby we were unable to detect any significant amounts of **17d,e**. On the other hand, we presumed and proved that **1b**-dialkyl phosphonate adducts are in fact not one isomer, but they exist in the equilibrium **17A** $\rightleftharpoons$ **17B**. As stated in the report,[18] compounds **17d,e** respond to the ferric chloride reaction This seems in our opinion unlikely, since the hydroxyl function in **17A** is acidic (aliphatic) and not phenolic. Finally, some spectroscopic data attributed to the structure **17A** are rather compatible with **17B** or both together.

EXPERIMENTAL

All melting points are uncorrected. The IR (υ in cm^{-1}) were recorded in KBr pellets, using a Philips Infracord Spectrometer model PU 9712. The ^1H- and ^{13}C-NMR spectra were measured in $CDCl_3$ or [d_6] DMSO with a Joel-270 MHz Spectrometer, using TMS as an internal reference, δ are given in ppm, *J* in Hz, ^{31}P-NMR spectra were taken with a Varian CFT-20 (*vs.* external 85% H_3PO_4). The mass spectra were performed at 70 eV on a Shimadzu GCS-QP 1000 EX Spectrometer provided with a data system. Elemental analyses were carried out at the Microanalytical Center, Faculty of Science, Cairo University. The appropriate precautions in handling moisture-sensitive compounds were observed. All the reactions were performed under nitrogen.

I. ***Reaction of 3-Acetyl Coumarins* 1a,b *with Trisdimethylaminophosphine* 2.** A mixture of compound **1a**[24] or compound **1b**[25] (4.2 mmol) and dry CH_2Cl_2 (20 ml) was cooled to 5 °C and treated with triaminophosphine **2** (0.7 g, 4.2 mmol) in 5 ml of cold CH_2Cl_2 under N_2. There was an exothermic reaction; the solution became brown and the colour faded to yellow within 15 min (stirring). The reaction mixture was allowed to warm slowly to the room temperature and then further stirred for 3 h. The product residue after removing the solvent was triturated twice with pentane to give **4a** or **4b**, respectively. The yield of the crude ylides **4** was ~82%.

Trisdimethylamino 2-acetyl (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl) phosphorane **4a** was obtained as yellow needles (1.8 g, 72%), m.p. 163-165 °C (CH_2Cl_2-ether); [Found: C, 62.9; H 7.09; N, 10.52; P, 7.77. $C_{21}H_{28}N_3O_3P$ requires: C, 62.83; H, 7.03; N, 10.46; P, 7.72%]; IR (KBr): υ 1715 (C=O, lactone), 1683 (C=O, acetyl, **4Ba**), 1482 (enolate carbonyl); 1310, 875 (N-P). NMR ($CDCl_3$): δ_H 2.61, 2.64 (2*d, $^4J_{HP}$= 4.5 Hz; 2*3H, 2*C-CH_3, **4Aa** & **4Ba**), 2.72, 2.8 (2*d, $^3J_{HP}$= 10.7 Hz, 2*18H, 2*N-CH_3, **4Aa** & **4Ba**), 4.13 (d, $^2J_{cp}$= 24.4 Hz, 1H, C-1-**H**, **4Aa**), 4.55 (d, $^3J_{HP}$= 11.8 Hz, 1H, C-2-**H**, **4Ba**), 7.31-8.35 (m, 2*6H, Ar-**H**, **4Aa** & **4Ba**); δc 16.4, 16.8 (2*C-CH_3, **4Aa** & **4Ba**), 35.8 (d, $^1J_{cp}$= 144.6 Hz, HC-1-P, **4Aa**), 42.6 (d, $^2J_{cp}$= 7.3 Hz, C-2-H, **4Ba**), 45.2, 46.5 (2*d, $^2J_{cp}$= 7 Hz, 2*N-CH_3), 168.3, (C=O, lactone), 178 (C-O, **4Aa**), 188.2 (C=O, acetyl, **4Ba**); δp= 58.4, 64.6 ppm (1:3 *ratio*, **4Aa:4Ba**). MS (EI): *m/z* (%): M^+, found: 401 (18); requires: 401.47.

