Reactions of *ortho*-Quinones with Ethoxycarbonylmethylene(triphenyl)-phosphorane. Trapping of the *ortho*-Quinone Methanide Intermediates

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The reactions of the *ortho*-quinones (**5a–d**) with the phosphorus ylide (**6**) afforded, besides the expected coumarin derivatives (**10a–d**), compounds (**9d**), (**11b** and **c**), (**13**), and (**14**). When the reactions between compounds (**5a–d**) and (**6**) were carried out in the presence of ethyl vinyl ether (**20**) the pyran derivatives (**21a**, **b**, and **d**) and (**22a**, **b**, and **d**) were obtained as main products, by a [4 + 2] trapping process of the *ortho*-quinone methanide intermediates (**7a**, **b**, and **d**) with the dienophile (**20**). Similarly, the reaction between compounds (**5a**) and (**6**) in the presence of α-methylstyrene afforded mainly the pyrans (**23 I** and **II**). Compounds (**16**), (**19**), and (**24**) were also prepared and studied.

In 1969 Shechter and co-workers[1] reported that the reaction between equimolar amounts of phenanthrene-9,10-quinone (**5a**) and ethoxycarbonylmethylene(triphenyl)phosphorane (**6**) afforded a yellow compound, m.p. 158 °C, for which they suggested the structure ethyl (9,10-dihydro-10-oxo-9-phenanthrylidene)acetate (**7a**) (Scheme 1). Soon afterwards the same reaction was reinvestigated by Bestmann and Lang[2] and they proposed the structure ethyl dibenzo[5,6:7,8]coumarin-4-carboxylate† (**10a**) for the yellow product, m.p. 159 °C. Similar coumarin derivatives were also produced from the phosphorane (**6**) or its methyl analogue (**17**) with diones (**5a**), 1,2-naphthoquinone (**5b**), and 4-anilino-1,2-naphthoquinone. According to the reaction mechanism proposed by the authors, Wittig mono-olefination of the *ortho*-quinone used gives initially the corresponding *ortho*-quinone methanide intermediate (**7**). Michael addition of a second ylide species to intermediate (**7**) affords the phenoxy anion intermediate (**8**). Intramolecular Hofmann elimination of triphenylphosphine from zwitterion (**8**) gives the non-isolated (*o*-hydroxyaryl)fumarates (**9**), which by further lactonization result in the coumarin derivatives (**10**) (Scheme 1). A similar mono-olefination of *ortho*-quinones, followed by an inter- or intra-molecular Michael addition, was also found to proceed in reactions of *ortho*-quinones with some other mono-[1,2] as well as 1,3-, 1,4-, 1,5-, and 1,6-bis-ylides.[3]

Several data are available in the literature on the reactivity of *ortho*-quinone methanides, prepared as intermediates through elimination processes from suitable 2-hydroxybenzyl derivatives,[4] by oxidation of *ortho*-alkylphenols,[5] by treatment of aryloxymagnesium bromides with aldehydes,[6] and by thermal dissociation of their spiro dimers.[7] The *ortho*-quinone methanides usually add nucleophiles to the methanide carbon[8] and/or react with dienophiles in Diels–Alder reactions,[9] although several competing processes, leading to different products, can occur, depending on the particular reagents and reaction conditions employed.[10]

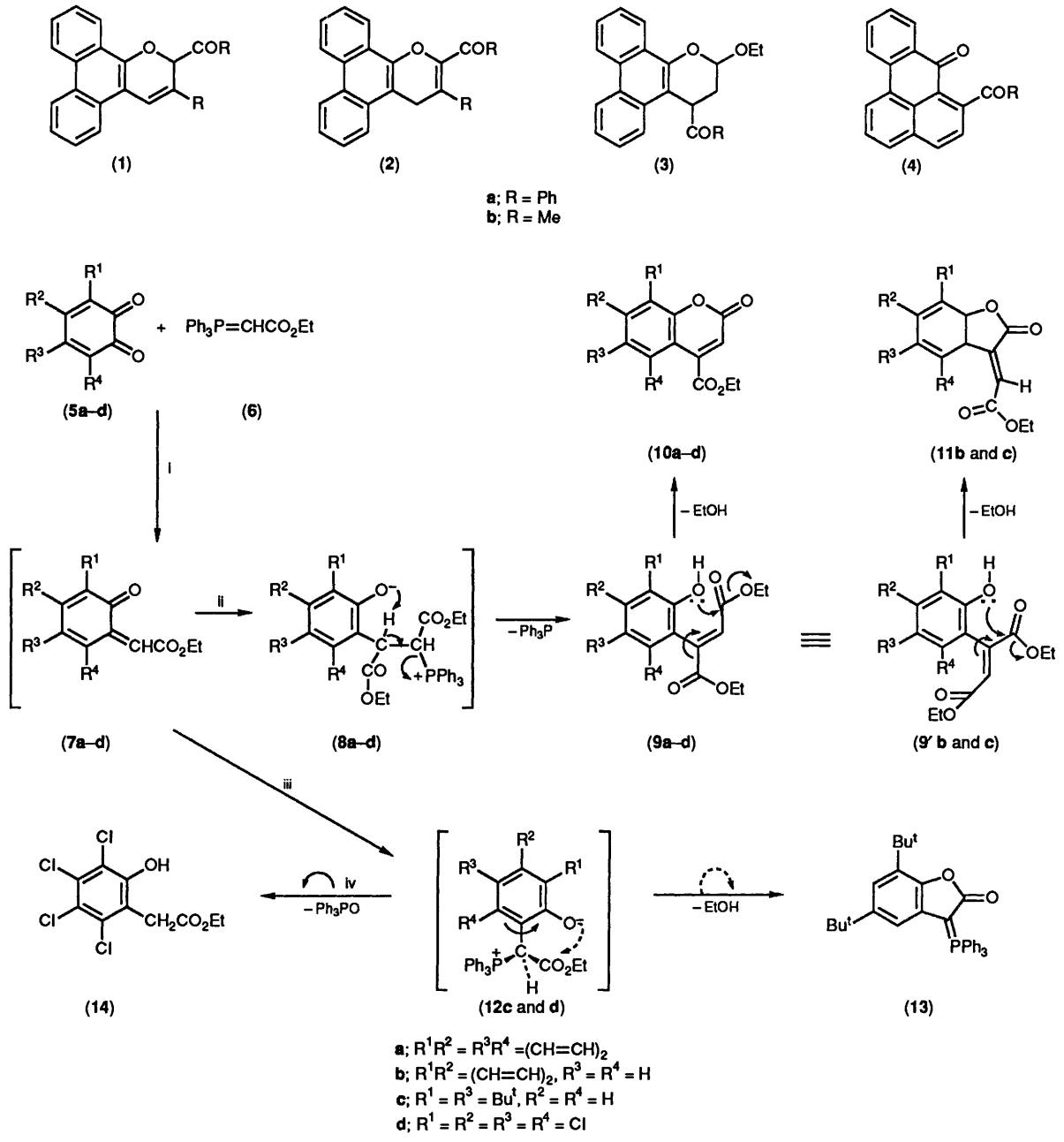
Very recently we reported[11] that the *ortho*-quinone methanide intermediates initially formed from the reactions of quinone (**5a**) with benzoyl- and acetyl-methylene(triphenyl)-phosphoranes react further with a second ylide molecule, mainly at their exocyclic carbonyl group, to give finally compounds (**1**) and/or (**2**), while in the presence of ethyl vinyl ether they are trapped by the dienophile to give the Diels–Alder cycloaddition products (**3**) (*cis* and *trans*) and (**4**) (by subsequent elimination of ethanol). The formation of compounds (**3**) predominates over the other competing reactions.

