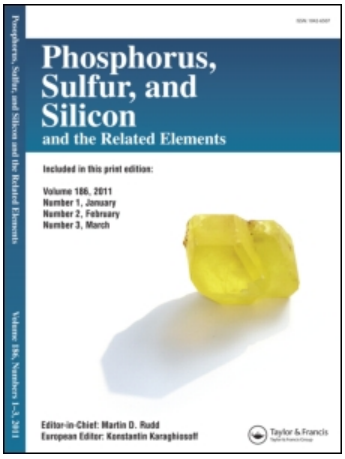

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THE REACTION OF 3-ACETYL COUMARIN WITH ALKYL PHOSPHITES AND PHOSPHONIUM YLIDES

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THE REACTION OF 3-ACETYL COUMARIN WITH ALKYL PHOSPHITES AND PHOSPHONIUM YLIDES

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Dialkyl phosphites reacted with 3-acetyl coumarin (**1**) at 100°C for about 5 h to give the phosphonates having structure **4.** Methylation of compounds **4** with ethereal solution of diazomethane gave the respective methyl ethers **5.** Treatment of **1** with trimethyl phosphite afforded a mixture of the phosphonates **5a** and **4a** whereas with triethyl phosphite gave a mixture of compounds **6** and **4b.** The reaction of phosphonium ylides **8a-d** with **1** in boiling toluene led to the formation of two isomers (E)-allylic (**9**) and (Z)-allylic (**10**). The structural assignments of all new compounds are based on IR and NMR (^1H, ^{13}C) spectra.

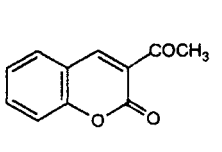
Keywords: 3-Acetyl coumarin; phosphonates; phosphonium ylides; NMR spectra (^1H, ^{13}C)

INTRODUCTION

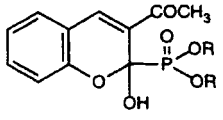
Recently, it has been reported[1] that 3-acetyl coumarin (**1**) reacted with di- and trialkyl phosphites in absence of solvents at 100°C to give the phosphonate structure **2.** Also, they claimed that the cyclic product **3** was obtained from the reaction of **1** with 2,4-bis(4-methoxyphenyl)-1,3,2,4 -dithiadiphosphetane 2,4-disulfide (Lawesson's Reagent) in boiling toluene. At first sight, these results are not satisfied. Moreover, the structural configuration **3** is unusual. This prompted us to reinvestigate these results for the reported reactions under the same experimental conditions. Also,

* Corresponding author

our studies include the reactivity of compound **1** towards stable ylide-phosphoranes **8.**



1



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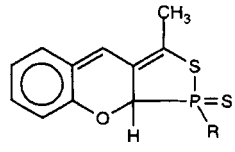
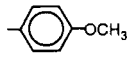
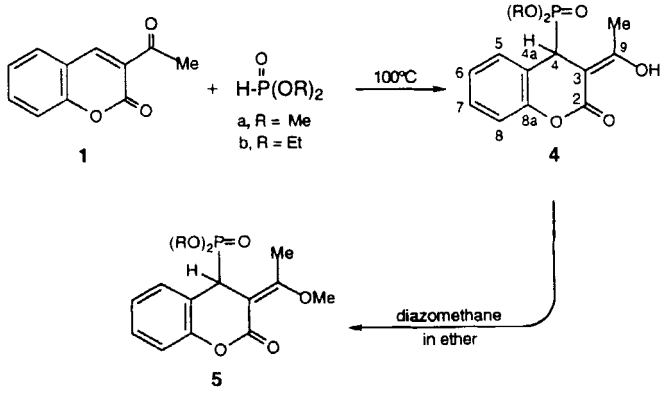


3, R = 

RESULTS AND DISCUSSIONS

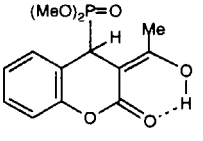
We have found 3-acetyl coumarin (**1**) reacted with dimethyl and diethyl phosphites without solvents at 100°C for about 5 h to give colorless crystalline products of the phosphonates **4** as only one isomer (Scheme 1) and not the reported structure **2.**[1]



SCHEME 1

Compounds **4** respond positively to the ferric chloride color reaction denoting the presence of the hydroxyl group. Their assigned structures

were established from elemental analyses, IR, NMR (^{31}P, ^{1}H, ^{13}C) and mass spectra (MS). The ^{31}P NMR spectrum of **4a,** taken as an example, showed a positive chemical shift δ 25.37 ppm (vs 85% H_3PO_4) which indicates the phosphonate structure.[2] Its ^{1}H NMR spectrum reveals the presence of a doublet at δ 2.24 ppm with coupling constant J_{HP} = 3.0 Hz, for the protons of methyl group located at carbon-9 and two doublets at δ 3.58, 3.67 ppm with $^{3}J_{HP}$ = 10.6 Hz, corresponding to the two methoxy groups which are diastereotopic. Also, the spectrum shows a doublet centered at δ 4.16 ppm with coupling constant $^{2}J_{HP}$=22.0 Hz, ascribed to the proton at C-4 which attached to phosphorus atom and a singlet for the hydroxylic proton at C-9 appeared at more downfield with chemical shift δ 13.30 ppm, correlated to the intramolecular hydrogen bonding with the lactonic carbonyl at position 2.[3] The phenyl protons at C-5 and C-8 appeared as two doublets at δ 7.08, 7.17 ppm with J_{HH}= 7.6 Hz, whereas the other two protons at C-6 and C-7 presented as a multiplets in the region δ 7.15–7.40 ppm. The ^{13}C NMR spectrum of **4a** exhibits a doublet at δ 37.5 ppm with characteristic coupling constant $^{1}J_{PC}$= 143.8 Hz, due to C-4. It also shows two singlets at δ 19.4 ppm, corresponding to the methyl carbon at C-9 and at δ 168.8 ppm, for C-2. The chemical shift values and coupling constant with phosphorus atom J_{PC} are presented in the experimental part. Further evidence supporting structure **4a** is the appearance of the lactonic carbonyl in the IR spectrum at 1649 cm^{-1}. This low frequency of the carbonyl band is attributed to the formation of an intramolecular hydrogen bonding with the hydroxyl group at C-9.[4]