Trisdimethylamino 2-acetyl (3H)benzo[b](1H-3-oxo-pyran-1-yl)phosphorane **4b** was obtained as yellow needles (1.1 g, 68.4%), m.p. 108-109 °C (cyclohexane). [Found: C, 58.19; H, 7.38; N, 11.84; P, 8.88. $C_{17}H_{26}N_3O_3P$ requires: C, 58.11; H,7.46; N,11.96; P, 8.81%]; IR (KBr): υ 1710 (C=O, lactone), 1678 (C=O, acetyl, **4Bb**), 1487 (enolate carbonyl), 1320, 870 (N-P). NMR ($CDCl_3$): δ_H 2.55, 2.64 (2*d, $^4J_{HP}$= 3.8 Hz,

2*3H, 2*C-CH_3, 4Ab & 4Bb), 2.72, 2.83 (2*d, 2*18H, $^3J_{HP}$= 10.7 Hz, N-CH_3, **4Ab & 4Bb)**, 4.21 (d, $^2J_{HP}$= 22.5 Hz, 1H, C-1-H, **4Ab)**, 4.45 (d, $^3J_{HP}$= 11.8 Hz, 1H, C-2-H, **4Bb)**, 7.34-7.98 (m, 2*4H, Ar-H, **4Ab & 4Bb)**; δc 17.2, 17.5 (2*C-CH_3, **4Ab & 4Bb)**, 35.2 (d, $^1J_{cp}$= 143.3 Hz, HC-P, **4Ab)**, 44.1 (d, $^2J_{cp}$= 7.2 Hz, C-2-H, **4Bb)**, 46.2, 46.5 (2*d, $^2J_{cp}$= 7.4 Hz, 2*N-CH_3), 163.5 (C=O, lactone), 174 (C-O, **4Ab)**, 191.7 (C=O, acetyl, **4Bb)**; δp 54.3, 63.6 ppm (1:3 *ratio*) **4Ab** and **4Bb**, respectively). MS (EI): *m/z* (%): M^+, found: 351 (22); requires: 351.4.

***Action of Water on Triaminoylides* 4a,b.** When a solution of the ylide **4a** or **4b** (1g) in MeOH (20 ml) containing water (2 ml) was refluxed for 2 h, a mixture of 3-acetyl 5,6-benzocoumarin **1a**, its reduced form **6a** and hexamethylphosphorustriamide $[(CH_3)_2N]_3P=O$, was formed. The latter was detected in the distillate (^{31}P-NMR, δp= 24.3 ppm). Fractional crystallization of the residual material from cyclohexane afforded the coumarin derivative **6a** (280 mg, 48%) as colourless crystals, m.p. 133.5 °C (acetone). [Found: C, 74.88; H, 4.92. $C_{15}H_{12}O_3$ requires C, 74.97; H, 5.04%]; IR (KBr): υ 1718 (C=O, lactone), 1673 (C=O, acetyl). ^{1}H-NMR ($CDCl_3$): δ 2.53 (s, 3H, C-CH_3), 2.87 (d, J_{HH}= 8.4 Hz, 2H, C-1-H_2), 4.32 (t, J_{HH}= 8.4 Hz, 1H, C-2-H), 7.32 - 8.34 (m, 6H, Ar-H). MS (EI): *m/z* (%): M^+, found: 240 (100); requires: 240.11.

Similarly, compound **6b** was obtained by the action of H_2O on **4b** (1g) as colourless crystals (280 mg, 52%), m.p. 109 °C (cyclohexane). [Found: C, 69.53; H, 5.24. $C_{11}H_{10}O_3$ requires: C, 69.46; H, 5.3%]; IR (KBr): 1725 (C=O, lactone), 1670 (C=O, acetyl). ^{1}H-NMR: δ 2.55 (s, 3H, CH_3), 2.68 (d, J_{HH}= 8 Hz, 2H, C-1-H_2), 4.26 (t, J_{HH}= 8 Hz, 1H, C-2-H), 7.32-7.87 (m, 4H, Ar-H). MS (EI): *m/z* (%): M^+, found: 190(100); requires: 190.2.

