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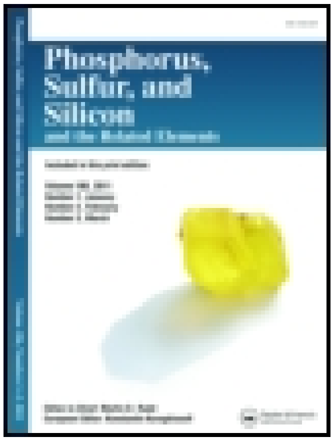

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Thiones as Reactive Intermediates in Condensations of Diketones with Aromatics Mediated by Tetraphosphorus Decasulfide

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THIONES AS REACTIVE INTERMEDIATES IN CONDENSATIONS OF DIKETONES WITH AROMATICS MEDIATED BY TETRAPHOSPHORUS DECASULFIDE

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Phenanthrene-9,10-quinone and P_4S_{10} react with phenols on being heated to give oxathiins, e.g., ***9*** *the dioxin* ***22****, ethers, e.g.,* ***14*** *arylphenanthrenols, e.g.,* ***10*** *and furanols, e.g.,* ***17*** *in addition to sulfides, e.g.,* ***26*** *and disulfides, e.g.,* ***25****. Under similar conditions benzil gives thiophene derivatives, e.g.,* ***2****. Most of the reactions appear to proceed via thione intermediates but some of the products are also formed when P_4S_{10} is absent.*

Keywords: Diketones; furans; tetraphosphorus decasulfide; thiones; thiophenes

INTRODUCTION

Condensations of diketones with aromatics have provided several types of polycarbocyclic compounds.[1,2] With the object of preparing polycyclics containing thiophene rings, we have investigated reactions between aromatic 1,2-diketones and phenols in the presence of tetraphosphorus decasulfide, P_4S_{10}.

RESULTS AND DISCUSSION

The reaction between benzil, P_4S_{10} and either phenol or catechol at 170°C gave 2-phenylbenzothiophene **1** (14.7%) and tetraphenylthiophene **2** (24.8%). The phenols took no part in the reaction and when omitted the same products were obtained together with a small amount (3.9%) of the thienothiophene **3**. A similar reaction between thenil,[3]

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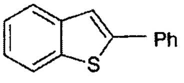
phenol, and P_4S_{10} gave a little (1.8%) of the thienothiophene **4** the UV absorption of which resembled that[4] of the parent thienothiophene **5**. Intramolecular cyclisation again occurred and the phenol was not incorporated into the product.

To encourage intermolecular reaction we replaced benzil by phenanthrene-9,10-quinone in which the carbonyl groups are part of a rigid structure and have a *cis* orientation. The quinone reacted with phenol and P_4S_{10} at 160°C to give the oxathiin **7** (10.6%) (where 'A' represents the partial formula **6**), the ether **14** (16.1%), and the diol **10** (21.5%). The UV absorption shown by the diol **10** and by the other arylphenanthrenols **11–13** produced in related reactions closely resembles that[5] of phenanthren-9-ol and indicates the nature of the major aromatic system present. As with all the other phenanthrene derivatives described here, only a partial interpretation of the NMR signals for the aromatic protons of these compounds is possible. Some of the low-field signals can be assigned to the "bay" protons[6] at C-4 and C-5, and to those[7] at C-1 and C-8 if heteroatom substituents are present in the *peri* positions as in the oxathiin **7**. In the diol **10** the aryl protons of the hydroxyphenyl group appear as a deceptively simple AA′XX′ system and so establish that the hydroxy group is at C-4′. Of the two hydroxy proton signals at δ 5.50 and 8.50, the former can be assigned to the hydroxy group is at C-9 which is shielded by the ring current of the C-10 aryl substituent. The hydroxy protons of the simple analogue biphenyl-2,2′-diol give a signal[8] at δ 5.65. In the diacetate of **10** the protons of the C-9 acetoxy group are shielded in a similar manner, the signal at δ 2.10 being close to that[9] shown by 2-acetoxybiphenyl at δ 2.08.

The reaction of catechol with phenanthrenequinone and P_4S_{10} gave two products, the dioxin **22** (18.6%) and the furanol **17** (38.7%). The NMR spectrum of the former shows a highly symmetrical AA′XX′ multiplet for the four aryl protons of the *o*-phenylenedioxy group so confirming the symmetrical structure of the molecule. The UV absorption of the acetate of the furanol **17** resembles closely that[10] of the unsubstituted furan **16** and indicates the nature of the polycyclic aromatic system present. The other acetates derived from the related furanols **18–21** show similar UV spectra. The NMR spectrum of the furanol **17** shows the expected three-proton AMX system for the protons at C-11, -12, and -13; the signal at lowest field (δ 7.97) results from the proton at C-13 which is close to C-1 and is further deshielded by the ring current in the phenanthrene system.

Phenanthrenequinone also reacted with catechol at 160°C in the absence of P_4S_{10} to give the dioxin **22** and the furanol **17**, both in much lower yield, and the triol **11** (15.9%). The structure of the last-named in which arylation has occurred *ortho* to an hydroxy group rather than *para* follows from its NMR and mass spectra. Thus the aryl protons of the dihydroxyphenyl group show signals typical of an AMX system, the coupling constants resembling those found for the corresponding protons in the furanol **17**. The presence of hydroxy groups at C-9 and -2′ explains the ready loss of water from the molecular ion to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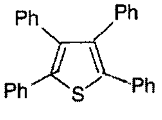
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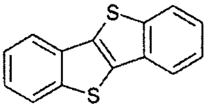
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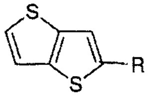
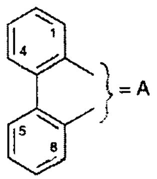

4. R = 2-thienyl
5. R = H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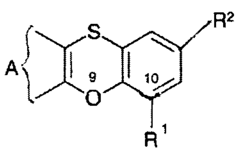
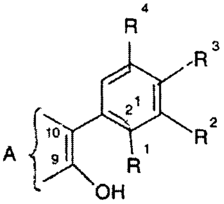
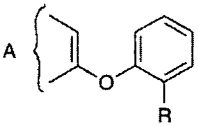
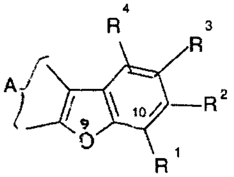
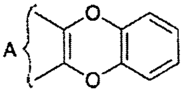

7. $R^1 = R^2 = H$
8. $R^1 = H$; $R^2 = OAc$
9. $R^1 = OH$; $R^2 = H$


10. $R^3 = OH$; $R^1 = R^2 = R^4 = H$
11. $R^1 = R^2 = OH$; $R^3 = R^4 = H$
12. $R^1 = R^3 = OH$; $R^2 = R^4 = H$
13. $R^1 = R^4 = OH$; $R^2 = R^3 = H$


14. R = H
15. R = OH


16. $R^1 = R^2 = R^3 = R^4 = H$
17. $R^1 = OH$; $R^2 = R^3 = R^4 = H$
18. $R^2 = OH$; $R^1 = R^3 = R^4 = H$
19. $R^3 = OH$; $R^1 = R^2 = R^4 = H$
20. $R^1 = R^2 = OH$; $R^3 = R^4 = H$
21. $R^2 = R^4 = OH$; $R^1 = R^3 = H$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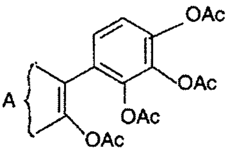
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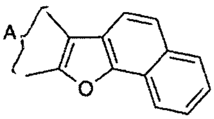
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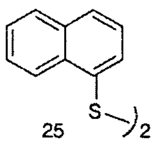
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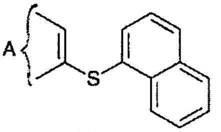
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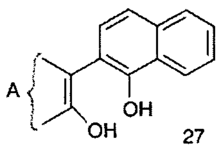
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produce a polycyclic furan ion-radical the subsequent fragmentation of which resembles that of the molecular ion derived from the furanol **17**. The NMR spectrum of the triacetate derived from the triol **11** shows proton signals at δ 1.82, 2.17, and 2.31 the first two of which we assign to the protons of the acetoxy groups at C-9 and C-2′, respectively, both of which are shielded by the adjoining aromatic rings.

