Reactions of 3-Triphenylphosphoranylidene-[*b*]fused Furan-2(3*H*)-ones with some Salicylaldehydes: New Synthesis of 3-(2-Hydroxyaryl)-coumarins and Coumestans

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Reactions of the ylide **1** and *o*-hydroxybenzaldehydes **2a–c** gave, depending on the reaction conditions, 3-(2-hydroxyphenyl)coumarin derivatives **5a–c**, 3-(2-hydroxybenzylidene)benzo[*b*]furan-2(3*H*)-one **4** and, in one step, the coumestan derivative **6**. Reaction of the ylide **11** with **2a** resulted in the coumarin derivative **13** and the coumestan derivative **14**.

Coumestans, 6*H*-benzofuro[3,2-*c*][1]benzopyran-6-ones, constitute an important class of naturally occurring compounds many of which have been isolated from natural sources.[1] They possess a variety of biological activities, such as estrogenic, antibacterial, antifungal and phytoalexine activity.[2] Several methods,[2,3] in general, are known for the synthesis of these compounds but they are multi-step and give low yields. Such methods involve coupling of *in situ* generated *o*-quinones, by potassium ferricyanide[3a] or mushroom tyrosinase[2a] oxidation of catechols, by 4-hydroxycoumarins or oxidation of the latter by (diacetoxy)iodoarenes;[3b] or oxidation of 3-(2-hydroxyaryl)-coumarins by using DDQ[3c] or lead tetraacetate[3d] as oxidizing agent.

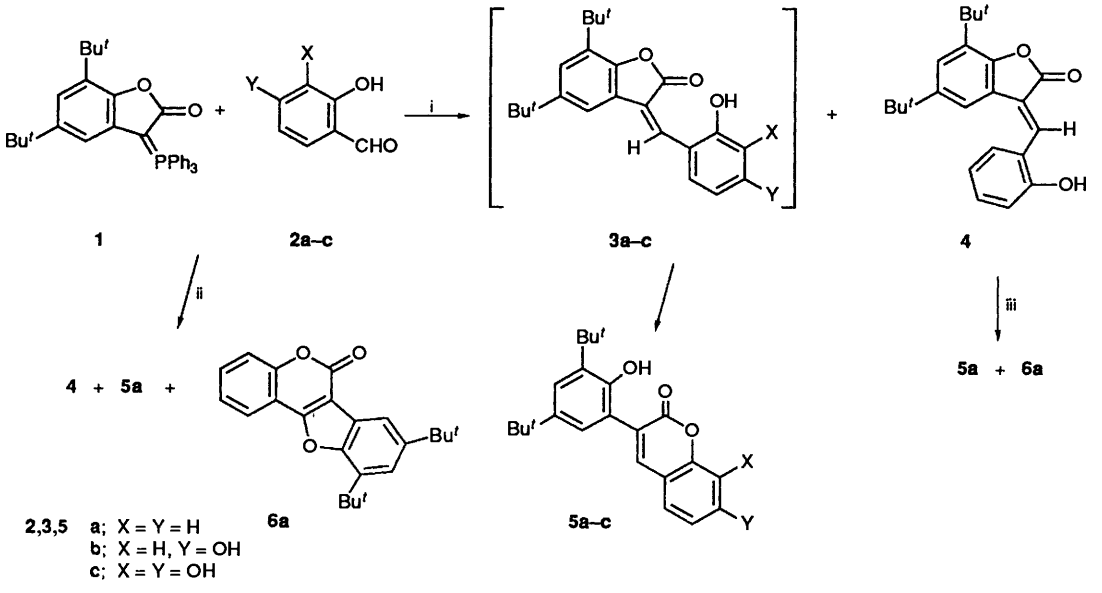
The above mentioned 3-(2-hydroxyaryl)coumarins show phytoalexin activity[4] and they are prepared by condensation of salicylaldehydes with phenylacetic acid derivatives,[3d,5–7] or coumaran-2(3*H*)-one in the presence of base.[8] However, these reactions are not very convenient owing to the difficulty in obtaining the substituted phenylacetic acid esters. A further approach to the synthesis of these compounds is a multi-step procedure involving a reaction of *o*-lithiated anisole with diethyl oxalate, Wittig reaction of the resulting adduct with 2-methoxybenzylidene(triphenyl)phosphorane giving ethyl α-aryl-cinnamates and, finally, cyclization of the latter with pyridine hydrochloride.[3c]

