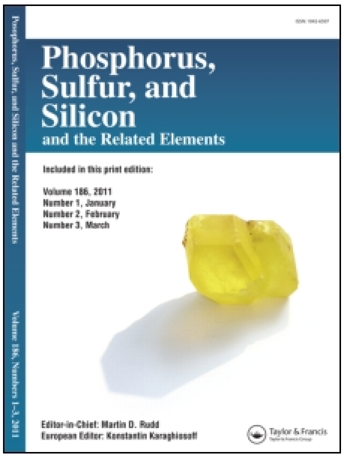

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Synthesis of Some [1,3]Benzodioxoles via the Reaction of *o*-Quinones with Phosphorus Ylides

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SYNTHESIS OF SOME [1,3]BENZODIOXOLES VIA THE REACTION OF *o*-QUINONES WITH PHOSPHORUS YLIDES

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3,5-Di(tert-butyl)benzo-1,2-quinone ***1c****, phenanthrene-9,10-quinone* ***11****, and 1,2-naphthoquinone* ***18*** *react with 1-phenylethylidene(triphenyl)phosphorane* ***2j****, cyclopentylidene(triphenyl)phosphorane* ***2k****, cyclohexylidene(triphenyl)phosphorane* ***2l****, and tetrahydro-2-furanylmethylidene(triphenyl)phosphorane* ***8*** *to give the corresponding 2-substituted [1,3]benzodioxoles* ***5–7****,* ***10****,* ***12–14****,* ***20–22*** *in low to high yields, instead of Wittig products, with exception of 11,12-dihydro-10*H*-cyclopenta[b]phenanthro[9,10-d]furan* ***17****. A possible explanation for these reaction sequences is discussed.*

Keywords: [1,3]Benzodioxoles; *o*-quinones; phosphorus ylides

The reactions of *o*-quinones with phosphorus ylides can lead to the formation of both expected and unexpected interesting compounds depending on the quinone and the ylide used.

Only a few double or bis-Wittig reactions of *o*-quinones with mono and especially with bis-ylides have been reported.[1–7] Usually the reaction proceeds through an initial Wittig mono-olefination of the quinone with formation of a reactive *ortho*-quinone methanide intermediate, which is further transformed to benzofuran or benzopyran derivatives.[1,5,8–16]

The formation of [1,3]benzodioxole derivatives, instead of Wittig reaction products, also has been reported to proceed in reactions between

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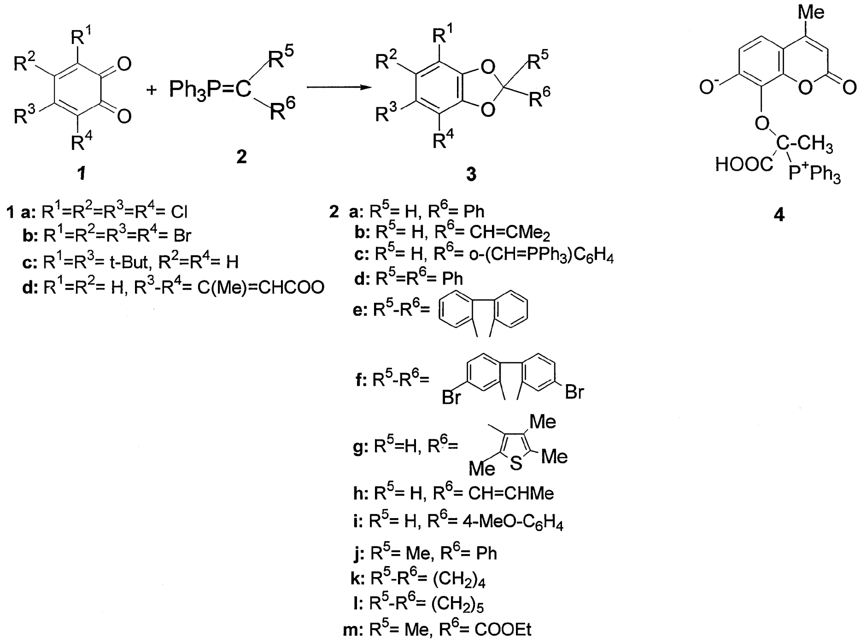
certain *o*-quinones and phosphorus ylides. Bestmann and Lang[8] reported in 1969 that tetrachloro-*o*-benzoquinone **1a** reacts with benzylidene(triphenyl)phosphorane **2a** to give 2-phenylmethylene-4,5,6,7-tetrachloro-1,3-benzodioxole **3** (R^1=R^2=R^3=R^4=Cl, R^5=H, R^6=Ph) and triphenylphosphine. The corresponding [1,3]benzodioxoles **3** also were obtained from the reaction of the same *o*-quinone **1a** with ylides **2b**,[17] **2c**,[2] **2d–f**,[18] and **2g**,[5] as well as from the reactions of **2d–f** with quinone **1b**.[18] The formation of the corresponding 1,3-dioxoles in high yields (82–90%), instead of Wittig products also was reported to proceed in the reactions of 3,5-di(tert-butyl)benzo-1,2-quinone **1c** with ylides **2d–f** (Scheme 1).[19]

Then we reported that the reactions of 4-methylchromene-2,7,8-trione **1d** with ylides **2b**, **2h**, **2i**,[20] as well as with ylides **2j–l**[21] afford the corresponding fused 1,3-dioxolocoumarin derivatives **3** in 4–37% yields. The reaction of **1d** with ylide **2m** gave, in addition to the corresponding dioxole **3** (7%), the betaine **4** as the major product (28%) (Scheme 1).[21]

In connection with these studies we report now our results on the reactions of ylides **2j**, **2k**, **2l**, **8** with *o*-quinones **1c**, **11**, **18**, which lead to the formation of the title compounds in low to high yields (10–90%).