The reaction of resorcinol with phenanthrenequinone in the presence of P_4S_{10} gave the expected products, the furanol **18** (58.0%) and the triol **12** (9.0%). When the reaction was repeated with the omission of the P_4S_{10} the same products were obtained but in significantly different yields (5.0% and 27.0% respectively). Hydroquinone behaved in a similar fashion giving the furanol **19** (30.8%), the triol **13** (9.6%), and a little of an oxathiinol which we isolated as the acetate **8** which shows UV absorption resembling that of the unsubstituted oxathiin **7**.

Phloroglucinol reacted with phenanthrenequinone and P_4S_{10} at 220°C to produce the furandiol **21** (11.4%) which gives an aromatic proton NMR signal at unusually low field (ca. δ 9.87). We assign this to H-1 which is strongly deshielded[11] by the nearby hydroxy group at C-13. The deshielding of the C-13 acetoxy protons of the corresponding diacetate is likewise a consequence of the proximity of the phenanthrene ring system. Several products resulted from the reactions between pyrogallol and phenanthrenequinone. With P_4S_{10} at 160°C we obtained the *mono* hydroxy furans **17** (7.5%) and **18** (12.5%) which we had previously prepared from catechol and resorcinol. When the P_4S_{10} was omitted the products were the expected furandiol **20** (12.4%) and the corresponding uncyclised tetraol which we isolated as the tetra-acetate **23** (13.6%) because it rapidly underwent aerial oxidation.

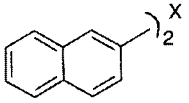
The products from the reactions of naphthols with phenanthrenequinone and P_4S_{10} proved to be more diverse. 1-Naphthol gave the naphthofuran **24** (74.8%), the disulfide **25** (11.0%), and the naphthylthiophenanthrene **26** (2.2%). The UV absorption of the naphthofuran shows a marked resemblance to that of its benzenoid analogue **16**. The NMR spectrum of the monosulfide **26** shows a two-proton multiplet centered at δ 8.43 which we assign to the *peri* protons at C-8 and -8′. In the absence of P_4S_{10} 1-naphthol reacted with phenanthrenequinone to give the expected products, the naphthofuran **24** (6.9%) and the corresponding diol **27** (47.2%). The NMR signals for the shielded hydroxy protons of the latter appear at δ 5.43 and 5.58 while the mass spectrum shows the characteristic ready loss of water from the molecular ion. 2-Naphthol behaved in a completely different fashion. It failed to react when heated with phenanthrenequinone alone and in the presence of P_4S_{10} gave the ether **28** (7.9%) and small amounts of the sulfide **29**, the disulfides **30** and **31**, and the naphthylthionaphthol **32**. There was no evidence of any phenanthrene-naphthalene bond formation.

Lawesson's reagent,[12] the dimer of *p*-methoxyphenylthionophosphinesulfide, resembles P_4S_{10} in its abiliity to convert ketones into thiones, and we briefly examined its effect on reactions between phenanthrenequinone and various phenols at 160°C. Phenol itself produced no recognisable products but catechol gave the dioxin **22** (3.5%), the disulfide **31** (12.9%), the furanol **17** (14.4%), the oxathiinol **9** (4.1%), and the hydroxyether **15** (8.4%). The oxathiinol and the hydroxyether show UV absorption resembling that of the parent compounds **7** and **14** respectively. Similar reactions with resorcinol and with hydroquinone gave the furanols **18** (45.7%) and **19** (56.5%).

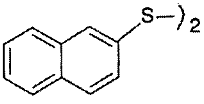
We also examined the reactions of P_4S_{10} with other cyclic dicarbonyl compounds. Acenaphthenequinone gave a little of the thiophene **33** while *o*-chloranil afforded a compound $C_{12}HCl_7OS$ (3.3%) which we formulate as the hydroxydibenzothiophene **34**, and which is presumably derived from the corresponding octa-chloro compound **35**. Calculations based on the dimensions of dibenzothiophene[13] show that the chlorine atoms at C-4 and -5 in **35** overlap considerably. Replacement of one of these by the less bulky hydroxy group at some point in the reaction procedure would be facilitated as this would reduce the distortion present in the molecule.

The plethora of products obtained together with the wide range of yields suggest that more than one reaction mechanism is involved. The sulfur-containing compounds clearly result from the mono- and dithiones formed[14] from the reactants and P_4S_{10}. Now the thione group can behave[15] as a dipolar system $[R_2\overset{+}{C}\text{-}\overset{-}{S} \leftrightarrow R_2\overset{-}{C}\text{-}\overset{+}{S}]$ or as a diradical $R_2\dot{C}\text{-}\dot{S}$ and mechanisms involving such entities can account for all the products obtained in the present work. Thus the dithione formed from benzil may be represented as the diradical **36**; double ring-closure and subsequent dehydrogenation by sulfur would give the thienothiophene **3**. The formation of many of the other products involves a reduction step which appears to be the extrusion of sulfur from the molecule. For example monocyclization of the diradical **36** and thiiran formation gives the diradical **37** which by hydrogen atom migration and loss of sulfur from the thiiran group,[16] gives the thiophene **1**. The thienothiophene **4** can be derived in a similar manner from thenil. Dimerisation of the diradical **36** would lead to the tricyclic structure **38** which would lose sulfur from both the thiiran and dithietan[17] rings giving the thiophene **2**. The thiophenes **33** and **35** would be formed in a similar manner.

The 2-naphthyl sulfides and disulfides appear to result from the thione **39** corresponding to the keto tautomer[18] of 2-naphthol. "Polar" dimerization of this and subsequent elimination of hydrogen sulfide would give the sulfide **29** while reaction with 2-naphthol and loss of hydrogen sulfide would lead to the ether **28**. "Radical" dimerization of the thione followed by dehydrogenation by sulfur would provide the disulfide **30** while a comparable radical substitution reaction between the thione and 2-naphthol would lead to the hydroxysulfide **32**. The disulfide **31** presumably results from a radical dimerization of the dithione formed from phenanthrenequinone which leads to a diradical such as



28. X = O
29. X = S



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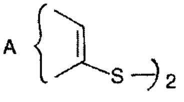

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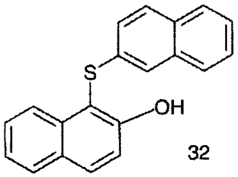

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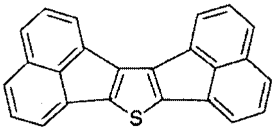

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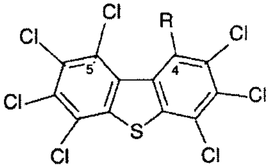
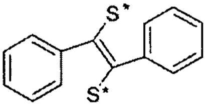


34. R = OH
35. R = Cl



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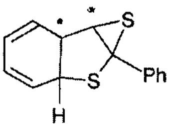

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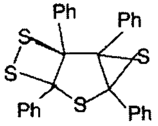

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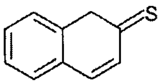

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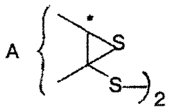

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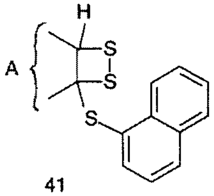

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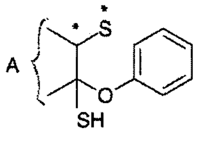

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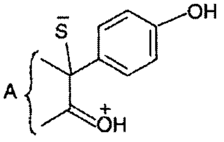

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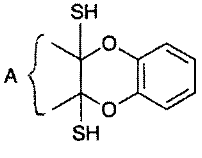

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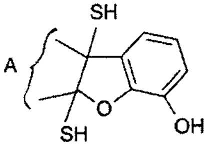
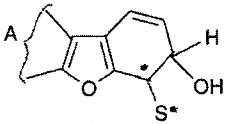
40. Abstraction of hydrogen from the phenol present in the reaction followed by extrusion of sulfur then occurs. In its reaction with phenanthrenequinone and P_4S_{10} 1-naphthol resembled its 2-isomer in giving the disulfide **25** but it also afforded the mixed sulfide **26**. We suggest that in the latter case the thione produced from the keto tautomer of 1-naphthol adds by a radical process to the dithione derived from phenanthrenequinone to give, after hydrogen atom migration, the dithietan **41** which finally loses two atoms of sulfur.

