Reactions of *o*-Quinones with some Bis-phosphonium Salts in the Presence of Lithium Ethoxide

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Reactions of the 1,3-bis-phosphonium salts (**2a–d**) with phenanthrene-9,10-quinone (**1**) in the presence of lithium ethoxide gave the phenanthro derivatives (**3**), (**4**), (**5**), and (**7**) respectively, instead of the expected bis-Wittig reaction products. However, from the reaction of the salt (**2c**) the bis-Wittig product (**6**) was also obtained, but in very low yield. On the other hand, reactions of 1,6- and 1,5-bis-phosphonium salts (**18**) and (**26**) with *o*-quinones (**1**), (**20**), and (**21**) resulted in the formation of 9-(*o*-hydroxyaryl)phenanthrenes (**22**)—(**24**) and 1-(*o*-hydroxyaryl)acenaphthylenes (**28**) and (**29**). Reaction mechanisms involving initial Wittig reaction of one carbonyl group with one ylide group are proposed. Bromination of (**22**) and (**28**) and dehydrobromination of the bromo derivatives (**33**) and (**35**) produced gave the annelated furan derivatives (**34**) and (**36**) respectively.

Several unsaturated cyclic compounds have been prepared by treatment of bis-phosphonium salts with a base in the presence of dicarbonyl compounds, through a double reaction, termed a bis-Wittig reaction.[1–3] It is assumed that the double condensation occurs stepwise, generally after the *in situ* pre-formation of the corresponding bis-ylide.

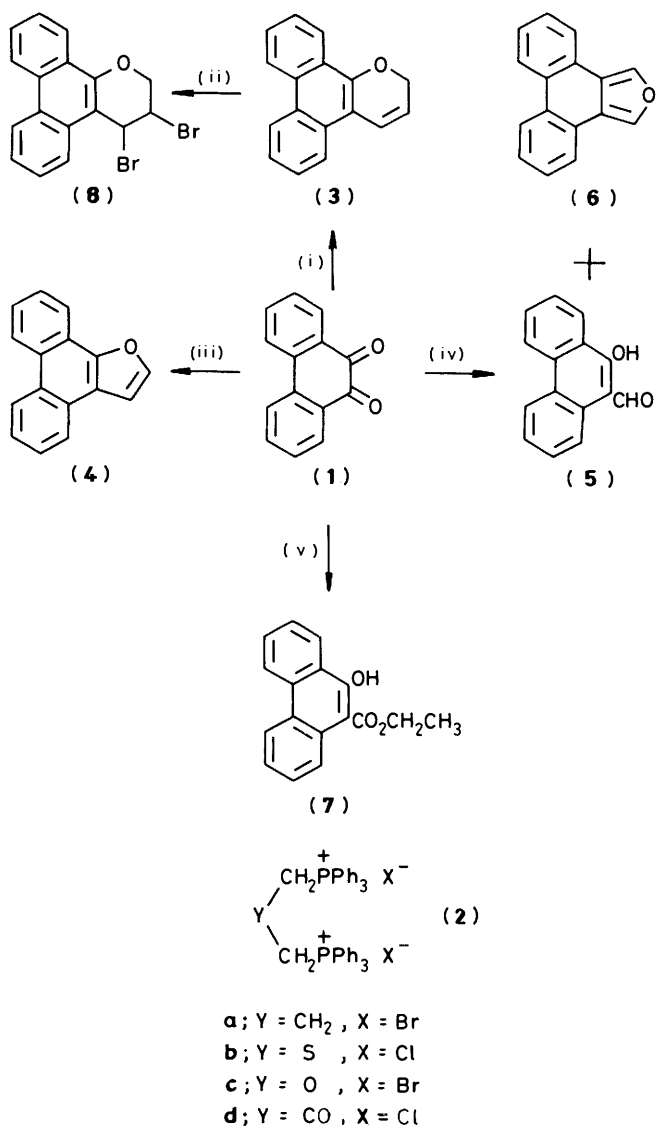
Although the reactions of cyclobutane-1,2-dione and cyclobutadienequinones with bis-ylides, leading to unsaturated cyclic products through bis-Wittig olefination, are well known,[4] the reactions of *o*-benzoquinones with bis-ylides have not yet been studied thoroughly. It is, however, reported that reactions of *o*-benzoquinones with mono-ylides result initially to the formation of *o*-quinomethanes. These reactive conjugated systems usually undergo a Michael addition by another ylide molecule although in some cases a second Wittig reaction is observed.[5]

Recently we reported the one-step synthesis of some polycyclic aromatic compounds through bis-Wittig reactions between hexa-*P*-phenyl-*o*-phenylenebismethylenediphosphorane and *o*-quinones.[6] Soon after, Minsky and Rabinovitz prepared by a similar reaction procedure some polycyclic hydrocarbons, using a phase-transfer-catalysed bis-Wittig reaction.[7] In the present paper we describe the reaction of 1,3-bis-phosphonium salts (**2a—d**) with phenanthrene-9,10-quinone (**1**) and the reactions of 1,6- and 1,5-bis-phosphonium salts (**18**) and (**26**) with *o*-quinones (**1**), (**20**), and (**21**), in the presence of lithium ethoxide. Some reactions of the (*o*-hydroxyaryl)-phenanthrene and -acenaphthylene derivatives (**22**) and (**28**) produced are also reported.

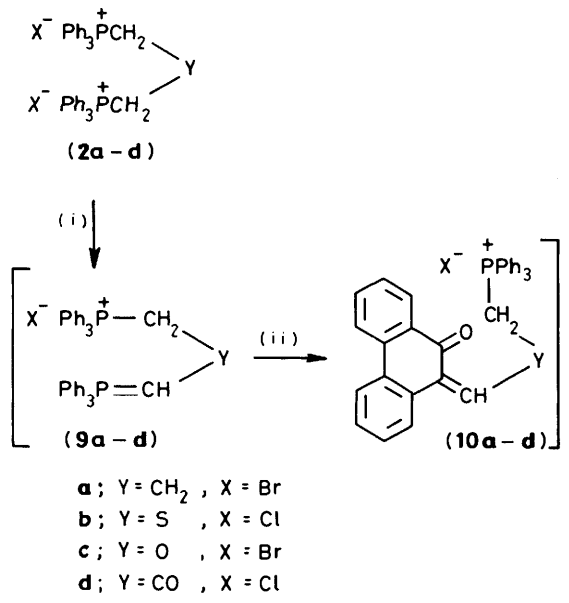
Results and Discussion

A solution of equimolar amounts of phenanthrene-9,10-quinone (**1**) and a 1,3-bis-phosphonium salt (**2a—d**) in dry dimethylformamide (DMF) was treated at room temperature with a dry ethanolic solution of lithium ethoxide for 18 h. After neutralisation with hydrochloric acid and extraction with ether the reaction mixtures were subjected to column chromatography and compounds (**3**)—(**7**) (Scheme 1) were isolated as reaction products.