Recently[9] we studied reactions of nitrile oxides with ethyl *o*-hydroxycinnamate, obtained by Wittig reaction of *o*-hydroxybenzaldehyde **2a** with ethoxycarbonylmethylene(triphenyl)-phosphorane, and cyclization of the resulting 1,3-dipolar cycloaddition products to 3-aryl-4*H*-[1]benzopyrano[3,4-*d*]isoxazol-4-ones. Also, very recently, we prepared the ylides **1** and **11** by a versatile method employing ethoxycarbonylmethylene-(triphenyl)phosphorane and 3,5-di-*tert*-butyl-*o*-benzoquinone or phenanthrene-9,10-quinone respectively, in the presence of an excess of triphenylphosphine.[10]

In continuation of our interest in coumarin chemistry we now report our results on the reactions of the ylide **1** with some salicylaldehydes and of the ylides **11** with **2a**, performed at different temperatures. Furthermore, some transformations of the synthesized adducts **4** and **5b** are reported.

Results and Discussion

Reactions of the ylide **1** with salicylaldehydes **2a–c** and the resulting products are depicted in Scheme 1. A mixture of the aldehyde **2a** and the ylide **1** in toluene was heated under reflux for 48 h and the reaction mixture was then subjected to column chromatography to give the benzopyranone **5a** (84%) and the benzofuranone **4** (14%). The IR spectrum of compound **5a** showed absorption at 1665 cm^{-1} (C=O) in the range for 3-arylcoumarin carbonyl (1660–1710 cm^{-1}),[1c,3c,3d] while the ^1H NMR spectrum showed a singlet at δ 7.87 characteristic of 4-H of coumarins.[3d] In the IR spectrum of compound **4** the absorption, at 1746 cm^{-1} is characteristic for γ-lactone carbonyl

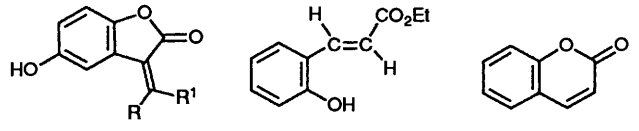


Scheme 1 *Reaction conditions:* i, toluene, reflux; ii, reflux; iii, xylene, reflux

stretching (1748–1765 cm^{-1}).[8,11] The chemical shift for the olefinic proton (δ 7.95) in the NMR spectrum of compound **4** is in good agreement with the suggested (*E*)-configuration, since this value is very close to the corresponding, earlier reported,[11] chemical shift for the (*E*)-compound **7** (δ 7.72), while the value for the olefinic proton of the (*Z*)-compound **8** is δ 6.72.

Wittig olefination of **2a** by **1** could account for the formation of products produced in the reaction studied. Compound **4** has the (*E*)-configuration, while the coumarin derivative **5a** is obtained by intramolecular cyclization of the (*Z*)-intermediate **3a** (Scheme 1). These are analogous with ethyl 2-hydroxycinnamate **9** and coumarin **10** reaction products of Wittig olefination of **2a** by ethoxycarbonylmethylene(triphenyl)phosphorane.[9] A similar cyclization has previously been reported[8] for 3-(2-hydroxyphenyl)coumarin by treatment of 3-(2-hydroxybenzylidene)coumaran-2(3*H*)-one at 80 °C by triethylamine or upon irradiation of the corresponding coumaranone.

In order to investigate the possibility of obtaining compound **5a** by cyclization of compound **4**, we refluxed a solution of the γ-lactone **4** in dry xylene for 6 days. Separation of the reaction



7 R = *p*-C_6H_4OH, R^1 = H
8 R = H, R^1 = *p*-C_6H_4OH

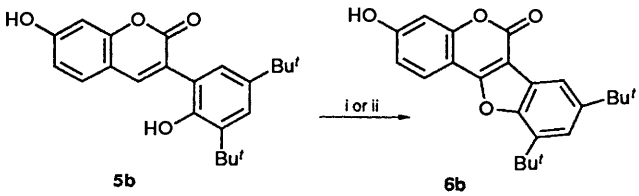
9 **10**

mixture by preparative TLC gave the coumarin derivative **5a** (17%), a new compound 2,4-di-*tert*-butyl-6*H*-benzofuro[3,2-*c*]-[1]benzopyran-6-one **6a** (63%) and unchanged lactone **4** (17%). The IR spectrum of compound **6a** showed absorption at 1745 cm^{-1}, the frequency range for carbonyl stretching in coumestans (1730–1740 cm^{-1}), and no hydroxy group absorption. No singlet signals in the range for aromatic protons appeared in ^1H NMR spectrum of this compound, while the mass spectrum and elemental analysis confirmed the suggested coumestan structure for **6a**. Obviously the coumarin derivative **5a** is produced by thermal cyclization of the γ-lactone **4** and then is possibly oxidized at high temperature to the coumestan derivative **6a** (Scheme 1).