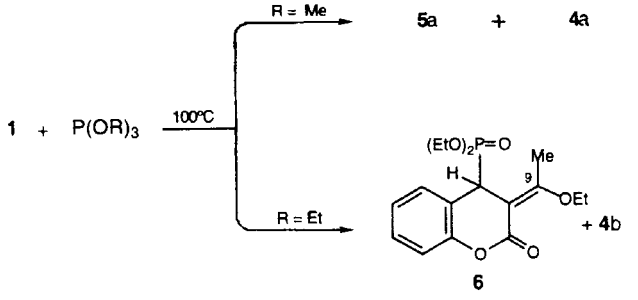


4a

Treatment of the phosphonates **4a,b** with ethereal solution of diazomethane at room temperature led to the formation of the respective methyl ethers **5a** and **5b** (Scheme 1). These adducts showed the absence of color on testing with ferric chloride and the ^{1}H, ^{13}C NMR spectra are consistent with their structures (*cf.* Experimental).

Trimethyl phosphite reacted with 3-acetyl coumarin (**1**) without solvents at 100°C for about 8 h to give a mixture of the phosphonate derivatives **5a**

and **4a** (Scheme 2) and not the reported structure **2**.[1] The formation of compound **4a** is due to the non-avoidable moisture during the reaction. The phosphonates **4a** and **5a** were separated by column chromatography on silica gel as colorless crystalline products and their assigned structures were verified by mp, mixed mp, comparative IR and ^{1}H NMR spectra with an authentic samples *(vide supra).*

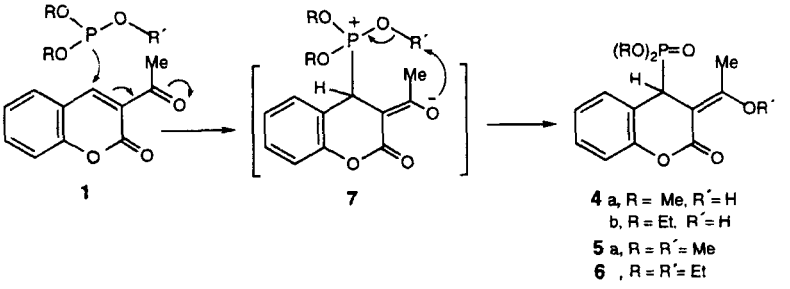


SCHEME 2

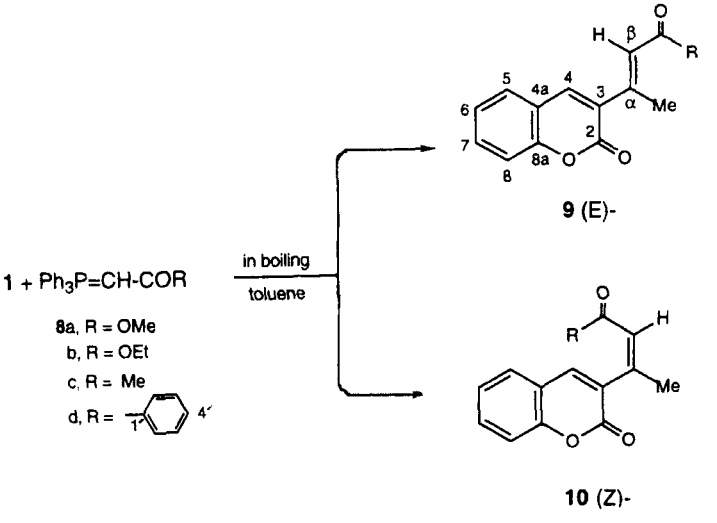
Similarly, triethyl phosphite reacted with **1** without solvent at 100°C to yield a mixture of the phosphonates **6** and **4b** (Scheme 2) which were separated by column chromatography. The identity of compound **4b** was established by comparison with its mp and ^{1}H NMR spectrum with a specimen prepared from the reaction of **1** with diethyl phosphite. The structure of the phosphonate **6** gives a compatible elemental analyses, molecular weight determination (MS), IR, ^{1}H and ^{13}C NMR spectra *(cf.* Experimental).

When we examined coumarin towards its reaction with di- and trialkyl phosphites at 100°C, no reaction takes place. This means that the presence of an electron-withdrawing group (acetyl group) at carbon-3 in 3-acetyl coumarin **(1)** facilitate the nucleophilic attack of the phosphite phosphorus to the carbon atom in position 4 to form the phosphonium species **7** which afforded the final products **4, 5a** or **6** (Scheme 3).