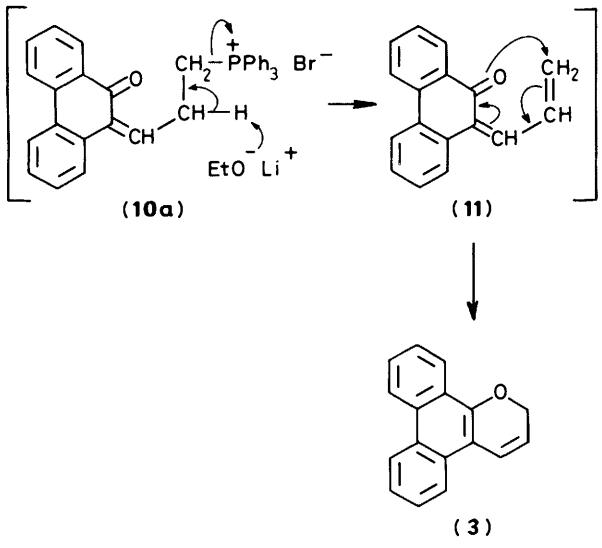
Compounds (**4**), (**5**), (**6**) and (**7**), obtained in 8, 58, 2, and 8% yield respectively, are known and have properties identical with those given in the literature. 2*H*-Phenanthro[9,10-*b*]pyran (**3**) was prepared in 26% yield and by bromination with bromine in carbon tetrachloride gave 3,4-dibromo-3,4-dihydro-2*H*-phenanthro[9,10-*b*]pyran (**8**) in 70% yield. The proposed structures for compounds (**3**) and (**8**) were confirmed by their elemental



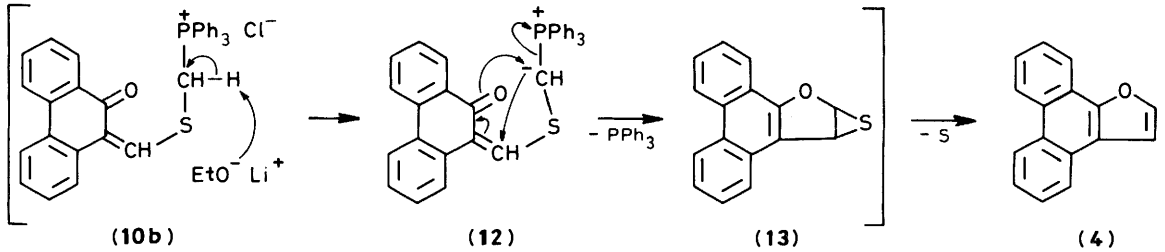
Scheme 1. *Reagents:* (i) (**2a**), EtOLi, DMF; (ii) Br_2, CCl_4; (iii) (**2b**), EtOLi, DMF; (iv) (**2c**), EtOLi, DMF; (v) (**2d**), EtOLi, DMF.



Scheme 2. *Reagents:* (i) EtOLi; (ii) (**1**).



Scheme 3.



Scheme 4.

analyses and spectral data (^{1}H n.m.r., i.r., m.s., u.v.). It should be noted that the expected bis-Wittig product (**6**) was isolated only from the reaction of salt (**2c**), and in very low yield. All attempts to detect or isolate bis-Wittig products from the other reactions failed.

In order to explain the formation of the unexpected products (**3**), (**4**), (**5**), and (**7**) we propose the multistep mechanism sequences shown in Schemes 2—7. It is reasonable to assume that a Wittig reaction between the ylides (**9a—d**) produced and the quinone (**1**), leading to the intermediate *o*-quinomethane derivatives (**10a—d**), is the first step in all the reactions studied (Scheme 2). The following steps, involving further attack of the base, are greatly influenced by the nature of the group Y of the intermediates (**10a—d**).

Hofmann elimination of a β-hydrogen and triphenylphosphine from (**10a**) by attack of the base, followed by intramolecular cyclisation of the produced intermediate (**11**),[8] gives compound (**3**) (Scheme 3).

Phenanthro[9,10-*b*]furan (**4**) is formed from (**10b**) through an intermolecular Michael addition by the carbanion of the free ylide group of the intermediate ylide (**12**) produced and desulphurisation of the annelated thiirane-derivative (**13**) (Scheme 4).

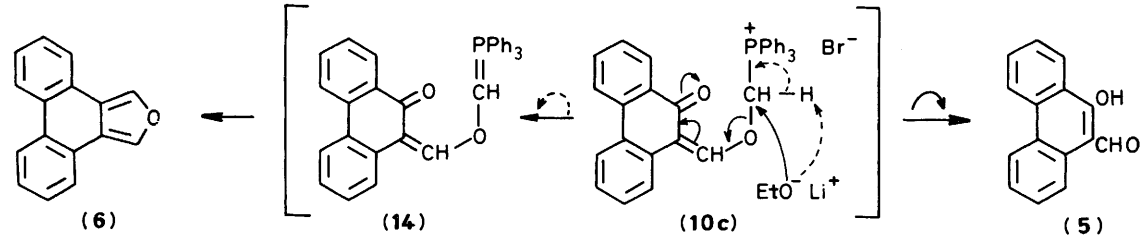
Nucleophilic attack by the base on the α-carbon of the phosphonium salt (**10c**), followed by fission of the neighbouring C–O bond and aromatisation of the phenanthrene ring system, can explain the formation of 10-hydroxyphenanthrene-9-carbaldehyde (**5**). Besides this predominant process, formation of the ylide (**14**) leads *via* an intramolecular Wittig reaction, to the preparation of phenanthro[9,10-*c*]furan (**6**) (Scheme 5).

The formation of ethyl 10-hydroxyphenanthrene-9-carboxylate (**7**) from (**10d**) could be explained by assuming an attack by an ethoxy group on the methine carbon of (**10d**). The proposed mechanism is believed to involve an intramolecular Michael addition by the oxygen anion on the mesomeric form (**15b**) of the ylide (**15a**) produced; aromatisation of the quinone ring, followed by opening of the oxirane ring of (**16**) then occurs. Finally substitution of the acetylide with an ethoxy group through nucleophilic attack on the ketone (**17**) by the base leads to compound (**7**) (Scheme 6).

