Reactions of Ethoxycarbonylmethylene(triphenyl)phosphorane with some *ortho*-Quinones in the Presence of Triphenylphosphine, Alcohols and Acetic Anhydride

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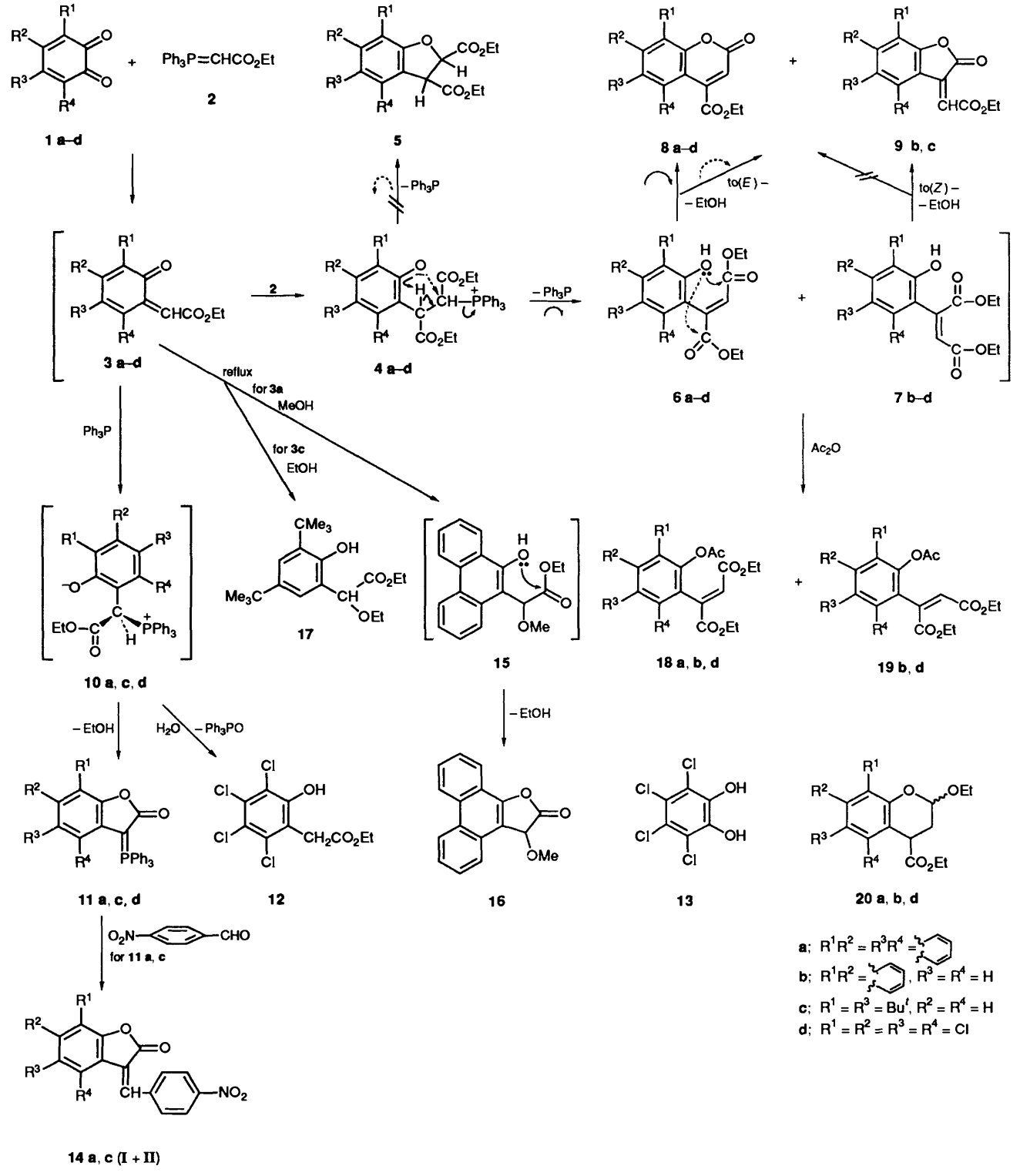
The reactions of *ortho*-quinones **1a**, **1c** and **1d** with ylide **2** in the presence of triphenylphosphine afforded the ylides **11a**, **11c** and **11d** and compound **12**. The reactions of **1a** and **1c** with **2** in refluxing methanol or ethanol gave compounds **16** and **17** respectively, while the reactions of **1a–d** with **2** in acetic anhydride yielded the acetates **18a**, **18b**, **18d** and **19b**, **19d**, the furan derivative **24** and the ylide **25**. Compounds **8** and **9** were also obtained in most of the above reactions. Wittig reactions of ylides **11a**, **11c** with *p*-nitrobenzaldehyde and of ylide **2** with coumarins **8a** and **29** resulted in compounds **14a**, **14c**, **26** and **30** respectively. The transformations of compounds **18**, **19** into **8**, **9** as well as of compound **26** into **28** were also studied.