3-Acetyl coumarin **(1)** reacted with stabilized phosphonium ylides **(8a-d)** in toluene under reflux temperature to give a mixture of two isomers **9a-d** and **10a-d** (examined by TLC) and triphenylphosphine oxide (Scheme 4). The reaction is very slow and accelerated by using controlled



SCHEME 3



SCHEME 4

amounts of benzoic acid as a catalyst in the reaction medium. The two isomers **9** and **10** were separated by column chromatography as colorless crystalline products and their structures were established by different spectroscopic techniques as well as elemental analyses and molecular weight determination (MS). The ^{1}H NMR spectra of both two isomers **9** and **10** reveal the presence of a olefinic proton as an ill-defined quartet with coupling constant $J_{HH} \simeq 1.6$ Hz and the methyl protons on the same double

bond appeared as a doublet signal ($J_{HH} \simeq$ 1.6 Hz. This observation confirm the presence of an allylic rigid configuration,[5,6] The structures of the two isomers **9a** (E-allylic) and **10a** (Z-allylic) as representative examples were fully interpreted *via* ^{1}H and ^{13}C NMR. The ^{1}H NMR spectra of (E)-isomer **9a** show the methyl protons attached to a double bond of the α, β-unsaturated ester resonate as a doublet at δ 2.52 ppm and the olefinic proton on the same double bond appeared as a quartet at δ 6.44 ppm while in case of (Z)- isomer **10a,** the methyl and olefinic protons are located at δ 2.20 and 6.06 ppm, respectively. The ^{13}C NMR spectra gave a chemical shift values of the methyl carbon of (E)-allylic form **9a** at δ 17.6 ppm and for (Z)-allylic **10a** at δ 24.9 ppm. These observed data in ^{1}H and ^{13}C NMR spectra of compounds **9a** and **10a** show the chemical shift values consistent with that in the literature for related systems.[3] The other (E)-allylic **(9b-d)** and (Z)-allylic **(10b-d)** isomers were established through similar spectroscopic data (*cf.* Experimental).

CONCLUSION

The results obtained in this investigation from the reaction of 3-acetyl coumarin (**1**) with di- and trialkyl phosphites gave a novel type of the phosphonates **4a, 4b, 5a, 6** and not the reported structure **2**.[1] Also, compound **1** reacted with stabilized phosphonium ylides **(8)** to form a mixture of two isomers having structures **9** (E-allylic) and **10** (Z-allylic).

EXPERIMENTAL

Melting points were determined on Electrothermal digital-melting-point apparatus and are uncorrected. The IR spectra were recorded in KBr disks, on a Jasco Fourier Transform Infrared spectrophotometer Model FT/IR-3000E. The NMR spectra were measured in $CDCl_3$, on a Varian Gemini-200 spectrometer for ^{1}H, ^{31}P and on a JEOL EX-270 spectrometer for ^{13}C. Chemical shifts are given in positive values downfield from internal tetramethylsilane (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). The mass spectra (MS) were determined at 70 eV on a Finnigan MAT SSQ 7000 spectrometer.

The ^{13}C NMR chemical shift values of all compounds presented in this paper are based on the related carbons in coumarin. [7,8]

3-Acetyl Coumarin (1)

This compound was prepared as described by Trivedi.[9] IR cm^{-1}: strong bands at 1741 (C=O, lactone); 1677 (C=O, acetyl). ^1H NMR: δ 2.72 (s, 3H, CH_3); 7.28–7.75 (m, 4H, ArH); 8.51 (s, 1H,. H at C-4). ^{13}C NMR: δ 30.1 (CH_3), 116.5 (C-8), 118.1 (C-4a), 124.4 (C-3), 124.9 (C-6), 130.2 (C-5), 134.3 (C-7), 147.3 (C-4), 155.2 (C-8a), 159.1 (C=O), lactone), 195.4 (C=O, acetyl).

Reaction of 3-Acetyl Coumarin (1) with Dimethyl Phosphite.

Compound **1** (2.0 g, 10.6 mmole) was added to a freshly distilled dimethyl phosphite (5 ml) and the mixture was heated at 100°C. After about 5 h, excess dimethyl phosphite was removed under reduced pressure and the residual substance triturated with petroleum ether (bp 60–80°C) to give colorless crystals of the phosphonate **4a** (2.70 g, 85% yield), recrystallized from dry benzene, mp 129–130°C. Anal. Calcd. for $C_{13}H_{15}O_6P$: C, 52.35 ; H, 5.07: P, 10.39. Found : C, 52.39; H, 5.01; P, 10.43%. IR cm^{-1}: 1649 (lactonic C=O, bonded); 1600 (C=C); 1252 (P=O); 1053, 1012 (P-O-CH_3). ^{31}P NMR: δ 25.37 ppm. ^1H NMR: δ 2.24 (d, J_{HP} = 3.0 Hz, 3H, CH_3); 3.58, 3.67 [2d, J_{HP}= 10.6 Hz, 6H, $P(OCH_3)_2$]; 4.16 (d, J_{HP} = 22.0 Hz, 1H, H at C-4); 7.08, 7.17 (2d, J_{HH} = 7.6 Hz, 2H, ArH at C-5 and C-8); 7.15–7.40 (m, 2H, ArH at C-6 and C-7); 13.30 (s, 1H, OH). ^{13}C NMR : δ 19.4 (s, CH_3 at C-9); 37.5 (d, $^1J_{PC}$ = 143.8 Hz, C-4); 53.5, 53.7 [2d, $^2J_{PC}$ = 7.82 Hz, $P(OCH_3)_2$]; 88.7 (d, $^2J_{PC}$ = 8.81 Hz, C-3); 116.8 (d, $^4J_{PC}$ = 3.91 Hz, C-8); 117.2 (d, $^2J_{PC}$= 7.82 Hz, C-4a); 124.2 (d, $^4J_{PC}$ = 2.93 Hz, C-6); 128.7 (d, $^5J_{PC}$= 3.91 Hz, C-7); 129.3 (d, $^3J_{PC}$ = 4.89 Hz, C-5); 150.6 (s, C-8a); 168.8 (s, C-2); 178.8 (d, $^3J_{PC}$= 5.87 Hz, C-9). MS: m/z (relative intensity) 298 (M^+, 15%), 281 (1), 271 (7), 255 (41), 223 (4), 215 (2), 189 (100), 171 (25), 147 (9), 127 (2), 110 (8), 91 (3) and 63 (1).