Repetition of the reaction between the ylide **1** and the aldehyde **2a** at the boiling point of the latter (*ca.* 196 °C) for 30 h afforded, after separation by column chromatography, compound **5a** (39%), the coumestan derivative **6a** (33%) and the lactone **4** (26%).

Treatment of 2,4-dihydroxybenzaldehyde **2b** with the ylide **1** in refluxing toluene for 9 days and separation of the reaction mixture by column chromatography gave the benzopyranone **5b** (75%) along with unchanged aldehyde **2b** (19%) and the ylide **1** (20%); no product analogous to compound **4** was isolated. The structure of compound **5b** was confirmed by its analytical and spectral data.

Thermal cyclization of compound **5b** in refluxing xylene for 4 days afforded the benzopyranone **6b** (43%) (Scheme 2),



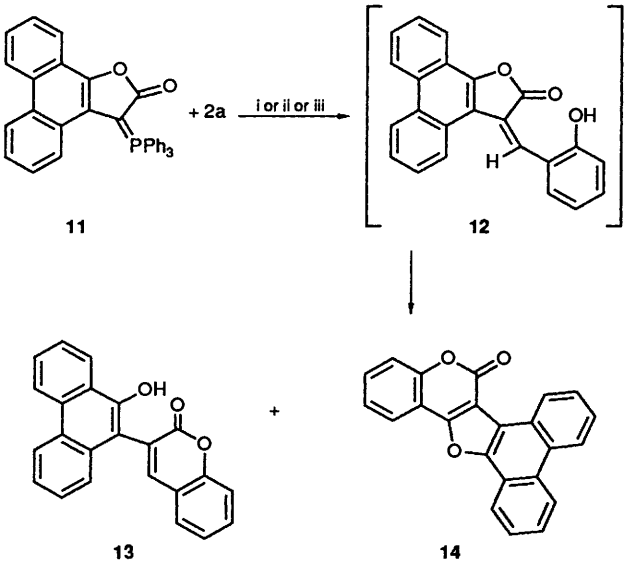
5b **6b**

Scheme 2 *Reaction conditions:* i, xylene, reflux; ii, DDQ, toluene, reflux

compound identical with the oxidation product (92%) of the coumarin **5b** by DDQ in toluene refluxed for 20 h; analytical and spectral data support the structural assignment **6b** for this product.

The reaction of 2,3,4-trihydroxybenzaldehyde **2c** with the ylide **1** in boiling toluene for 6 days gave, after separation of the reaction mixture by column chromatography, the benzopyranone **5c** (60%). Efforts to repeat the above reactions of the ylide **1** with the aldehydes **2b** or **2c** at 160–170 °C without solvent resulted in sublimation of these aldehydes.

Reaction of the aldehyde **2a** with the phenanthrofuranone **11** in refluxing toluene for 9 days gave a precipitate of the ylide **1** (78%), while the filtrate, separated by preparative TLC, gave the phenanthro[*b*]furo[3,2-*c*][1]benzopyranone **14** (3%) and the [1]benzopyranone **13** (13%) (Scheme 3). The structures of



11 **12** **13** **14**

Scheme 3 *Reaction conditions:* i, toluene, reflux; ii, reflux; iii, diglyme, reflux

compounds **13** and **14** were established on the basis of analytical and spectral results. The above reaction when carried out in boiling diglyme (*ca.* 160 °C) for 48 h gave increased yields of the coumestan **14** (13%) and coumarin **13** (73%) a result which suggested that with diglyme as solvent a one-step procedure for the preparation of coumestans and/or 3-(2-hydroxyaryl)coumarins was possible.

Repetition of the reaction between the aldehyde **2a** and the ylide **11** without solvent at the boiling point of **2a** for 48 h gave after crystallization of the reaction mixture and subsequent separation of the filtrate by preparative TLC coumestan **14** (60%) and the coumarin derivative **13** (11%).