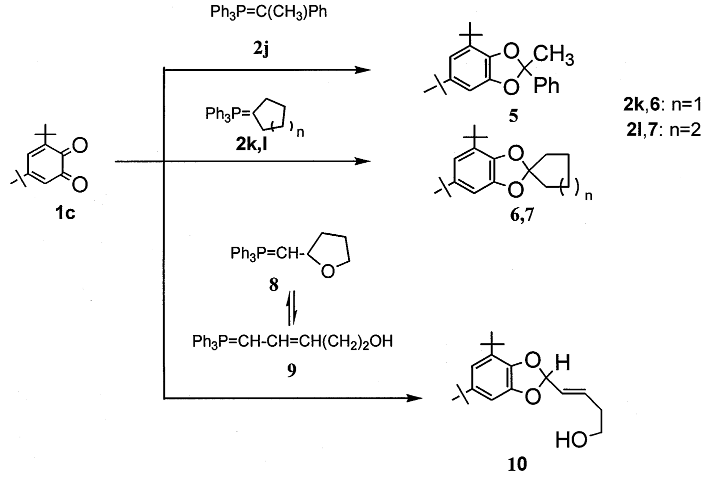
SCHEME 1

RESULTS AND DISCUSSION

The reactions studied and the products obtained are depicted in Schemes 2, 3, and 4.

We studied first the reaction of 3,5-di(tert-butyl)benzo-1,2-quinone **1c** with 1-phenylethylidene(triphenyl)phosphorane **2j**, prepared from 1-phenylethyl(triphenyl)phosphonium bromide, by using different bases and experimental conditions. Treatment of a methylene chloride solution of **1c** and the phosphonium salt under vigorous stirring with aqueous lithium hydroxide solution (Method A), for 24 h at room temperature (r.t.) and separation of the reaction mixture by column chromatography gave 4,6-di(tert-butyl)-2-methyl-2-phenyl-1,3-benzodioxole **5** in 90% yield. When a mixture of equimolar amounts of **1c** and the phosphonium salt in dioxane, which contained a small amount of water, was treated with potassium carbonate under reflux (Method B) for 20 h unreacted quinone **1c** (19%) and product **5** (92%, based on the quinone consumed) were obtained. We also tried the reaction at 0°C under N_2 atmosphere, by treating a THF solution of equimolar amounts of the above reactants with n-BuLi (Method C) for 18 h at r.t. Separation of the reaction mixture by column chromatography gave unreacted **1c** (18%) along with compound **5** (83%, based on the quinone consumed) (Scheme 2).

The reactions of quinone **1c** with ylide **2k** and ylide **2l**, prepared in situ from the corresponding phosphonium bromides,

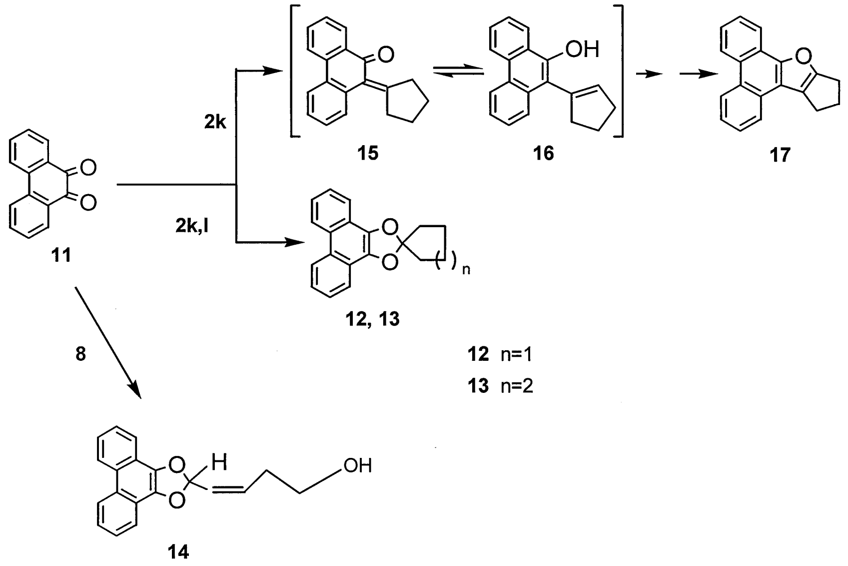


SCHEME 2

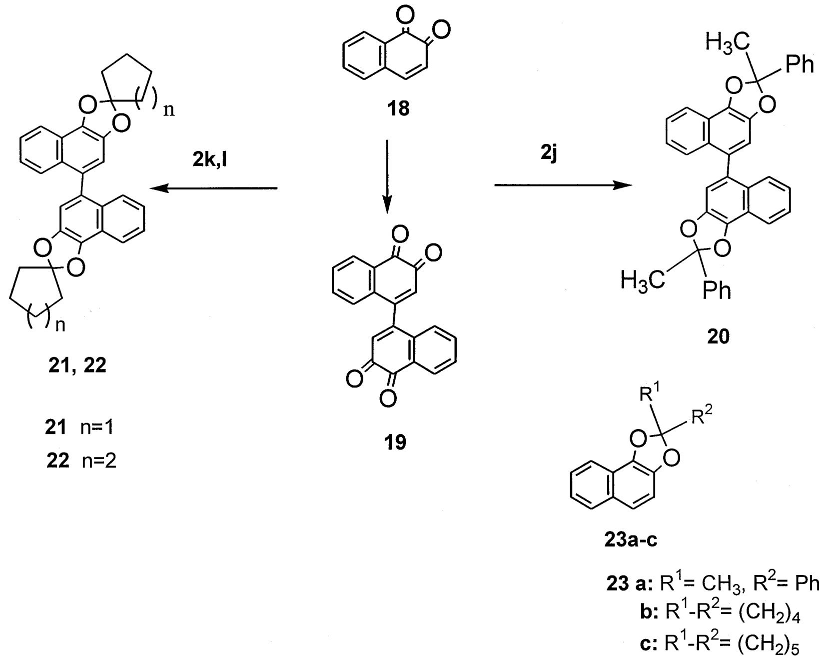
according to Method B afforded 4′,6′-di(tert-butyl)spirocyclopentane-1,2′-benzodioxole **6** and 4′,6′-di(tert-butyl)spirocyclohexane-1,2′-benzodioxole **7** in 69% and 38% yield respectively.