The formation of the oxathiin **7** could proceed via the adduct **42** which would then undergo successive cyclization, hydrogen atom migration, and loss of hydrogen sulfide. Hydrogen atom migration from sulfur to carbon in the diradical **42** and subsequent loss of sulfur from the resulting dithietan would give the ether **14**. The formation of the carbon-carbon bond in the phenanthrenediol **10** suggests that the phenol present undergoes electrophilic attack by the monothione to give the dipolar species **43** which after cyclization to a hydroxythiiran and loss of sulfur provides the diol. Although the ether **14** and the diol **10** do not contain sulfur their formation nevertheless requires the presence of P_4S_{10} (and consequently the production of the intermediate thiones) because phenol and phenanthrenequinone failed to react when heated together. The dioxin **22** appears to result from nucleophilic addition of both hydroxy groups of catechol to the dithione followed by elimination of hydrogen sulfide and sulfur from the intermediate dithiol **44**. A similar addition involving only one of the hydroxy groups and subsequent cyclization would provide the isomeric dithiol **45**, which would fragment in a similar manner to give the furanol **17**. The formation of the products from the other phenols can be explained by similar reaction sequences. The unexpected monohydric furanols **17** and **18** obtained from pyrogallol must result from the thiones derived from the keto tautomers of the furandiol **20**. For example the thione **46** could undergo hydrogen migration and thiiran formation followed by extrusion of sulfur to give the furanol **18**.

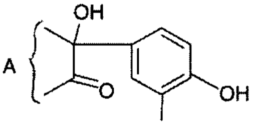
When P_4S_{10} was omitted the combined yields of all the products from the reactions of catechol and of resorcinol with phenanthrenequinone were considerably lower than when P_4S_{10} was present. Presumably the formation of the triol **11** now occurred via the intermediate hydroxyketone **47** which then underwent reduction by the excess of catechol present followed by dehydration. We associate the relatively high yield of the triol **13** with its being derived from hydroquinone which is a particularly good reducing agent. Similar conventional mechanisms each involving a reduction step can be devised for the formation of the furanols obtained under comparable conditions.



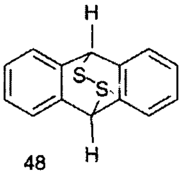
45



46



47



48

The efficient conversion of anthraquinone into anthracene (76.9%) by treatment with P_4S_{10} in the presence of phenol appears to occur via the corresponding dithione. This would abstract hydrogen atoms from the phenol forming the dithietan **48** which would then lose sulfur.

EXPERIMENTAL

IR spectra were recorded for KBr discs and UV absorption spectra for methanolic solutions (except where indicated); ε values are given in units of $dm^3mol^{-1}cm^{-1}$ and infl denotes an inflexion. ^1H NMR spectra were measured at 220 MHz for solutions in deuterochloroform (unless otherwise stated) with tetramethylsilane as internal standard. Mass spectra were obtained using electron impact at 70 eV. TLC and PLC were performed using Merck Kieselgel GF_{254}. "Light petroleum" refers to the fraction b.p. 60–80°C. The yields of products are based on the initial weights of the dicarbonyl compounds (or, where appropriate, of the naphthols) used and were not optimalized.

Reaction of Benzil with P_4S_{10} to Give 1, 2, and 3

(a) A mixture of benzil (5 g, 23.81 mmol), phenol (5 g, 53.19 mmol), and P_4S_{10} (Aldrich, 5 g, 11.26 mmol) was heated under nitrogen at 170°C with stirring for 2 h and poured into water. Extraction with chloroform afforded a solid which on being subjected to PLC using light petroleum gave two bands. The faster-moving of these afforded 2-phenylbenzothiophene **1** (734 mg, 3.50 mmol, 14.7%), m.p. 173–174°C (lit.,[19] 175–176°C) which crystallized from light petroleum (Found: M^+, 210.0495. Calc. for $C_{14}H_{10}S$: *M*, 210.0502); *m/z* 210 (100%, M^+), 178 (5, M-S), 165 (10, M-CHS), and 105 (5, M^{2+}); λ_{max} (Et_2O)/nm 234 (log ε

4.31), 256 (4.11), 260infl (4.10), 301 (4.37), and 318infl (4.14); ν_{max}/cm^{-1} 758 and 688 (5 adjacent ArH) and 745 (4 adjacent ArH); δ_H 7.1–8.0 (m, ArH). The slower-moving band afforded tetraphenylthiophene **2** (1.143 g, 2.95 mmol, 24.8%) m.p. 183–184°C (lit.,[20] 184–185°C) from light petroleum. (Found: M$^+$, 388.1289. Calc. for $C_{28}H_{20}S$: *M*, 388.1286); *m*/*z* 388 (100%, M$^+$), 354 (10, M-H_2S), 310 (3, M-C_6H_6), and 278 (2, 310-S); λ_{max} (Et_2O)/nm 248 (log ε 4.43), and 313 (4.22); ν_{max}/cm^{-1} 760, 750, 708, and 696 (5 adjacent ArH); δ_H 7.0–7.4 (m, ArH).

(b) A similar reaction between benzil and P_4S_{10} alone gave three products after PLC. The fastest-moving component crystallized from light petroleum to give benzthieno[3,2-*b*]benzothiophene **3** (220 mg, 0.92 mmol, 3.9%) m.p. 210–212°C (lit.,[21] 215–216°) (Found: M$^+$, 240.0062. Calc. for $C_{14}H_8S_2$: *M*, 240.0066); *m*/*z* 240 (100%, M$^+$), 208 (5, M-S), 195 (3, M-CHS), and 120 (5, M^{2+}); λ_{max} (Et_2O)/nm 240 (log ε 4.19), 256 (4.17), 264 (4.21), 296infl (4.18), 306 (4.22), 316infl (4.07), and 330 (3.87); ν_{max}/cm^{-1} 742 (4 adjacent ArH), δ_H 7.25–7.58 and 7.65–7.97 (both 4H, m, ArH). The other products were the phenylthiophenes **1** (572 mg, 2.72 mmol, 11.5%) and **2** (1.035 g, 2.67 mmol, 22.4%).

Reaction of 2,2′-Thenil with P_4S_{10} to Give 4

The product from a similar reaction between 2,2′-thenil[3] (2 g, 9.01 mmol), phenol (4 g, 42.55 mmol), and P_4S_{10} (2 g, 4.50 mmol) at 160°C was dissolved in chloroform and washed with aqueous sodium hydroxide. The alkali-insoluble material on being subjected to PLC using light petroleum gave 2-(2′-thienyl)thieno[3,2-b]thiophene **4** (35 mg, 0.16 mmol, 1.8%), m.p. 96–98°C (from light petroleum). (Found: M$^+$, 221.9631. $C_{10}H_6S_3$ requires *M*, 221.9631); *m*/*z* 222 (100%, M$^+$), 190 (28, M-S), 177 (52, M-CHS), 164 (10, M-C_2H_2S), and 145 (17, 177-S); λ_{max}/nm 253 (log ε 3.82), 306infl (3.96), 327 (4.07) and 343infl (3.90); ν_{max}/cm^{-1} 1610 aromatic C=C), 805 and 695 (3 and 2 adjacent ArH); δ_H 7.00–7.06 (1H, m, ArH) and 7.19–7.37 (5H, m, ArH).