Similarly, the phosphonate **4b** was formed from the reaction of **1** with diethyl phosphite under the same experimental conditions described above.

Phosphonate 4b

(78% yield), recrystallized from benzene, mp 147–148°C. Anal. Calcd. for $C_{15}H_{19}O_6P$: C, 55.22; H, 5.87; P, 9.49. Found : C, 55.31; H, 5.83; P, 9.40%. IR cm^{-1}: 1718 (C=O, lactone); 1608 (C=C); 1211 (P=O); 1057, 1020 (P-O-C_2H_5).^{1}H NMR : δ 1.17, 1.25 [2t, J_{HH}= 7.0 Hz, 6H, $P(OCH_2\mathbf{CH_3})_2$]; 2.24 (d, J_{HP} = 3.0 Hz, 3H, CH_3); 3.80–4.10 [m, 4H, $P(\mathbf{OCH_2}CH_3)_2$]; 4.14 (d, J_{HP}=22.2 Hz, 1H, H at C-4); 7.07, 7.16 (2d, J_{HH}= 7.8 Hz and 7.2 Hz, 2H, ArH at C-5 and C-8); 7.22–7.40 (m, 2H, ArH at C-6 and C-7); 13.30 (s, 1H, OH). ^{13}C NMR: δ 16.25, 16.34 [2s, P $(OCH_2\mathbf{CH_3})_2$]; 19.6 (s, CH_3 at C-9); 37.9 (d, $^1J_{PC}$ = 143.8 Hz, C-4); 63.0, 63.2[2d $^2J_{PC}$=7.83 Hz, $P(OCH_2CH_3)_2$]; 89.1 (d, $^2J_{PC}$= 8.80 Hz, C-3); 116.8 (d, $^4J_{PC}$ =3.91 Hz, C-8), 117.6 (d, $^2J_{PC}$= 7.83 Hz, C-4a); 124.5 (d,$^4J_{PC}$ = 2.94 Hz, C-6); 129.1 (d, $^5J_{PC}$=3.92Hz, C-7); 129.4 (d, $^3J_{PC}$ = 4.89 Hz, C-5); 150.7 (d, $^3J_{PC}$= 5.87 Hz, C-8a); 169.0 (s, C-2); 178.8 (d, $^3J_{PC}$= 5.87 Hz, C-9). MS : m/z (relative intensity) 326 (M^{+}·22%), 299 (12), 283 (27), 243 (7), 227 (9), 189 (100), 171 (30), 147 (9), 138 (16), 111 (16) and 82 (8).

The above mentioned compounds **4a** and **4b** respond positively to ferric chloride color reaction, giving brown color.

Reaction of Diazomethane with Phosphonate 4a.

To ethereal solution of diazomethane (50 ml) (from 5 g nitrosomethylurea), compound **4a** (0.30 g, 1.0 mmole) was added portionwise. Evolution of nitrogen was observed. After 2 h, the colorless crystals was collected and recrystallized from benzene petroleum ether (bp 60–80°C) to give the phosphonate **5a** (0.30 g, 97% yield), mp 180–181°C. Anal. Calcd. for $C_{14}H_{17}O_6P$: C, 53.85; H, 5.49; P, 9.92. Found: C, 53.81; H, 5.53; P, 9.88%. IR cm^{-1}; 1716 (C=O, lactone); 1604 (C=C); 1257 P=O); 1055, 1018 (P-O-CH_3). ^{1}H NMR: δ 2.51 (d, J_{HP}= 5.2 Hz, 3H, CH_3): 3.55, 3.69 [2d, J_{HP} = 10.6 Hz, 6H, $P(OCH_3)_2$]; 3.87 (s, 3H, OCH_3 at C-9); 4.72 (d, J_{HP} = 24.4 Hz, 1H, H at C-4); 7.016, 7.098 (2d, J_{HH} = 8.6 Hz and 7.2 Hz, 2H, ArH at C-5 and C-8); 7.23, 7.30 (two double of triplets, J_{HH} = 7.6 Hz and 2.0 Hz, 2H, ArH at C-6 and C-7). ^{13}C NMR: δ 14.8 (d, $^4J_{PC}$ = 2.93 Hz, CH_3 at C-9); 35.8 (d, $^1J_{PC}$ = 140.8 Hz, C-4); 53.1, 53.2 [2d, $^2J_{PC}$ = 7.82 Hz, $P(OCH_3)_2$]; 55.5 (s, OCH_3at C-9), 96.2 (d, $^2J_{PC}$ = 9.78 Hz, C-3); 116.3 (d, $^4J_{PC}$ = 2.94 Hz, C-8); 118.1 (d, $^2J_{PC}$ = 7.82 Hz, C-4a);

123.7 (d,$^4J_{PC}$= 3.93 Hz, C-6); 128.5 (d, $^5J_{PC}$= 2.94 Hz, C-7); 128.8 (d, $^3J_{PC}$ = 4.89 Hz, C-5); 151.0 (d, $^3J_{PC}$= 5.87 Hz, C-8a); 163.6 (s, C-2); 169.8 (d, $^3J_{PC}$ = 7.83 Hz, Hz, C-9). MS: m/z (relative intensity) 313 (M^+ +1, 94%), 312 (72), 297 (16), 281 (27), 279 (7), 217 (8), 203 (100), 187 (29), 171 (99), 160 (10), 145 (60), 127 (18), 115 (82), 109 (75), 89 (50), 79 (33) and 63 (14).