***Reaction of Amino-ylides* 4a,b *with Hydrogen Chloride*.** A solution of **4a** (1 g) in dry CH_2Cl_2 (20 ml) was cooled to 0 °C and treated with anhydrous HCl gas to saturation. The yellow solution became colourless; the solvent was removed at reduced pressure, after 15 min., the solid (0.89 g, 82%) of the aminophosphonium salt **7a** was obtained, m.p. 155 °C (CH_2Cl_2 - ether). [Found: C, 57.48; H, 6.58; Cl, 7.98; N, 9.52; P, 7.14. $C_{21}H_{29}ClN_3O_3P$ requires: C, 57.59; H, 6.68; Cl, 8.09; N, 9.59; P, 7.07%]; NMR ($CDCl_3$): δ_H 2.55 (d, $^4J_{HP}$= 4.1 Hz, 3H, -CH_3), 2.76 (d, $^3J_{HP}$= 10 Hz, 18H, N-CH_3), 4.15 (d.d, J_{HP}= 24.2 Hz, J_{HH}= 12.8 Hz, 1H, HC-P), 4.63 (d.d, J_{HP}= 10.3 Hz, J_{HH}= 12.8 Hz, 1H, C-2-H), 7.36-8.4 (m, 6H, Ar-H); δp 53.2 ppm. MS (EI): *m/z* (%): M^+, found: 440/438 (33/100); requires: 437.92.

Similarly, Compound **7b** was obtained by the action of HCl gas on **4b** (1 g) as colourless material (0.88 g, 80%), m.p. 95 °C (acetone-light petroleum). [Found: C, 52.55; H, 6.95; Cl, 9.04; N, 10.78; P, 8.05. $C_{17}H_{27}ClN_3O_3P$ requires: C, 52.64; H, 7.02; Cl, 9.14; N, 10.83; P, 7.98%]; NMR ($CDCl_3$): δ_H 2.56 (d, $^4J_{HP}$ = 3.8 Hz, 3H, -CH_3), 2.77 (d, J_{HH}= 10 Hz, 18H, N-CH_3), 4.12 (d.d, J_{HP}= 23.7 Hz, J_{HH}= 13.2, 1H, HC-P), 4.56 (d.d, $^3J_{HP}$= 8.8 Hz, J_{HH}= 13.2 Hz, 1H, C-2-H), 7.26 - 7.78 (m, 4H, Ar-H); δp = 52.5 ppm. MS (EI): *m/z*: M^+, found: 389, 387 (33/100); requires: 387.86.

***Wittig Reaction of Amino-ylides* 4a,b.** To a solution of toluene (20 ml) containing 1g of **4a** (or **4b**), benzaldehyde (1 ml) was added. The reaction mixture was heated at the reflux temperature for 5 h and the solvent was, then evaporated. The residual material was washed thrice with cold light petroleum to give 1-benzylcoumarins **8a** and **8b**, respectively.

2-Acetyl 1-benzyl-(3H)naphtho[2,1-b]poyran-3-one **8a** was obtained as colourless crystals (0.6 g, 62%), m.p. 168-170 °C (CH_3CN). [Found: C, 80.39; H, 4.82. $C_{22}H_{16}O_3$ requires: C, 80.47; H, 4.91%]; IR (KBr): υ 1728 (C=O, lactone), 1685 (C=O, acetyl). ^{1}H-NMR ($CDCl_3$): δ_H 2.64 (s, 3H, C-CH_3), 2.88 (s, 2H, -CH_2), 7.31 - 8.34 (m, 11H, Ar-H). MS (EI): *m/z* (%): M^+, found: 328 (100); requires: 328.37.

2-Acetyl-1-benzyl-(3H)benzo[b]pyran-3-one **8b** was obtained as colourless crystals (0.55 g, 69%), m.p. 131-132 °C (CH_2Cl_2-ether). [Found: C, 77.74; H, 4.96. $C_{18}H_{14}O_3$ requires: C, 77.68; H, 5.07%]; IR (KBr): υ 1720 (C=O, lactone), 1677 (C=O, acetyl). ^{1}H-NMR($CDCl_3$), δ 2.62 (s, 3H, C-CH_3), 2.75 (s, 2H, -CH_2), 7.35-8.24 (m, 9H, Ar-H). MS (EI): *m/z* (%): M^+, found: 278 (100); requires: 278.31.

The ^{31}P-NMR spectrum of the reaction mixture prior to work up had a strong signal at δp= 24.8 ppm, $[(CH_3)_2N]_3P=O$, and some unidentified resonances.

Action of Heat on Amino-ylides **4a,b**. Compound **4a** (or **4b**) 0.5 g was heated in a cold finger sublimator at 250 °C (bath temperature) under reduced pressure (5 mm/Hg) for 30 min. The substance that sublimed was collected, recrystallized from the appropriate solvent to give pale yellow crystals, proved to be 3-acetyl 5,6-benzocoumarin **4a** or 3-acetyl coumarin **4b**, respectively (identified by m.p. and mixed m.ps. and comaparative IR spectra).