REACTIONS OF PHENANTHRENEQUINONE AND P_4S_{10} WITH PHENOLS

P_4S_{10} (1 g, 2.25 mmol) was added to a stirred mixture of phenanthrenequinone (1 g, 4.81 mmol) and the phenol (4 g) at 160°C under nitrogen. After being heated at 160°C for 2 h the mixture was poured into water, extracted with chloroform, and the chloroform layer was washed with aqueous sodium hydroxide. Acidification of the latter afforded the phenolic components. Both the neutral and the phenolic fractions were separated by PLC (which also removed sulfur) using light petroleum and chloroform respectively, and the components were purified by crystallization.

1. With Phenol (42.55 mmol) to Give 7, 10, and 14

The neutral fraction gave rise to two bands, the faster-moving component crystallizing from chloroform-light petroleum to give benzo[b]phenanthro[9,10-e]oxathiin **7** as plates (153 mg, 0.51 mmol, 10.6%) m.p. 167–168.5°C (Found: M^+, 300.0607. $C_{20}H_{12}OS$ requires *M*, 300.0608); *m/z* 300 (71%, M^+), 271 (10, M-CHO), 268 (100, M-S), 239 (29, 268-CHO), 150 (10, M^{2+}), 134 (17, 268^{2+}), and 119.5 (15, 239^{2+}); λ_{max}/nm 248 (log ε 4.71), 264infl (4.71), 293infl (3.92), 309 (3.88), 321 (3.90), 341 (3.49), 348infl (3.42), and 354 (3.40); ν_{max}/cm^{-1} 1628 and 1604 (aromatic C=C), 760 and 745 (4 adjacent ArH); δ_H 7.00–7.25 (2H, m, ArH), 7.38–7.78 (5H, m, ArH), 7.92–8.02 (1H, m, ArH), and 8.27–8.75 (4H, m, 1-, 4-, 5-, and 8-H). The slower-moving component crystallized from benzene-ethanol to give 9-phenoxyphenanthrene **14** (209 mg, 0.78 mmol, 16.1%) as needles m.p. and mixture m.p. with an authentic specimen 79–80°C (lit,[22] 80–81°) (Found: M^+, 270.1047. Calc. for $C_{20}H_{14}O$: *M*, 270.1044); *m/z* 270 (100%, M^+), 241 (18, M-CHO), 176 (11, M-PhOH), and 165 (14, M-PhCO); λ_{max}/nm 247infl (log ε 4.66), 253 (4.68), 273infl (4.15), 287 (3.91), 298 (3.92), 335 (2.97), and 352 (3.00); ν_{max}/cm^{-1} 1630, 1594, 1588 (aromatic C=C), 768, 727, and 692 (5 adjacent ArH), and 752 (4 adjacent ArH); δ_H 7.04–7.23 (4H, m, ArH), 7.28–7.42 (2H, m, ArH), 7.45–7.77 (5H, m, ArH), 8.27–8.38 (1H, m, 8-H) and 8.55–8.73 (2H, m, 4- and 5-H).

The alkali-soluble fraction afforded a solid which crystallized from chloroform-light petroleum to give 10-phenylphenanthrene-4′,9-diol **10** (296 mg, 1.03 mmol, 21.5%) m.p. 165–167°C (Found: M^+, 286.0995. $C_{20}H_{14}O_2$ requires: *M*, 286.0993); *m/z* 286 (100%, M^+), 257 (8, M-CHO), 218 (36, M-C_4H_4O), 126 (16, 218-C_6H_4O), and 94 (12, C_6H_6O); λ_{max}/nm 251 (log ε 4.51), 274infl (4.16), 300infl (3,86), 343 (3.17), and 361 (3.11); ν_{max}/cm^{-1} 3400 (phenolic OH), 1595 (aromatic C=C), 830 (2 adjacent ArH) and 760 (4 adjacent ArH); δ_H 5.50 (1H, brs, 9-OH), 6.61, 6.66, 6.97, and 7.02 (each 1H, s, AA′XX′, 3′-, 5′-, and 2′-, 6′-H), 7.33–7.56 (3H, m, ArH), 7.61–7.85 (3H, m, ArH), 8.03–8.15 (2H, m, 4- and 5-H), and 8.50 (1H, brs, 4′-OH). The diacetate m.p. 128–130°C crystallized from chloroform-light petroleum [Found: (M^+-CH_2CO), 328.1102. $C_{22}H_{16}O_3$ requires: *M*, 328.1099]; *m/z* 370 (1%, M^+), 328 (68, M-CH_2CO), 286 (100, 328-CH_2CO), 257 (32, 286-CHO), 239 (11, 257-H_2O), and 218 (20, 286-C_4H_4O); λ_{max}/nm 241infl (log ε 4.93), 259infl (4.44), 268infl (4.37) and 335 (3.73); ν_{max}/cm^{-1} 1755 and 1720 (aryl acetate CO), 1608 (aromatic C=C), 825 (2 adjacent ArH), and 747 (4 adjacent ArH); δ_H 2.10 and

2.35 (each 3H, s, 9- and 4′-$MeCO_2Ar$), 6.92–7.98 (10 H, m, ArH), and 8.65–8.90 (2H, m, 4- and 5-H).

2. With Catechol (36.36 mmol) to Give 11, 17, and 22

The neutral fraction, after further PLC using light petroleum-chloroform, crystallized from the same solvent to give benzo[b]-phenanthro[9,10-e]dioxin **22** as needles (254 mg, 0.89 mmol, 18.6%) m.p. 212–214°C (Found: M^+, 284.0837. $C_{20}H_{12}O_2$ requires *M*, 284.0837); *m/z* 284 (100%, M^+), 255 (45, M-CHO), 226 (15, M-2CHO), 202 (4, M-$C_4H_2O_2$), 142 (18, M^{2+}), 113 (14, 226^{2+}), and 101 (8, 202^{2+}); λ_{max}/nm 236infl (log ε 4.54), 243 (4.58), 256infl (4.22), 265infl (4.13), 335 (3.52), and 371infl (3.10); ν_{max}/cm^{-1} 1597 (aromatic C=C), and 751 (4 adjacent ArH); δ_H 6.81–7.10 (4H, AA′XX′m, 10-, 11-, 12-, and 13-H), 7.15–7.70 (4H, m, ArH), 8.12–8.25 (2H, m, 1- and 8-H), and 8.48–8.70 (2H, m, 4- and 5-H).

The alkali-soluble fraction crystallized from light petroleum-chloroform to give benzo[b]phenanthro[9,10-d]furan-10-ol **17** as needles (528 mg, 1.86 mmol, 38.7%) m.p. 265–267°C (Found: M^+, 284.0837. $C_{20}H_{12}O_2$ requires: *M*, 284.0837.); *m/z* 284 (100%, M^+), 255 (6, M-CHO), 226 (22, M-2CHO), 178 (11, $C_{14}H_{10}$), 142 (17, M^{2+}), and 113 (17, 226^{2+}); λ_{max}/nm 250 (log ε 4.65), 264 (4.64), 281 (4.12), 308 (4.15), 320 (4.08), 341 (3.41), and 359 (3.55); ν_{max}/cm^{-1} 3400 (phenolic OH), 1592 (aromatic C=C), 780 (3 adjacent ArH) and 755 (4 adjacent ArH); δ_H [$(CD_3)_2CO + 10\%$ $(CD_3)_2SO$], 7.09 (1H, dd, *J* 1 and 8, 11-H), 7.32 (1H, dd, *J* 8 and 8, 12-H), 7.67–7.91 (4H, m, ArH), 7.97 (1H, dd, *J* 1 and 8, 13-H), 8.50–8.58 (1H, m, 1-H), 8.70–8.76 (1H, m, 8-H), and 8.88–9.07 (2H, m, 4- and 5-H). The acetate crystallized from light petroleum as needles m.p. 170–171°C (Found: M^+, 326.0942. $C_{22}H_{14}O_3$ requires: *M*, 326.0943); *m/z* 326 (24%, M^+), 284 (100, M-CH_2CO), 255 (6, 284-CHO), and 226 (11, 255-CHO); λ_{max}/nm 240infl (log ε 4.43), 252 (4.57), 261 (4.56), 282 (4.02), 296 (4.01), 306 (4.14), 319 (4.15), 339 (3.40), and 353 (3.37); ν_{max}/cm^{-1} 1764 (aryl acetate CO), 1591 (aromatic C=C), 759 (3 adjacent ArH), and 731 (4 adjacent ArH); δ_H 2.53 (3H, s, $MeCO_2Ar$), 7.22–7.28 (1H, m, 11-H), 7.39–7.48 (1H, m, 12-H), 7.60–7.82 (4H, m, ArH), 8.17–8.26 (1H, m, 13-H), 8.44–8.51 (1H, m, 1-H), 8.54–8.61 (1H, m, 8-H), and 8.67–8.77 (2H, m, 4- and 5-H).