When quinone **1c** was treated with tetrahydro-2-furanylmethyl-(triphenyl)phosphonium bromide, as described in Method B, for 45 h, it gave (*E*)-4-[4,6-di(tert-butyl)benzo[d][1,3]dioxol-2-yl-3-buten-1-ol **10** in 27% yield along with 3,5-di(tert-butyl)-1,2-benzenediol (38%) and unreacted quinone **1c** (25%). Obviously, tautomerization of the expected ylide **8** initially formed to the ylide **9** via the opening of the tetrahydrofuran ring; the reaction conditions[22] and further reaction of the latter with **1c** can account for the formation of the product **10** obtained (Scheme 2).

The reactions between phenanthrene-9,10-quinone **11** and ylides **2k**, **2l**, **8** were carried out according to Method B and gave spirocyclopentane-1,2′-phenanthro[9,10-d][1,3]dioxole **12** (17%), spirocyclohexane-1,2′-phenanthro[9,10-d][1,3]dioxole **13** (16%), and (*Z*) 4-(phenanthro[9,10-d][1,3]dioxol-2-yl)-3-buten-1-ol **14** (55%) respectively (Scheme 3). From the reaction of **11** and **2k** in addition to product **12**, 11,12-dihydro-10*H*-cyclopenta[b]phenathro[9,10-d]furan **17** also was obtained in 6% yield (obviously via an initial Wittig monoolefination of **11**) followed by tautomerization-aromatization of the *o*-quinone methanide **15** formed to the *o*-hydroxy derivative **16** and further cyclization of the latter, as is suggested in Scheme 3.



SCHEME 3



SCHEME 4

The reaction of commercial 1,2-naphthoquinone **18** with the ylide **2j** according to Method B resulted in a complicated mixture of products. Separation of the reaction mixture by column chromatography gave from the faster moving band 2-methyl-2-phenyl-5-(2-methyl-2-phenylnaphtho[1,2-d][1,3]dioxol-5-yl)-naphtho[1,2-d][1,3]dioxole **20** in 20% yield (Scheme 4). The structure suggested for this product agrees well with the recorded analytical and spectral data, and especially with the MS, ^{1}H-NMR, and the ^{13}C-NMR data, which reveal the symmetry of the structure. The recorded ^{1}H-NMR spectrum of the product in question exhibited a two proton singlet at δ 7.12 ppm for the two symmetric 4-H, 4′-H of the two joined dioxolo-naphthalene systems, in good agreement with the suggested 5,5′-linkage, for its two moieties.

The similar products **21** and **22** (Scheme 4) also were obtained in 32% and 38% yield, respectively, from the reactions of the same quinone **18** with ylides **2k** and **2l**, under the same conditions, as it was established from the analytical and spectral data of these products. Obviously products **20–22** are the 5,5′-dimers of the expected, but not isolated or detected monomeric dioxoles **23a–c**, respectively (Scheme 4), and were formed via dimerization of them, or, more probably, compounds **20–22** were produced from the reaction of the known[24] bis-quinone **19**, formed by dimerization of quinone **18** and the ylides. Although in other reactions of quinone **18** with some ylides, studied previously by us, only products of the monomeric quinone **18** were obtained,[4,10] the transformation of **18** into the bis-quinone **19** by its treatment with ethyl azidoformate also has been reported[24] without comments.

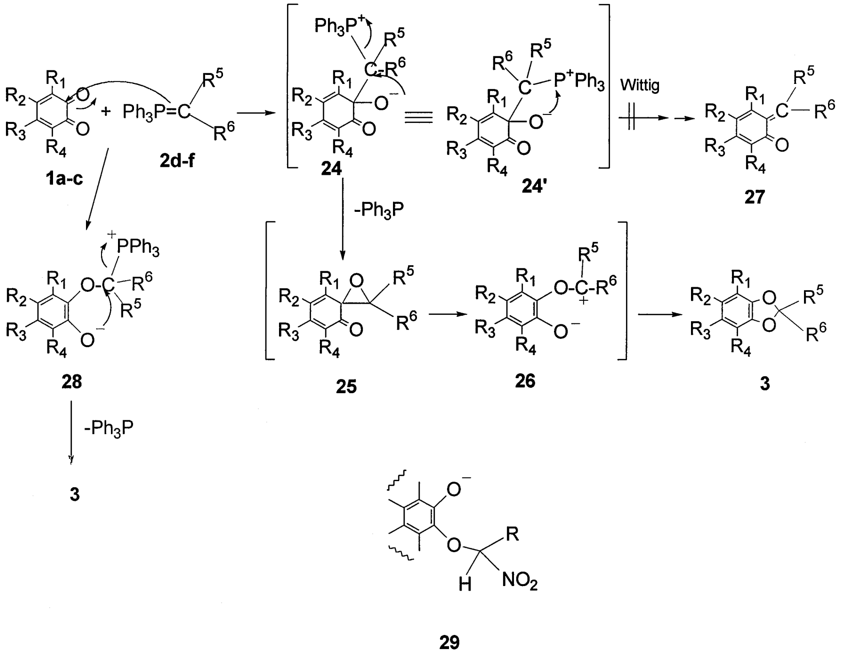
When a dioxane solution of the quinone used in the above reactions was treated under reflux with potassium carbonate and in the absence of any of the above phosphonium salts, the starting quinone was quickly converted to a tarry mass which remained at the bottom of the TLC plate. Furthermore, when in a control experiment pure quinone **18**, obtained from a commercial sample by column chromatography, was treated with ylide **2j** under the conditions described above, compound **20** was again formed, as indicated by TLC examination of the reaction mixture.