II. Reaction of 3-Acetyl Coumarins 1a,b with Trialkyl Phosphites.

(a) Reaction of 1a with* 10a,b. *General Procedure: A mixture of **1a** (1g, 4.2 mmol) and trimethyl- **10a** or triethyl phosphite **10b** was refluxed in dry toluene solution (30 ml). After the reaction was completed (TLC, ~ 8 h), the volatile materials were evaporated, *in vacuo*, and the residual substance was triturated thrice with hot cyclohexane and then recrystallized from the appropriate solvent to give **12a** or **12b**, respectively.

Dimethyl 2-ethyl-1-ene-1-methylether (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **12a** was obtained as colourless crystals (1.1 g, 72%), m.p. 156 °C (benzene). [Found: C, 59.58; H, 5.2; P, 8.62. $C_{18}H_{19}O_6P$ requires: C, 59.67; H, 5.28; P, 8.55%]; IR (KBr): υ 1711 (C=O, lactone), 1260 (P=O), 1100 (P-O-C). NMR (d_6-DMSO): δ_H 2.55 (d, $^4J_{HP}$= 4.2 Hz, 3H, C-CH_3); 3.55, 3.75 (2*d, J_{HH}= 8.2, $^3J_{HP}$= 3.7 Hz, 6H, P-O-CH_3); 3.88 (s, 3H, C-OCH_3), 4.75 (d, $^2J_{HP}$ = 24.5 Hz, 1H, H-C-P), 7.15-8.35 (m, 6H, Ar-H), δc 16.2 (C-CH_3), 33.8 (d, $^2J_{cp}$= 143.3 Hz, HC-P), 53.5 (C-O-CH_3), 62.4 (P-O-CH_3), 88.3 (d, $^2J_{cp}$= 8 Hz, C-2), 158.4 (d, $^3J_{cp}$= 3.6 Hz, = C-O-C), 169.5 (C=O, lactone); δp= 22.29 ppm. MS (EI): *m/z* (%): M^+, found: 362 (66); requires: 362.33.

Diethyl 2-ethyl-1-ene-1-ethylether (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **12b** was obtained as colourless crystals (1.3 g, 78%), m.p. 144 °C (CH_2Cl_2). [Found: C, 62.43; H, 6.32; P, 7.78. $C_{21}H_{25}O_6P$ requires: C, 62.37; H, 6.23; P, 7.66%]; IR (KBr): υ 1719 (C=O, lactone), 1265 (P=O), 1050 (P-O-C). NMR (d_6-DMSO): δ_H 0.87-1.23 (m, 3*d, *overlapped*, 9H, P-O-C-CH_3 & C-O-CH_3), 2.47 (d, $^4J_{HP}$= 2.8 Hz, 3H, C-CH_3), 3.73-4.07 (m, 3*q, 6H, P-O-CH_2 & C-O-CH_2), 4.82 (d, $^2J_{HP}$= 24.5 Hz. 1H, HC-P), 7.25-8.43 (m, 6H, Ar-H); δc 16.5 (C-CH_3), 18.2 (d, $^2J_{cp}$= 8.2 Hz, P-O-C-CH_3), 18.4 (-C-O-C-CH_3), 34.2 (d, $^1J_{cp}$= 148.6 Hz, HC-P), 62.2 - 64.6 (m, P-O-CH_2- & C-O-CH_2), 91.3 (d, $^2J_{cp}$= 8.3 Hz. C-2), 162.3 (d. $^3J_{cp}$=

4.1 Hz, =C-O-C), 169.9 (C=O, lactone); δp= 22.54 ppm. MS (EI): *m/z* (%): M^+, found: 404 (35); requires: 404.4.

(b) ***Reaction of* 1a *with* 10c.** Reaction of **1a** with triisopropyl phosphite **10c** was carried out in refluxing toluene, similar to the general procedure, using the same amounts. After evaporation of the volatile materials, *in vacuo*, **17c** and **12c** were obtained, respectively, by column chromatography [silica gel / light petroleum (b.r. 60-80 °C)] with increasing amounts of chloroform.