When the above experiment was repeated using only catechol and phenanthrenequinone the yields of the dioxin **22** (1.5%) and of the furanol **17** (3.1%) were much lower. The phenolic fraction now afforded a second product which crystallized from chloroform-light petroleum to give 10-phenylphenanthrene-2′,3′,9-triol **11** as needles (231 mg, 0.76 mmol, 15.9%) m.p. 184–186°C (Found: M^+, 302.0941. $C_{20}H_{14}O_3$ requires:

M, 302.0943); *m/z* 302 (100%, M^+), 284 (5, M-H_2O), 273 (8, M-CHO), 255 (6, 284-CHO), 226 (6, 255-CHO), 165 (8, $C_{13}H_9$), 142 (13, 284^{2+}), 127.5 (7, 255^{2+}), and 113 (14, 226^{2+}); λ_{max}/nm 255 (log ε 4.60), 272infl (4.16), 301 (3.95), 341 (3.34), and 358 (3.23); ν_{max}/cm^{-1} 3460 (phenolic OH), 1618 and 1595 (aromatic C=C), 761 and 757 (3 and 4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.72 (1H, dd, *J* 1.5 and 9, 4′-H), 6.87 (1H, dd, *J* 9 and 9, 5′-H), 6.98 (1H, dd, *J* 1.5 and 9, 6′-H), 7.30–8.00 (6H, m, ArH and ArOH), 8.36–8.47 (1H, m, 8-H), and 8.67–8.95 (2H, m, 4- and 5-H). The triacetate crystallized from chloroform-light petroleum as needles, m.p. 155–156°C (Found: M^+, 428.1264. $C_{26}H_{20}O_6$ requires: *M*, 428.1260); *m/z* 428 (2%, M^+), 386 (74, M-CH_2CO), 344 (51, M-2CH_2CO), 302 (100, M-3CH_2CO), 284 (20, 302-H_2O), 273 (12, 302-CHO), 255 (8, 284-CHO), and 226 (6, 255-CHO); λ_{max}/nm 249infl (log ε 4.50), 255 (4.55), 268infl (4.10), 274infl (3.96), 287 (3.84), and 298 (3.86); ν_{max}/cm^{-1} 1760 (aryl acetate CO), 1599 (aromatic C=C), 794 and 760, (3 and 4 adjacent ArH); δ_H 1.82, 2.17, and 2.31 (each 3H, s, 9-, 2′-, and 3′-$MeCO_2Ar$), 7.20–7.75 (8H, m, ArH), 7.82–7.89 (1H, m, 8-H), and 8.67–8.77 (2H, m, 4- and 5-H).

3. With Resorcinol (36.36 mmol) to Give 12 and 18

There was no neutral fraction. The alkali-soluble fraction afforded two products the faster-moving of which crystallized from chloroform to give benzo[b]phenanthro[9,10-d]furan-11-ol **18** as needles (793 mg, 2.79 mmol, 58.0%) m.p. 227–228°C (Found: M^+, 284.0845, $C_{20}H_{12}O_2$ requires: *M*, 284.0837); *m/z* 284 (100%, M^+), 255 (7, M-CHO), 226 (10, M-2CHO), 142 (21, M^{2+}), 127.5 (4, 255^{2+}), and 113 (8, 226^{2+}); λ_{max}/nm 260 (log ε 4.61), 283infl (4.18), 298 (3.95), 320 (4.22), 332 (4.28), 346infl (3.65), and 366 (3.43); ν_{max}/cm^{-1} 3300 (phenolic OH), 1596 (aromatic C=C). 806 (2 adjacent ArH), and 754 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 7.07 (1H, dd, *J* 2 and 10, 12-H), 7.27 (1H, d, *J* 2, 10-H), 7.35–7.78 (5H, m, ArH and ArOH), 8.26 (1H, d, *J* 10, 13-H), 8.30–8.37 (1H, m, 1-H), 8.56–8.63 (1H, m, 8-H), and 8.66–8.82 (2H, m, 4- and 5-H). The acetate, m.p. 197–200°C, crystallized from chloroform-light petroleum (Found: M^+, 326.0940. $C_{22}H_{14}O_3$ requires: *M*, 326.0943); *m/z* 326 (15%, M^+), 284 (100, M-CH_2CO), 255 (6, 284-CHO), and 226 (11, 255-CHO); λ_{max}/nm 242infl (log ε 4.50), 252 (4.66), 282 (4.15), 296 (4.08), 309 (4.26), 322 (4.31), 341 (3.53), and 360 (3.45); ν_{max}/cm^{-1} 1758 (aryl acetate CO), 1589 (aromatic C=C), 808 (2 adjacent ArH), and 761 (4 adjacent ArH); δ_H 2.41 (3H, s, $MeCO_2Ar$), 7.26 (1H, dd, *J* 2 and 9, 12-H), 7.34 (1H, d, *J* 2, 10-H), 7.53–7.97 (4H, m, ArH), 8.34 (1H, d, *J* 9, 13-H, and 8.47–8.97 (4H, m, 1-, 4-, 5-, and 8-H).

The slower-moving band gave 10-phenylphenanthrene-2′,4′,9-triol **12** (130 mg, 0.43 mmol, 9.0%) m.p. 175–177°C (Found: M$^+$, 302.0944. $C_{20}H_{14}O_3$ requires: *M*, 302.0942); *m/z* 302 (100%, M$^+$), 284 (11, M-H_2O), 273 (8, M-CHO), 255 (5, 273-H_2O), 231(8, 273-C_2H_2O), 215 (6, M-3CHO), 165 (7, $C_{13}H_9$), and 142 (7, 284^{2+}); λ_{max}/nm 251 (log ε 4.41), 277 (4.11), 310infl (3.87), 344 (3.05) and 362 (2.87); ν_{max}/cm^{-1} 3350 (phenolic OH), 1595 (aromatic C=C), 840 (2 adjacent ArH) and 757 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.37–6.76 (2H, m, ArH), 7.02–7.09 (1H, m, ArH), 7.37–8.30 (7H, m, ArH and ArOH), 8.40–8.57 (2H, m, ArH and ArOH), 8.70–8.84 (2H, m, 4- and 5-H).

Repetition of the reaction without the addition of P_4S_{10} gave the furanol **18** (5.0%) and the triol **12** (27.0%).