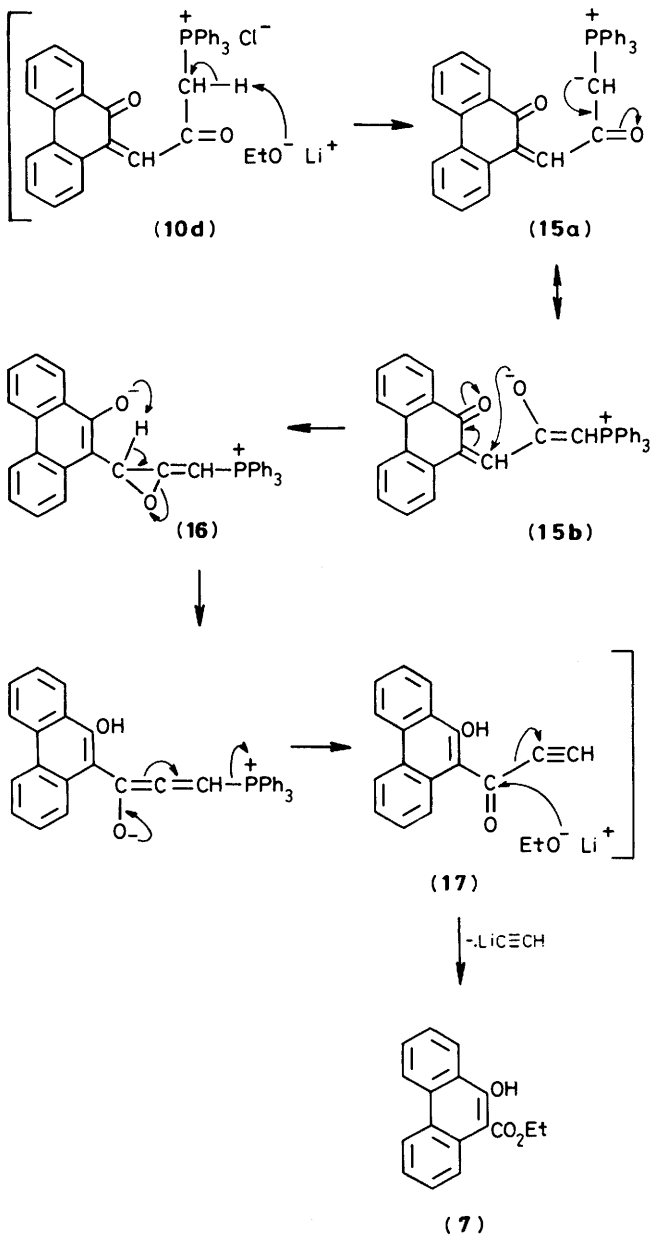
The intermediates (**12**), (**14**), and (**15**) (Schemes 4, 5, and 6) can also be produced through Wittig mono-olefination of (**1**) *via* the preformed bis-ylides from salts (**2b**), (**2c**), and (**2d**) respectively.

When a mixture of equimolar amounts of 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**18**) and phenanthrene-9,10-quinone (**1**) in dry DMF was treated with lithium ethoxide at room temperature under nitrogen, 9,9′-biphenanthryl-10-ol (**22**) was obtained as crystals in 33% yield (Scheme 7). The expected cyclic product from a bis-Wittig olefination was neither isolated nor detected in the reaction mixture.

The proposed structure for compound (**22**) is based primarily on the mass spectral data with supporting evidence coming from i.r., ^{1}H n.m.r., and u.v. spectra, and elemental analysis. The mass spectrum showed a molecular ion at *m/z* 370 (100%), followed by fragmentations to the ions *m/z* 353, 352, 341, 340, 339 by loss of HO$^{\cdot}$, H_2O, $\overset{+}{C}H{=}O$, $CH_2{=}O$ and $CH_2{=}\overset{+}{O}H$ respectively. The presence of the hydroxy group was also

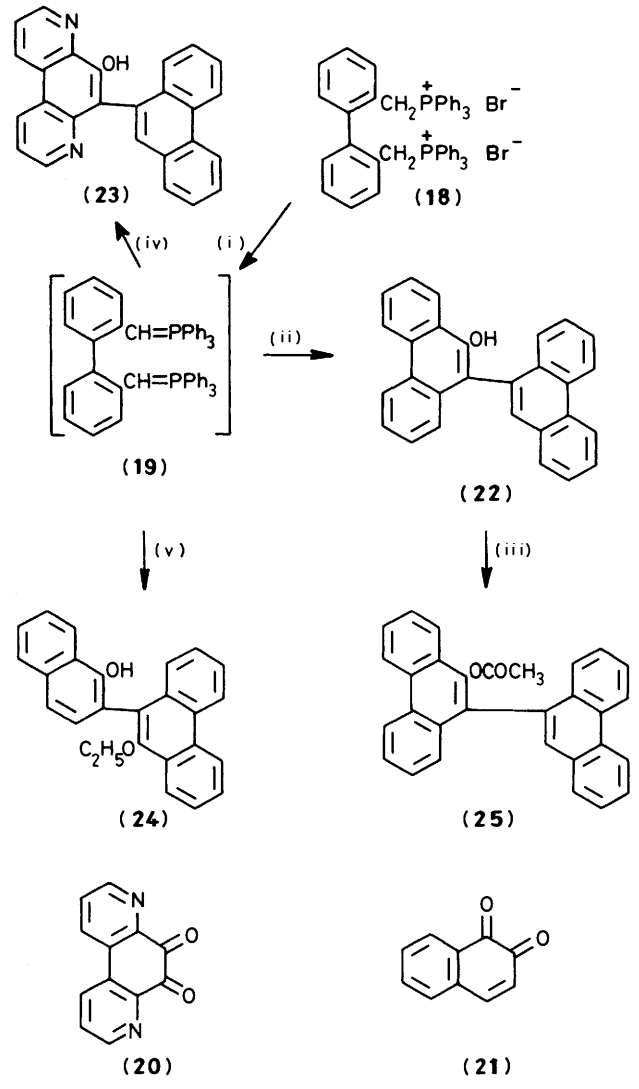


Scheme 5.

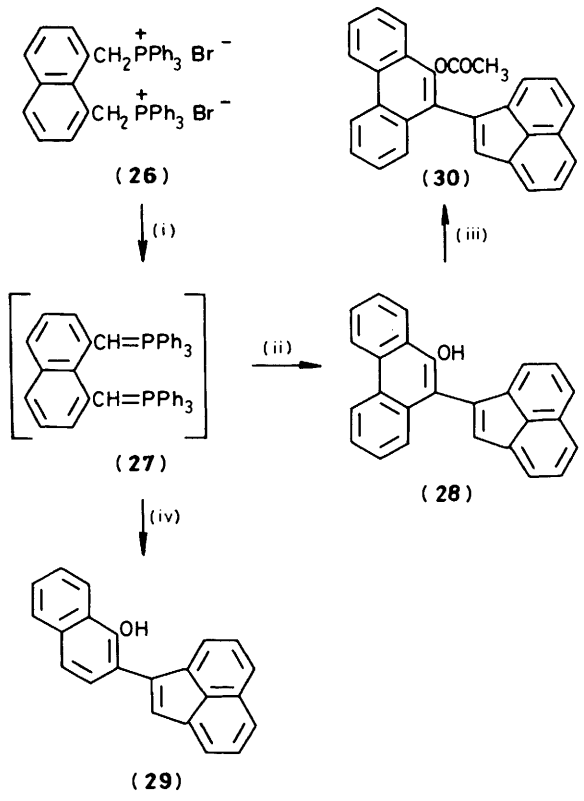


Scheme 6.