Diisopropyl 2-ethyl-1-en-1-ole (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **17c** was obtained (9:1, *v/v*) as colourless crystals (0.3 g, 18%), m.p. 129.5 °C (CH_3CN). [Found: C, 62.46; H, 6.17; P, 7.78. $C_{21}H_{25}O_6P$ requires: C, 62.37; H, 6.23; P, 7.66%], IR (KBr): υ 3803 (OH, **17Ac**), 1718 (C=O, lactone), 1647 (C=O, acetyl, **17Bc**), 1623 (C=C, ylidene, **17Ac**) 1261 (P=O), 1010, 990 (P-O-C). NMR (d_6-DMSO): δ_H 0.87-1.25 [2*2d (m), 2*12H, 2*P-O-C$(CH_3)_2$], 2.43, 2.47 (2*d, $^4J_{HP}$= 2.8 Hz, 2*3H, 2*C-CH_3), 4.21-4.53 (2*2 septs., 2*1H, 2*P-O-CH), 4.82, 5.13 (2*d, $^2J_{HP}$= 24.2 Hz, 2*1H, 2*HC-P, **17Ac** & **17Bc**), 5.28 (d, $^3J_{HP}$= 8.5 Hz, C-2-H, **17Bc**), 7.25-8.43 (m, 6H, Ar-H), 13.18 (s, 1H, -OH, *exchangeable with D_2O*, **17Ac**); δc: 19.3, 19.5 (2*C-CH_3), 22.5-24.7 [2*d, 2*P-O-C- $(CH_3)_2$, 34.5, 34.8 (2*d, $^1J_{cp}$= 144.6 Hz, 2*HC-P), 70.15-70.26 (m, 2*P-O-CH), 91.3 (d, $^2J_{cp}$= 8.8 Hz, P-C-C-2, **17Bc**), 163.1 (d, $^2J_{cp}$= 8.8 Hz, PC-C-2=, **17Ac**), 169.5 171.2 (2*C=O, lactone), 205.2 (C=O, acetyl, **17Bc**); δp = 21.2, 21.54 ppm (2:1 *ratio*, **17Bc**: **17Ac**). MS: *m/z* (%): M^+, found: 404(33); requires: 404.4

Diisopropyl 2-ethyl-1-ene-1-isopropylether (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **12c** was obtained (up to 8:2, *v/v*) as colourless crystals (0.49 g, 29%), m.p. 165 °C (acetone), [Found: C, 64.46; H, 6.92; P, 6.82. $C_{24}H_{31}O_6P$ requires: C, 64.56; H, 7.00; P, 6.94%]; IR(KBr): υ 1710 (C=O, lactone), 1263 (P=O), 1015, 990 (P-O-C). NMR (d_6-DMSO): δ_H 0.87 [d, J_{HH}= 6.5 Hz, 6H, C-O-$(CH_3)_2$], 0.95-1.23 [2*d of d (m), 12H, P-O-C$(CH_3)_2$], 2.43 (d, $^4J_{HP}$ = 2.6 Hz, C-CH_3), 4.22-4.68 (3*septs. (m), 2H & 1H, P-O-CH- & CO-CH-), 4.85 (d, $^2J_{HP}$= 23.6 Hz, 1H, HC-P), 7.25-8.43 (m, 6H, Ar-H); δc 19.78 (d, C-CH_3), 23.5, 24.1 [2d, P-O-C-$(CH_3)_2$], 35.7 (d, $^1J_{HP}$= 143.2 Hz, HC-P), 70.1-70.5 (m, P-O-CH & C-O-CH), 169.8 (C=O, lactone); δp= 22.88 ppm. MS (EI): *m/z* (%) : M^+, found: 446(48); requires: 446.49.

(c) ***Reaction of* 1b *with* 10a,b.** A mixture of **1b** (1 g, 5.3 mmol) and trimethyl-**10a** or triethyl phosphite **10b** (6 mmol) was refluxed in toluene for ~ 10 h. After removing the volatile materials, *in vacuo*, the residue was triturated with hot pentane and left to cool. The solid so formed was collected and recrystallized from the appropriae solvent to give **12d** (74%) or **12e** (76%). The identities of **12d** and **12e** (m.p., IR, ^1H-, ^{13}C- and ^{31}P-NMR) are exactly the same as previously described.[18] There was no indication for the formation of any **1a**-dialkyl phosphonate adducts **17d,e**, at least under our described conditions.

(d) ***Reaction of* 1b *with* 10c.** Triisopropyl phosphite **10c** reacted with **1b** whereas the procedure and the work up are the same (with **10a,b**), using the same amounts. After evaporation of the solvent, the residual material was subjected to column chromatography on silica gel. The column was then developed with hexane containing increasing amounts of chloroform to give **17f** and **12f**, respectively.