Bestmann and Lang reported[1] in 1969 that the reactions of *ortho*-quinones **1a–b** and of 4-anilino-1,2-naphthoquinone with ethoxycarbonylmethylene(triphenyl)phosphorane **2**, as well as with its methoxy analogue, afford the corresponding 4-alkoxycarbonylcoumarins **8**, *via* the suggested intermediates **3**, **4**, **6**, depicted in Scheme 1. Recently Soliman *et al.* reported[2] that reaction of the same ylides with benzo[*a*]phenazine-8,9-dione gives the corresponding dialkyl 1,2-dihydrofuro-1,2-dicarboxylates **5**, again *via* intermediates **3** and **4**. Very recently[3] we found that the reactions of **2** with *o*-quinones **1a–d** in dichloromethane solutions afford, besides the coumarins **8a–d**, the γ-lactones **9b** and **9c**, the hydroxy derivatives **6d** (33%) and **12** (8%) and the ylide **11c** (3%), according to the mechanisms proposed in Scheme 1. We also found that, when the reactions between **2** and **1a–c** are carried out in ethyl vinyl ether solution and the ylide **2** is added portionwise into the reaction mixture, the intermediates *o*-quinone methanides **3a**, **3b**, **3d** are trapped by the dienophile to give the corresponding *cis*- and *trans*-pyran derivatives **20a**, **20b**, **20d** in a high total yield. Similarly, the 2-methyl-2-phenyl disubstituted pyran derivative was also obtained as the main product from the reactions between **1a** and **2** in the presence of α-methylstyrene, whereas 4-acyl- or 4-benzoyl-substituted pyrans were obtained from the reactions between **1a** and the ylides $Ph_3P{=}CHCOR$ (R = Me, Ph) in ethyl vinyl ether solution.[4] These results show that the corresponding Wittig monoolefination products initially formed can be trapped easily and under mild conditions by dienophiles, as can the other known *o*-quinone methanides,[5] though these intermediates are also very reactive towards the starting ylides used and the triphenylphosphine, generated *in situ*. In connection with these studies we now report our results on the reactions of the ylide **2** with some *o*-quinones, performed (a) in the presence of an excess of triphenylphosphine; (b) in refluxing methanol or ethanol and (c) in hot acetic anhydride solutions. Furthermore, the reaction between **1a** or **8a** and **2** at high temperature, the Wittig reaction of ylides **11a** and **11c**, prepared for reactions (a), as well as some transformations of the triesters **18** and **19**, are reported.

Results and Discussion

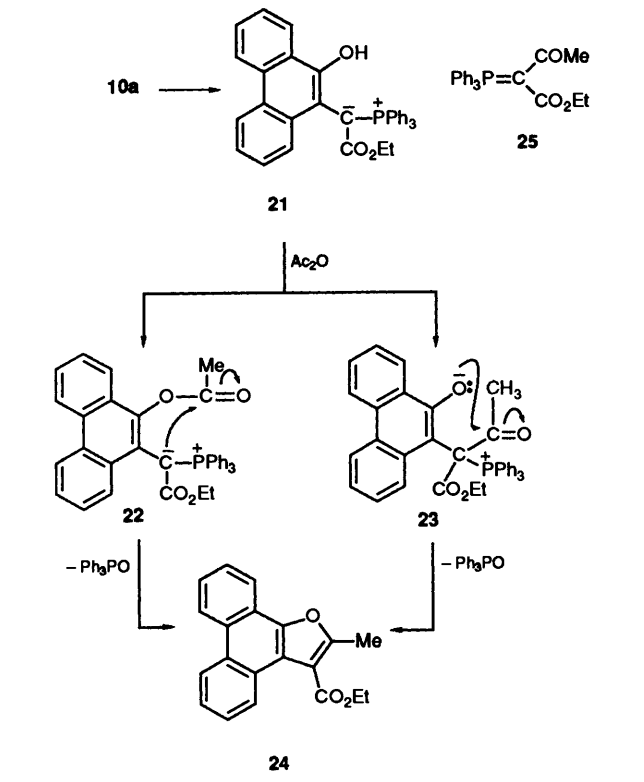
The title reactions studied and the products obtained are depicted in Schemes 1–3. To a stirred dichloromethane solution of a mixture of quinone **1a** (1 equiv.) and triphenylphosphine (3 equiv.), the ylide **2** (1 equiv.) was added at room temperature and portionwise, during 2 h. The mixture was then stirred for further 20 h at ambient temperature and was afterwards heated at reflux for 48 h to give, on cooling, crystals of 3-(triphenylphosphoranylidene)phenanthro[9,10-*b*]furan-2(3*H*)-one[6] **11a** in 79% yield. The reaction between **1c**, triphenylphosphine and ylide **2** (added during 4 h) for 24 h at room temperature afforded, after separation of the reaction mixture by column chromatography 5,7-di-*tert*-butyl-3-triphenylphosphoranylidenebenzo[*b*]furan-2(3*H*)-one[6] **11c** (49%), along with ethyl 6,8-di-*tert*-butyl-2-oxo-2*H*-chromene-4-carboxylate[3] **8c** (12%) and 5,7-di-*tert*-butyl-3-ethoxycarbonylmethylenebenzo[*b*]furan-2(3*H*)-one[3] **9c** (6%). When the reaction was carried out by immediate addition of the ylide **2** and the reaction mixture was then stirred for 45 h at room temperature, the ylide **11c** was obtained in 60% yield. Compounds **11a** and **11c** are identical with those prepared previously in 63 and 58% yield respectively[6] under dry conditions and nitrogen atmosphere from the reactions of quinones **1a** and **1c** with (2,2-diethoxyvinylidene)triphenylphosphorane and triphenylphosphine. The tetrachloroquinone **1d** proved to react with triphenylphosphine under the conditions described above. Thus, when triphenylphosphine was added to a dichloromethane solution of **1d**, an exothermic reaction took place immediately and before addition of the ylide, finally yielding tetrachlorocatechol **13** (69%), obviously *via* the further hydrolysis of the initially formed triphenyldioxaphospholene intermediate. The quinone **1a** reacts with triphenylphosphine in a similar way, but at a higher temperature (70 °C).[7] When the quinone **1d** was added portionwise to a stirred dichloromethane solution of equimolar amounts of triphenylphosphine and of ylide **2** and the reaction mixture was stirred for further **24** h at room temperature and then subjected to column chromatography, compound **13** (13%), ethyl (3,4,5,6-tetrachloro-2-hydroxyphenyl)acetate[3] **12** (37%) and 4,5,6,7-tetrachloro-3-triphenylphosphoranylidenebenzo[*b*]furan-2(3*H*)-one **11d** (2%) were obtained. Although this experimental procedure leads again to the formation of the desired *o*-quinone methanide **3d** and further to its trapping by triphenylphosphine, the betaine thus produced is mainly hydrolysed to the hydroxy derivative **12**, prior to the expected lactonization to the stable ylide **11d**. A possible explanation for the predominant formation of compound **12** to compound **11d**, suggested by a referee, is that the electron withdrawing effects of the four chlorine substituents in **10d** reduce the electron density of the phenoxy anion, thereby rendering it less nucleophilic. A similar electronic effect can also explain the reported[3] isolation of the hydroxy derivative **6d** (in 33% yield) and the carbonyl absorption of compound **11d** at ν/cm^{-1} 1710. It should be noted that the same C=O bond in