confirmed by the i.r. band at 3 524 cm^{-1}. The ^1H n.m.r. spectrum displayed a four-proton multiplet at δ 9.02—8.65 assigned to 4-,4′-,5-, and 5′-H of the biphenanthryl ring system,[9] two sets of multiplets at δ 8.58—8.83 (1 H) and 8.08—7.26 (12 H), as well as a broad singlet at δ 5.46 (1 H) which disappeared on addition of D_2O without any change in the rest of the spectrum. The u.v. spectrum is very similar to that given for phenanthrene-9,10-diol monoacetate.[10] The presence of the hydroxy group was further confirmed by esterification of compound (**22**) with acetic anhydride to give the acetate (**25**) and by conversion of (**22**) into a fused furan derivative (**34**) as described below. The formation of compound (**34**) proves beyond any doubt the existence of this OH group in the 10-position of (**22**).



Scheme 7. *Reagents:* (i) EtOLi, EtOH–DMF, room temp.; (ii) (**1**); (iii) Ac_2O, H_2SO_4; (iv) (**20**); (v) (**21**)

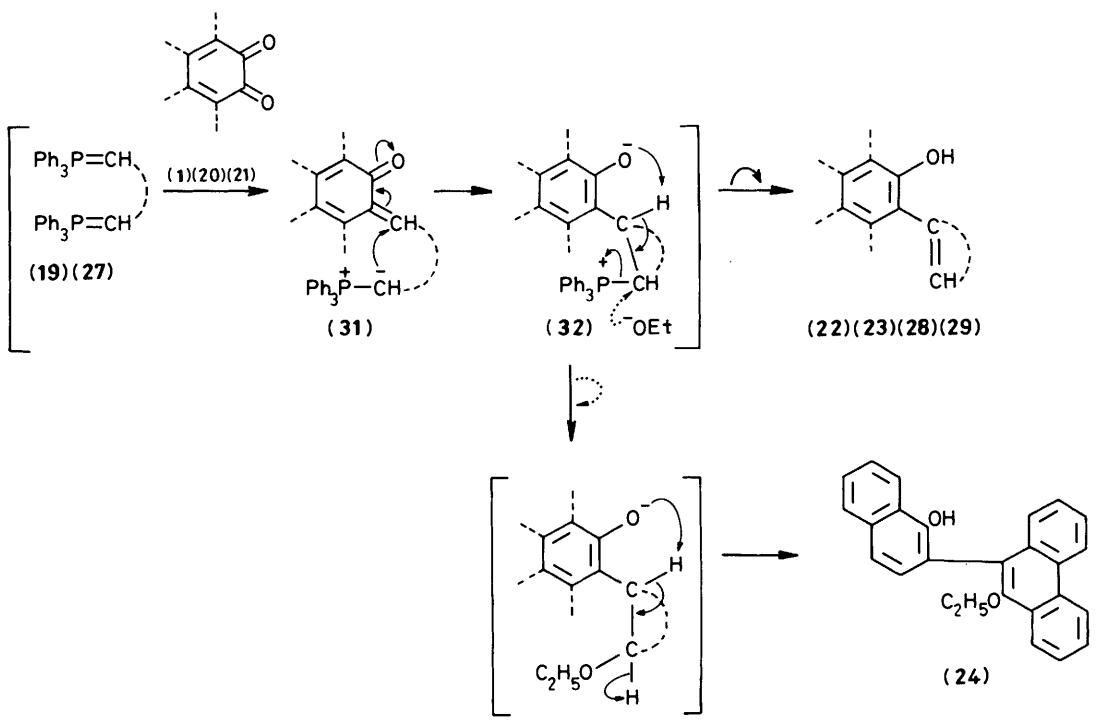


Scheme 8. *Reagents:* (i) EtOLi, EtOH–DMF, room temp.; (ii) (**1**); (iii) Ac_2O, H_2SO_4; (iv) (**21**)

Similarly, the reaction of 4,7-phenanthroline-5,6-dione (**20**) with the salt (**18**) resulted to the preparation of 6-(9-phenanthryl)-4,7-phenanthroline-5-ol (**23**) in 12% yield, consistent with the structural assignments supported by spectral data. In contrast to the above described results, the reaction of 1,2-naphthoquinone (**21**) with the salt (**18**) gave under the same conditions 9-ethoxy-10-(1-hydroxy-2-naphthyl)phenanthrene (**24**) in 8% yield. However, we failed to isolate the corresponding de-ethoxy derivative [9-(1-hydroxy-2-naphthyl)phenanthrene]. It should also be noted that the corresponding ethoxy derivatives of (**22**) and (**23**) were neither isolated nor detected in the previously described reactions. The structure proposed for compound (**24**) was confirmed by its spectral data, which showed the correct molecular ion and the presence of an hydroxy and an ethoxy group, as well as the presence of the phenanthrene ring system.

After the above results we investigated the reactivity of quinones (**1**) and (**21**) with 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide (**26**) under the same reaction conditions. As shown in Scheme 8, both reactions of (**26**) resulted again in the formation of hydroxy derivatives, 10-(acenaphthylen-l-yl)phenanthrene-9-ol (**28**) and 1-(1-hydroxy-2-naphthyl)acenaphthylene (**29**) in 49 and 6% yield respectively (Scheme 8). Compounds (**28**) and (**29**) showed consistent ^1H n.m.r., i.r., u.v., and mass spectra. The observed broad singlet at δ 5.98 in the ^1H n.m.r. spectrum of (**28**), attributed to the hydroxy proton, was removed on addition of deuterium oxide. Treatment of the alcohol (**28**) with acetic anhydride gave the ester (**30**).

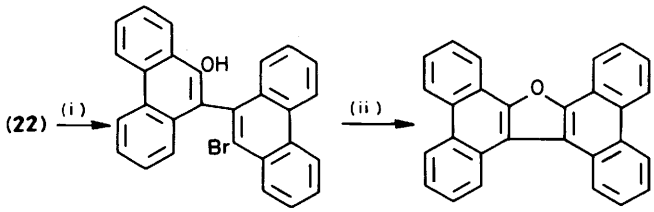
The mechanism in Scheme 9 is proposed to explain the formation of 9-(*o*-hydroxyaryl)phenanthrenes (**22**)—(**24**) and 1-(*o*-hydroxyaryl)acenaphthylenes (**28**) and (**29**) from (**18**) and (**26**) respectively. The bis-ylides (**19**) and (**27**) produced from (**18**) and (**26**) give, *via* Wittig mono-olefination of quinones (**1**), (**20**), and (**21**), an *o*-quinomethane-ylide intermediate (**31**). An intramolecular Michael addition by the carbanion of the ylide group to this quinomethane conjugated system (**31**), instead of a second Wittig reaction, leads to the intermediate (**32**). Finally, intramolecular abstraction of a β-hydrogen by the phenoxy anion and elimination of triphenylphosphine results in the formation of compounds (**22**),



Scheme 9.