In conclusion, the reactions of 3-triphenylphosphoranylidene[*b*]fused furan-2(3*H*)-ones in refluxing 2-hydroxybenzaldehyde **2a** provide an easy synthetic route for the preparation of coumestans in one step and in good yields. Also, the reactions of the above ylides with salicylaldehydes allow the preparation of 3-(2-hydroxyaryl)coumarins and/or the corresponding coumestans depending on the solvent, which is used for reflux.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 1310 spectrophotometer. ^1H NMR spectra were recorded with deuteriochloroform as solvent on a Bruker AW (80 MHz) spectrometer with $SiMe_4$ as internal standard. Coupling constants (*J*) are given in Hz. Mass spectra were determined on

a VG-250 spectrometer with ionization energy maintained at 70 eV.

Reactions of 5,7-*Di*-tert-*butyl*-3-*triphenylphosphoranylidene*-*benzofuran*-2(3H)-*one* **1** *with* o-*Hydroxybenzaldehyde* **2a**.—(*a*) To a stirred solution of the aldehyde **2a** (61 mg, 0.5 mmol) in dry toluene (5 cm^3) the ylide **1** (0.253 g, 0.5 mmol) was added at once. The reaction mixture was heated under reflux for 48 h after which it was cooled to room temperature and evaporated. The residue was chromatographed on silica gel [dichloromethane–hexane (2:1)] to give as the first fraction 3-(2-*hydroxy*-3,5-*di*-tert-*butylphenyl*)-2H-[1]*benzopyran*-2-*one* **5a** as pale yellow crystals (0.174 g, 84%), m.p. 187–189 °C (from dichloromethane–hexane) (Found: C, 79.1; H, 7.2. $C_{23}H_{26}O_3$ requires C, 78.8; H, 7.5%); ν_{max}(Nujol)/cm^{-1} 3200br, 1665, 1605, 1560 and 1235; δ_H($CDCl_3$) 1.32 (9 H, s), 1.46 (9 H, s), 7.07 (1 H, d, *J* 2.5), 7.16–7.71 (5 H, m), 7.87 (1 H, s) and 10.34 (1 H, br s, exchanged with D_2O); *m/z* 350 (M^+, 72%), 336 (31), 335 (100), 307 (4), 279 (53), 160 (11) and 57 (40). Further elution gave 5,7-*di*-tert-*butyl*-3-(2-*hydroxybenzylidene*)*benzo*[b]*furan*-2(3H)-*one* **4** as yellow crystals (24 mg, 14%), m.p. 197–199 °C (from dichloromethane) (Found: C, 79.0; H, 7.6. $C_{23}H_{26}O_3$ requires C, 78.8; H, 7.5%); ν_{max}(Nujol)/cm^{-1} 3435, 1746, 1620, 1595 and 1128; δ_H($CDCl_3$) 1.27 (9 H, s), 1.44 (9 H, s), 5.62 (1 H, br s, exchanged with D_2O), 6.75–7.12 (2 H, m), 7.28–7.76 (4 H, m) and 7.95 (1 H, s); *m/z* 350 (M^+, 52%), 336 (17), 335 (100), 279 (45) and 57 (76).

(*b*) A mixture of the aldehyde **2a** (44 mg, 0.36 mmol) and the ylide **1** (0.181 g, 0.36 mmol) was heated under reflux (*ca* 196 °C) for 30 h. After cooling, the reaction mixture was chromatographed on silica gel [dichloromethane–hexane (1:1)] to give three fractions. The first fraction gave compound **5a** (49 mg, 39%). The second fraction gave 2,4-*di*-tert-*butyl*-6H-*benzofuro*[3,2-c][1]*benzopyran*-6-one **6a** (41 mg, 33%), m.p. > 300 °C (from dichloromethane–hexane) (Found: C, 79.5; H, 7.1. $C_{23}H_{24}O_3$ requires C, 79.3; H, 6.95%); ν_{max}(Nujol)/cm^{-1} 1745, 1630, 1600, 1235 and 1085; δ_H($CDCl_3$) 1.42 (9 H, s), 1.58 (9 H, s), 7.38–7.61 (5 H, m) and 8.02 (1 H, d, *J* 2.5); *m/z* 348 (M^+, 16%), 334 (6), 333 (24), 277 (3) and 57 (100). The last fraction afforded compound **4** (32 mg, 26%).

Cyclization of Compound **4**.—The lactone **4** (35 mg, 0.1 mmol) dissolved in dry *o*-xylene (6 cm^3) when heated and the solution was refluxed for 6 days. After the solution had cooled, it was evaporated under reduced pressure. Preparative TLC of the residue on silica gel [dichloromethane–hexane (1:1)] afforded the coumarin **5a** (6 mg, 17%) the coumestan **6a** (22 mg, 63%) and unchanged lactone **4** (6 mg, 17%).