Diisopropoyl 2-ethyl-1-en-ole (3H)benzo[b](1H-3-oxo-pyran-1-yl)phosphonate **17f** was obtained (9:1, v/v) as colourless crystals (390 mg, 21%), m.p. 112-114 °C (cyclohexane). [Found: C, 57.55; H, 6.46; P, 8.83. $C_{17}H_{23}O_6P$ requires: C, 57.62; H, 6.54; P, 8.74%]; IR (KBr): υ 3820 (OH, **17Af**), 1715 (C=O, lactone), 1648 (C=O, acetyl, **17Bf**), 1622 (C=C, ylidene, **17Af**), 1247 (P=O), 1030 (P-O-C). NMR ($CDCl_3$): δ_H 0.91-1.213 [2*2d, (m) 2*12H, 2*P-O-C$(CH_3)_2$], 2.46, 2.51 (2*d, $^4J_{HP}$= 2.5 Hz, 2*3H, 2*C-CH_3), 4.17-4.35 (2*2 septs. (m), 2*1H, 2*P-O-CH), 4.65, 4.82 (2*d, $^2J_{HP}$= 24.5 Hz, 2*1H, HC-P, **17Af** & **17Bf**), 5.03 (d, $^3J_{HP}$= 4.5 Hz, C-2-H, **17Bf**), 7.25-7.73 (m, 4H, Ar-H), 13.36 (s, 1H, -OH, *exchangeable with* D_2O, **17Af**), δc 14.6, 15.3 (2*C-CH_3), 18.6, 19.5 [2*d, 2*P-O-C$(CH_3)_2$], 35.4, 35.8 (2*d, $^1J_{cp}$= 142.3 Hz, 2*HC-P), 65.7, 66.3 (m, 2*P-O-CH), 93.6 (d, $^2J_{cp}$= 8.6 Hz, P-C-C-2, **17Bf**), 158.7 (d, $^2J_{cp}$= 8.2 Hz, P-C-C-2=, **17Af**), 168.6, 169.4 (2*C=O, lactone), 196.8 (C=O, acetyl, **17Bf**); δp= 24.26, 24.68 ppm (2:1 *ratio,* **17Bf**: **17Af**). MS: *m/z* (%): M^+, found: 354 (60); requires: 354.35.

Diisopropyl 2-ethyl-1-ene-1-isopropylether (3H)benzo[b](1H-3-oxo-pyran-1-yl)phosphonate **12f** was obtained (up to 8:2, *v/v*) as colourless crystals (690 mg, 31%), m.p. 96-97 °C (pentane). [Found: C, 60.68; H, 7.28; P, 7.89. $C_{20}H_{29}O_6P$ requires: C, 60.59; H 7.37; P, 7.81%]; IR (KBr): υ 1715 (C=O, lactone), 1268 (P=O), 1020, 995 (P-O-C). NMR ($CDCl_3$): δ_H 0.82 [d, J_{HH}= 7.2 Hz, 6H, C-O-C$(CH_3)_2$], 0.98-1.25 [2*d of d (m), 12H, P-O-C$(CH_3)_2$], 2.54 (d, $^4J_{HP}$= 2.5 Hz, C-CH_3), 4.02-4.44 (3*septs (m), 3H, P-O-CH- & C-O-CH-), 4.66 (d, $^2J_{HP}$= 24.2 Hz, 1H, HC-P), 7.23-7.74 (m, 4H, Ar-H); δc 19.53 (d, C-CH_3), 20.2, 20.88 [2d, P-O-C(CH_3)], 34.6 (d, $^1J_{HP}$= 144.5 Hz, HC-1), 67.6-69.8 (m, P-O-CH & C-O-CH), 168.5 (C=O, lactone); δp= 24.73 ppm. MS (EI): *m/z* (%): M^+, found: 396 (55); requires: 396.43.

Similar results were obtained by allowing the reactions to proceed at 105 °C in the absence of solvent for ~8 h (yield ~ 72%).

III. Reaction of 3-Acetyl Coumarins 1a,b with Dialkyl Phosphonates.

(a) ***Reaction of* 1a *with* 15a-c. *General procedure***: A mixture of **1a** (1g, 4.2 mmol) and dialkyl phosphonate (dimethyl-**15a**, diethyl-**15b** or diisopropyl phosphonate **15c**) was refluxed in dry toluene solution (30 ml). After the reaction was completed (TLC, ~ 16 h), the volatile materials were evaporated, *in vacuo*, the residue was triturated with hot pentane and left to cool. The solid so formed was collected and recrystallized from the appropriate solvent to give **17a-c**.