(23), (28), and (29). However, in the case of naphthoquinone (21) the ethoxy derivative (24) was formed probably *via* the same intermediate (32) through nucleophilic substitution of triphenylphosphine with an ethoxy group of the base, followed by proton abstraction and hydride elimination. It should be mentioned that this sequence seems less favourable than that leading to products (22), (23), (28), and (29).

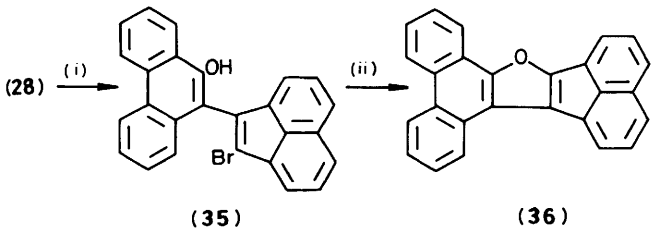
Treatment of compound (22) with bromine in carbon tetrachloride gave 10′-bromo-9,9′-biphenanthryl-10-ol (33) which was dehydrobrominated on being heated with copper(I) oxide in quinoline to provide the known[11] diphenanthro[9,10-*b*:9′,10′-*d*]furan (34) in 39% yield. The proposed structure of compound (33) was established by its spectral data and by its conversion into the furan derivative (34).



(33) (34)

Reagents: (i) Br_2, CCl_4; (ii) Cu_2O, quinoline, 170 °C, 48 h

Similarly, starting from compound (28) we prepared 10-(2-bromoacenaphthylen-1-yl)phenanthrene-9-ol (35) and acenaphtho[1,2-*b*]phenanthro[9,10-*d*]furan (36) in 62 and 38% yield respectively.



(35) (36)

Reagents: (i) Br_2, CCl_4; (ii) Cu_2O, quinoline, 170 °C, 48 h

In conclusion, the title reactions proceed through a Wittig olefination of only one carbonyl group of the *o*-quinone. Generally, it is believed that the tendency for aromatisation of the quinone ring system acts as the driving force in the transformations which follow on from the formation of the initially formed quinomethane intermediate. In addition, the reaction sequences proposed for these transformations may be considered stereochemically more favoured than those for an intermolecular Wittig reaction. The reactions of *o*-quinones with 1,6- and 1,5-bis-phosphonium salts (18) and (26) provide a synthetic route to symmetric or asymmetric *o*-hydroxybiaryls, which by bromination and dehydrobromination can be converted into annelated polycyclic furans.

The title reactions were repeated under the same conditions and gave reproducible results. No efforts to optimize yields were made.

Experimental

M.p.s. are uncorrected and were determined on a Kofler hot-stage apparatus. U.v. spectra were recorded on a Shimadzu UV-210A spectrophotometer for solutions in 95% ethanol. I.r. spectra were obtained with a Perkin-Elmer 297 spectrophotometer using KBr discs. ^1H N.m.r. spectra were recorded with deuteriochloroform or carbon tetrachloride as solvent on a Varian A60-A spectrometer, with tetramethylsilane as internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6L mass spectrometer. The ionisation energy was maintained at 70 eV. Earlier reported procedures were used for the preparation of the phosphonium salts (2a),[12] (2b),[13] (2c),[14] (2d),[15] (18),[16] and (26).[17] Light petroleum refers to the fraction of b.p. 40—60 °C.

Reactions of Phenanthrene-9,10-quinone (1) *with* 1,3-*Bis-phosphonium Salts* (2a—c)*: General Procedure. Preparation of Compounds* (3), (4), (5), *and* (6).—A solution of the quinone (1) (10 mmol) and the corresponding bis-phosphonium salt (2a—c) (10 mmol, dried at 110—120 °C/0.2 mmHg over P_2O_5) in dry DMF (350 ml) was stirred under nitrogen for 3 h at room temperature while a solution of lithium ethoxide (from 0.31 g of lithium) in ethanol (50 ml) was added dropwise. The mixture was stirred for a further 18 h and then poured into a mixture of conc. hydrochloric acid (350 ml) and ice (*ca.* 200 g) and extracted with ether. The extract was washed with water (4 × 200 ml), dried (Na_2SO_4). and concentrated under reduced pressure. The residue was chromatographed on silica gel (300 g) with chloroform as eluant, 25-ml fractions being collected. Products (3), (4), and (6) were eluted from the corresponding reaction mixtures with some triphenylphosphine, in fractions 20—32, and were purified by preparative t.l.c. Compound (5) was eluted after compound (6).

2H-*Phenanthro*[9,10-b]*pyran* (3) was eluted from the column as a mixture with triphenylphosphine and was purified by sublimation *in vacuo* (124 °C/4 mmHg) (0.9 g, 26%), m.p. 111—112 °C (from light petroleum) (Found: C, 88.1; H, 5.2. $C_{17}H_{12}O$ requires C, 87.90; H, 5.21%); $\lambda_{max.}$ (95% EtOH) 230, 273, 278sh, 284sh, 325sh, 338, 352sh, and 370 nm (log ε 4.49, 4.32, 4.26, 4.06, 3.81, 3.90, 3.84, and 3.59); $\nu_{max.}$(KBr) 3 060, 3 030, 2 942, 2 910, 2 840, 1 630, 1 598, 1 570, 1 487, 1 440, 1 380, 1 310, 1 224, 1 156, 1 114, 1 015, 750, 738, 717, and 705 cm^{-1}; δ($CDCl_3$) 8.73—8.20 (3 H, m), 8.08—7.40 (5 H, m), 7.12 (1 H, dt, *J* 10 and 1.5 Hz), 5.90 (1 H, dt, *J* 10 and 3.8 Hz), and 4.93 (2 H, dd, *J* 3.8 and 1.5 Hz); *m/z* 233 (19%), 232 (M^+, 100), 231 (94), 215 (9), 204 (9), 203 (27), 202 (51), 201 (10), 200 (11), 176 (7), and 116 (6).