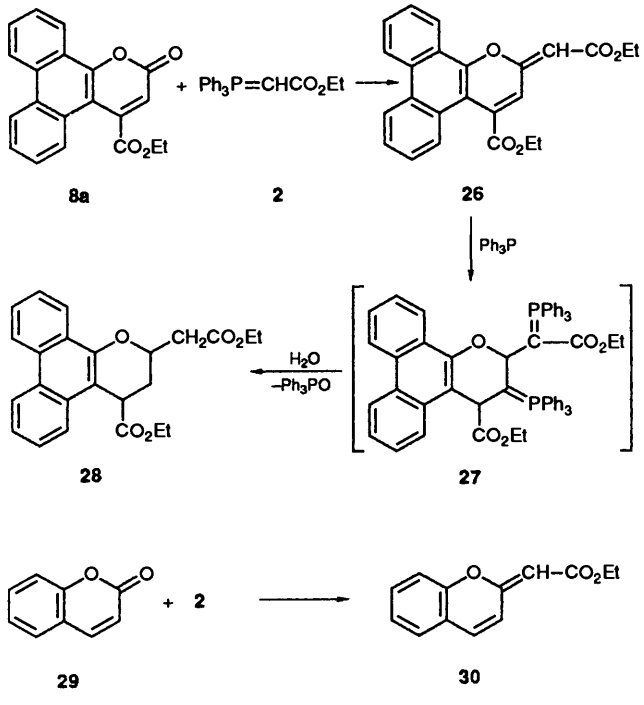
Scheme 1

compounds **11a** and **11c** appeared[6] at ν/cm^{-1} 1680. The recorded spectral data for compound **11d** are in agreement with the suggested ylide form.

Treatment of compound **11a** with 4-nitrobenzaldehyde in refluxing dichloromethane for 48 h afforded 3-(4-nitrobenzylidene)phenanthro[9,10-*b*]furan-2(3*H*)-one **14a** in 17% yield. When the same reaction was carried out in refluxing toluene, compound **14a** was again obtained, but in 67% yield. By a similar treatment of ylide **11c** with 4-nitrobenzaldehyde in a refluxing dichloromethane solution, the two isomeric 5,7-di-*tert*-butyl-3-(4-nitrobenzylidene)benzofuran-2(3*H*)-ones **14c**$_{I}$ (38%) and **14c**$_{II}$ (49%) were isolated. All these Wittig products exhibited the carbonyl band in the range ν/cm^{-1} 1765–1780, like other similar 3-alkylidenebenzofuran-2(3*H*)ones.[8] More evidence is necessary for the configurational assignment of the products **14** though the *Z*-configuration seems more favourable for **14a** due to expected reduced steric hindrance. The Wittig reaction of naphtho[2,1-*b*]furan-1,2-dione with ylide **2** and also with its methoxy analogue has also been used[2] for the preparation of similar alkyl 2-oxonaphtho[2,1-*b*]furan-1(2*H*)-



Scheme 2



Scheme 3

ylideneacetates, though recently it has been reported that the reactions of some furan-2,3-diones with the same ylides lead to the Wittig olefination of the lactonic carbonyl and not of the keto carbonyl.[9]

When the reaction of quinone **1a** with ylide **2** was carried out in refluxing methanol and the ylide was added portionwise, the expected[10] Michael addition of the methanol to the corresponding *o*-quinone methanide intermediate **3a** predominated over all the other competing reactions of **3a**, leading originally to the formation of ether **15**. Thus, to a precipitate of quinone **1a** in refluxing methanol the ylide **2** (1.2 equiv.) was added in portions during 4 h and the reaction mixture was heated at reflux for further 20 h, until all the quinone was consumed, to give, after filtration, crystals of 3-methoxyphenanthro[9,10-*b*]furan-2(3*H*)-one **16** (31%), obviously by further lactonization of the ether **15** initially formed. Separation of the filtrate by column chromatography afforded an additional amount of **16** (17%, total yield 48%), along with ethyl 2-oxo-2*H*-dibenzo-[*f*,*h*]chromene-4-carboxylate[3] **8a** (35%). Treatment of quinone **1c** with **2** in refluxing methanol resulted in the formation of a mixture of ethyl and methyl derivatives, obviously by part transesterification of the original ethyl derivatives, which were only roughly separated by chromatography and not further studied. After that the reaction of **1c** with **2** was carried out in refluxing ethanol for 29 h to give ethyl (3,5-di-*tert*-butyl-2-hydroxyphenyl)ethoxyacetate **17** (5%), along with compounds **8c**[3] (43%), **9c**[3] (5%) and **11c**[6] (4%).

We next studied the reactions between the quinones **1a–d** and the ylide **2** in the presence of acylating agents, in an effort to trap the suggested intermediates **6** and/or **7** by their acylation into the corresponding acetoxy derivatives **18** and/or **19**, and to shed more light into the problem concerning the formation and the configuration of the γ-lactones **9b** and **9c** obtained previously.[3] We note that further lactonization of the ethyl fumarate intermediates **6** could lead to formation of the coumarins **8** and/or to formation of the (*E*)-γ-lactones **9**. That was previously suggested by us for compounds **9b** and **9c** on the basis of their ^{1}H NMR spectra.[3] Furthermore, the lactonization of the ethyl maleate intermediates **7** could lead only to the formation of the (*Z*)-γ-lactones **9**.