Reaction of Diazomethane with Phosphonate 4b.

Compound **4b** (0.33 g, 1.0 mmole) was added in a small portions to ethereal solution of diazomethane (50 ml). The reaction proceeded with evolution of nitrogen. After 3 h, the ethereal solution was evaporated under reduced pressure followed by addition of petroleum ether (bp 60–80°C). The solid product, thus formed, was crystallized from chloroform/n-hexane to give colorless crystals of the phosphonate **5b** (0.32 g, 94% yield), mp 104–105°C. Anal. Calcd. for $C_{16}H_{21}O_6P$:C, 56.47 ; H, 6.22 ; P, 9.10. Found C, 56.59 ; H, 6.17 : P, 9.18%. IR cm^{-1}: 1726 (C=O, lactone) ; 1616 (C=C) ; 1248 (P=O); 1047 (P-O-C_2H_5). ^1H NMR : δ 1.13, 1.24 [2t, J_{HH} = 7.2 Hz, 6H, P(OCH_2 **CH_3**)$_2$]; 2.51 (d, J_{HP} = 5.0 Hz, 3H, CH_3); 3.85 (s, 3H, OCH_3 at C-9); 3.70–4.11 [m, 4H, P(**OCH_2** CH_3)$_2$]; 4.69 (d, J_{HP} = 24.4 Hz, 1H, H at C-4) ; 7.01, 7.09 (2d, J_{HH} = 8.2 Hz and 7.8 Hz, 2H, ArH at C-5 and C-8) ; 7.21, 7.30 (two double of triplets, J_{HH} = 7.6 Hz and 2.2 Hz, 2H, ArH at C-6 and C-7). ^{13}C NMR : δ 14.6 (d, $^4J_{PC}$ = 2.93 Hz, CH_3 at C-9); 15.6, 15.8 [2d, $^3J_{PC}$= 5.87 Hz, P(OCH_2**CH_3**)$_2$]; 36.2 (d, $^1J_{PC}$= 140.8 Hz, C-4); 55.0 (s, OCH_3 at C-9); 62.1 62.3 [2d, $^2J_{PC}$=7.82 Hz, P(**OCH_2**CH_3)$_2$]; 96.4 (d, $^2J_{PC}$ = 9.78 Hz, C-3) ; 116.0 (d, $^4J_{PC}$= 2.94 Hz, C-8) ; 118.2 (d, $^2J_{PC}$= 7.83 Hz, C-4a); 123.4 (d,$^4J_{PC}$=2.94 Hz, C-6) ; 128.1 (d, $^5J_{PC}$ = 2.93 Hz, C-7); 128.6 (d, $^3J_{PC}$= 4.89 Hz, C-5) ; 150.8 (d, $^3J_{PC}$=4.89 Hz, C-8a); 163.5 (s, C-2) ; 169.2 (d, $^3J_{PC}$= 8.81 Hz, C-9). MS : m/z (relative intensity) 341 (M^+ +1, 93%), 340 (80), 325 (26), 309 (17), 297 (3), 251 (2), 217 (3), 204 (66), 187 (10), 171 (100), 145 (30), 115 (73), 89 (19), 81 (11) and 65 (5).

Reaction of 1 with Trimethyl Phosphite

A mixture of **1** (1.88 g, 10 mmole) and freshly distilled trimethyl phosphite (5 ml) was heated at 100°C without solvent for about 8 h and then allowed to stand overnight. The colorless crystals, thus formed, was fil-

tered off, washed with petroleum ether (bp 60–80°C) and then recrystallized from benzene-petroleum ether to give a product identical in all respects with the phosphonate **5a** (0.9 g) (mp, mixed mp, comparative IR and ^{1}H NMR spectra) *(vide supra).* The filtrate was evaporated under reduced pressure and chromatographed on silica gel, using acetone and *n*-hexane as eluent to give two fractions. The first fraction (75–70% *n*-hexane) yielded colorless crystals (0.21 g, 7% yield), proved to be **4a** (mp and mixed mp with an authentic sample). The second fraction (70–65% *n*-hexane) afforded another quantity of the phosphonate **5a** (0.43 g) (the total yield 1.33 g, 43%).