In connection with this study we now report our results on the reactions of ylide (**6**) with *ortho*-quinones (**5a–d**), carried out in dichloromethane and in ethyl vinyl ether solutions. The reactions between compounds (**5a**) and (**6**) in α-methylstyrene solution, as well as some transformations of the products obtained, are also reported.

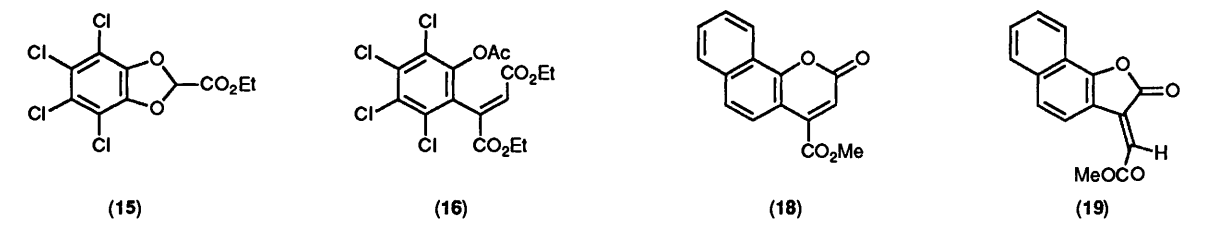
Results and Discussion

The reactions of ylide (**6**) with quinones (**5a–d**) were studied first in dichloromethane solutions and the products obtained are depicted in Scheme 1. A dichloromethane solution of quinone (**5a**) and the ylide (**6**) (2 mol equiv.) was heated under reflux for 4 h and the reaction mixture was then subjected to column chromatography to give a yellow solid (75%), m.p. 158–159 °C, identical in all respects with compound (**10a**) reported by Bestmann and Lang.[2] Repetition of the reaction between equimolar amounts of substrates (**5a**) and (**6**) afforded again only compound (**10**) (45%). Compound (**10a**) also appeared to be the sole product, detectable by TLC, when the reaction was performed with excess (up to 10 mol equiv.) of quinone (**5a**), and even at room temperature. These results show that the non-isolated intermediate (**7a**) is much more reactive than the starting quinone towards the ylide (**6**), and is finally converted into compound (**10a**). The reaction of quinone (**5b**) with the phosphorane (**6**) gave, besides compound (**10b**) (50%), reported previously,[2] (*E*)-3-ethoxycarbonylmethylenenaphtho[1,2-*b*]-furan-2(3*H*)-one (**11b**) (7%). The reaction of 3,5-di-t-butyl-1,2-benzoquinone (**5c**) with ylide (**6**) gave ethyl 6,8-di-t-butyl-2-oxo-2*H*-chromene-4-carboxylate (**10c**) (38%), (*E*)-5,7-di-t-butyl-3-ethoxycarbonylmethylenebenzofuran-2(3*H*)-one (**11c**) (28%), and 5,7-di-t-butyl-3-triphenylphosphoranylidenebenzofuran-2(3*H*)-one (**13**)[12] (3%). When the same reaction was carried out at room temperature, compounds (**10c**) (24%), (**11c**) (38%), and (**13**) (2%) were again obtained. Treatment of tetrachloro-1,2-benzoquinone (**5d**) with ylide (**6**) in refluxing dichloromethane solution afforded diethyl (2,3,4,5-tetrachloro-6-hydroxyphenyl)-fumarate (**9d**) (33%) as the major product, along with ethyl 5,6,7,8-tetrachloro-2-oxo-2*H*-chromen-4-carboxylate (**10d**) (2%) and the unexpected ethyl (2,3,4,5-tetrachloro-6-hydroxy-

† Ethyl 2-oxo-2*H*-dibenzo[*f*,*h*]chromene-4-carboxylate.