Although it is known[11] that phosphorus ylides react easily with acylating agents to give at first acyl salts and further on the corresponding acyl ylides, we initially tried the reaction between compounds **1a** and **2** (2 equiv.) in ethyl acetate solution, at room temperature. Separation of the reaction mixture by column chromatography gave only compound **8a** (69%). Next a solution of quinone **1a** and ylide **2** (2 equiv.) in excess of acetic anhydride, used also as a solvent, was kept at room temperature for 24 h to yield the expected acetoxy compound **18a** (28%) and compound **8a** (53%). When the same reaction was carried out at 60 °C, compounds **18a** (62%), **8a** (25%) and the unexpected ethyl 2-methylphenanthro[9,10-*b*]furan-3-carboxylate **24** (7%) were obtained. Further transformation of the intermediate **10a** (Scheme 1) to the *o*-hydroxy ylide **21**, followed firstly by acetylation of **21** into the ester ylide **22** and then by an intramolecular Wittig reaction of the ylide group with the carbonyl of the ester group[12] of intermediate **22**, can account for the formation of the furan derivative **24** (Scheme 2). As an alternative process to compound **24** could also be considered the acylation of **21** to the phosphonium derivative **23**, followed by an intramolecular attack of the hydroxy to the acetyl carbonyl of **23** to the same betaine intermediate, as known from the Wittig reaction of **22**, and in analogy to the reported previously 'internal Wittig' reaction.[13] The intermediate **23** could also be formed by the Wittig monoolefination of quinone **1a** with the stable and less reactive[14] ylide **25**,[11b] generated *in situ* by acetylation of a part of **2**, and by further attack of the corresponding *o*-quinone methanide thus formed, with triphenylphosphine. However, in a control experiment it was found that a mixture of compounds **1a** and **25** remained unchanged, even after reflux for 24 h in chloroform. In agreement with the proposed structure **24** the product under question showed in the ^{1}H NMR spectrum the characteristic low field absorptions for the fused phenanthrofuran system,[4] along with those for the methyl and ethoxycarbonyl substituents, as well as correct molecular ion and analytical data.

The reaction between **1b**, **2** and acetic anhydride at 60 °C for

10 h afforded the acetoxy isomers **18b** (36%) and **19b** (23%) along with the coumarin derivative **8b**[3] (9%). When the quinone **1c** was treated with ylide **2** in acetic anhydride solution under the same conditions, only compounds **8c** (4%), **9c** (73%) and the ylide **25** (19%) were obtained. Probably, the bulky substituent R^1 (Bu^t) in the intermediates **6c** and/or **7c** prevents the intermolecular attack of the adjacent hydroxy by the acetic anhydride. Finally the reaction between compounds **1d** and **2** in acetic anhydride afforded compounds **18d**[3] (33%), **19d** (24%) and **25** (27%). Compound **18d** is identical in all respects with that previously obtained by treatment of the isolated compound **6d** with acetic anhydride.[3]

The suggested *trans*-configuration **18a**, for the sole acetoxy product, obtained from quinone **1a**, and **18b**, **18d** for the major acetoxy isomers obtained from quinones **1b** and **1d** respectively, is based on the one hand on the fact that in absence of the acetic anhydride only the coumarin **8a** and mainly the coumarin **8b** are obtained from quinones **1a** and **1b**, obviously *via* the further δ-lactonization of the fumarate intermediates **6a** and **6b**, and on the other hand on the fact that the isolated compound **6d** was converted by prolonged heating in refluxing toluene quantitatively (89%) into the coumarin **8d**.[3] The recorded chemical shifts for the olefinic proton in the ^1H NMR spectra of compounds **18a**, **18b**, **18d** and **6d**[3] are very similar to each other and also to those of γ-lactones **9b** and **9c**, and are quite different from those recorded for the acetoxy maleates **19b** and **19d**. This observation can be used as an evidence in favour of the (*E*)-configuration of compounds **9b** and **9c**, as it was previously suggested by us.[3] Furthermore, when an ethanolic solution of compound **18a** was heated at reflux for 6 h in presence of hydrochloric acid, it afforded only compound **8a** in almost 100% yield. Compound **18d** gave, under the same conditions, quantitatively the hydroxy derivative **6d**. Unfortunately, both the acetoxy compounds **18b** and **19b** were found to give, by a similar treatment, both the lactonization products **8b** and **9b**. When an ethanolic solution of **18b**, containing hydrochloric acid, was left to stand at room temperature for 64 h, and the reaction mixture was then separated by column chromatography, compounds **8b** (52%) and **9b** (7%), along with some unreacted starting compound **18b** (34%) were obtained. By a similar treatment of the isomer **19b** for only 9 h the starting compound **19b** (40%), the coumarin **8b** (41%) and the γ-lactone **9b** (16%), identical in all respects with that obtained from **18b**, were isolated from the reaction mixture. Although the conversion of both acetoxy compounds **18b** and **19b** to the same lactonization products proves beyond any doubt that they are configurational and not *peri*-isomers, it does not confirm with any certainty the route of formation and the configuration of the compounds under question. It is also of interest to notice once more that the γ-lactones **9** were obtained only from quinones with R^4 = H.

In an unsuccessful effort to trap the intermediate **3a** *via* coumarin **29**, we found that dissolution of quinone **1a** in an excess (5 equiv.) of melted coumarin **29** and further portionwise addition of ylide 2 (1.5 equiv.) to the heated mixture led to compound **8a** (47%) and ethyl (3,4-dihydro-4-ethoxycarbonyl-2*H*-phenanthro[9,10-*b*]pyran-2-yl)acetate **28** (12%), along with triphenylphosphine and triphenylphosphine oxide. No trapping products[15] of the intermediate **3a** by coumarin **29** were detected or isolated from the reaction mixture. We considered that compound **28** was formed from compound **8a** according to the reaction sequence depicted in Scheme 3. In agreement with the above consideration, when a toluene solution of equimolar amounts of compounds **2** and **8a** was heated at reflux for 3 days, it gave ethyl (4-ethoxycarbonyl-2*H*-phenanthro[9,10-*b*]pyran-2-ylidene)acetate **26** in 48% yield. Furthermore, a toluene solution of compound **26** and triphenylphosphine (2.5 equiv.) was heated at reflux for 48 h and the reaction mixture was then separated by column chromatography to give compound **28** in 18% yield. Coumarin **29** also reacted with ylide **2**, but at higher temperatures. A mixture of equimolar amounts of compounds **2** and **29** was heated at 115–120 °C for 48 h to give ethyl (2*H*-benzo[*b*]pyran-2-ylidene)acetate **30** (35%). The recorded spectral data (^1H NMR, IR and MS) and the analytical data of the knew compounds of Scheme 3 support the structures proposed for them, although more evidence is necessary for their configurational assignment. It is of interest to notice that the reported reactions of some other lactones with phosphorus ylides did not give the normal Wittig olefination products.[16] It must also be pointed out that attack of triphenylphosphine to the Wittig product **26**, and further transformation of the initial phosphonium derivative thus formed to the final product **28**, can proceed in more than one step, the bis-ylide **27**, depicted in Scheme 3, being one of the possible intermediates. Similar reactions of triphenylphosphine with maleic anhydrides, maleimides and isomaleimides to give the corresponding phosphorus ylides have been known since 1968.[17]