Phenanthro[9,10-*b*]furan (4) was separated from triphenylphosphine by preparative t.l.c. on silica gel [ether–light petroleum (3:7)] (0.17 g, 8%), m.p. 116—118 °C (from light petroleum (lit.,[18] 118—119 °C); $\lambda_{max.}$ (95% EtOH) 237, 249, 254, 280, 290, 302, 320, 335 and 352 nm (log ε 4.48, 4.72, 4.81, 4.17, 4.02, 4.09, 2.90, 3.08, and 3.11); δ(CCl_4) 8.65—8.42 (2 H, m), 8.30—7.83 (2 H, m), 7.66—7.33 (5 H, m), and 7.03 (1 H, d, *J* 2 Hz); *m/z* 219 (7%), 218 (M^+, 100), 190 (9), 189 (45), 179 (19), 178 (32), 177 (20), 176 (35), and 152 (28).

10-Hydroxyphenanthrene-9-carbaldehyde (5) was crystallised from chloroform–light petroleum (1.29 g, 58%), m.p. 134—135 °C (lit.,[19] 135—136 °C); δ($CDCl_3$) 14.54 (1 H, s), 10.63 (1 H, s), 8.63—8.05 (4 H, m), and 7.92—7.40 (4 H, m); *m/z* 223 (27%), 222 (M^+, 100), 221 (43), 194 (46), 193 (5), 176 (15), 165 (92), 164 (28), and 163 (31).

Phenanthro[9,10-*c*]furan (6) was separated from triphenylphosphine by preparative t.l.c. on silica gel [carbon tetrachloride–light petroleum (1:1)] (43 mg, 2%), m.p. 99—102 °C (from light petroleum) (lit.,[20] 102—103 °C); $\lambda_{max.}$ (95% EtOH) 230sh, 236, 246, 253, 262sh, 281, 291, 303, 317, 331, and 353 nm (log ε 4.40, 4.43, 4.52, 4.55, 4.30, 3.72, 3.68, 3.71, 3.25, 3.30, and 2.70); *m/z* 219 (19%), 218 (M^+, 100), 190 (20), 189 (74), 188 (13), 187 (21), 178 (31), 177 (35), 176 (38), 152 (45), and 151 (23).

Reaction of Phenanthrene-9,10-quinone (1) *with the Salt* (2d)*: Preparation of Ethyl* 10-*Hydroxyphenanthrene-9-carboxylate* (7).—The reaction was carried out according to above described general procedure using compound (1) (10 mmmol), (2d) (10

mmol; dried at 100 °C/0.2 mmHg over P_2O_5), and a slight excess of lithium ethoxide (23 mmol). After being stirred for 18 h at room temperature the reaction mixture was poured into water (400 ml) and then was worked up and separated according to the general procedure. Compound (**7**) was eluted as a mixture with some unchanged quinone (**1**). The mixture was further separated by preparative t.l.c. on silica gel [chloroform–light petroleum (3:2)] to give the ester (**7**) (0.21 g, 8%), m.p. 108—109 °C (from ethanol) (lit.,[21] 109 °C); δ($CDCl_3$) 13.28 (1 H, s), 8.90—8.27 (4 H, m), 7.80—7.32 (4 H, m), 4.58 (2 H, q, *J* 7 Hz), and 1.50 (3 H, t, *J* 7 Hz); *m/z* 267 (9%), 266 (M^+, 45), 237 (2), 222 (3), 221 (23), 220 (100), 193 (2), and 164 (34); $\nu_{max.}$ ($CHCl_3$) 3 500, 3 200, 3 000, 2 910, 2 830, 1 635, 1 580, 1 440, 1 360, 1 320, 1 300, 1 220, 1 180, 1 150, 1 010, 835, and 780 cm^{-1}.

Bromination of Compound (**3**). *Preparation of* 3,4-*Dibromo*-3,4-*dihydro*-2H-*phenanthro*[9,10-b]*pyran* (**8**).—To a solution of compound (**3**) (46 mg, 0.2 mmol) in carbon tetrachloride (6 ml) was added a 10% solution of bromine (0.25 mmol) in carbon tetrachloride (0.4 ml). The mixture was stirred at room temperature for 3 h, the solvent was evaporated off under reduced pressure, and the residue was separated by preparative t.l.c. on silica gel [ether–light petroleum (2:3)] to give compound (**8**) (54 mg, 70%), m.p. 103—104 °C (from chloroform–light petroleum) (Found: C, 52.3; H, 3.2. $C_{17}H_{12}Br_2O$ requires C, 52.04; H, 3.08%); $\nu_{max.}$ (KBr) 3 055, 3 030, 2 940, 2 910, 2 840, 1 598, 1 487, 1 440, 1 380, 1 310, 1 220, 1 160, 1 114, 1 015, 750, 740, 720, and 665 cm^{-1}; δ($CDCl_3$) 8.75—8.32 (3 H, m), 8.20—7.97 (1 H, m), 7.87—7.48 (4 H, m), 5.45—5.33 (1 H, m), 4.72—4.62 (2 H, m), and 4.57—4.42 (1 H, m); *m/z* 394/392 (2%)/390 (M^+), 313/311 (10), 312/310 (16), 233 (13), 232 (82), 231 (100), 230 (9), 203 (24), 202 (15), and 200 (14).

Reactions of the Quinones (**1**), (**20**), and (**21**) *with the Dibromides* (**18**) *and* (**26**): *General Procedure. Preparation of Compounds* (**22**), (**23**), (**24**), (**28**), *and* (**29**).—A solution of 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**18**) or 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide (**26**) (10 mmol; dried at 150 °C/0.1 mmHg over P_2O_5) and the corresponding quinone (**1**), (**20**), or (**21**) (10 mmol) in dry DMF (350 ml) was stirred under nitrogen for 3 h at room temperature, while a solution of lithium ethoxide (from 0.36 g of lithium) in ethanol (50 ml) was added dropwise; the mixture was stirred for a further 15 h and then was poured into a mixture of conc. hydrochloric acid (300 ml) and ice (*ca.* 200 g) [except for reaction of compound (**20**), where only water was used] and extracted with ether. The extract was washed with water (5 × 150 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was then chromatographed on silica gel (300 g) with chloroform as eluant, 25-ml fractions being collected. Products (**22**), (**23**), (**24**), (**28**), (**29**) were always eluted generally in fractions 25—35, after triphenylphosphine and 2,2′-dimethylbiphenyl or 1,8-dimethylnaphthalene, produced from (**18**) or (**26**), respectively, and before the unchanged quinone and triphenylphosphine oxide. The following compounds were prepared in this way.

9,9′-*Biphenanthryl*-10-*ol* (**22**) was recrystallised from chloroform–light petroleum as crystals (1.29 g, 35%), m.p. 218—219 °C (Found: C, 90.5; H, 4.8. $C_{28}H_{18}O$ requires C, 90.78; H, 4.90%); $\nu_{max.}$(Nujol) 3 524, 3 063, 1 620, 1 242, 1 150, 890, 755, and 736 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 276, 284sh, 298, 306sh, 316sh, 340, and 358 nm (log ε 4.47, 4.31, 4.27, 4.03, 3.64, 3.43, and 3.36); δ($CDCl_3$) 9.02—8.33 (5 H, m), 8.08—7.26 (12 H, m), and 5.46 (1 H, s, removed by D_2O, OH); *m/z* 371 (31%), 370 (M^+, 100), 353 (12), 352 (16), 342 (6), 341 (16), 340 (12), 339 (30), 326 (10), and 176 (10).