The analytical and spectral data (MS, IR, ^{1}H-NMR, ^{13}C-NMR) of all 1,3-dioxoles prepared agree well with the structures suggested for them (see Experimental section).

From the experimental and the literature data presented in this article we can notice that the formation of 1,3-dioxoles instead of an initial Wittig olefination mainly was observed in the reactions of hindered *o*-quinones **1a–c** as well as in the reactions of the hindered phosphoranes **2d–f, 2j–l** and that in the cases of reactions between the above *o*-quinones and ylides the corresponding 1,3-dioxoles are formed almost quantitatively. 1,3-Dioxoles also were formed, but in lower yield, from the reactions of the less hindered quinones **1d**, **11**, **18** (**19**) with ylides **2j–l**, **8** (**9**), as well as from the reactions between quinone **1a** and ylides **2a–c**, **2g–i**.

It is obvious that the 1,3-dioxole formation is favored when the *o*-quinone or the ylide used bear bulky substituents in the proximity of their carbonyl carbon and their carbanionic carbon respectively. However, it must be noted that in contrast to above observations Wittig olefination also has been observed to proceed between the quinones **1a**, **1c** and the ylides $Ph_3P{=}COOR$, $Ph_3P{=}CHCOR$, $Ph_3P{=}CBr_2$[6,13,14] as well as between the ylide **2e** and quinone **11**.[1] Sidky and Boulos[18] and later Abdou[19] suggested the following mechanistic reaction sequence **1** + **2** → **24** → **25** → **26** → **3** (Scheme 5) in order to explain the formation of 1,3-dioxoles **3** from the reactions between **1a–c** and **2d–f**.

According to their suggested mechanism, nucleophilic carbon attack on the carbonyl carbon of quinone **1** by the phosphorane **2** yields the betaine species **24**, like in the first step of the normal Wittig reaction. Subsequent anti elimination of triphenylphospine results in the formation of the intermediate epoxide **25**, which isomerizes to the stable



SCHEME 5

1,3-dioxole **3** through the dipolar form **26** or directly by an orbital symmetry allowed conversion.

We consider that an intermediate betaine conformer **24** suitable for the anti elimination of triphenylphosphine is highly hindered—much more hindered than the conformer **24′**—which however is more suitable for the continuation of the Wittig reaction sequence. This means that the suggested[19,22] original nucleophilic attack by the ylide to the carbonyl carbon of quinone seems to be not very possible. The formation of an intermediate betaine **28** (Scheme 5), followed by ring closure—triphenylphosphine elimination also could lead to the formation of 1,3-dioxoles **3**. Betaine **28** is less hindered and its intermediacy can also explain the isolation of betaine **4** (Scheme 1) previously reported.[21]

Ohshiro et al.[25] reported the formation of 1,3-dioxoles from the reaction between nitroalkanes and *o*-quinones. They suggested that the nitroalkane anion formally added to the cabonyl oxygen of the *o*-quinone to give the intermediate **29** (Scheme 5), similar to **28**, which by further cyclization–elimination of $^{-}NO_2$ affords 1,3-dioxoles. One of the possible mechanism of this abnormal addition is electron transfer from anion to the quinone and subsequent radical coupling in the solvent cage.

Although a similar mechanism can also be suggested for the formation of 1,3-dioxoles **3** via **28** from hindered *o*-quinones and phosphoranes, more evidence is necessary to explain their abnormal behavior with certainty. Finally we note, that in contrast to the reaction of the O-methyl monoxime of quinone **11** with ylides $Ph_3P{=}CHCOR$ (R=Ph, OEt), which proceeded via an initial Wittig monoolefination of the quinone carbonyl,[26–28] the reactions of the O-methyl monoximes of hindered quinones **1b**, **1d** with ylides $Ph_3P{=}CHR$ (R=Ar, COOEt, COOMe, $CH{=}CR'_2$) afforded the corresponding 2-R substituted benzoxazoles[29,30] and the reactions with ylides $Ph_3P{=}C(CH_2R)COOEt$ ($R = CH_3$, Ph, H) gave 2*H*-[b][1,4]benzoxazine derivatives[31] instead of any Wittig product.

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 as Nujol mulls except otherwise stated. NMR spectra were recorded on a Bruker AM 300 (300 MHz, and 75 MHz for ^1H and ^{13}C, respectively, using $CDCl_3$ as solvent and TMS as an internal standard. *J* values are reported in Hz. Mass spectra were determined on a VG-250 spectrometer at 70 eV under Electron Impact (EI) conditions, or on a Perkin Elmer API 100 Sciex Simple quadrupole under Electrospray Ionization (ESI) conditions. High resolution mass spectra (HRMS) were recorded on an Ionspec mass spectrometer under Matrix-Assisted Laser Desorption-Ionization Fourier Transform Mass Spectrometer (MALDI-FTMS) conditions with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Microanalyses were performed on a Perkin-Elmer 2400-II Element analyzer. THF was refluxed over sodium and benzophenone and distilled, when the mixture turned blue. Silica gel N°60, Merck A.G. has been used for column chromatographies.