In conclusion, the reactions between *o*-quinones and alkoxymethylene(triphenyl)phosphoranes are of significant synthetic value, since they can be used for the preparation of several different compounds, depending on the particular reagents present and the reaction conditions applied.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were recorded with deuteriochloroform as solvent on a Bruker AW 80 (80 MHz) spectrometer with $SiMe_4$ as internal standard. Coupling constant values, *J*, are given in Hz. Mass spectra were determined on a VG-250 spectrometer with ionization energy maintained at 70 eV.

Reactions of o-*Quinones* **1a**, **1c**, **1d** *with Ylide* **2** *in the Presence of Triphenylphosphine.*—(*a*) To a stirred solution of phenanthrene-9,10-quinone **1a** (0.104 g, 0.5 mmol) and triphenylphosphine (0.393 g, 1.5 mmol) in dichloromethane (5 cm^3) the ylide **2** (0.174 g, 0.5 mmol) was added portionwise during 2 h. The reaction mixture was then stirred for a further 20 h at ambient temperature and then for a further 48 h under reflux and then was cooled to room temperature to give crystals of 3-(triphenylphosphoranylidene)phenanthro[9,10-*b*]furan-2-(3*H*)-one **11a** (195 mg, 79%), m.p. 250–252 °C (decomp.) (from dichloromethane) (lit.,[6] m.p. 252 °C).

(*b*) To a stirred solution of 3,5-di-*tert*-butyl-1,2-benzoquinone **1c** (0.22 g, 1 mmol) and triphenylphosphine (0.786 g, 3 mmol) in dichloromethane (6 cm^3) the ylide **2** (0.348 g, 1 mmol) was added portionwise during 4 h and the reaction mixture was stirred for further 24 h at room temperature and then evaporated to dryness. Chromatography on silica gel with dichloromethane as the eluent gave three fractions. The first fraction gave 5,7-di-*tert*-butyl-3-ethoxycarbonylmethylenebenzo-[*b*]furan-2(3*H*)-one **9c** (20 mg, 6%), m.p. 119–121 °C (from hexane) (lit.,[3] m.p. 119–121 °C). The second fraction gave ethyl 6,8-di-*tert*-butyl-2-oxo-2*H*-chromene-4-carboxylate **8c** (41 mg, 12%), m.p. 113–115 °C (from hexane) (lit.,[3] m.p. 113–115 °C). The third fraction gave 5,7-di-*tert*-butyl-3-triphenylphosphoranylidenebenzo[*b*]furan-2(3*H*)-one **11c** (0.248 g, 49%) m.p. 247–249 °C (from methanol) (lit.,[6] m.p. 249 °C).

When the same reaction between *o*-quinone **1c** (0.44 g, 2 mmol), triphenylphosphine (1.572 g, 6 mmol) and the ylide **2** (0.696 g, 2 mmol) was carried out by adding them at once in dichloromethane (17 cm^3) under stirring and the reaction mixture was stirred for 48 h at room temperature and then was

concentrated to a small volume, crystals of compound **11c** were obtained (0.605 g, 60%).

(*c*) To a stirred solution of triphenylphosphine (0.262 g, 1 mmol) and ylide **2** (0.348 g, 1 mmol) in dichloromethane (10 cm^3) tetrachloro-1,2-benzoquinone **1d** (0.246 g, 1 mmol) was added portionwise during 2 h and the reaction mixture was then stirred for further 24 h at room temperature. After evaporation of the solvent, the residue was chromatographed on silica gel with dichloromethane as the eluent. Triphenylphosphine (34 mg) was eluted first. The second fraction gave ethyl (3,4,5,6-tetrachloro-2-hydroxyphenyl)acetate **12** (0.116 g, 37%), m.p. 129–131 °C (dichloromethane–hexane) (lit.,[3] m.p. 129–131 °C). The third fraction gave tetrachlorocatechol **13** (33 mg, 13%), m.p. 193–195 °C (from ethanol) (lit.,[18] m.p. 194–195 °C). The next fraction gave 4,5,6,7-*tetrachloro*-3-*triphenylphosphoranylidenebenzo*[b]*furan*-2(3H)-*one* **11d** (11 mg, 2%), m.p. 275–277 °C (from dichloromethane) (Found: C, 58.3; H, 3.15. $C_{26}H_{15}Cl_4O_2P$ requires C, 58.7; H, 2.8%); ν_{max}(Nujol)/cm^{-1} 1710; δ_H($CDCl_3$) 7.34–7.84 (m); *m*/*z* 538 (M^+ + 8, 1%), 536 (M^+ + 6, 2), 534 (M^+ + 4, 6), 532 (M^+ + 2, 23), 530 (M^+, 8) and 165 (100).

When the reaction between triphenylphosphine (0.131 g, 0.5 mmol), the quinone **1d** (0.246 g, 1 mmol) and the ylide **2** (0.348 g, 1 mmol) in dichloromethane (5 cm^3) was carried out as above, and then hexane was added to the reaction mixture, crystals of compound **11d** (24 mg, 4.5%) were precipitated. When the quinone **1d** (62 mg, 0.26 mmol) and triphenylphosphine (0.198 g, 0.75 mmol) was first dissolved in dichloromethane (2 cm^3) a spontaneous reaction between them took place, before the addition of the ylide **2**, yielding tetrachlorocatechol **13** (44 mg, 69%).