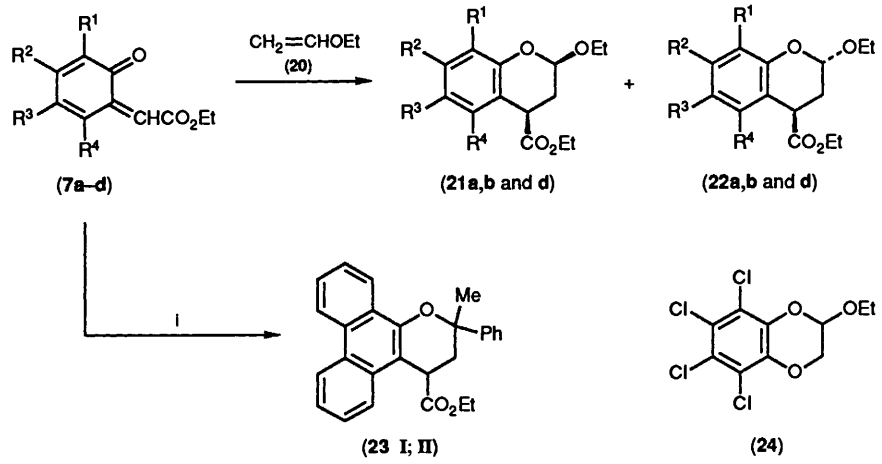


Scheme 1. *Reagents:* i, (Wittig); ii, (6) (Michael); iii, PPh_3; iv, water.



phenyl)acetate (**14**) (8%). When the same reaction was carried out at room temperature compounds (**9d**) (22%), (**10d**) (11%), and (**14**) (11%) were again obtained. Although tetrahalogeno-1,2-benzoquinones, previously used in reactions with phosphorus ylides, gave, instead of Wittig products, 1,3-benzodioxole derivatives,[2,3b,13] the expected dioxole (**15**) was not isolated from the reaction mixture. Treatment of compound (**9d**) with acetic anhydride gave the acetoxy derivative (**16**) (79%). Finally we studied the reaction of quinone (**5b**) with ylide $Ph_3P{=}CHCO_2Me$ (**17**) in refluxing dichloromethane solution. Separation of the reaction mixture by column chromatography gave, besides the coumarin (**18**)[2] (60%), (*E*)-3- methoxycarbonylmethylenenaphtho[1,2-*b*]furan-2(3*H*)-one (**19**) (5%).

Obviously compounds (**10a–d**) and (**18**) are produced *via* the



a; $R^1R^2 = R^3R^4 = (CH{=}CH)_2$
b; $R^1R^2 = (CH{=}CH)_2$, $R^3 = R^4 = H$
c; $R^1R^3 = Bu^t$, $R^2 = R^4 = H$
d; $R^1 = R^2 = R^3 = R^4 = Cl$

Scheme 2. *Reagents:* i, CH_2=CMePh [only for (**7a**].

corresponding intermediates (**7**)–(**9**), suggested by Bestmann and Lang.[2] The 3-alkoxycarbonylmethylene-γ-lactones (**11b** and **c**) and (**19**), obtained only from quinones (**5b** and **c**), are also produced through a further γ-lactonization of the appropriate dialkyl (*o*-hydroxyaryl)butenedioates, generated from intermediates (**8**). It seems logical to consider that they have the (*E*)-configuration, since they are formed from the same fumarate intermediates (**9**) and also since they lead to coumarins (**10b** and **c**) and (**18**), respectively, as suggested in Scheme 1. A conformation similar to (**9**'**b** and **c**) is not favoured over that for the intermediates (**9a** and **d**), due to the bulky R^4-substituent, and only coumarins (**10a** and **d**) are obtained from quinones (**5a** and **d**). Consistent with this proposal, a solution of the isolated compound (**9d**), when heated under reflux in toluene for 6 days, gave only compound (**10d**) (89%). Although the recorded ^1H NMR spectra of the isolated γ-lactones, and especially the chemical shifts of their 4-H atoms, are in good agreement with the suggested structures (**11b** and **c**) and (**19**), more evidence is necessary to confirm with certainty their (*E*)-configuration, since γ-lactonization of the other possible alkyl (*o*-hydroxyaryl)-maleate precursors, generated from zwitterions (**8**), can lead to formation of the corresponding (*Z*)-isomers. It is of interest that there are only a few methods in the literature for the synthesis of 3-alkylidenebenzofuran-2(3*H*)-ones, such as the Wittig reaction of benzofuran-2(3*H*)-one with phosphorus ylides,[14] the thermal rearrangement of γ-aryloxycrotonates,[15] and very recently the oxidative ring opening of substituted oxepino[2,3-*b*]benzofurans.[16]

The formation of compounds (**13**) and (**14**) from quinones (**5c**) and (**5d**) respectively can be explained by assuming a Michael addition of triphenylphosphine, generated *in situ* from the intermediates (**8**), to the quinone methanide intermediates (**7c** and **d**). The further transformation of betaines (**12c** and **d**) depends probably upon their predominant conformation, affected by the nature of their R^4-substituent (H and Cl respectively). The direct lactonization of the favourable conformer (**12c**), suggested in Scheme 1, affords the stable ylide (**13**). On the other hand prior attack by water at the phosphonium group of the intermediate (**12d**) occurs mainly in the more favoured conformation bearing its aryloxy and carbethoxy groups in a fairly *anti* spatial arrangement, followed by triphenylphosphine oxide elimination to account for the formation of product (**14**). A study aimed at attaining a high-yield preparation of products similar to (**13**) and (**14**) from reactions between *ortho*-quinones and ylide (**6**) is in progress.