4. With Hydroquinone (36.36 mmol) to Give 8, 13, and 19

There was no neutral fraction but the phenolic fraction afforded three products. The fastest-moving of these crystallized from light petroleum-chloroform to give benzo[b]phenanthro[9,10-d]furan-12-ol **19** as needles (420 mg, 1.48 mmol, 30.8%) m.p. 218–219°C (Found: M$^+$, 284.0828. $C_{20}H_{12}O_2$ requires: *M*, 284.0837); *m/z* 284 (100%, M$^+$), 255 (6, M-CHO), 226 (9, M-2CHO), 142 (19, M^{2+}), and 113 (11, 226^{2+}); λ_{max}/nm 259 (log ε 4.46), 285 (3.89), 310infl (4.13), 315 (4.16), 327 (4.19), 341infl (3.62), and 361 (3.31); ν_{max}/cm^{-1} 3260 (phenolic OH), 1611 and 1586 (aromatic C=C), 806 (2 adjacent ArH), and 745 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 7.08 (1H, dd, *J* 2 and 10, 11-H), 7.64 (1H, d, *J* 10, 10-H), 7.68–7.86 (5H, m, ArH and ArOH), 7.90 (1H, d, *J* 2, 13-H), 8.41–8.48 (1H, m, 1-H), 8.58–8.66 (1H, m, 8-H), and 8.84–8.93 (2H, m, 4- and 5-H). The acetate, m.p. 187–188.5°C, crystallized from chloroform-light petroleum (Found: M$^+$, 326.0944. $C_{22}H_{14}O_3$ requires: *M*, 326.0943); *m/z* 326 (28%, M$^+$), 284 (100, M-CH_2CO), 255 (10, 284-CHO), and 226 (14, 255-CHO); λ_{max}/nm 254 (log ε 4.56), 263infl (4.53), 281 (3.98), 299infl (3.99), 308 (4.18), 321.5 (4.24), 340 (3.46), and 358 (3.43); ν_{max}/cm^{-1} 1751 (aryl acetate CO), 1613 and 1587 (aromatic C=C), 812 (2 adjacent ArH), and 750 (4 adjacent ArH); δ_H 2.41 (3H, s, $MeCO_2Ar$), 7.11–7.20 (1H, m, 11-H), 7.53–7.77 (5H, m, ArH), 7.97 (1H, brs, 13-H), 8.32–8.43 (2H, m, 1- and 8-H), and 8.55–8.69 (2H, m, 4- and 5-H).

The next fraction afforded a mixture of phenols which, after acetylation and further PLC using light petroleum-chloroform (9:1), gave benzo[b]phenanthro[9,10-e]oxathiin-12-yl acetate **8** (10 mg, 0.03 mmol, 0.6%) as needles, m.p. 181–183°C (Found: M$^+$, 358.0671. $C_{22}H_{14}O_3S$ requires: *M*, 358.0663); *m/z* 358 (54%, M$^+$), 316 (100, M-CH_2CO), 287 (6, 316-CHO), 284 (23, 316-S), 258 (12, 287-CHO), 255 (6, 284-CHO), and 226 (7, 255-CHO); λ_{max}/nm 244infl (log ε 4.52), 285 (4.39). 307infl (4.10), 322infl (4.02), and 344infl (3.82); ν_{max}/cm^{-1} 1765 (aryl acetate CO), 1594 (aromatic C=C), 811 (2 adjacent ArH), and 762 (4 adjacent ArH); δ_H 2.26 (3H, s, $MeCO_2Ar$), 6.85–7.96 (7H, m, ArH), 8.31–8.40 (1H, m, 8-H), 8.44–8.52 (1H, m, 1-H), and 8.57–8.71 (2H, m, 4- and 5-H).

The slowest-moving fraction crystallized from chloroform to give 10-phenylphenanthrene-2′,5′,9-triol **13** (140 mg, 0.46 mmol, 9.6%) as needles, m.p. 190.5–191.5°C (Found: M^+, 302.0941. $C_{20}H_{14}O_3$ requires: *M*, 302.0943); *m/z* 302 (100%, M^+), 284 (9, M-H_2O), 273 (7, M-CHO), 255 (6, 273-H_2O), 226 (6, 255-CHO), 202 (9, $C_{16}H_{10}$), 189 (7, $C_{15}H_9$), 165 (9, $C_{13}H_9$), 142 (16, 284^{2+}), 127.5 (6, 255^{2+}), and 113 (11, 226^{2+}); λ_{max}/nm 252 (log ε 4.56), 273infl (4.14), 303 (4.04), 341 (3.18), and 358 (3.18); ν_{max}/cm^{-1} 3300 (phenolic OH), 1595 (aromatic C=C), 816 (2 adjacent ArH), and 756 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.69–7.02 (3H, m, 3′-,4′-, and 6′-H), 7.38–8.02 (8H, m, ArH and ArOH), 8.37–8.50 (1H, m, 8-H), and 8.66–8.87 (2H, m, 4- and 5-H).

Repetition of the reaction with the omission of P_4S_{10} gave the furanol **19** (10.2%) and the triol **13** (45.1%).

5. With Phloroglucinol (31.75 mmol) at 220°C to Give 21

The phenolic fraction afforded benzo[b]phenanthro[9,10-d]furan-11,13-diol **21** (148 mg, 0.49 mmol, 11.4%) which crystallized from chloroform as needles m.p. 235–238°C (Found: M^+, 300.0774. $C_{20}H_{12}O_3$ requires *M*, 300.0786); *m/z* 300 (100%, M^+), 271 (4, M-CHO), and 150 (22, M^{2+}); λ_{max}/nm 254 (log ε 4.03), 265 (4.03), 320 (3.57), 331 (3.58), 352infl (3.01) and 368 (2.81); ν_{max}/cm^{-1} 3445 (phenolic OH), 1628 (aromatic C=C), and 754 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.62 and 6.83 (each 1H, d, *J* 1.5, 12- and 10-H), 7.59–7.85 (4H, m, ArH), 8.37–8.44 (1H, m, 8-H), 8.72–8.97 (3H, m, 4- and 5-H and 11-OH), 9.79 (1H, brs, 13-OH), and 9.83–9.92 (1H, m, 1-H). The diacetate had m.p. 191–193°C (Found: M^+, 384.0994. $C_{24}H_{16}O_5$ requires *M*, 384.0997); *m/z* 384 (24%, M^+), 342 (25, M-CH_2CO), 300 (100, M-2CH_2CO), 271 (8, 300-CHO), and 213 (8, 300-3CHO); λ_{max}/nm 242infl (log ε 4.43), 253 (4.60), 261infl (4.58), 281infl (4.12), 298infl (4.01), 311 (4.17), 323 (4.17), 340 (3.41), and 358 (3.32); ν_{max}/cm^{-1} 1761 (aryl acetate CO), 1621 and 1580 (aromatic C=C), and 758 (4 adjacent ArH); δ_H 2.39 and 2.58 (each 3H, s, 11- and 13-$MeCO_2Ar$), 7.06 and 7.48 (each 1H, brs, 10- and 12-H), 7.60–7.75 (4H, m, ArH), 8.40–8.47 (1H, m, 8-H), 8.66–8.77 (2H, m, 4- and 5-H), and 8.96–9.03 (1H, m, 1-H).

Repetition of the reaction in the absence of P_4S_{10} gave the same furandiol **21** in lower (4.2%) yield.

6. With Pyrogallol (31.75 mmol) to Give 17, 18, 20, and 23

The phenolic fraction afforded the furanol **17** (103 mg, 0.38 mmol, 7.5%) and its isomer **18** (170 mg, 0.60 mmol, 12.5%) identical with the products obtained from the reactions with catechol and with resorcinol. Repetition of the reaction without the addition of P_4S_{10} gave a phenolic fraction which was separated by PLC using chloroform-acetone (9:1). The faster-moving component crystallized from chloroform to give benzo[b]phenanthro[9,10-d]furan-10,11-diol **20** (179 mg, 0.60 mmol, 12.4%) as needles m.p. 235–237°C (Found: M^+, 300.0774. $C_{20}H_{12}O_3$ requires: *M*, 300.0785); *m/z* 300 (100%, M^+), 226 (9, M-CHO—CO—OH), and 150 (20, M^{2+}); λ_{max}/nm 252 (log ε 4.54), 277infl (4.23), 318 (3.98), 327 (3.98), 348infl (3.51), and 364 (3.39); ν_{max}/cm^{-1} 3320 (phenolic OH). 1610 (aromatic C=C), 790 (2 adjacent ArH), 755 and 740 (4 adjacent ArH); δ_H[$(CD_3)_2CO$] 7.11 (1H, d, *J* 8, 12-H), 7.65–7.80 (6H, m, ArH), 7.83 (1H, d, *J* 8, 13-H), 8.43–8.51 (1H, m, 1-H), 8.65–8.72 (1H, m, 8-H), and 8.86–8.95 (2H, m, 4- and 5-H).