Wittig Reactions of Ylides **11a** *and* **11d** *with* p-*Nitrobenzaldehyde. Preparation of Compounds* **14a** *and* $\mathbf{14c_{I,II}}$.—(*a*) To a solution of ylide **11a** (0.107 g, 0.216 mmol) in toluene (17 cm^3) *p*-nitrobenzaldehyde (33 mg, 0.218 mmol) was added and the reaction mixture was heated under reflux for 48 h. After the evaporation of the solvent the residue was triturated with dichloromethane to yield red crystals of 3-(4-*nitrobenzylidene*)*phenanthro*[9,10-b]*furan*-2(3H)-*one* **14a** (53 mg, 67%), m.p. 256–258 °C (from dichloromethane) (Found: C, 74.75; N, 4.1; H, 3.9. $C_{23}H_{13}NO_4$ requires C, 75.2; N, 3.8; H, 3.6%); ν_{max}(Nujol)/cm^{-1} 3020, 1765, 1595, 1520 and 1345; δ_H($CDCl_3$) 7.48–7.92 (4 H, m), 7.98–8.50 (6 H, m) and 8.64–8.94 (3 H, m); *m*/*z* 367 (M^+, 100%), 339 (42), 294 (30), 293 (33), 292 (23), 265 (38) and 263 (47).

(*b*) A solution of the ylide **11c** (95 mg, 0.19 mmol) and *p*-nitrobenzaldehyde (29 mg, 0.19 mmol) in dichloromethane (4 cm^3) was heated under reflux for 48 h. After evaporation of the solvent, the residue was separated by preparative TLC on silica gel [hexane–dichloromethane (1:1)]. The faster moving band afforded 5,7-*di*-tert-*butyl*-3-(4-*nitrobenzylidene*)*benzo*[b]*furan*-2(3H)-*one* $\mathbf{14c_I}$ (27 mg, 38%), m.p. 162–164 °C (dichloromethane–hexane) (Found: C, 73.15; N, 3.9; H, 6.35. $C_{23}H_{25}NO_4$ requires C, 72.8; N, 3.7; H, 6.6%); ν_{max}(Nujol)/cm^{-1} 1769, 1618, 1590, 1520 and 1340; δ_H($CDCl_3$) 1.40 (9 H, s), 1.46 (9 H, s), 7.27 (1 H, s), 7.39 (1 H, s), 7.57 (1 H, s) and 8.17–8.38 (4 H, m); *m*/*z* 379 (M^+, 70%), 363 (100) and 335 (16). The next band gave the other *isomer* $\mathbf{14c_{II}}$ (35 mg, 49%), m.p. 183–185 °C (dichloromethane–hexane) (Found: C, 73.2; N, 3.3; H, 6.9. $C_{23}H_{25}NO_4$ requires C, 72.8; N, 3.7; H, 6.6%); ν_{max}(Nujol)/cm^{-1} 1779, 1630, 1600, 1525 and 1340; δ_H($CDCl_3$) 1.23 (9 H, s), 1.42 (9 H, s), 7.34–7.44 (2 H, m), 7.77 (1 H, s), 7.82 (2 H, d, *J* 7.2) and 8.35 (2 H, d, *J* 7.2); *m*/*z* 379 (M^+, 56%), 363 (100) and 335 (8). The later moving band gave *p*-nitrobenzaldehyde (3 mg).

3-*Methoxyphenanthro*[9,10-b]*furan*-2(3H)-*one* **16**.—To a stirred suspension of quinone **1a** (0.208 g, 1 mmol) in methanol (10 cm^3) heated at reflux was added the ylide **2** (0.418 g, 1.2 mmol) portionwise over 4 h and the reaction mixture was then refluxed for a further 20 h under stirring. The hot reaction mixture was then filtrated to give crystals of *compound* **16** (81 mg, 31%), m.p. 220–222 °C (decomp.) (from methanol) (Found: C, 77.1; H, 4.3. $C_{17}H_{12}O_3$ requires C, 77.25; H, 4.6%); ν_{max}(Nujol)/cm^{-1} 1815; δ_H($CDCl_3$) 3.31 (3 H, s), 7.34 (1 H, s, partially overlapped by $CHCl_3$), 7.56–7.90 (5 H, m), 8.27–8.44 (1 H, m) and 8.57–8.74 (2 H, m); *m*/*z* 264 (M^+, 44%), 236 (56), 221 (100), 220 (81) and 205 (19). The filtrate was evaporated to dryness. Chromatography on silica gel with dichloromethane–hexane (3:1) as eluent gave first an additional amount of compound **16** (35 mg, 13%), total yield 44%. The next fraction gave compound **8a** (0.112 g, 35%).

Ethyl (3,5-*Di*-tert-*butyl*-2-*hydroxyphenyl*)*ethoxyacetate* **17**.—To a solution of quinone **1c** (0.44 g, 2 mmol) in ethanol (17 cm^3), heated at reflux, was added the ylide **2** (0.696 g, 2 mmol) over 5 h and the reaction mixture was then refluxed for a further 24 h. The solvent was evaporated and the oily residue was triturated with ether to yield crystals of compound **11c** (45 mg, 4%). The filtrate was evaporated to dryness. Chromatography of the residue on silica gel with hexane–dichloromethane (3:1→1:1) as eluent gave three fractions. The first fraction gave compound **9c** (24 mg, 4%). The second fraction gave compound **17** (35 mg, 5%), m.p. 125–127 °C (from hexane) (Found: C, 71.15; H, 9.9. $C_{20}H_{32}O_4$ requires C, 71.4; H, 9.6%); ν_{max}(Nujol)/cm^{-1} 3400 and 1735; δ_H($CDCl_3$) 1.25 (3 H, t, *J* 6.4), 1.38 (3 H, t, *J* 7.2), 3.60 (2 H, q, *J* 6.4), 4.19 (2 H, q, *J* 7.2), 5.35 (1 H, s), 7.27 (1 H, s) and 8.68 (1 H, s); *m*/*z* 336 (M^+, 18%), 335 (66), 318 (16), 307 (35), 305 (43), 291 (17), 277 (44), 263 (38), 234 (44), 233 (99), 232 (64), 230 (60), 218 (35) and 217 (100). The third fraction afforded compound **8c** (0.285 g, 43%).