Furthermore we studied the reactions of ylide (**6**) with quinones (**5a–d**) in the presence of ethyl vinyl ether (**20**), used in excess as solvent, and the products obtained are depicted in Scheme 2. A mixture of equimolar amounts of compounds (**5a**) and (**6**) in excess of the ether (**20**) was heated under reflux for 3 h and the reaction mixture was then separated by column chromatography to give ethyl *cis*-(**21a**) (36%) and *trans*-2-ethoxy-3,4-dihydro-2*H*-phenanthro[9,10-*b*]pyran-4-carboxylate (**22a**) (8%), along with compound (**10a**) (24%). When the reaction was carried out by portionwise addition of compound (**6**) to a solution of quinone (**5a**) in the ether (**20**), heated under reflux, during 3 h and the reaction mixture was refluxed for a further 1 h, compounds (**21a**) (57%), (**22a**) (17%), and (**10a**) (10%) were obtained. The latter procedure was then applied to the reactions of ylide (**6**) with quinones (**5b–d**). Reaction of quinone (**5b**) afforded compounds (**21b**) (7%), (**22b**) (54%), and (**10b**) (15%). No [4 + 2] cycloaddition product was obtained from the similar treatment of quinone (**5c**) with ylide (**6**), probably due to the expected strong steric hindrance of the bulky R^1-substituent ($R^1 = Bu^t$). Only compounds (**10c**) (25%) and (**11c**) (17%) were isolated from the corresponding reaction mixture. Finally the reaction of quinone (**5d**) with ylide (**6**) in the presence of dienophile (**20**) afforded compounds (**21d**) (17%), (**22d**) (6%), (**9d**) (17%), (**10d**) (2%), and (**14**) (3%), as well as 5,6,7,8-tetrachloro-2-ethoxy-2,3-dihydro-1,4-benzodioxine (**24**) (5%), through a [4 + 2] cycloaddition of **20** to the 1,4-heterodiene system of the starting quinone (**5d**).

The suggested *cis*- and *trans*-configurations for compounds (**21a**, **b**, and **d**) and (**22a**, **b**, and **d**) respectively, although not established with certainty, are supported by the recorded ^1H NMR chemical shifts and coupling constants of their pyran protons and especially those of 2-H, as in the case of compounds (**3**).[11] The determined coupling constants of 2-H in the recorded ^1H NMR spectra are 2.8 and 6.0 Hz for compound (**21a**), 2.4 and 2.4 Hz for (**22a**), 2.7 and 4.9 Hz for (**21b**), 2.3 and 3.4 Hz for (**22b**), 2.8 and 5.9 Hz for (**21d**), and 2.2 and 2.2 Hz for (**22d**). In all cases the larger of the two coupling constants observed for the isomer suggested as *cis* is greater than those of the corresponding isomer, suggested as *trans*, in agreement with the literature.[17]

In order to investigate further whether the above described

trapping [4 + 2] cycloadditions are applicable to dienophiles other than the ether (**20**), we first treated quinone (**5a**) with ylide (**6**) in α-methylstyrene solution, under the conditions described for compound (**20**). Separation of the reaction mixture by column chromatography gave the expected cycloproducts (**23I**) (36%) and (**23II**) (13%), along with compound (**10a**) (28%). More evidence is necessary for the configurational assignment of the first two products.

In conclusion, the reactions of *ortho*-quinones with alkoxycarbonylmethylene(triphenyl)phosphoranes provide an easy route for the preparation not only of the previously reported coumarins (**10**) but also of γ-lactones (**11**), as well as for the convenient preparation of the pyran derivatives (**21**) and (**22**), depending on the *ortho*-quinone and the additional reagents used. Steric effects of the R^1 and especially of the R^4 substituents in intermediates (**7**), (**9**), and (**12**) interfere with their further transformations, described in Schemes 1 and 2.

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 Model AW 80 (80 MHz) or on a Varian VXR-300 (300 MHz) spectrometer, with $SiMe_4$ as internal standard. ^{13}C NMR spectra were obtained at 75 MHz on a Varian VXR-300 spectrometer, for deuteriochloroform solution, with $SiMe_4$ as internal reference. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6L spectrometer (with ionization energy maintained at 70 eV).

General Procedure for the Reaction of Ylide (**6**) *with Quinones* (**5a–d**) *in Dichloromethane*.—A solution of the appropriate quinone (**5a–d**) (1 mmol) and ylide (**6**) (0.636 g, 2 mmol) in dry dichloromethane (10 ml) was heated at reflux until all the quinone was consumed (30 min–20 h; the reactions were monitored by TLC). After removal of the solvent the residue was chromatographed on silica gel with hexane–dichloromethane (1:1) as eluant. According to this general procedure the following products were prepared:

Ethyl 2-oxo-2*H*-dibenzo[*f,h*]chromene-4-carboxylate (**10a**) was obtained from quinone (**5a**) as yellow crystals (0.25 g, 75%), m.p. 158–159 °C (from EtOH) (lit.,[2] 158 °C); ν_{max}(KBr) 3 090, 2 940, and 1 725 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.52 (3 H, t, *J* 7 Hz), 4.67 (2 H, d, *J* 7 Hz), 6.70 (1 H, s), 7.43–7.93 (5 H, m), and 8.25–8.67 (3 H, m); *m/z* 319 (22%), 318 (M^+, 100), 290 (35), 262 (17), 246 (11), 245 (22), 218 (16), and 189 (41). The reaction between equimolar amounts of compounds (**5a**) and (**6**) under the same conditions also gave compound (**10a**) (45%).

(E)-*Ethyl* (2,3-*dihydro*-2-*oxonaphtho*[1,2-b]*furan*-3-*ylidene*)*acetate* (**11b**) was obtained from quinone (**5b**) as yellow crystals (19 mg, 7%), m.p. 187–189 °C (from $CHCl_3$–hexane) (Found: C, 71.9; H, 4.7. $C_{16}H_{12}O_4$ requires C, 71.63; H, 4.51%); ν_{max}(Nujol) 1 790, 1 710, and 1 625 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.38 (3 H, t, *J* 7.2 Hz), 4.36 (2 H, q, *J* 7.2 Hz), 6.90 (1 H, s), 7.43–7.76 (3 H, m), 7.82–7.99 (1 H, m), 8.04–8.21 (1 H, m), and 8.56 (1 H, d, *J* 8.8 Hz, 4-H); *m/z* 269 (19%), 268 (M^+, 100), 240 (56), 223 (21), 212 (44), 196 (21), 195 (44), 190 (17), 168 (51), and 139 (79).

Ethyl 2-oxo-2*H*-benzo[*h*]chromene-4-carboxylate (**10b**) was also obtained from quinone (**5b**) [eluted after (**11b**)] as yellow crystals (0.135 g, 50%), m.p. 147–148 °C (from $CHCl_3$–hexane) (lit.,[2] 148 °C); ν_{max}(Nujol) 3 095, 1 725, and 1 630 cm^{-1}; δ_H(80 MHz; $CDCl_3$), 1.44 (3 H, t, *J* 8 Hz), 4.49 (2 H, q, *J* 8 Hz), 6.97 (1 H, s), 7.50–8.05 (4 H, m), 8.19 (1 H, d, *J* 8.8 Hz), and 8.46–8.67 (1 H, m).