Reaction of Quinone 1c with Ylide 2j

Method A (Phase Transfer Catalysis)

To a stirred solution of quinone **1c** (0.66 g, 3 mmol) and 1-phenylethyl(triphenyl)phosphonium bromide (1.341 g, 3 mmol) in methylene chloride (45 ml) a freshly prepared 5N lithium hydroxide solution (7.5 ml) was added at once and the two-phase reaction mixture was further stirred at r.t. for 24 h. The organic phase was separated and the aqueous layer was extracted with methylene chloride (3 × 45 ml).

The combined organic phases were dried over sodium sulfate, the solvent was removed in a rotary evaporator, and the residue was subjected to column chromatography, using hexane/ethyl acetate mixtures as eluent.

Reactions of Quinones 1c, 11, 18 with Ylides 2j–l, 8

Method B (General Procedure)

To a stirred mixture of quinone **1c**, **11**, **18** (3 mmol), the corresponding phosphonium salt (3 mmol) and potassium carbonate (3.6 mmol) in dry dioxane (15 ml), water (98 mg) was added and the mixture was heated under reflux for 4–72 h. After cooling at r.t. the precipitate was filtered and washed with methylene chloride. The filtrates were combined, the solvents were removed in a rotary evaporator, and the residue was subjected to column chromatography. Mixtures of n-hexane with increasing amounts of ethyl acetate or methylene chloride were used as eluents. In addition to the reaction products, unreacted starting quinones were eluted generally after the products described, unless otherwise stated. Quinone **1c** was recovered from the reactions with ylides: **2j** (**1c** recovered 127 mg, 19%); **2k** (150 mg, 23%); **2l** (98 mg, 15%); **8** (170 mg, 26%). Quinone **11** was recovered from the reactions with ylides: **2j** (**11** recovered 134 mg, 21%); **2k** (245 mg, 39%); **2l** (313 mg, 50%); **8** (98 mg, 16%).

Reactions of Quinones 1c, 11 with Ylide 2j

Method C (General Procedure)

1-Phenylethyl(triphenyl)phosphonium bromide (0.66 g, 3.3 mmol) was suspended in dry THF (50 ml) under dry N_2. n-Butyllithium (3.63 mmol) in hexane (2.27 ml) was added to the stirred mixture (at r.t. in the case of **1c**, at 0°C in the case of **11**) and stirring was continued for 7 min. The red solution was then added to a solution of the quinone **1c**, **11** (3 mmol) in dry THF (35 ml) at the same temperature, under N_2. The red color was discharged and the reaction mixture was stirred for further 18–24 h. The solvent was removed in a rotary evaporator. The residue was extracted with methylene chloride (3 × 100 ml) and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography, using mixtures of n-hexane with methylene chloride or with ethyl acetate as eluents. In addition to the reaction products obtained, unreacted starting quinone **1c** (119 mg, 18%), **11** (289 mg, 46%) were recovered from the reactions, eluted after the products obtained.

*4,6-Di(***tert***-butyl)-2-methyl-2-phenyl-1,3-benzodioxole 5*

It was obtained from the reaction between **1c** and **2j** with Method A (90%) or with Method B (20 h, 92%), or with Method C (18 h, 83%), m.p. 53–55°C (hexane). Anal. Calcd. for $C_{22}H_{28}O_2$, C 81.4, H 8.7. Found; C 81.8, H 8.8. IR cm^{-1} 3025, 1592; NMR: ^{1}H, δ_H 1.26 (s, 9H), 1.38 (s, 9H), 1.95 (s, 3H), 6.76 (s, 2H), 7.28–7.38 (m, 3H), 7.62 (d, 2H, $J = 6.7$); ^{13}C, δ_C 27.5, 29.6, 31.7, 34.1, 34.7, 104.1, 115.0, 115.9, 125.0, 128.2, 128.5, 131.4, 142.1, 142.2, 144.2, 147.0; EIMS: m/z 324 (M$^+$, 65%), 309 (66), 267 (13), 247 (26), 207 (78), 191 (48), 147 (92), 105 (76), 91 (100), 77 (83).

*4′,6′-Di(***tert***-butyl)spirocyclopentane-1,2′-[1,3]benzodioxole 6*

It was obtained from the reaction between **1c** and **2k**, prepared in situ from cyclopentyl(triphenyl)phosphonium bromide with Method B (21 h, 69%), m.p. 57–58°C (ether/hexane). Anal. Calcd. for $C_{19}H_{28}O_2$, C 79.1, H 9.8. Found: C 79.3, H 10.1. IR cm^{-1} 3050, 1590; NMR: ^{1}H, δ_H 1.27 (s, 9H), 1.34 (s, 9H), 1.78–1.92 (m, 4H), 2.07 (t, 4H, $J = 6.5$), 6.70 (s, 1H), 6.74 (s, 1H); ^{13}C, δ_C 23.3, 29.4, 31.7, 34.0, 34.7, 37.1, 101.0, 103.7, 114.6, 126.1, 131.1, 143.7, 145.4, 147.3; EIMS: m/z 288 (M$^+$, 7%), 273 (16), 192 (6), 179 (17), 106 (100), 104 (21), 77 (37), 57 (27).