Reaction of Quinone **1a** *with Ylide* **2** *in Ethyl Acetate*.—A solution of quinone **1a** (0.104 g, 0.5 mmol) and ylide **2** (0.348 g, 1 mmol) in ethyl acetate (5 cm^3) was stirred at room temperature. The reaction was monitored by TLC examination of the mixture. After 2 h all the starting quinone was consumed. The solvent was evaporated and the residue was chromatographed on silica gel, with hexane–dichloromethane (1:1) as eluent to give ethyl 2-oxo-2*H*-dibenzo[*f*,*h*]chromene-4-carboxylate **8a** (0.11 g, 69%), m.p. 158–159 °C (from ethanol) (lit.,[1] m.p. 158 °C).

Reactions of Quinones **1a–d** *with Ylide* **2** *in Acetic Anhydride. Preparation of Compounds* **18a**, **18b**, **18d**, **19b**, **19d** *and* **24**.—(*a*) A solution of quinone **1a** (0.416 g, 2 mmol) and ylide **2** (1.392 g, 4 mmol) in acetic anhydride (5 cm^3) was heated at *ca* 60 °C for 8 h. The reaction mixture was then poured into water (30 cm^3) and extracted with ether (4 × 40 cm^3). The extract was dried over Na_2SO_4 and evaporated to dryness. Chromatography on silica gel with hexane–ethyl acetate (9.9:0.1→9:1) as eluent gave three fractions. The first fraction gave *ethyl* 2-*methylphenanthro*[9,10-b]*furan*-3-*carboxylate* **24** (44 mg, 7%), m.p. 109–110 °C (dichloromethane–hexane) (Found: C, 78.8; H, 5.4. $C_{20}H_{16}O_3$ requires C, 78.9; H, 5.3%); ν_{max}(Nujol)/cm^{-1} 1705 and 1615; δ_H($CDCl_3$) 1.47 (3 H, t, *J* 8.0), 2.80 (3 H, s), 4.50 (2 H, d, *J* 8.0), 7.43–7.79 (4 H, m), 8.18–8.37 (1 H, m), 8.57–8.79 (2 H, m) and 9.04–9.26 (1 H, m); *m*/*z* 304 (M^+, 100%), 278 (16), 277 (30), 276 (24), 275 (51), 231 (16), 230 (19), 202 (59) and 152 (27). The second fraction afforded compound **8a** (0.16 g, 25%). The third fraction gave colourless crystals of *diethyl* (10-*acetoxy*-9-*phenanthryl*)*fumarate* **18a** (0.503 g, 62%), m.p. 70–72 °C (from ethanol) (Found: C, 70.8; H, 5.6. $C_{24}H_{22}O_6$ requires C, 70.9; H, 5.5%); ν_{max}(Nujol)/cm^{-1} 1760, 1725 and 1720; δ_H($CDCl_3$) 0.63 (3 H, t, *J* 8.0), 1.10 (3 H, t, *J* 9.0), 2.35 (3 H, s), 3.81 (2 H, q, *J* 9.0), 4.19 (2 H, q, *J* 8.0), 7.26–7.92 (6 H, m) and 8.42–8.79 (2 H, m); *m*/*z* 407 (15%), 406 (M^+, 24), 364 (100), 318 (64) and 290 (53).

When the same reaction between compounds **1a** and **2** in acetic anhydride was carried out at room temperature compounds **8a** (53%) and **18a** (28%) were again obtained.

(*b*) The reaction between quinone **1b** (0.158 g, 1 mmol) and ylide **2** (0.696 g, 2 mmol) in acetic anhydride (2 cm^3) at 60 °C for 10 h was carried out and the reaction mixture was worked up, as described above for quinone **1a**, to give, from the first fraction, compound **8b** (23 mg, 9%), m.p. 147–148 °C (chloroform–hexane) (lit.,[1] m.p. 148 °C). The next fraction gave *diethyl* (1-*acetoxy*-2-*naphthyl*)*maleate* **19b** (83 mg, 23%), m.p. 52–54 °C (from ethanol) (Found: C, 67.3; H, 5.55. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.7%); ν_{max}(Nujol)/cm^{-1} 1760 and 1720; δ_H($CDCl_3$) 1.29 (6 H, t, *J* 7.2), 2.42 (3 H, s), 4.25 (2 H, q, *J* 7.2), 4.34 (2 H, q, *J* 7.2), 6.30 (1 H, s) and 7.34–7.91 (6 H, m); *m*/*z* 356 (M^+, 78%), 312 (100), 266 (54) and 240 (42).

(*c*) The reaction between the quinone **1c** (0.44 g, 2 mmol) and the ylide **2** (1.392 g, 4 mmol) in acetic anhydride (5 cm^3) for 24 h, at room temperature, was carried out and the reaction mixture was worked up as above to give first compound **9c** (0.48 g, 73%). The next fraction afforded compound **8c** (26 mg, 4%). The third fraction gave ylide **25** (0.302 g, 19%), m.p. 171–173 °C (dichloromethane–hexane) (lit.,[11b] m.p. 172–174 °C).

(*d*) The reaction of quinone **1d** (0.492 g, 2 mmol) with ylide **2** (1.392 g, 4 mmol) in acetic anhydride at 60 °C for 30 min was carried out and the reaction mixture was worked up as described for quinone **1a**. The following fractions were eluted. The fraction eluted first gave **18d** (0.29 g, 33%), m.p. 61–63 °C (from hexane) (lit.,[3] m.p. 61–63 °C). The next fraction afforded *diethyl* (2-*acetoxy*-3,4,5,6-*tetrachlorophenyl*)*maleate* **19d** (0.21 g, 24%), oil (Found: C, 43.0; H, 3.1. $C_{16}H_{14}Cl_4O_6$ requires C, 43.3; H, 3.2%); ν_{max}(liquid film)/cm^{-1} 1787, 1735, 1725, 1640 and 1560; δ_H($CDCl_3$) 1.23 (3 H, t, *J* 7.0), 1.32 (3 H, t, *J* 7.4), 2.31 (3 H, s), 4.21 (2 H, q, *J* 7.0), 4.28 (2 H, q, *J* 7.4) and 6.21 (1 H, s); *m*/*z* 448 (M^+ + 6, 0.8%), 446 (M^+ + 4, 4), 444 (M^+ + 2, 9) and 442 (M^+, 6). The next fraction gave triphenylphosphine oxide (0.46 g, 83%) and the following fraction afforded ylide **25** (0.425 g, 27%).