(E)-*Ethyl* (5,7-*di-t-butyl*-2,3-*dihydro*-2-*oxobenzo*[b]*furan*-3-*ylidene*)*acetate* (**11c**) was obtained from quinone (**5c**) as yellow crystals (92 mg, 28%), m.p. 119–121 °C (from hexane) (Found: C, 72.9; H, 7.6. $C_{20}H_{26}O_4$ requires C, 72.70; H, 7.93%); ν_{max}(Nujol) 1 800, 1 722, 1 652, and 1 602 cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.36 (9 H, s), 1.38 (3 H, t, *J* 7.2 Hz), 1.41 (9 H, s), 4.35 (2 H, q, *J* 7.2 Hz), 6.88 (1 H, s, vinylic H), 7.47 (1 H, d, *J* 2 Hz, 6-H), and 8.56 (1 H, d, *J* 2 Hz, 4-H); δ_C(75 MHz; $CDCl_3$) 14.20, 29.54, 31.50, 34.37, 34.98, 61.38, 120.51, 123.14, 124.35, 128.37, 132.01, 133.16, 133.91, 147.17, 164.99, and 168.26; *m/z* 331 (7%), 330 (M^+, 32), 316 (23), 315 (100), 287 (9), 285 (9), 271 (3), 259 (2), 257 (3), 243 (4), 231 (3), 217 (5), 199 (9), and 150 (3).

Ethyl 6,8-*di-t-butyl*-2-*oxo*-2H-*chromene*-4-*carboxylate* (**10c**) was also obtained from quinone (**5c**) [eluted after (**11c**)] as yellow crystals (0.126 g, 38%), m.p. 113–115 °C (from hexane) (Found: C, 72.6; H, 7.7. $C_{20}H_{26}O_4$ requires C, 72.70; H, 7.93%); ν_{max}(Nujol) 3 095, 1 728, and 1 580 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.36 (9 H, s), 1.39 (3 H, t, *J* 7 Hz), 1.51 (9 H, s), 4.46 (2 H, q, *J* 7 Hz), 6.83 (1 H, s), 7.64 (1 H, d, *J* 2 Hz), and 8.00 (1 H, d, *J* 2 Hz); *m/z* 331 (11%), 330 (M^+, 53), 317 (5), 316 (37), 315 (100), 287 (7), 285 (5), 271 (4), 259 (4), 231 (8), 217 (6), 199 (6), and 150 (4).

5,7-Di-t-butyl-3-triphenylphosphoranylidenebenzofuran-2(3*H*)-one (**13**) was further obtained from quinone (**5c**) [eluted after (**10c**)] (15 mg, 3%), m.p. 247–249 °C (from CH_2Cl_2) (lit.,[12] 249 °C).

The same amounts of compounds (**5c**) and (**6**) as quoted above gave, on reaction for 3 h at room temperature, compounds (**11c**) (38%), (**10c**) (24%), and (**13**) (2%).

Ethyl 5,6,7,8-*tetrachloro*-2-*oxo*-2H-*chromene*-4-*carboxylate* (**10d**) was obtained from quinone (**5d**) (7 mg, 2%), m.p. 155–157 °C (from CH_2Cl_2) (Found: C, 40.5; H, 1.6. $C_{12}H_6Cl_4O_4$ requires C, 40.48; H, 1.70%); ν_{max}(Nujol) 1 753, 1 730, and 1 600 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.40 (3 H, t, *J* 8 Hz), 4.44 (2 H, q, *J* 8 Hz), and 6.55 (1 H, s); *m/z* 360 (M^+, 6%), 358 (M^+, 21), 356 (M^+, 48), 354 (M^+, 43), 330 (3), 328 (6), 326 (5), 295 (11), 293 (41), 291 (41), 287 (11), 285 (52), 283 (100), 281 (81), 258 (17), 256 (43), 254 (27), 229 (36), 227 (67), and 225 (52).

Ethyl (2,3,4,5-*tetrachloro*-6-*hydroxyphenyl*)*acetate* (**14**) was also obtained from quinone (**5d**) [eluted after (**10d**)] (24 mg, 8%), m.p. 129–131 °C (from CH_2Cl_2–hexane) (Found: C, 37.5; H, 2.3. $C_{10}H_8Cl_4O_3$ requires C, 37.77; H, 2.54%); ν_{max}(Nujol) 3 280 and 1 714 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 8 Hz), 3.91 (2 H, s), 4.19 (2 H, q, *J* 8 Hz), and 6.33 (1 H, br s, removed by D_2O); *m/z* 322 (M^+, 1%), 320 (M^+, 3), 318 (M^+, 6), 316 (M^+, 5), 276 (3), 274 (12), 272 (27), 270 (20), 249 (7), 248 (10), 247 (32), 246 (34), 245 (69), 244 (62), 243 (52), 242 (47), 220 (3), 218 (16), 216 (30), 214 (22), and 109 (100).

Diethyl (2,3,4,5-*tetrachloro*-6-*hydroxyphenyl*)*fumarate* (**9d**) was also obtained from quinone (**5d**) [eluted after (**14**)] (0.131 g, 33%), m.p. 76–78 °C (from ethyl acetate–hexane) (Found: C, 41.6; H, 2.85. $C_{14}H_{12}Cl_4O_5$ requires C, 41.82; H, 3.01%); ν_{max}(Nujol) 3 350, 1 730, 1 720, and 1 640 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.14 (3 H, t, *J* 7 Hz), 1.26 (3 H, t, *J* 7 Hz), 4.10 (2 H, q, *J* 7 Hz), 4.27 (2 H, q, *J* 7 Hz), 5.90 (1 H, br s, removed by D_2O), and 7.18 (1 H, s); *m/z* 406 (M^+, 2%), 404 (M^+, 10), 402 (M^+, 15), 400 (M^+, 13), 369 (19), 367 (50), 365 (51), 362 (10), 360 (14), 358 (41), 356 (71), 354 (58), 339 (22), 337 (23), 310 (18), 308 (19), 292 (38), 290 (38), 284 (54), 282 (100), and 280 (79).