The slower-moving component (253 mg) darkened on exposure to the air and was therefore acetylated. PLC using chloroform gave 10-phenylphenanthrene-2′,3′,4′,9-tetrayl tetra-acetate **23** (179 mg, 0.37 mmol, 13.6%), m.p. 196–199°C after crystallization from chloroform-light petroleum. [Found: $(M\text{-}CH_2CO)^+$, 444.1200. $C_{26}H_{20}O_7$ requires: *M*, 444.1209]: *m/z* 486 (1%, M^+), 444 (79, M-CH_2CO), 402 (64, 444-CH_2CO), 360 (64, 402-CH_2CO), 318 (100, 360-CH_2CO), 300 (25, 318-H_2O), 289 (17, 318-CHO), 271 (7, 289-H_2O), 231 (7, 289-2CHO), and 165 (8, $C_{13}H_9$); λ_{max}/nm 243infl (log ε 4.52), 261infl (4.42), 271infl (4.32), and 329 (3.69); ν_{max}/cm^{-1} 1775 (aryl acetate CO), 1602 (aromatic C=C), 822 (2 adjacent ArH), and 752 (4 adjacent ArH); δ_H 1.95, 2.18, 2.35, and 2.38 (each 3H, s, 9-, 2′-, 3′-, and 4′-$MeCO_2Ar$.), 6.97 (1H, d, *J* 8, 5′-H), 7.15-7.83 (6H, m, ArH), 7.92–7.99 (1H, m, 8-H), and 8.54–8.76 (2H, m, 4- and 5-H).

7. With 1-Naphthol (27.78 mmol) to Give 24, 25, 26, and 27

The neutral fraction afforded three components the fastest-moving of which was 1,1′-dinaphthyl disulfide **25** (487 mg, 1.53 mmol, 11.0%) which crystallized from light petroleum in plates, m.p. 91°C (lit.,[23] 91°C) (Found: M^+, 318.0528 Calc. for $C_{20}H_{14}S_2$: *M*, 318.0537); *m/z* 318 (52%, M^+), 286 (9, M-S), 254 (9, M-2S), 159 (100, M-$C_{10}H_7S$), and 115 (97, C_9H_7); λ_{max}/nm 305 (log ε 3.80); ν_{max}/cm^{-1} 1588 (aromatic C=C), 789 (3 adjacent ArH), and 768 (4 adjacent ArH); δ_H 7.08–7.85 (12H, m, ArH), and 8.24–8.44 (2H, m, 8- and 8′-H).

The next product was 9-(1-naphthylthio)phenanthrene **26** (35 mg, 0.01 mmol, 2.2%) which crystallized from light petroleum-chloroform in plates m.p. 59–60°C (Found: M^+, 336.0968. $C_{24}H_{16}S$ requires: *M*, 336.0973); *m/z* 336 (100%, M^+), 335 (17, M-H), 302 (26, M-H_2S), 210 (17, M-$C_{10}H_6$), 209 (18, M-$C_{10}H_7$), 168 (11, M^{2+}), 165 (33, $C_{13}H_9$), 160 (32, $C_{10}H_8S$), 159 (39, $C_{10}H_7S$), 128 (9, $C_{10}H_8$), and 115 (45, C_9H_7); λ_{max}/nm 256 (log ε 4.74), 263infl (4.71), and 344 (3.52); ν_{max}/cm^{-1} 1582 (aromatic C=C), 785 (3 adjacent ArH), 764, 759, and 742 (4 adjacent ArH); δ_H 7.17–7.91 (12H, m, ArH), 8.35–8.52 (2H, m, 8- and 8′-H), and 8.55–8.79 (2H, m, 4- and 5-H).

The slowest-moving component crystallized from light petroleum-chloroform to give naphtho[1,2-b]phenanthro]9,10-d]furan **24** (1.143 g, 3.50 mmol, 74.8%) as plates, m.p. 208–210°C (Found: M^+, 318.1049. $C_{24}H_{14}O$ requires: *M*, 318.1045); *m/z* 318 (100%, M^+) 289 (16, M-CHO), 159 (20, M^{2+}), 144.5 (10, 289^{2+}); λ_{max}/nm 252 (log ε 4.53), 267 (4.56), 278infl (4.47), 316 (4.08), 326 (4.08), 333 (402), 340 (3.80), 348 (3.82), and 360 (3.20); ν_{max}/cm^{-1} 1610 (aromatic C=C), 803 (2 adjacent ArH), 765, 755, and 742 (4 adjacent ArH); δ_H (C_6D_6) 7.20–7.84 (9H, m, ArH), 8.09–8.18 (1H, m, ArH) and 8.41–8.60 (4H, m, ArH). The phenolic fraction contained only unchanged 1-naphthol.

Repetition of the reaction without the addition of P_4S_{10} gave a neutral fraction containing the furan **24** (6.9%). The phenolic fraction afforded 10-(2′-naphthyl)phenanthrene-1′,9-diol **27** (763 mg, 2.27 mmol, 47.2%) m.p. 201–203°C which crystallized from light petroleum-chloroform (Found: M^+, 336.1158. $C_{24}H_{16}O_2$ requires: *M*, 336.1150); *m/z* 336 (100%, M^+), 318 (18, M-H_2O), 307 (12, M-CHO), 289 (20, 318-CHO), 278 (5, 307-CHO), 165 (23, $C_{13}H_9$), and 159 (12, 318^{2+}); λ_{max}/nm 238 (log ε 4.73), 252 (4.72), 278 (4.39), 300 (4.16), 310infl (4.12), 323infl (3.90), 341 (3.44), and 360 (3.36); ν_{max}/cm^{-1} 3505 (phenolic OH), 1595 (aromatic C=C), 808 (2 adjacent ArH), 760 and 748 (4 adjacent ArH); δ_H 5.43 and 5.58 (each 1H, s, ArOH), 7.29–7.90 (10H, m, ArH), 8.30–8.45 (2H, m, 8- and 8′-H), and 8.60–8.75 (2H, m, 4- and 5-H). The diacetate crystallized from light petroleum-chloroform in needles m.p. 178–180°C (Found: M^+, 420.1361. $C_{28}H_{20}O_4$ requires *M*, 420.1361); *m/z* 420 (1%, M^+), 378 (33, M-CH_2CO), 336 (100, 378-CH_2CO), 318 (17, 336-H_2O), 307 (8, 336-CHO), 289 (10, 307-H_2O) and 165 (10, $C_{13}H_9$); λ_{max}/nm 228 (log ε 4.78), 251infl (4.69), 256 (4.72), 271infl (4.41), and 298 (4.12); ν_{max}/cm^{-1} 1764 (aryl acetate CO), 1596 (aromatic C=C), 809 (2 adjacent ArH), 761 and 750 (4 adjacent ArH); δ_H 1.94 and 2.07 (each 3H, s, 1′- and 9-$MeCO_2Ar$), 7.40–8.01 (12H, m, ArH), and 8.69–8.80 (2H, m, 4- and 5-H).