Conversion of **18a** *into* **8a**.—A solution of compound **18a** (67 mg, 0.165 mmol) and concentrated hydrochloric acid (0.5 cm^3) in ethanol (3 cm^3) was heated at reflux for 6 h. Then the reaction mixture was cooled to room temperature to give crystals of compound **8a** (52 mg, 99%).

Conversion of **18b** *into* **8b** *and* **9b**.—A solution of compound **18b** (0.116 g, 0.326 mmol) and concentrated hydrochloric acid (0.5 cm^3) in ethanol (3 cm^3) was left to stand for 64 h at room temperature. The solvent evaporated to dryness. Separation by preparative TLC on silica gel [hexane–dichloromethane (1:1)] afforded from the faster moving band compound **9b** (6 mg, 7%), m.p. 187–189 °C (chloroform–hexane) (lit.,[3] m.p. 187–189 °C). The next band gave compound **8b** (51 mg, 52%). The slower moving band gave unchanged compound **18b** (39 mg, 34%).

Conversion of **19b** *into* **8b** *and* **9b**.—A solution of compound **19b** (82 mg, 0.23 mmol) and concentrated hydrochloric acid (0.5 cm^3) in ethanol (3 cm^3) was stirred for 9 d at room temperature. The solvent evaporated to dryness. Chromatography on silica gel with dichloromethane–hexane (1:1) gave three fractions. The first fraction afforded compounds **9b** (10 mg, 16%). The second fraction gave compound **8b** (25 mg, 41%). The third fraction gave unreacted compound **19b** (36 mg, 40%).

Conversion of **18d** *into* **6d**.—A solution of compound **18d** (20 mg, 0.045 mmol) and concentrated hydrochloric acid (0.3 cm^3) in ethanol (2 cm^3) was heated at reflux for 24 h. The solvent evaporated to dryness to give diethyl (2,3,4,5-tetrachloro-6-hydroxyphenyl)fumarate **6d** (18 mg, 100%), m.p. 76–78 °C (ethyl acetate–hexane) (lit.,[3] m.p. 76–78 °C).

Ethyl (4-*Ethoxycarbonyl*-2H-*phenanthro*[9,10-b]*pyran*-2-*ylidene*)*acetate* **26**.—A solution of compound **8a** (0.318 g, 1 mmol) and ylide **2** (0.348 g, 1 mmol) in toluene (5 cm^3) was heated at reflux for 3 d. The solvent evaporated to dryness in a rotary evaporator. Chromatography on silica gel with ethyl acetate–hexane (1:2) gave compound **26** (0.186 g, 48%), m.p. 140–141 °C (from ethanol) (Found: C, 74.1; H, 5.3. $C_{24}H_{20}O_5$ requires C, 74.2; H, 5.2%); ν_{max}(Nujol)/cm^{-1} 1735, 1730, 1680, 1630 and 1600; δ_H($CDCl_3$) 1.25 (3 H, t, *J* 9.0), 1.49 (3 H, t, *J* 9.0), 4.28 (2 H, q, *J* 9.0), 4.60 (2 H, q, *J* 9.0), 5.56 (1 H, s), 7.40–7.93 (6 H, m) and 8.16–8.64 (3 H, m); *m*/*z* 389 (25%), 388 (M^+, 92), 343 (19), 316 (89), 288 (18) and 214 (100). The next fraction afforded unreacted compound **8a** (99 mg, 31%).

Ethyl (3,4-*Dihydro*-4-*ethoxycarbonyl*-2H-*phenanthro*[9,10-b]*pyran*-2-*yl*)*acetate* **28**.—(*a*) A solution of compound **26** (78 mg, 0.2 mmol) and triphenylphosphine (0.131 g, 0.5 mmol) in toluene (5 cm^3) was heated at reflux for 48 h. The solvent was evaporated to dryness. Chromatography on silica gel with hexane–dichloromethane (1:1) as eluent gave compound **28** (14 mg, 18%), m.p. 70–72 °C (from ethanol) (Found: C, 73.3; H, 6.3. $C_{24}H_{24}O_5$ requires C, 73.45; H, 6.2%); ν_{max}(Nujol)/cm^{-1} 1740, 1730 and 1625; δ_H($CDCl_3$) 1.02–1.87 (6 H, m), 2.20–2.84 (4 H, m), 3.50–4.15 (6 H, m), 7.05–7.82 (5 H, m) and 8.40–8.72 (3 H, m); *m*/*z* 392 (M^+, 56%), 320 (48) and 248 (100).

(*b*) To a stirred melted mixture of quinone **1a** (0.208 g, 1 mmol) and coumarin **29** (0.73 g, 5 mmol), heated at *ca.* 70 °C, ylide **2** (0.522 g, 1.5 mmol) was added in portions during 2 h. The reaction mixture was separated by column chromatography on silica gel. Elution with hexane–ethyl acetate (9:1) gave three fractions. The first fraction gave compound **28** (47 mg, 12%). The second fraction gave coumarin **29** (0.701 g, 96%) and the third fraction gave compound **8a** (0.149 g, 47%).

Ethyl (2H-*Benzo*[b]*pyran*-2-*ylidene*)*acetate* **30**.—A mixture of coumarin **29** (0.292 g, 2 mmol) and ylide **2** (0.696 g, 2 mmol) was heated in an oil bath at *ca.* 115 °C for 48 h, and then chromatographed on silica gel with hexane–ethyl acetate (2:1) as eluent to give compound **30** (0.151 g, 35%), m.p. 75–76 °C (from ethanol) (Found: C, 72.3; H, 5.6. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.6%); ν_{max}(Nujol)/cm^{-1} 1695sh, 1680 and 1600; δ_H($CDCl_3$) 1.27 (3 H, t, *J* 9.0), 4.16 (2 H, q, *J* 9.0), 5.38 (1 H, s), 6.88–7.36 (5 H, m) and 7.83 (1 H, d, *J* 14); *m*/*z* 216 (M^+, 40%), 171 (87) and 114 (100).

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Paper 1/03700E
Received 19*th July* 1991
Accepted 2*nd October* 1991