*4′,6′-Di(***tert***-butyl)spirocyclohexane-1,2′-[1,3]benzodioxole 7*

It was obtained from the reaction between **1c** and **2l**, prepared in situ from cyclohexyl(triphenyl)phosphonium bromide with Method B (72 h, 38%), m.p. 64–65°C (ether/hexane). Anal. Calcd. for $C_{20}H_{30}O_2$, C 79.4, H 10.0. Found: C 79.7, H 10.1. IR cm^{-1} 3060, 1590; NMR: ^{1}H, δ_H 1.28 (s, 9H), 1.35 (s, 9H), 1.42–1.59 (m, 2H), 1.68–1.81 (m, 4H), 1.83–1.99 (m, 4H), 6.70 (s, 1H), 6.73 (s, 1H); ^{13}C, δ_C 23.3, 24.7, 29.4, 31.7, 34.0, 34.7, 35.2, 103.9, 114.5, 117.1, 131.2, 142.3, 143.6, 147.1; EIMS: m/z 303 (M$^+$+H, 18%), 302 (100, M$^+$), 287 (90), 259 (30), 231 (4), 81 (13).

*(***E***)4-[4,6-Di(***tert***-butyl)benzo[d][1,3]dioxol-2-yl]-3-buten-1-ol 10*

It was obtained from the reaction between **1c** and **8**, prepared in situ from tetrahydro-2-furanylmethyl(triphenyl)phosphonium bromide with Method B (45 h, 27%) (eluted after unreacted **1c**), m.p. 59–61°C (hexane). IR cm^{-1} 3300, 1665, 1590, 1480; NMR: ^{1}H, δ_H 1.28 (s, 9H), 1.35 (s, 9H), 1.37 (brs, 1H), 2.42 (q, 2H, $J = 6.4$), 3.75 (t, 2H, $J = 6.4$), 5.85 (dd, 1H, $J = 6.4$, 15.3), 6.11 (dt, 1H, $J = 6.4$, 15.3), 6.34 (d, 1H, $J = 6.4$), 6.72 (d, 1H, $J = 1.7$), 6.76 (d, 1H, $J = 1.7$); ^{13}C, δ_C 29.5, 31.6, 34.0, 34.7, 35.3, 61.4, 104.0, 109.4, 115.2, 127.7, 131.5, 134.6, 142.6, 144.4, 147.3; EIMS: m/z 304 (M$^+$, 100%), 273 (17), 259 (43), 243 (13), 233 (22), 217 (16), 207 (29), 191 (28), 175 (16), 145 (20), 131 (29), 115 (35), 105 (33); MALDIHRMS (DHB): m/z 304.2037 $[M]^+$. $C_{19}H_{28}O_3$ requires m/z 304.2033.

Spirocyclopentane-1,2′-phenanthro[9,10-d][1,3]dioxole 12

It was obtained from the reaction between **11** and **2k**, prepared in situ from cyclopentyl(triphenyl)phosphonium bromide with Method B, (19 h, eluted after **17**, 17% yield), m.p. 116–118°C (DCM/hexane). Anal. Calcd. for $C_{19}H_{16}O_2$, C 82.6, H 5.8. Found: C 82.6, H 5.7. IR cm^{-1} 3050, 1600, 1510; NMR: ^1H, δ_H 1.90–2.03 (m, 4H), 2.26 (t, 4H, $J = 7.3$), 7.48–7.64 (m, 4H), 7.91 (d, 2H, $J = 8.3$), 8.64 (d, 2H, $J = 8.3$); ^{13}C, δ_C 23.5, 37.6, 120.1, 121.5, 123.2, 124.2, 126.7, 126.9, 128.7, 137.3; EIMS: m/z 276 (M^+, 100%), 247 (87), 210 (22), 194 (12), 191 (11), 181 (65), 163 (83), 152 (98).

Spirocyclohexane-1,2′-phenanthro[9,10-d][1,3]dioxole 13

It was obtained from the reaction between **11** and **2l**, prepared in situ from cyclohexyl(triphenyl)phosphonium bromide with Method B (67 h, 10%), m.p. 106–108°C (ether/hexane) Anal. Calcd. for $C_{20}H_{18}O_2$, C 82.7, H 6.25. Found: C 82.4, H 6.2. IR cm^{-1} 3050, 1600, 1515; NMR: ^1H, δ_H 1.47–1.67 (m, 2H), 1.77–1.95 (m, 4H), 2.09 (t, 4H, $J = 6.0$), 7.50–7.63 (m, 4H), 7.93 (d, 2H, $J = 8.4$), 8.66 (d, 2H, $J = 8.3$); ^{13}C, δ_C 23.3, 24.8, 35.3, 119.9, 120.1, 120.2, 123.2, 124.1, 126.6, 126.7, 137.2; EIMS: m/z 291 (M^++H, 52%), 290 (73, M^+), 248 (18), 247 (16), 210 (34), 209 (18), 182 (36), 181 (52), 180 (17), 164 (30), 152 (60), 82 (37), 81 (100).