6-(9-*Phenanthryl*)-4,7-*phenanthrolin*-5-*ol* (**23**) was recrystallised from chloroform–light petroleum as crystals (0.45 g, 12%), m.p. 221—222 °C (Found: C, 83.35; H, 4.5; N, 7.3. $C_{26}H_{16}N_2O$ requires C, 83.85; H, 4.33; N, 7.52%); $\nu_{max.}$(Nujol) 3 310, 3 062, 1 625, 1 580, 1 240, 1 202, 1 155, 920, 780, 770, and 748 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 253, 278, 287, 303sh, 320sh, 350sh, 366sh, and 438 nm (log ε 4.50, 4.52, 4.47, 4.13, 3.89, 3.04, 2.78, and 2.00); δ[$(CD_3)_2SO$] 9.42—8.58 (6 H, m), 8.02—6.90 (9 H, m), and 6.57 (1 H, br s); *m/z* 373 (28%), 372 (M^+, 100), 371 (48), 370 (11), 355 (3), 354 (8), 342 (2), 3.41 (5), and 196 (53).

9-*Ethoxy*-10-(1-*hydroxy*-2-*naphthyl*)*phenanthrene* (**24**) was recrystallised from chloroform–light petroleum as crystals (0.29 g, 8%), m.p. 211—212 °C (Found: C, 85.6; H, 5.4. $C_{26}H_{20}O_2$ requires C, 85.71; H, 5.5%); $\nu_{max.}$ (KBr) 3 500, 3 075, 3 055, 2 975, 2 925, 2 884, 1 617, 1 591, 1 449, 1 388, 1 377, 1 361, 1 268, 1 229, 1 174, 1 117, 758, 738, and 720 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 256, 267sh, 276sh, 287, 298, 330, and 339sh nm (log ε 4.85, 4.43, 4.29, 4.23, 4.24, 3.84, and 3.84); δ($CDCl_3$) 8.80—8.45 (2 H, m), 8.38—7.29 (1 H, m), 7.88—6.93 (11 H, m), 4.95 (1 H, br s), 4.17 (2 H, q, *J* 7 Hz), and 1.55 (3 H, t, *J* 7 Hz); *m/z* 366 (25%), 365 (92), 364 (M^+, 100), 363 (13), 338 (7), 337 (49), 336 (97), 335 (26), 321 (19), 320 (45), 319 (25), 318 (37), 317 (25), 290 (30), 289 (97), 276 (81), and 265 (98).

10-(*Acenaphthylen*-1-*yl*)*phenanthren*-9-*ol* (**28**) was recrystallised from chloroform–light petroleum as crystals (1.61 g, 47%), m.p. 124—125 °C (Found: C, 90.6; H, 4.7. $C_{26}H_{16}O$ requires C, 90.67; H, 4.68%); $\nu_{max.}$ (Nujol) 3 440, 3 060, 1 620, 1 590, 1 205, 1 077, 1 025, 860, 820, 760, and 750 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 256sh, 273sh, 301sh, 311, 323, 338sh, 357, and 408sh nm (log ε 4.62, 4.32, 4.16, 4.03, 4.18, 3.91, 3.60, and 3.26); δ($CDCl_3$) 8.82—8.30 (3 H, m), 7.98—7.12 (12 H, m), and 5.98 (1 H, br s); *m/z* 345 (24%), 344 (M^+, 100), 343 (36), 342 (59), 327 (7), 326 (5), 316 (11), 315 (33), 314 (16), 313 (38), 172 (5), and 163 (8).

1-(1-*Hydroxy*-2-*naphthyl*)*acenaphthylene* (**29**) was recrystallised from chloroform–light petroleum as crystals (0.18 g, 6%), m.p. 132—133 °C (Found: C, 89.9; H, 4.8.$C_{22}H_{14}O$ requires C, 89.77; H, 4.79%); $\nu_{max.}$ (Nujol) 3 500, 3 059, 1 606, 1 578, 1 240, 1 037, 818, 766, and 743 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 258, 268sh, 278sh, 313, 326, 342sh, 354sh, and 421 nm (log ε 4.31, 4.16, 4.02, 4.03, 3.87, 3.67, and 3.38); δ($CDCl_3$) 8.48—8.17 (1 H, m), 7.97—7.12 (12 H, m), and 6.25 (1 H, br s); *m/z* 295 (24%), 294 (M^+, 100), 293 (30), 292 (11), 266 (13), 265 (37), 264 (10), and 263 (23).

Reactions of Compounds (**22**) *and* (**28**) *with Acetic Anhydride: Preparation of Compounds* (**25**) *and* (**30**).—9,9′-*Biphenanthryl*-10-*yl acetate* (**25**). A mixture of the alcohol (**22**) (76 mg, 0.2 mmol), acetic anhydride (1.08 g, 10 mmol), and conc. sulphuric acid (3 drops) was stirred at room temperature for 7 h. The reaction mixture was filtered and the precipitate was washed with water to give the acetate (**25**) (74 mg, 88%), m.p. 226—228 °C (from chloroform–light petroleum) (Found: C, 87.0; H, 4.8. $C_{30}H_{20}O_2$ requires C, 87.35; H, 4.89%); $\nu_{max.}$(KBr) 3 062, 2 927, 2 843, 1 760, 1 602, 1 590, 1 485, 1 444, 1 425, 761, 748, and 724 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 257, 271, 279, 288, 301, 325sh, 333, 342, 349, and 358sh nm (log ε 4.93, 4.55, 4.39, 4.24, 4.27, 3.06, 2.87, 2.74, 2.70, and 2.00); δ($CDCl_3$) 8.96—8.68 (4 H, m), 8.08—7.28 (13 H, m), and 1.86 (3 H, s); *m/z* 413 (6%), 412 (M^+, 17), 372 (5), 371 (30), 370 (100), 369 (22), 368 (8), 353 (10), 352 (13), 341 (30), 340 (25), 339 (61), 337 (20), and 326 (15).