Reaction of 1 with Triethyl Phosphite

A mixture of **1** (1.88 g, 10 mmole) and triethyl phosphite (6 ml) was heated at 100°C for 8 h (examined by TLC). Then, the clear solution was evaporated under reduced pressure and chromatographed on silica gel using acetone and *n*-hexane as eluent to give two fractions. The first fraction (75–70% *n*-hexane) afforded colorless crystalline product, proved to be the phosphonate **4b** (1.12 g, 34% yield) by its mp and mixed mp with an authentic sample previosly reported. The second fraction (70–65% *n*-hexane) gave colorless crystals of the phosphonate **6** (0.34 g, 10% yield). recrystallized from benzene /*n*-hexane, mp 113–114°C. Anal. Calcd. for $C_{17}H_{23}O_6P$:C. 57.63; H. 6.54; P, 8.74. Found : C, 57.54 : H, 6.60; P, 8.81%. IR cm^{-1}: 1728 (C=O, lactone): 1606 (C=C); 1247 (P=O): 1043 (P-O-C_2H_5). ^{1}H NMR :δ 1.12, 1.23 [2t, J_{HH} =7.0 Hz, 6H, P(OCH$_2$**CH$_3$**)$_2$];1.36 (t, J_{HH} =7.0 Hz, 3H, OCH$_2$**CH$_3$** at C-9); 2.49 (d, J_{HP} = 5.2 Hz, 3H, CH_3 at C-9); 3.84 (m, 2H, **OCH$_2$**CH$_3$ at C-9); 4.06 [m, 4H, P(**OCH$_2$**CH$_3$)$_2$]; 4.70 (d, J_{HP} = 24.4 Hz, 1H, H at C-4); 7.00, 7.08 (2d, J_{HH} = 8.0 Hz and 2.0 Hz, 2H, ArH at C-5 and C-8); 7.21, 7.32 (two double of triplets, J_{HH}= 7.4 Hz and 2.2 Hz, ArH at C-6 and C-7). ^{13}C NMR : δ 15.0 (s, OCH$_2$**CH$_3$** at C-9); 15.6 (d, $^4J_{PC}$= 2.93 Hz, CH_3 at C-9); 16.1, 16.3 [2d, $^3J_{PC}$ = 5.87 Hz, P(OCH$_2$**CH$_3$**)$_2$]; 36.6 (d, $^1J_{PC}$ = 140.8 Hz, C-4); 62.5, 62.8 [2d, $^2J_{PC}$= 6.84 Hz, P(**OCH$_2$**CH$_3$)$_2$]; 64.1 (s, **OCH$_2$**CH$_3$ at C-9); 96.7 (d, $^2J_{PC}$= 9.78 Hz, C-3); 116.4 (d, $^4J_{PC}$ =2.94 Hz, C-8); 118.7 (d, $^2J_{PC}$ =6.84 Hz, C-4a); 123.8 (d, $^4J_{PC}$ = 3.91 Hz, C-6); 128.6 (d, $^5J_{PC}$ = 3.92 Hz, C-7); 129.1 (d, $^3J_{PC}$= 4.89 Hz, C-5); 151.3 (d, $^3J_{PC}$ = 5.87 Hz, C-8a); 164.1 (s, C-2); 169.3 (d, $^3J_{PC}$ = 8.80 Hz, C-9). MS: m/z (relative intensity) 355 (M^+ +1, 100%), 325 (12), 309 (15), 279 (2), 245

(3), 217 (93), 189 (92), 171 (85), 145 (26), 143 (13), 115 (36), 91 (23), 81 (18) and 65 (9).

Reaction of 3-Acetyl Coumarin (1) with Methoxycarbonylmethylene(triphenyl) phosphorane (8a)

A mixture of 1 (0.57 g, 3.0 mmole) and ylide **8a**[10] (1.17g, 3.5 mmole) in dry toluene (20 ml) was heated under reflux for about 20 h. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel using acetone /*n*-hexane as eluent. The first fraction (95–94% *n*-hexane) gave colorless crystals of (E)-methyl 3-(2-oxo-2H-1-benzopyran-3-yl)-2-butenoate **(9a)** (0.11 g, 15% yield), recrystallized from benzene/n-hexane, mp 164–165°C. Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found :C, 68.90; H, 4.79%. IR cm^{-1}: 1720, 1701 (C=O, lactone and C=O, ester); 1608 (C=C). ^1H NMR : δ 2.52 (d, J_{HH} = 1.4 Hz, 3H, CH_3); 3.76 (s, 3H, OCH_3); 6.44 (q, J_{HH} = 1.4 Hz, H at C-β); 7.22–7.62 (m, 4H, ArH); 7.74 (s, 1H; H at C-4). ^{13}C NMR : δ 17.6 (CH_3 at C-α); 51.3 (OCH_3); 116.4 (C-8); 118.8 (C-4a); 120.7 (C-β); 124.6 (C-6); 128.2 (C-5); 129.7 (C-3), 132.1 (C-7); 140.1 (C-4); 150.1 (C-α); 153.5 (C-8a); 159.0 (C-2); 166.7 (C=O, ester). MS : m/z (relative intensity) 244 (M^+, 59%), 229 (7), 212 (29), 185 (100), 156 (11), 141 (9), 128 (41), 115 (18), 89 (7) and 63 (10). The second fraction (94–93% n-hexane) yielded colorless crystalline product of (Z)-methyl 3-(2-oxo-2H-1-benzopyran-3-yl)-2-butenoate **(10a)** (0.44 g, 60% yield), recrystallized from benzene/*n*-hexane, mp 129–130°C. Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found : C, 68.71; H, 4.83%. IR cm^{-1}: 1707 (C=O, ester and C=O, lactone); 1606 (C=C). ^1H NMR : δ 2.20 (d, J_{HH} = 1.6 Hz, 3H, CH_3); 3.62 (s, 3H, OCH_3); 6.06 (q, J_{HH}= 1.6 Hz, 1H, H at C-β); 7.20–7.60 (m, 4H, ArH); 7.48 (s overlaped, 1H, H at C-4). ^{13}C NMR : δ 24.9 (CH_3 at C-α); 51.2 (OCH_3); 116.0 (C-8); 118.8 (C-4a); 120.6 (C-β); 124.3 (C-6); 127.7 (C-5); 128.9 (C-3); 131.3 (C-7); 138.5 (C-4); 148.8 (C-α); 153.4 (C-8a); 158.9 (C-2); 165.5 (C=O, ester). MS : m /z (relative intensity) 244 (M^+, 95%), 229 (11), 213 (48); 201 (2), 185 (100), 184 (81), 171 (5), 156 (11), 141 (8), 128 (33), 115 (13), 89 (4) and 63 (4). The third fraction (80–65% *n-hexane)* afforded colorless crystals of triphenylphosphine oxide (0.83 g, 86% yield) (mp and mixed mp).