(Z) 4-(Phenanthro[9,10-d][1,3]dioxol-2-yl)-3-buten-1-ol 14

It was obtained from the reaction between **11** and **8**, prepared in situ from tetrahydro-2-furanylmethyl(triphenyl)phosphonium bromide with Method B (72 h, 55%) (eluted after unreacted **11**), m.p. 87–88°C (DCM/hexane). IR cm^{-1} (KBr) 4323, 3050, 1636, 1600; NMR: ^1H, δ_H 1.22 (t, 1H, $J = 7.1$), 1.99–2.06 (m, 1H), 2.22–2.78 (m, 1H), 3.90–3.96 (m, 1H), 4.01–4.06 (m, 1H), 5.26 (ddt, 1H, $J_1 = 1.5$, $J_2 = 3.7$, $J_3 = 8.8$), 5.90 (dd, 1H, $J_1 = 3.7$, $J_2 = 9.9$), 7.16 (dd, 1H, $J_1 = 1.5$, $J_2 = 9.9$), 7.52 (, 1H, $J = 8.1$), 7.56–7.65 (m, 3H), 7.99 (d, 1H, $J = 8.1$), 8.26 (d, 1H, $J = 7.7$), 8.61 (d, 2H, $J = 8.4$); ^{13}C, δ_C 36.9, 59.2, 101.3, 121.0, 121.9, 122.6, 123.0, 124.4, 126.7, 127.0, 134.7, 147.3; ESIMS: m/z 293 $[MH]^+$; MALDIHRMS (DHB): m/z 292.1090 $[M]^+$. $C_{19}H_{16}O_3$ requires m/z 292.1093.

*11,12-Dihydro-10*H*-cyclopenta[b]phenanthro-[9,10-d]furan 17*

It was obtained from the reaction between **11** and **2k**, prepared in situ from cyclopentyl(triphenyl)phosphonium bromide with Method B (19 h, eluted before **12**, 6%), m.p. 156–158°C (methylene chloride/hexane). Anal. Calcd. for $C_{19}H_{14}O$, C 88.3, H 5.5. Found: C 88.1, H 5.5. IR cm^{-1} 3050, 1605; NMR: ^{1}H, δ_H 2.62–2.79 (m, 2H), 2.99 (t, 2H, $J = 6.1$), 3.09 (t, 2H, $J = 6.3$), 7.53–7.72 (m, 4H), 8.08 (d, 1H, $J = 8.0$), 8.28 (d, 1H, $J = 8.0$), 8.70 (dd, 2H, $J = 2.3$ and $J = 7.3$); ^{13}C, δ_C 24.0, 25.0, 28.1, 106.3, 119.0, 120.0, 123.0, 123.2, 123.3, 124.6, 124.8, 124.9, 126.7, 126.9, 127.6, 127.9, 128.1, 153.2, 161.5; EIMS: m/z 258 (M^+, 100%), 257 (33), 231 (60), 215 (38), 210 (58), 209 (19), 202 (58), 189 (15), 181 (58), 165 (22), 152 (52).

2-Methyl-2-phenyl-5-(2-methyl-2-phenylnaphtho-[1,2-d][1,3]dioxol-5-yl)-naphtho[1,2-d][1,3]dioxole 20

It was obtained from the reaction between **18** and **2j**, prepared in situ from 1-phenylethyl(triphenyl)phosphonium bromide with Method B (18 h, 20%), m.p. 209–211°C (methylene chloride/hexane). IR cm^{-1} (methylene chloride) 3040, 1625, 1595, 1460, 1260, 1170; NMR: ^{1}H, δ_H 2.15 (s, 3H), 7.04–7.20 (m, 2H), 7.29–7.44 (m, 5 H), 7.69–7.73 (m, 2H), 7.92 (d, 1H, $J = 7.6$); ^{13}C, δ_C 27.2, 91.8, 113.0, 117.9, 119.9, 123.7, 125.0, 125.8, 127.2, 128.3, 128.9, 129.2, 131.9, 140.4, 141.6, 142.1; EIMS: m/z 522 (M^+, 54%), 508 (8), 420 (44), 419 (21), 405 (7), 318 (50), 317 (22), 289 (21), 103 (100), 77 (75); MALDIHRMS (DHB): m/z 522.1835 $[M]^+$. $C_{36}H_{26}O_4$ requires m/z 522.1826.

5′-(Spirocyclopentane-1,2′-naphtho[1,2-d][1,3]dioxol-5′-yl)spirocyclopentane-1,2′-naphtho[1,2-d][1,3]dioxole 21

It was obtained from the reaction between **18** and **2k**, prepared in situ from cyclopentyl(triphenyl)phosphonium bromide with Method B (18 h, 32%), m.p. 239–242°C (ethyl acetate/hexane). IR cm^{-1} (methylene chloride) 3040, 1630, 1600, 1260; NMR: ^{1}H, δ_H 1.85–2.0 (m, 8H), 2.20–2.34 (m, 8H), 7.08 (t, 2H, $J = 7.6$), 7.12 (s, 2H), 7.30 (d, 2H, $J = 7.6$), 7.38 (t, 2H, $J = 7.6$), 7.86 (d, 2H, $J = 7.6$); ^{13}C, δ_C 23.4, 37.5, 112.7, 119.5, 119.8, 123.5, 125.6, 127.2, 128.5, 128.9, 131.5, 140.6, 142.2; EIMS: m/z 450 (M^+, 49%), 422 (20), 385 (7), 356 (10), 338 (11), 271 (15), 226 (59), 225 (22), 215 (28), 202 (15), 67 (100); MALDIHRMS (DHB): m/z 450.1818 $[M]^+$. $C_{30}H_{26}O_4$ requires m/z 450.1825.