Dimethyl 2-ethyl-1-en-1-ole (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **17a** was obtained as colourless crystals (1.1 g, 75%), m.p. 111-112 °C (cyclohexane). [Found: C, 58.71; H, 4.86; P, 8.81. $C_{17}H_{17}O_6P$ requires: C, 58.62; H, 4.92; P, 8.89%], IR (KBr): υ 3875 (OH, **17Aa**), 1705 (C=O), 1080 (P-O-C). NMR (d_6-DMSO): δ_H 2.53, 2.55 (2*d, 2*$^4J_{HP}$= 2.6 Hz, 2*3H, 2*C-CH_3), 3.55-3.83 (2*2d(m), 2*6H, 2*P-O-CH_3), 4.45, 4.63 (2*d, $^2J_{HP}$= 24.3 Hz, 2*1H, 2*HCP, **17Aa** & **17Ba**), 5.07 (d, $^3J_{HP}$= 8.5 Hz, C-2-H, **17Bd**), 7.31-7.77 (m, 4H, Ar-H), 12.83 (5, 1H, -OH, *exchangeable with* D_2O, **17Aa**); δc 17.6, 18.1 (2*C-CH_3), 35.8, 36.8 (2*d, $^1J_{cp}$= 14.37 Hz, 2*HC-P), 62.-63.5 (2*2d (m), 2*P-O-CH_3), 84.7 (d, $^2J_{cp}$= 10.2 Hz, P-CH-HC-2, **17Ba**), 155.8 (d, $^2J_{cp}$= 10.8 Hz, P-CH-C-2=, **17Aa**), 167.8, 189.2 (2*C=O, lactone), 194.3 (C=O, acetyl, **17Ba**); δp= 21.5, 22.88 ppm (2.5:1*ratio*, **17Ba**:**17Aa**). MS (EI): *m/z* (%): M^+, found: 348 (75): requires: 348.3.

Diethyl 2-ethyl-1-en-1-ole (3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **17b** was obtained as colourless crystals (1.3 g. 80%), m.p. 105-106 °C (pentane). [Found: C, 60.76: H, 5.54; P, 8.29. $C_{19}H_{21}O_6P$

requires: C, 60.64; H, 5.62; P, 8.23%]; IR (KBr): υ 3810 (OH, **17Ab**), 1719 (C=O, lactone), 1686 (C=O, acetyl, **17Bb**), 1623 (C=C, ylidene, **17Ab**), 1261 (P=O), 1069 (P-O-C). NMR (d_6-DMSO): δ_H 0.92-1.23 (2*2d(m), 2*6H, 2*P-O-CH_3), 2.52, 2.58 (2*d, $^4J_{HP}$= 2.5 Hz, 2*3H, 2*C.CH_3); 3.78-4.03 (2*2q (m), 2*2H, 2*P-O-CH_2), 4.73, 5.12 (2*d, $^1J_{HP}$= 24.8 Hz, 2*1H, 2*-HCP), 5.35 (d, $^3J_{HP}$= 8.3 Hz, 1H, P-CH-C-2-H, **17Bb**), 7.31-8.32 (m, 2*6H, 2*Ar-H), 12.85 (s, 1H, OH, **17Ab**); δp= 20.95, 21.73 ppm (2.3:1*ratio*, **17Bb**: **17Ab**). MS: *m/z* (%) : M^+, found: 376 (56); requires: 376.36.

Disopropyl 2-ethyl-1-en-1-ole(3H)naphtho[2,1-b](1H-3-oxo-pyran-1-yl)phosphonate **17c** was obtained as colourless crystals (1.2 g, 72%), and identified by m.p., mixed m.ps. and comparative IR spectra with the corresponding reference sample (see supra).

(b) ***Reaction of* 1b *with* 15a-c.** A mixture of **1b** (1g, 5.3 mmol) and **15a**, **15b** or **15c** was heated under reflux in toluene solution (30 ml). After the reaction was completed (TLC, ~ 10 h), the volatile materials were evaporated, *in vacuo*, and the residual substance was then triturated with cyclohexane and left to cool. The solid so formed was collected and recrystallized from the appropriate solvent to give **17d-f.**