When the above reaction was performed using benzoic acid (0.2 g) as a catalyst, the reaction was completed after about 8 h.

Reaction of 1 with Ethoxycarbonylmethylene(triphenyl)phosphorane (8b)

Compound **1** (0.57 g, 3.0 mmole) reacted with ylide **8b**[10](1.22 g, 3.5 mmole) in dry toluene (20 ml) under the same experimental conditions described above to give three fractions. The first fraction (96–95% *n*-hexane) yielded colorless crystals of (E)-ethyl 3-(2-oxo-2H-1-benzopyran-3-yl)-2-butenoate **(9b)** (0.14 g, 18% yield), recrystallized from benzene-petroleum ether (bp 60–80°C), mp 114–115°C. Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.76 ; H, 5.46. Found : C, 69.68 ; H, 5.51%. IR cm^{-1}: 1714 (C=O, lactone); 1678 (C=O, ester); 1612 (C=C). ^1H NMR : δ 1.31 (t, J_{HH}= 7.2 Hz, 3H, OCH_2 **CH_3**); 2.52 (d, J_{HH}= 1.2 Hz, 3H, CH_3); 4.21 (q, J_{HH}= 7.2 Hz, 2H, **OCH_2**CH_3); 6.41 (q, J_{HH}=1.2 Hz, 1H, H at C-β); 7.22–7.62 (m, 4H, ArH); 7.74 (s, 1H, H at C-4). ^{13}C NMR : δ 14.2 (CH_3, ester), 17.6 (CH_3 at C-α); 60.0 (CH_2, ester); 116.4 (C-8); 118.8 (C-4a); 121.2 (C- β); 124.5 (C-6); 128.2 (C-5); 129.8 (C-3); 132.1 (C-7); 140.0 (C-4); 149.7 (C-α); 153.5 (C-8a); 159.0 (C-2); 166.2 (C=O, ester). MS : m /z (relative intensity) 258 (M^+, 36%), 247 (10), 229 (18), 213 (21), 207 (32), 185 (100), 171 (46), 155 (7), 144 (14), 128 (31), 115 (33), 102 (6), 89 (9), 77 (6) and 63 (10). The second fraction (95–93% *n-hexane)* yielded colorless crystals of (Z)-ethyl 3-(2-oxo-2H-1-benzopyran-3-yl)-2-butenoate **(10b)** (0.43 g, 55% yield), recrystallized from benzene-petroleum ether (bp 60–80°C), mp 110–111°C. Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found : C, 69.82 ; H, 5.35%. IR cm^{-1}: 1720 (C=O, lactone) ; 1699 (C=O, ester). ^1H NMR: δ 1.15 (t, J_{HH}= 7.2 Hz, 3H, OCH_2**CH_3**); 2.194 (d, J_{HH}= 1.6 Hz, 3H, CH_3); 4.06 (q, J_{HH}= 7.2 Hz, 2H, **OCH_2**CH_3); 6.046 (q, J_{HH}= 1.6 Hz, 1H, H at C-β); 7.20–7.60 (m, 4H, ArH); 7.48 (s overlaped, 1H, H at C-4). ^{13}C NMR : δ 13.9 (CH_3, ester); 24.9 (CH_3at C-α) 60.0 (CH_2, ester); 116.4 (C-8); 118.8 (C-4a); 121.1 (C-β); 124.3 (C-6); 127.7 (C-5); 129.0 (C-3); 131.3 (C-7); 138.4 (C-4); 148.3 (C-α); 153.3 (C-8a); 159 (C-2); 165.0 (C=O, ester). MS : m /z (relative intensity) 258 (M^+, 43%), 229 (7), 213 (23), 207 (6), 185 (100), 171 (10), 128 (17)), 115 (11), 89 (3), 63 (3) and 51 (2), The third fraction (80–65% *n*-hexane) gave colorless crystals of triphenylphosphine oxide (0.88 g, 91% yield) (mp and mixed mp).

Reaction of 1 with Acetylmethylene(triphenyl)phosphorane (8c)

To a mixture of compound **1** (0.38 g, 2.0 mmole) and ylide **8c**[11] (0.95 g, 3.0 mmole) in dry toluene (10 ml) benzoic acid (0.25 g) was added. The