Reactions of the Ylide **1** *with* 2,4-*Dihydroxybenzaldehyde* **2b**.—(*a*) A stirred solution of the ylide **1** (0.253 g, 0.5 mmol) and the aldehyde **2b** (69 mg, 0.5 mmol) in boiling toluene (7 cm^3) was heated under reflux for 9 days and then evaporated under reduced pressure. Column chromatography of the residue on silica gel with ethyl acetate–hexane (3:4) as eluent gave (i) 3-(3,5-*di*-tert-*butyl*-2-*hydroxyphenyl*)-7-*hydroxy*-2H-[1]*benzopyran*-2-*one* **5b** (0.137 g, 75%), m.p. 257–259 °C (from dichloromethane–hexane) (Found: C, 75.2; H, 7.45. $C_{23}H_{26}O_4$ requires C, 75.45; H, 7.15%); ν_{max}(Nujol)/cm^{-1} 3534sh, 3268br, 1661, 1592, 1250 and 1225; δ_H($CDCl_3$) 1.32 (9 H, s), 1.45 (9 H, s), 6.8–7.0 (2 H, m), 7.03 (1 H, d, *J* 2.2), 7.2–7.5 (2 H, m) and 7.82 (1 H, s); *m/z* 366 (M^+, 4%), 349 (3), 311 (6), 267 (4), 252 (5), 207 (22) and 57 (100); (ii) unchanged aldehyde **2b** (13 mg, 19%); (iii) unchanged ylide **1** (51 mg, 20%) and (iv) triphenylphosphine oxide (0.108 g, 78%).

(*b*) A mixture of the ylide **1** (0.101 g, 0.2 mmol) and the aldehyde **2b** (28 mg, 0.2 mmol) was heated at *ca.* 160 °C. After 60 min a sublimated solid, which seemed to be the aldehyde **2b**, was obtained.

Cyclization of Compound **5b**.—(*a*) *Heating in boiling* o-*xylene*. Dissolution occurred when a stirred mixture of the coumarin **5b** (40 mg, 0.109 mmol) in dry *o*-xylene (4 cm^3) was heated and the solution was refluxed for 4 days. Cooling gave a tarry precipitate (12 mg). Concentration of the filtrate followed by preparative TLC on silica gel [ethyl acetate–hexane (1:2)] gave from the faster moving band 2,4-*di*-tert-*butyl*-9-*hydroxy*-6H-*benzofuro*[3,2-c][1]*benzopyran*-6-*one* **6b** (17 mg, 43%), m.p. 245–247 °C (from dichloromethane) (Found: C, 75.75; H, 6.4. $C_{23}H_{24}O_4$ requires C, 75.8; H, 6.65%); ν_{max}(CH_2Cl_2)/cm^{-1} 3570, 1730, 1625, 1595 and 1260; δ_H($CDCl_3$) 1.41 (9 H, s), 1.57 (9 H, s), 6.55 (1 H, br s, exchanged with D_2O), 6.87–7.06 (2 H, m), 7.39 (1 H, d, *J* 2.5), 7.92 (1 H, d, *J* 8.2) and 7.99 (1 H, d, *J* 2.5); *m/z* 364 (M^+, 93%), 350 (22), 349 (100), 321 (7), 293 (18), 184 (24) and 57 (52). The next band afforded unchanged coumarin **5b** (11 mg, 28%).

(*b*) *Oxidation of compound* **5b** *with DDQ*. To a stirred solution of compound **5b** (52 mg, 0.14 mmol) in boiling toluene (10 cm^3) was added DDQ (32 mg, 0.14 mmol). The mixture was refluxed for 20 h, filtered and evaporated and the residue chromatographed on silica gel, with ethyl acetate–hexane (1:2) as eluent to give the coumestan **6b** (47 mg, 92%).