10-(*Acenaphthylen*-1-*yl*)-9-*phenanthryl acetate* (**30**). Similarly, reaction of compound (**28**) (100 mg, 0.3 mmol) with acetic anhydride (1.5 ml, 15 mmol) in the presence of conc. sulphuric acid (5 drops) gave the *acetate* (**30**) (90 mg, 80%), m.p. 138—139 °C (from chloroform–light petroleum) (Found: C, 86.8; H, 4.5. $C_{28}H_{18}O_2$ requires C, 87.02; H, 4.69%; $\nu_{max.}$ (KBr) 3 060, 2 920, 2 845, 1 760, 1 618, 1 593, 1 490, 1 448, 1 424, 1 220, 1 155, 1 030, 1 010, 821, 768, 752, and 721 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 255, 273sh, 302sh, 314, 330, 347sh, 367sh, and 419sh nm (log ε 4.49, 4.13, 3.94, 4.01, 4.03, 3.77, 3.40, and 3.11); δ($CDCl_3$) 8.78—8.47 (2 H, m), 8.32—7.27 (13 H, m), and 1.77 (3 H, s); *m/z* 387 (3%),

386 (M^+, 10), 346 (4), 345 (29), 344 (100), 343 (27), 342 (29), 327 (6), 326 (5), 316 (9), 315 (29), 314 (17), 313 (27), 312 (3), 311 (8), and 223 (3).

Bromination of Compounds (**22**) *and* (**28**)*: Preparation of Compounds* (**33**) and (**35**).—*10′-Bromo-9,9′-biphenanthryl-10-ol* (**33**). To a solution of compound (**22**) (0.25 g, 0.68 mmol) in carbon tetrachloride (30 ml) was added bromine (0.1 ml, 1.95 mmol) and the mixture was stirred under reflux for 6 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with chloroform–light petroleum (1:1) as eluant to give the *bromide* (**33**) (0.165 g, 60%), m.p. 225—227 °C (from chloroform) (Found: C, 74.6; H, 3.7. $C_{28}H_{17}BrO$ requires C, 74.83; H, 3.79%); $\nu_{max.}$(Nujol) 3 484, 3 060, 1 592, 1 209, 1 004, 815, 745, and 673 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 257, 278sh, 287sh, 299, 312sh, 331sh, 348, and 366 nm (log ε 5.08, 4.51, 4.38, 4.36, 4.11, 3.63, 3.52, and 3.50); δ($CDCl_3$) 8.87—8.17 (5 H, m), 8.02—6.87 (11 H, m), and 5.41 (1 H, s); *m/z* 4.51/449 (36%), 450/448 (M^+, 100), 369 (14), 368 (18), 352 (20), 351 (7), 350 (11), 341 (14), 340 (22), 339 (53), 338 (7), 337 (19), and 176 (14).

10-(2-Bromoacenaphthylen-1-yl)phenanthrene-9-ol (**35**). To a solution of compound (**28**) (0.105 g, 0.3 mmol) in carbon tetrachloride (10 ml) was added a solution of bromine (0.09 g, 1.12 mmol) in carbon tetrachloride (10 ml) and the mixture was stirred at room temperature for 3 h. The solvent was evaporated off under reduced pressure and the residue was recrystallised from ether–light petroleum to give the *bromide* (**35**) (0.08 g, 62%), m.p. 92—93 °C (from ether–light petroleum) (Found: C, 73.45; H, 3.6. $C_{26}H_{15}BrO$ requires C, 73.75; H, 3.54%); $\nu_{max.}$ (Nujol) 3 300, 3 060, 1 590, 1 215, 1 035, 768, 748, and 653 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 260sh, 276, 302sh, 313, 327, 342sh, 349sh, 356sh, 379sh, and 428sh nm (log ε 4.62, 4.29, 4.13, 4.22, 4.18, 3.92, 3.83, 3.62, 3.43, and 3.11); δ($CDCl_3$) 8.78—8.27 (3 H, m), 8.00—7.10 (11 H, m), and 5.68 (1 H, s); *m/z* 425/423 (3%), 424/422 (M^+, 12), 344 (35), 343 (100), 342 (42), 315 (31), 314 (21), 313 (49), 312 (8), and 311 (16).

Bromination of compound (**28**) under reflux gave, besides compound (**35**), other products with more than one bromo substituent.

Dehydrobromination of Compounds (**33**) *and* (**35**)*: Preparation of Compounds* (**34**) *and* (**36**).—*Diphenanthro*[9,10-b:9′,10′-d]*furan* (**34**). A mixture of compound (**33**) (50 mg, 0.11 mmol) and copper(I) oxide (16 mg, 0.11 mmol) in dry quinoline (1.5 ml) was stirred at 170 °C for 48 h. The reaction mixture was neutralised with dil. hydrochloric acid and then extracted with chloroform (2 × 25 ml). The extract was dried (Na_2SO_4), the solvent was removed, and the residue was chromatographed on silica gel with chloroform as eluant. A mixture of the pentacycle (**34**) and some unchanged (**33**) was collected which was further separated by preparative t.l.c. on silica gel, with chloroform–light petroleum (4:6) as developer. The faster moving band gave the pentacycle (**34**) (16 mg, 39%), m.p. 308—310 °C (from chloroform–light petroleum) (lit.,[11] 310 °C); $\nu_{max.}$ (Nujol) 3 077, 3 060, 1 590, 1 490, 1 225, 1 210, 1 110, 1 010, and 745 cm^{-1}; $\lambda_{max.}$($CHCl_3$) 266sh, 277sh, 298, 313sh, 337sh, 355sh, 372sh, 384sh, and 403sh nm (log ε 4.44, 4.33, 4.09, 3.99, 3.74, 3.58, 3.41, 3.26, and 3.08); δ($CDCl_3$) 9.04—8.52 (8 H, m) and 8.02—7.50 (8 H, m); *m/z* 369 (22%), 368 (M^+, 100), 367 (71), 366 (75), 340 (24), 339 (63), 338 (32), 337 (91), 311 (22), 184 (33), 170 (36), and 169 (40).

Acenaphtho[1,2-b]*phenanthro*[9,10-d]*furan* (**36**). Similarly, treatment of compound (**35**) (36 mg, 0.085 mmol) with copper(I) oxide (13.5 mg, 0.085 mmol) in quinoline (0.5 ml) gave the *pentacycle* (**36**) (11 mg, 39%), m.p. 313—315 °C (from chloroform) (Found: C, 90.75; H, 4.0. $C_{26}H_{14}O$ requires C, 91.22; H, 4.09%); $\lambda_{max.}$($CHCl_3$) 256, 267sh, 276sh, 317sh, 327, 353sh, 373, and 442 nm (log ε 4.08, 3.98, 3.90, 3.88, 3.91, 3.26, 3.04, and 2.79); $\nu_{max.}$(KBr) 3 050, 1 610, 1 490, 1 201, 1 033, 762, and 748 cm^{-1} *m/z* 343 (34%), 342 (M^+, 100), 313 (36), 312 (6), 311 (15), 310 (5), 285 (9), 283 (25), 282 (24), 281 (29), 280 (31), 279 (10), 256 (45), 255 (11), 254 (65), 247 (10), 246 (11), 245 (15), 220 (26), and 202 (36).

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