When the ylide (**6**) was added portionwise during 15 min to a solution of quinone (**5d**) at room temperature compounds (**10d**) (11%), (**14**) (11%), and (**9d**) (22%) were obtained.

Conversion of Fumarate (**9d**) *into the Coumarin* (**10d**).—A solution of compound (**9d**) (75 mg, 0.19 mmol) in dichloromethane (4 ml) was heated at reflux for 24 h. After evaporation of the solvent the starting compound was recovered. Dry toluene (4 ml) was then added to the residue and the mixture was refluxed for 6 days. Evaporation of the solvent and trituration of the residue with hexane afforded compound (**10d**) (59 mg, 89%).

Conversion of Fumarate (**9d**) *into Diethyl* (2-*Acetoxy*-3,4,5,6-*tetrachlorophenyl*)*fumarate* (**16**).—A mixture of compound (**9d**) (40 mg, 0.1 mmol), acetic anhydride (0.3 ml), and conc. sulphuric acid (2 drops) was stirred at room temperature for 6 h. The reaction mixture was poured into water (5 ml) and extracted with dichloromethane (3 × 3 ml). The extract was washed with water (2 × 2 ml), dried (Na_2SO_4), and concentrated to give *compound* (**16**) (35 mg, 79%), m.p. 61–63 °C (from hexane) (Found: C, 43.5; H, 2.9. $C_{16}H_{14}Cl_4O_6$ requires C, 43.27; H, 3.18%); ν_{max}(Nujol) 1 790, 1 735, 1 725, and 1 655 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.10 (3 H, t, *J* 7 Hz), 1.23 (3 H, t, *J* 7 Hz), 2.21 (3 H, s), 4.07 (2 H, q, *J* 7 Hz), 4.24 (2 H, q, *J* 7 Hz), and 7.14 (1 H, s); *m/z* 448 (M^+, 0.3%), 446 (M^+, 1), 444 (M^+, 1.6), 442 (M^+, 1.5), 411 (4), 409 (12), 407 (13), 404 (2), 402 (3), 400 (2), 369 (21), 367 (60), 365 (67), 285 (48), 283 (100), 281 (85), 256 (62), and 254 (48).

Reaction of Quinone (**5b**) *with Methoxycarbonylmethylene*(*triphenyl*)*phosphorane* (**17**).—*Preparation of compounds* (**18**) *and* (**19**). The reaction between quinone (**5b**) (1.58 g, 10 mmol) and ylide (**17**) (6.68 g, 20 mmol) in dry dichloromethane (100 ml) for 24 h was carried out and the reaction mixture was worked up according to the above described procedure for ylide (**6**). (E)-*Methyl* (2,3-*dihydro*-2-*oxonaphtho*[1,2-b]*furan*-2-*ylidene*)*acetate* (**19**) was eluted first (0.130 g, 5%), m.p. 170–171 °C (from $CHCl_3$–hexane) (Found: C, 70.6; H, 3.85. $C_{15}H_{10}O_4$ requires C, 70.86; H, 3.96%); ν_{max}(Nujol) 1 795, 1 720, and 1 620 cm^{-1}; δ_H(300 MHz; $CDCl_3$) 3.92 (3 H, s), 6.91 (1 H, s), 7.56–7.66 (3 H, m), 7.87 (1 H, dd, *J* 1.5 and 7.4 Hz), 8.09 (1 H, dd, *J* 1.2 and 8.05 Hz), and 8.54 (1 H, d, *J* 8.8 Hz, 4-H); δ_C(75 MHz; $CDCl_3$) 52.38, 115.74, 119.26, 122.29, 123.34, 123.75, 124.09, 127.10, 128.30, 129.28, 134.28, 136.41, 153.99, 165.45, and 168.03; *m/z* 255 (19%), 254 (M^+, 100), 226 (98), 195 (67), and 139 (78).

Methyl 2-oxo-2*H*-benzo[*h*]chromene-4-carboxylate (**18**) was eluted next (1.61 g, 60%), m.p. 167–168 °C (from $CHCl_3$–hexane) (lit.,[2] 167 °C); δ_H(80 MHz; $CDCl_3$), 4.02 (3 H, s), 6.94 (1 H, s), 7.43–7.97 (4 H, m,), 8.11 (1 H, d, *J* 8.8 Hz), and 8.28–8.63 (1 H, m); *m/z* 225 (17%), 254 (M^+, 100), 226 (41), 195 (44), 167 (10), 139 (29), and 127 (2).

General Procedure for the Reaction of the Ylide (**6**) *with Quinones* (**5a–d**) *in Ethyl Vinyl Ether* (**20**).—(*a*) To a stirred suspension of the appropriate quinone (**5a** or **b**) (1 mmol) in ethyl vinyl ether (**20**) (5 ml), heated at reflux, was added the ylide (**6**) (0.348 g, 1 mmol) portionwise over 3 h and the mixture was refluxed for a further 1 h.