5′-(Spirocyclohexane-1,2′-naphtho[1,2-d][1,3]dioxol-5′-yl)spirocyclohexane-1,2′-naphtho[1,2-d][1,3]dioxole 22

It was obtained from the reaction between **18** and **2l**, prepared in situ from cyclohexyl(triphenyl)phosphonium bromide with Method B (18 h, 38%), m.p. 226–228°C (ether/hexane). IR cm^{-1} (methylene chloride) 3040, 1625, 1595, 1140; NMR: ^{1}H, δ_H 1.52–1.62 (m, 4H), 1,77–1.86 (m, 8H), 2.04–2.11 (m, 8H), 7.08 (t, 2H, $J = 7.6$), 7.12 (s, 2H), 7.30

(d, 2H, $J = 7.6$), 7.38 (t, 2H, $J = 7.6$), 7.87 (d, 2H, $J = 7.6$); ^{13}C, δ_C 23.6, 24.6, 35.9, 113.0, 119.7, 119.8, 123.3, 125.5, 127.2, 128.8, 128.9, 131.4, 140.5, 142.2; EIMS: m/z 478 (M^+, 100%), 435 (8), 397 (8), 271 (9), 226 (7), 215 (11), 202 (6), 81 (98); MALDIHRMS (DHB): m/z 478.2143 $[M]^+$. $C_{32}H_{30}O_4$ requires m/z 478.2139.

REFERENCES

[1] W. W. Sullivan, D. Ullman, and H. Shechter, *Tetrahedron Lett.*, 457 (1969).
[2] D. N. Nicolaides and K. E. Litinas, *J. Chem. Res. (S)*, 57 (1983); (*M*) 658 (1983).
[3] A. Minsky and M. Rabinovitz, *Synthesis*, 497 (1983).
[4] K. E. Litinas and D. N. Nicolaides, *J. Chem. Soc., Perkin Trans.*, **1,** 429 (1985).
[5] D. N. Nicolaides, K. E. Litinas, and N. G. Argyropoulos, *J. Chem. Soc., Perkin Trans.*, **1,** 415 (1986).
[6] W. M. Abdou, N. A. Ganoub, and N. M. Abd El-Rahman, *Phosphorus, Sulfur and Silicon*, **61,** 91 (1991).
[7] C. Yang, D. T. C. Yang, and R. G. Harvey, *Synlett*, 799 (1992).
[8] H. J. Bestmann and H. J. Lang, *Tetrahedron Lett.*, 2101 (1969).
[9] F. M. Soliman, K. M. Khalil, and G. Abdelnaim, *Phosphor and Sulfur*, **35,** 41 (1988).
[10] D. N. Nicolaides, D. A. Lefkaditis, P. S. Lianis, and K. E. Litinas, *J. Chem. Soc., Perkin Trans.*, **1,** 2329 (1989).
[11] C. J. Moody, C. W. Rees, and R. Thomas, *Tetrahedron*, **48,** 3589 (1992).
[12] D. N. Nicolaides, K. E. Litinas, D. A. Lefkaditis, et al., *J. Chem. Soc., Perkin Trans.*, **1,** 2107 (1994).
[13] D. N. Nicolaides, S. G. Adamopoulos, D. A. Lefkaditis, and K. E. Litinas, *J. Chem. Soc., Perkin Trans.*, **1,** 2127 (1990).
[14] D. N. Nicolaides, S. G. Adamopoulos, D. A. Lefkaditis, K. E. Litinas, and P. V. Tarantili, *J. Chem. Soc., Perkin Trans.*, **1,** 283 (1992).
[15] F. H. Osman, N. M. Abd El-Rahman, and F. A. El-Samahy, *Tetrahedron*, **49,** 8691 (1993).
[16] F. H. Osman and F. A. El-Samahy, *Phosphorus, Sulfur and Silicon*, **108,** 21 (1996).
[17] G. Gardillo, L. Merlini, and S. Servi, *Ann. Chim.* (Rome), **60,** 564 (1970).
[18] M. M. Sidky and L. S. Boulos, *Phosphorus and Sulfur*, **19,** 27 (1984).
[19] W. M. Abdou, *Phosphorus, Sulfur and Silicon*, **66,** 285 (1992).
[20] D. N. Nicolaides, C. Bezergiannidou-Balouctsi, K. E. Litinas, et al., *J. Chem. Res. (S)*, 108 (1993); (*M*) 826 (1993).
[21] K. C. Fylaktakidou, D. R. Gautam, D. J. Hadjipavlou-Litina, et al., *J. Chem. Soc., Perkin Trans.*, **1,** 3073 (2001).
[22] E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29,** 1746 (1964).
[23] A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 746 (1946).
[24] M. S. Chauhan, D. M. McKinnon, and R. G. Cooke, *Can. J. Chem.*, **55,** 2363 (1977).
[25] S. Itoh, K. Nii, M. Mure, and Y. Ohshiro, *Tetrahedron Lett.*, **28,** 3975 (1987).
[26] D. N. Nicolaides, K. E. Litinas, G. K. Papageorgiou, and J. Stephanidou-Stephanatou, *J. Heterocyclic Chem.*, **28,** 139 (1991).
[27] D. N. Nicolaides, R. W. Awad, G. K. Papageorgiou, and J. Stephanidou-Stephanatou, *J. Org. Chem.*, **59,** 1083 (1994).
[28] D. N. Nicolaides, R. W. Awad, G. K. Papageorgiou, and J. Stephanidou-Stephanatou, *Tetrahedron Lett.*, **37,** 1097 (1996).

[29] D. N. Nicolaides, G. K. Papageorgiou, and J. Stephanidou-Stephanatou, *Tetrahedron*, **45,** 4585 (1989).

[30] C. Bezergiannidou-Balouctsi, K. E. Litinas, E. Malamidou-Xenikaki, and D. N. Nicolaides, *Liebigs Ann. Chem.*, 1175 (1993).

[31] D. N. Nicolaides, D. R. Gautam, K. E. Litinas, C. Manouras, and K. C. Fylaktakidou, *Tetrahedron*, **57,** 9469 (2001).