Dimethyl ethyl-1-en-1-ole *(3H)benzo[b](1H-3-oxo-pyran-1-yl)phosponate* **17d** was obtained as colourless crystals (1.2 g, 77%), m.p. 129-130 °C[18] (cyclohexane). [Found: C, 52.41; H, 5.75; P, 10.29. $C_{13}H_{15}O_6P$ requires: C, 52.35; H, 5.07; P, 10.38%]; IR (KBr): υ 3808 (OH, **17Ad**), 1710 (C=O, lactone), 1647 (C=O, acetyl, **17Bd**), 1618 (C=C, ylidene, **17Ad**), 1258 (P=O), 1055 (P-O-C). NMR ($CDCl_3$): δ_H 2.41, 2.44 (2*d, 2*$^4J_{HP}$= 2.7 Hz, 2*3H, 2*C-CH_3), 3.53-3.78 (2*d(m), 2*6H, 2*P-O-CH_3), 4.24, 4.44 (2*d, $^2J_{HP}$= 22.8 Hz, 2*1H, 2*HC-P), 55.2-58.6 (2*2d (m), 2*P-O-CH_3), 87.5 (d, $^2J_{cp}$= 8.9 Hz, P-CH-HC-2, **17Bd**), 152.8 (d, $^2J_{cp}$= 10.5, P-CH-C-2=, **17Ad**), 168.8, 169.1 (2*C=O, lactone), 194.5 (C=O, acetyl, **17Bd**); δp 24.3, 25.2 ppm (3:1*ratio*, **17Bd**: **17Ad**). MS (EI) : *m/z* (%): M^+, found: 298 (28); requires: 298.24.

Diethyl 2-ethyl-1-en-1-ole (3H)benzo[b](1H-3-oxo-pyran-1-yl)phosphonate **17e** was obtained as colourless crystals (1.2 g, 70%), m.p. 142.5 °C (benzene, literature:[18] 147-148 °C). [Found: C, 55.28; H, 5.77; P, 4.55. $C_{15}H_{19}O_6P$ requires: C, 55.22; H, 5.87; P, 4.49%]; IR (KBr): υ 3800 (OH, **17Ae**), 1718 (C=O, lactone), 1640 (C=O, acetyl, **17Be**), 1610 (C=C, ylidene, **17Ae**), 1261 (P=O), 1055 (P-O-C). NMR ($CDCl_3$): δ_H 0.98-126 (2*2d(m), 2*6H, 2*P-O-C-CH_3), 3.72-4.08 (2*2q(m), 2*2H, 2*P-O-CH_2), 4.35, 4.55 (2*d, $^1J_{HP}$= 22.8 Hz, 2*1H, 2*HCP), 4.83 (d, $^3J_{HP}$= 8.8 Hz, 1H, P-CH-C-2-H, **17Be**), 7.23-7.78 (m, 2*4H, 2*Ar-H), 13.31 (s, 1H, OH, **17Ae**); δp= 23.7, 25.1 ppm (2.4:1 *ratio*, **17Be**: **17Ae**). MS (EI) : *m/z* (%) : M^+, found: 326 (33); requires: 326.22.

Diisopropyl 2-ethyl-1-en-1-ole (3H)benzo[b](1H-3-oxo-pyran-1-yl)phosphonate **17f** was obtained as colourless crystals (1.5 g, 80%) and proved (m.p., mixed m.ps. and comparative spectra) to be the one previously formed from the reaction of **1b** with **10c**.

Similar results were obtained when the reactants **1b** and **15a-c** were allowed to react at 105 °C in the absence of solvent for ~10 h (yields ~75%).

***Action of Heat on* 17a *and* 17d.** Compound **17a** (or **17d**, 0.5 g) was heated in a cold finger sublimator at 250 °C (bath temperature) under reduced pressure (8 mm/Hg) for 30 minutes. The compound that sublimed

was collected, recrystallized from ethyl alcohol to give **1a** or **1b** (~48%), respectively. Dimethyl phosphonate was detected in the receiver by the development of a violet colour on addition of 3,5-dinitrobenzoic acid in the presence of alkali.[26]

***Methylation of the phosphonates* 17a *and* 17d.** To a stirred solution of **17a** (or **17d**, 0.75 g) in dry acetone (50 ml) was added 3 g of anhydrous K_2CO_3. Stirring was continued at room temperature for 1 h, freshly distilled CH_3I (3 g) was then added and the reaction mixture was gently heated under reflux for 10 h. The inorganic and volatile materials were removed to give **12a** or **12d** (~65%), respectively, in a semi-solid form which solidified after being triturated with cold pentane. The identities of **12a** and **12d** were established by m.p., mixed m.ps. and comparative IR spectral determination with the corresponding samples.

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