(*b*) To a stirred solution of the appropriate quinone (**5c** or **d**) (1 mmol) in dichloromethane (2 ml) was added dropwise a solution of ylide (**6**) (1 mmol) and dienophile (**20**) (0.095 ml, 1 mmol) in dichloromethane (2 ml) during 45 min, and the mixture was then stirred for a further 24 h. In both methods (*a*) and (*b*), after evaporation of the solvent the residue was subjected to column chromatography on silica gel with hexane–dichloromethane (1:1) as eluant. Besides the following (described above) products (**10a**) (10%) obtained from quinone (**5a**), (**10b**) (15%) obtained from quinone (**5b**), (**10c**) (25%) and (**11c**) (17%) obtained from quinone (**5c**), and (**9d**) (17%), (**10d**) (2%), and (**14**) (3%) obtained from quinone (**5d**), the following [4 + 2] cycloproducts were also prepared according to this procedure:

cis-*Ethyl* 2-*ethoxy*-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran*-4-*carboxylate* (**21a**) was obtained from quinone (**5a**) (0.2 g, 57%), m.p. 110–111 °C (from aq. EtOH) (Found: C, 75.4; H, 6.5. $C_{22}H_{22}O_4$ requires C, 75.41; H, 6.33%); ν_{max} 1 730, 1 620, and 1 595 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.15 (3 H, t, *J* 7 Hz), 1.26 (3 H, t, *J* 7 Hz), 2.35–2.47 (2 H, m), 3.20–4.45 (5 H, m), 5.60 (1 H, dd, *J* 2.8 and 6.0 Hz, 2-H), 7.30–7.92 (5 H, m), and 8.26–8.65 (3 H, m); *m/z* 351 (8%), 350 (M^+, 31), 304 (18), 277 (26), 275 (17), 247 (13), 231 (100), 219 (26), 202 (50), 191 (39), 189 (52), 178 (25), 176 (21), and 165 (47).

trans-*Ethyl* 2-*ethoxy*-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran*-4-*carboxylate* (**22a**) was also obtained from quinone (**5a**) [eluted after (**21a**) and before (**10a**)] (60 mg, 17%), m.p. 105–106 °C (from aq. EtOH) (Found: C, 75.5; H, 6.5%); ν_{max}(Nujol) 1 735, 1 620, and 1 600 cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.09 (3 H, t, *J* 7.2 Hz), 1.12 (3 H, t, *J* 7.2 Hz), 2.31 (1 H, ddd, *J* 2.4, 7.2, and 13.8 Hz, 3-H^a), 2.92 (1 H, ddd, *J* 2.4, 2.4, and 13.8 Hz, 3-H^b), 3.66 (1 H, dq, *J* 7.2 and 9.3 Hz), 3.90 (1 H, dq, *J* 7.2 and 9.3 Hz), 4.02 (1 H, dq, *J* 7.2 and 10.8 Hz), 4.17 (1 H, dd, *J* 2.4 and 7.2 Hz, 4-H), 4.20 (1 H, dq, *J* 7.2 and 10.8 Hz), 5.54 (1 H, dd, *J* 2.4 and 2.4 Hz, 2-H), 7.47–7.68 (5 H, m), 8.35 (1 H, dd, *J* 1.6 and 7.7 Hz, 12-H), 8.64 (2 H, 2dd, *J* 1.5 and 7.7, and 1.3, 7.4 Hz, 8- and 9-H); *m/z* 351 (26%), 350 (M^+, 100), 304 (28), 277 (43), 275 (27), 247 (11), 231 (96), 219 (13), 202 (17), 192 (14), 189 (13), 178 (10), 176 (8), and 165 (13).

When a mixture of compounds (**5a**) and (**6**) in ethyl vinyl ether (**20**) was heated under reflux for 3 h, compounds (**21a**) (36%), (**22a**) (8%), and (**10a**) (24%) were obtained.

cis-*Ethyl* 2-*ethoxy*-3,4-*dihydro*-2H-*naphtho*[1,2-b]*pyran*-4-*carboxylate* (**21b**) was obtained from quinone (**5b**) (22 mg, 7%) as an oil (Found: C, 71.9; C, 6.7. $C_{18}H_{20}O_4$ requires C, 71.98; H, 6.71%); ν_{max}(Nujol) 1 725, 1 620, and 1 595 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.19 (3 H, t, *J* 7 Hz), 1.29 (3 H, t, *J* 7 Hz), 2.18–2.51 (2 H, m, 3-H_2), 3.68 (1 H, dd, *J* 2.7 and 7.0 Hz, 4-H), 4.03 (2 H, q, *J* 7 Hz), 4.21 (2 H, q, *J* 7 Hz), 5.22 (1 H, dd, *J* 2.7 and 4.9 Hz, 2-H), 7.14–7.83 (5 H, m), and 8.19 (1 H, dd, *J* 3.8 and 5.4 Hz, 10-H); *m/z* 301 (17%), 300 (M^+, 83), 255 (11), 254 (33), 228 (19), 227 (100), 226 (22), 225 (20), and 181 (59).

trans-*Ethyl* 2-*ethoxy*-3,4-*dihydro*-2H-*naphtho*[1,2-b]*pyran*-4-*carboxylate* (**22b**) was also obtained from compound (**5b**) [eluted after (**21b**) and before (**10b**)] (0.161 g, 54%) as an oil (Found: C, 71.8; H, 6.6%); ν_{max}(Nujol) 1 725, 1 625, and 1 600 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7 Hz), 1.19 (3 H, t, *J* 7.2 Hz), 2.20 (1 H, ddd, *J* 2.3, 7.2, and 13.8 Hz, C-H^a), 2.77 (1 H, ddd, *J* 3.4, 3.4, and 13.8 Hz, 3-H^b), 3.71 (1 H, dd, *J* 3.4 and 7.2 Hz, 4-H), 3.80 (2 H, q, *J* 7.2 Hz), 4.13 (2 H, dq, *J* 1.8 and 7 Hz), 5.41 (1 H, dd, *J* 2.3 and 3.4 Hz, 2-H), 7.07–7.84 (5 H, m), and 8.19 (1 H, dd, *J* 3.2 and 6.8 Hz, 10-H); *m/z* 301 (20%), 300 (M^+, 96), 255 (13), 254 (32), 228 (20), 227 (100), 226 (20), 225 (20), and 181 (67).