reaction mixture was heated under reflux for about 30 h (examined by TLC). After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel, using system : *n*-hexane, then *n*-hexane containing increase amounts of acetone. The first fraction (93% *n*-hexane) gave colorless crystals (0.25 g, 55% yield), identified as (E)- isomer (9c). Recrystallization from benzene/*n*-hexane, mp 147–148°C. Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found : C, 73.52, H, 5.39%. IR cm^{-1}: 1720 (C=O, lactone); 1674 (C=O, acetyl); 1606 (C=C). ^1H NMR : δ 2.30 (s, 3H, CH_3 acetyl); 2.46 (d, J_{HH}= 1.4 Hz, 3H, CH_3 at C-α); 6.88 (q, J_{HH}= 1.4 Hz, 1H, H at C-β); 7.20–7.65 (m, 4H, ArH); 7.78 (s, 1H, H at C-4). ^{13}C NMR : δ 17.5 (CH_3 at C-α); 32.0 (CH_3, acetyl); 116 (C-8) ; 118.9 (C-4a); 124.7 (C-6) : 128.1 (C-5); 128.3 (C- β); 129.7 (C-3); 132.3 (C-7); 140.6 (C-4); 147.1 (C-α); 153.6 (C-8a); 159.3 (C-2); 199.4 (C=O, acetyl). MS : m/z (relative intensity) 228 (M^+, 16%), 213 (14), 185 (100), 171 (12), 157 (20), 141 (28), 128 (72), 115 (54), 102 (12), 89 (16), 77 (24), 63 (36) and 51 (44). The Second fraction (91% n-hexane) afforded colorless crystals of (Z)-isomer **(10c)** (0.14 g, 30% yield), recrystallized from benzene/n-hexane, mp 91–92°C. Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found : C, 73.72; H, 5.41%. IR cm^{-1}: 1714 (C=O, lactone); 1690 (C=O, acetyl); 1604 (C=C). ^1H NMR : δ 2.167 (d, J_{HH}= 1.6 Hz, 3H, CH_3 at C-α); 2.171 (s overlaped, 3H, CH_3 acetyl); 6.38 (q, J_{HH}= 1.6 Hz, 1H, H at C-β); 7.20–7.60 (m, 4H, ArH); 7.46 (s overlaped, 1H, H at C-4). ^{13}C NMR : δ 24.7 (CH_3 at C-α); 30.5 (CH_3, acetyl); 116.4 (C-8); 118.8 (C-4a); 124.3 (C-6); 127.7 (C-5); 128.5 (C-β); 129.5 (C-3); 131.3 (C-7); 138.5 (C-4); 145.4 (C-α); 153.4 (C-8a) ; 159.0 (C-2); 197.4 (C=O, acetyl). MS : m /z (relative intensity) 228 (M^+, 12%), 213 (12), 185 (100), 157 (8), 141 (15), 128 (50), 115 (42), 83 (45), 63 (32) and 51 (38). The third fraction gave a colorless crystals of triphenylphosphine oxide (0.74 g, 89% yield) (mp and mixed mp with an authentic sample).

The reaction of **1** with **8c** in boiling toluene without addition of benzoic acid is completed after about 40 h.

Reaction of 1 with Benzoylmethylene(triphenyl)phosphorane (8d)

A solution of compound **1** (0.75 g, 4.0 mmole) and ylide **8d**[11](2.28 g, 6.0 mmole) in dry toluene (15 ml) was heated under reflux. Then, benzoic acid (0.5 g) was added to the reaction mixture with continuous heating for about 35 h (examined by TLC). Then, the solution evaporated to dryness

in presence of silica gel and subjected to column chromatography on silica gel, using n-hexane yielded colorless crystals of (E)- isomer **(9d)** (0.42 g, 36% yield,), recrystallized from chloroform-petroleum ether (bp 60–80°C), mp 127–128°C. Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found : C, 78.50; H, 4.92%. IR cm^{-1}:1712 (C=O, lactone); 1653 (C=O, benzoyl) ; 1591 (C=C). ^1H NMR : δ 2.49 (d, J_{HH}= 1.2 Hz, 3H, CH_3 at C-α); 7.25–7.65 (m, 7H, ArH); 7.70 (q, J_{HH}= 1.2 Hz, 1H, H at C-β); 7.87 (s, 1H, H at C-4); 7.95–8.15 (m, 2H, ArH). ^{13}C NMR : δ 18.5 (CH_3at C-α); 116.9 (C-8); 119.4 (C-4a); 125.1 (C-6); 127.1 (C-β); 128.7 (C-5); 129.0, 129.1 (C-2′, C-3′, C-5′, C-6′); 129.8 (C-3); 132.7 (C-7); 133.4 (C-4′); 139.0 (C-1′); 140.9 (C-4); 147.0 (C-α); 153.9 (C-8a); 159.8 (C-2); 192.8 (C=O, benzoyl). MS : m/z (relative intensity) 290 (M^+, 27%), 275 (21), 185 (100), 141 (18), 128 (62), 105 (74), 89 (21), 77 (75), 63 (28) and 51 (76). The second fraction (95–94% n-hexane) gave colorless crystalline product of (Z)- isomer **(10d)** (0.40 g, 35% yield), recrystallized from benzene/*n*-hexane, mp 136–137°C. Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found : C, 78.69 : H, 4.81%. IR cm^{-1}: 1728 (C=O, lactone); 1658 (C=O, benzoyl); 1600 (C=C).^1H NMR: δ 2.31 (d, J_{HH}= 1.6 Hz, 3H, CH_3 at C- α); 6.99 (q, J_{HH}= 1.6 Hz, 1H, H at C-β); 7.49 (s, 1H, H at C-4); 7.15–7.98 (m, 9H, ArH). ^{13}C NMR : δ 25.6 (CH_3at C-α); 117.0 (C-8); 119.3 (C-4a); 124.8 (C-6); 126.6 (C-β): 128.2 (C-5); 128.9, 129.0 (C-2′, C-3′, C-5′, C-6′); 130.1 (C-3); 131.8 (C-7) : 133.3 (C-4′); 138.3 (C-1′); 139.3 (C-4); 147.7 (C- α); 153.9 (C-8a): 159.5 (C-2); 191.3 (C=O, benzoyl). MS : m/z (relative intensity) 290 (M^+, 30%), 276 (26), 261 (10), 248 (13), 215 (8), 202 (9), 185 (100), 128 (56), 105 (81), 89 (21), 77 (90), 63 (32) and 51 (72). The third fraction (80–75% *n*-hexane) afforded colorless crystals of triphenylphosphine oxide (1.43 g, 85% yield) (mp and mixed mp).

When the above reaction was carried out in absence of benzoic acid, a very poor yield of the two isomers **9d** and **10d** was obtained after about 50 h .

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