Reactions of Ylide **1** *with* 2,3,4-*Trihydroxybenzaldehyde* **2c**.—(*a*) Dissolution occurred when a stirred mixture of the ylide **1** (0.253 g, 0.5 mmol) and the aldehyde **2c** (77 mg, 0.5 mmol) in toluene (20 cm^3) was heated and it was then refluxed for 6 days. The mixture was cooled, concentrated and subjected to column chromatography on silica gel [ethyl acetate–hexane (1:1)] to give 3-(3,5-*di*-tert-*butyl*-2-*hydroxyphenyl*)-7,8-*dihydroxy*-2H-[1]*benzopyran*-2-*one* **5c** (0.115 g, 60%), m.p. 259–261 °C (decomp.) (from dichloromethane–hexane) (Found: C, 72.4; H, 6.7. $C_{23}H_{26}O_5$ requires C, 72.2; H, 6.85%); ν_{max}(Nujol)/cm^{-1} 3540sh, 3320br, 1663, 1582, 1256, 1195 and 1170; δ_H($CDCl_3$) 1.32 (9 H, s), 1.44 (9 H, s), 6.93–7.09 (3 H, m), 7.39 (1 H, d, *J* 3) and 7.81 (1 H, s); *m/z* 382 (M^+, 15%), 367 (16), 339 (2), 311 (8), 267 (100), 239 (25) and 57 (25). Further elution afforded a mixture of unseparated aldehyde **2c**, ylide **1** and triphenylphosphine oxide.

(*b*) A mixture of the ylide **1** (0.182 g, 0.36 mmol) and the aldehyde **2c** (55 mg, 0.36 mmol) was heated at *ca.* 160 °C to give after 2 h a sublimate which seemed to be the aldehyde **2c**.

Reactions of 3-*Triphenylphosphoranylidenephenanthro*[b]-*furan*-2(3H)-*one* **11** *with* o-*Hydroxybenzaldehyde* **2a**.—(*a*) A stirred mixture of the ylide **11** (0.248 g, 0.5 mmol) and the aldehyde **2a** (61 mg, 0.5 mmol) in dry toluene (12 cm^3) was refluxed for 9 days. The mixture was cooled and the precipitated unchanged ylide **11** was filtered off (0.193 g, 78%); the filtrate was evaporated and the residue separated by preparative TLC [dichloromethane–hexane (1:1)] to give from the faster moving band 7H-*phenanthro*[b]*furo*[3,2-c][1]*benzopyran*-7-*one* **14** (5 mg, 3%), m.p. 275–277 °C (from chloroform–hexane) (Found: C, 81.8; H, 3.9. $C_{23}H_{12}O_3$ requires C, 82.1; H, 3.6%); ν_{max}(CH_2Cl_2)/cm^{-1} 1728, 1625 and 1260; δ_H($CDCl_3$) 7.42–7.88 (8 H, m), 8.02–8.22 (1 H, m), 8.33–8.41 (1 H, m) and 8.58–8.85 (2 H, m); *m/z* 336 (M^+, 100%), 308 (7), 280 (3), 279 (8), 252 (12), 250 (16), 224 (6) and 144 (14). The slower moving band afforded 3-(10-*hydroxy*-9-*phenanthryl*)-2H-[1]*benzopyran*-2-*one* **13** (22 mg, 13%), m.p. 232–234 °C (from dichloromethane–hexane) (Found: C, 81.6; H, 4.3. $C_{23}H_{14}O_3$ requires C, 81.65; H, 4.15); ν_{max}(Nujol)/cm^{-1} 3470br, 1695, 1600, 1585, 1250 and 1180; δ_H($CDCl_3$) 6.62 (1 H, br s), 7.11–7.82 (9 H, m), 7.95 (1 H, s) and 8.33–8.76 (3 H, m); *m/z* 338 (M^+, 100%), 321 (6), 310 (36), 293 (11), 282 (20), 281 (77), 253 (22) and 252 (45).

(b) Dissolution occurred when a stirred mixture of the ylide **11** (0.264 g, 0.53 mmol) and the aldehyde **2a** (65 mg, 0.53 mmol) in diglyme (10 cm^3) was heated and the solution was refluxed for 48 h. The cooled mixture evaporated and chromatographed on silica gel [dichloromethane–hexane (1:1)] to give the coumestan **14** (23 mg, 13%), the coumarin **13** (0.14 g, 73%) and unchanged ylide **11** (17 mg, 6%).

(c) A mixture of the ylide **11** (68 mg, 0.14 mmol) and the aldehyde **2a** (61 mg, 0.5 mmol) was heated under reflux (*ca* 196 °C) for 48 h. The cooled mixture was triturated with chloroform to give a precipitate, which upon dissolution in hot ethyl acetate afforded an insoluble tar (12 mg), while evaporation of the filtrate gave compound **14** (16 mg, 34%). Separation of the chloroform filtrate by preparative TLC [ethyl acetate–hexane (1:2)] afforded from the faster-moving band the coumestan **14** (12 mg, total yield 60%) and from the slower the coumarin derivative **13** (5 mg, 11%).

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