cis-*Ethyl* 5,6,7,8-*tetrachloro*-2-*ethoxy*-3,4-*dihydro*-2H-*benzo*[b]*pyran*-4-*carboxylate* (**21d**) was obtained from quinone (**5d**) [eluted after (**24**) and before (**22d**)] (67 mg, 17%), m.p. 108–110 °C (from CH_2Cl_2–hexane) (Found: C, 43.4; H, 3.6. $C_{14}H_{14}Cl_4O_4$ requires C, 43.31; H, 3.63%); ν_{max}(Nujol) 1 720 and 1 565 cm^{-1}; δ_H(300 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.1 Hz), 1.27 (3 H, t, *J* 7.1 Hz), 2.22–2.39 (2 H, m, 3-H_2), 3.68 (1 H, dq, *J* 7.1 and 9.6 Hz), 3.94 (1 H, dq, *J* 7.1 and 9.6 Hz), 4.05 (1 H, t, *J* 6.8 Hz, 4-H), 4.21 (2 H, q, *J* 7.1 Hz), and 5.35 (1 H, dd, *J* 2.8 and 5.9 Hz, 2-H); *m/z* 394 (M^+, 1%), 392 (M^+, 3), 390 (M^+, 15), 388 (M^+, 29), 386 (M^+, 22), 343 (7), 341 (5), 319 (11), 317 (48), 315 (100), 313 (79), 287 (17), 285 (16), and 269 (13).

trans-*Ethyl* 5,6,7,8-*tetrachloro*-2-*ethoxy*-3,4-*dihydro*-2H-*benzo*[b]*pyran*-4-*carboxylate* (**22d**) was also obtained from quinone (**5d**) [eluted after (**21d**) and before (**10d**)] (23 mg, 6%), m.p. 114–116 °C (from $CHCl_3$) (Found: C, 43.1; H, 3.4%); ν_{max}(Nujol) 1 725 and 1 505 cm^{-1}; δ_H(80 MHz; $CDCl_3$), 1.07 (3 H, t, *J* 7 Hz), 1.20 (3 H, t, *J* 7.2 Hz), 2.06 (1 H, ddd, *J* 2.2, 7.0, and 14.0 Hz, 3-H^a), 2.79 (1 H, ddd, *J* 2.2, 2.2, and 14.0 Hz, 3-H^b), 3.47–4.34 (5 H, m), and 5.42 (1 H, dd, *J* 2.2 and 2.2 Hz, 2-H); *m/z* 394 (M^+, 0.3%), 392 (M^+, 3), 390 (M^+, 11), 388 (M^+, 22), 386 (M^+, 17), 343 (6), 341 (5), 319 (12), 317 (49), 315 (100), 313 (82), 287 (18), 285 (17), 269 (16), 267 (10), 261 (8), 259 (16), and 257 (12).

5,6,7,8-*Tetrachloro*-2-*ethoxy*-2,3-*dihydro*-1,4-*benzodioxine* (**24**) was also obtained from quinone (**5d**) [eluted before compounds (**21d**) and (**22d**)] (15 mg, 5%), m.p. 100–102 °C (from CH_2Cl_2) (Found: C, 37.5; H, 2.4. $C_{10}H_8Cl_4O_3$ requires C,

37.77; H, 2.54%); ν_{max}(Nujol) 1 560 and 1 275 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.2 Hz), 3.79 (2 H, q, *J* 7.2 Hz), 4.17 (1 H, dd, *J* 1.7 and 11.0 Hz), 4.31 (1 H, dd, *J* 1.7 and 11.0 Hz), and 5.38 (1 H, dd, *J* 1.7 and 1.7 Hz); *m/z* 324 (M^+, 2%), 322 (M^+, 12), 320 (M^+, 50), 318 (M^+, 100), 316 (M^+, 79), 294 (2), 292 (7), 290 (13), 285 (10), 273 (13), 271 (10), 261 (22), 259 (35), 257 (23), 249 (17), 247 (36), 245 (30), 183 (12), and 181 (13).

Preparation of Compounds (**23I**) *and* (**23II**).—To a stirred solution of quinone (**5a**) (0.208 g, 1 mmol) in α-methylstyrene (3 ml), heated at 60 °C, was added the ylide (**6**) (0.348 g, 1 mmol) in portions during 2 h and the mixture was heated for a further 1 h. After cooling to room temperature, the mixture was subjected to column chromatography on silica gel with hexane–ethyl acetate (100:0–95:5) as gradient eluant. Three fractions were eluted. The first fraction afforded *ethyl 2-methyl-2-phenyl-3,4-dihydro-2H-phenanthro*[9,10-b]*pyran-4-carboxylate* (**23I**) (143 mg, 36%), m.p. 182–183 °C (from aq. EtOH) (Found: C, 81.7; H, 6.2. $C_{27}H_{24}O_3$ requires C, 81.79; H, 6.10%); ν_{max}(Nujol) 1 730, 1 625, and 1 600 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 1.07 (3 H, t, *J* 9 Hz), 1.75 (3 H, s), 2.33–3.15 (2 H, m), 3.80–4.00 (1 H, m), 4.15 (2 H, q, *J* 9 Hz), 7.05–7.82 (11 H, m), and 8.42–8.66 (2 H, m); *m/z* 397 (30%), 396 (M^+, 100), 350 (35), 323 (21), 307 (22), 279 (21), 245 (17), 234 (14), 233 (62), 206 (11), 205 (14), 202 (4), 165 (12), 129 (23), 118 (14), and 105 (86).

The second fraction gave the *isomer* (**23II**) (52 mg, 13%), m.p. 174–176 °C (from aq. EtOH) (Found: C, 81.7; H, 6.15%); ν_{max}(Nujol) 1 735, 1 625, and 1 600 cm^{-1}; δ_H(80 MHz; $CDCl_3$) 0.80 (3 H, t, *J* 9 Hz), 1.75 (3 H, s), 2.40–3.95 (3 H, m), 4.13 (2 H, q, *J* 9 Hz), 7.10–7.76 (11 H, m), and 8.50–8.76 (2 H, m); *m/z* 397 (26%), 396 (M^+, 100), 350 (30), 323 (33), 307 (23), 305 (7), 279 (20), 278 (10), 245 (14), 233 (57), 205 (9), 176 (9), 129 (24), 118 (42), and 105 (77).

The third fraction gave compound (**10a**) (28%).

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