8. With 2-Naphthol (27.78 mmol) to Give 28, 29, 30, 31, and 32

The neutral fraction gave rise to four bands, the fastest-moving of which was 2,2′-dinaphthyl disulfide **30** (205 mg, 0.64 mmol, 4.6%) which crystallized from light petroleum in plates, m.p. 138–139°C (lit.,[24] 139–140°C) (Found: M^+, 318.0544. Calc. for $C_{20}H_{14}S_2$: *M*, 318.0537); *m/z* 318 (63%, M^+), 254 (14, M-2S), 160 (57, M-$C_{10}H_6S$), 159 (77, M-$C_{10}H_7S$), 128 (12, $C_{10}H_8$), and 115 (100, C_9H_7); λ_{max}/nm 248 (log ε 3.51); ν_{max}/cm^{-1} 1583 (aromatic C=C), 813 (2 adjacent ArH), and 738 (4 adjacent ArH), δ_H 7.35–8.10 (m, ArH). The next band afforded 2,2′-dinaphthyl sulfide **29** (172 mg, 0.60 mmol, 4.3%) which crystallized from light petroleum in plates m.p. 148–150°C (lit.,[25] 151°C) (Found: M^+, 286.0811. Calc. for $C_{20}H_{14}S$: *M*, 286.0816); *m/z* 286 (100%, M^+), 284 (32, M-2H), 252 (15, 284-S), 143 (11, M^{2+}), 142 (9, 284^{2+}), and 115 (20, C_9H_7); λ_{max}/nm 230 (log ε 4.68), 256 (4.52), 275infl (4.24), 305 (4.03), and 332 (3.65); ν_{max}/cm^{-1} 1620 and 1587 (aromatic C=C), 812 (2 adjacent ArH), and 738 (4 adjacent ArH); δ_H 7.28–8.08 (10H, m, ArH), 8.47–9.11 (4H, m, ArH). The third band gave 2,2′-dinaphthyl ether **28** (295 mg, 1.09 mmol, 7.9%) which crystallized from light petroleum in needles m.p. 104–105°C (lit.,[26] 105°C) (Found: M^+, 270.1046. Calc. for $C_{20}H_{14}O$: *M*, 270.1044); *m/z* 270 (100%, M^+), 241 (20, M-CHO), 239 (9, 241-2H), 135 (14, M^{2+}), 127 (19, $C_{10}H_7$), and 115 (11, C_9H_7); λ_{max}/nm 235 (log ε 4.81), 263infl (4.54), 274infl (4.42), 286infl (4.20), 313 (3.68), and 328 (3.70); ν_{max}/cm^{-1} 1625 and 1592 (aromatic C=C), 809 (2 adjacent ArH), and 744 (4 adjacent ArH); δ_H 7.26–7.90 (m, ArH). The final band afforded 9,9′-diphenanthryl disulfide **31** (19 mg, 0.05 mmol, 1.9%) which crystallized from light petroleum-chloroform in plates, m.p. 189–190°C (lit.,[27] 202–204°C for a sample with a poor carbon analysis) (Found: M^+, 418.0832. Calc. for $C_{28}H_{18}S_2$: *M*, 418.0848); *m/z* 418 (31%, M^+), 386 (33, M-S), 354 (9, M-2S), 352 (354-2H), 210 (73, $C_{14}H_{10}S$), 209 (73, $C_{14}H_9S$), 178 (18, 210-S), 176 (17, 210-H_2S), and 165 (100, $C_{13}H_9$); λ_{max}/nm ($CHCl_3$) 259 (log ε 4.63), 301infl (4.10), and 352infl (3.57); ν_{max}/cm^{-1} 1600 (aromatic C=C), and 739 (4 adjacent ArH); δ_H 7.45–8.00 (12H, m, ArH), 8.47–8.53 (2H, m, 8- and 8′-H), and 8.59–8.85 (4H, m, 4-, 4′-, 5-, and 5′-H).

The phenolic fraction gave 1-(2′-naphthylthio)-2-naphthol **32** (25 mg, 0.08 mmol, 0.6%) m.p. 92°C (lit.,[28] 92°C) which crystallized from light petroleum-chloroform (Found: M^+, 302.0756. Calc. For $C_{20}H_{14}OS$: *M*, 302.0763); *m/z* 302 (91%, M^+). 269 (15, M-HS), 268 (6, M-H_2S), 241 (7, M-S-CHO), 239 (6, 268-CHO), 151 (11, M^{2+}), 128 (100, $C_{10}H_8$), and 115 (19, C_9H_7); λ_{max}/nm 233 (log ε 4.82), 238infl (4.74), 284 (4.08), 292infl (4.04), 325 (3.69), and 338 (3.73); ν_{max}/cm^{-1} 3360 (phenolic OH), 1618 and 1592 (aromatic C=C), 818 (2 adjacent ArH), and 743 (4 adjacent

ArH); δ_H 7.06–7.95 (13H, m, ArH and ArOH), and 8.14–8.26 (1H, m, 8-H). The acetate m.p. 118–120°C crystallized from light petroleum-chloroform. (Found: M^+, 344.0868. $C_{22}H_{16}O_2S$ requires: *M*, 344.0871); *m/z* 344 (44%, M^+), 302 (100, M-CH_2CO), 269 (19, 302-HS), 239 (10, 269-CH_2O), 144 (11, $C_{10}H_8O$), 128 (94, $C_{10}H_8$), and 115 (17, C_9H_7); λ_{max}/nm 244infl (log ε 4.52), 285 (4.39), 307infl (4.10), 322infl (4.02) and 334infl (3.82); ν_{max}/cm^{-1} 1760 (aryl acetate CO), 1590 (aromatic C=C), 810 (2 adjacent ArH), 762 and 743 (4 adjacent ArH); δ_H 2.25 (3H, s, $MeCO_2Ar$), 7.13–7.74 (10H, m, ArH), 7.84–8.02 (2H, m, ArH), and 8.41–8.51 (1H, m, 8-H).

REACTIONS OF PHENANTHRENEQUINONE WITH LAWESSON'S REAGENT (*p*-METHOXYPHENYLTHIONOPHOSPHINE SULFIDE DIMER) AND PHENOLS

1. With Catechol to Give 9, 11, 15, 17, 22, and 31

Lawesson's reagent[12] (2.03 g, 5.0 mmol) was added to a stirred mixture of phenanthrenequinone (1 g, 4.81 mmol) and catechol (5 g, 45.5 mmol) at 160°C. The mixture was heated at 160°C for 4 h and then treated as described above for the corresponding reactions with P_4S_{10}. The neutral fraction afforded the dioxin **22** (48 mg, 0.17 mmol, 3.5%) and the disulfide **31** (130 mg, 0.31 mmol, 12.9%). The phenolic fraction gave three products, the fastest-moving being the furanol **17** (196 mg, 0.69 mmol, 14.4%). The next band afforded 9-phenoxyphenanthren-2′ol **15** (115 mg, 0.40 mmol, 8.4%) which crystallized from light petroleum-chloroform in needles m.p. 103–105°C (Found: M^+, 286.0997. $C_{20}H_{14}O_2$ requires: *M*, 286.0993); *m/z* 286 (100%, M^+), 257 (6, M-CHO), 239 (6, 257-H_2O), 196 (16, $C_{14}H_{12}O$), 178 (57, $C_{14}H_{10}$), 176 (22, $C_{14}H_8$), and 165 (22, $C_{13}H_9$); λ_{max}/nm 252 (log ε 4.59), 280infl (4.13), 304 (3.98), 334 (3.51) and 349 (3.39); ν_{max}/cm^{-1} 3450 (phenolic OH), 1594 (aromatic C=C), 760 and 747 (4 adjacent ArH), δ_H [$(CD_3)_2SO$] 7.35–8.11 (9H, m, ArH and ArOH), 8.67–8.77 (1H, m, ArH), and 8.77–9.16 (4H, m, 4-, 5-, 8-, and 10-H). The slowest-moving band gave benzo[b]phenanthro[9,10-e]oxathiin-10-ol **9** (63 mg, 0.20 mmol, 4.1%) which crystallized from light petroleum-chloroform as needles m.p. 186–188°C (Found: M^+, 316.0561. $C_{20}H_{12}O_2S$ requires: *M*, 316.0558); *m/z* 316 (100%, M^+), 287 (11, M-CHO), 284 (20, M-S), 259 (8. 287-CO), 158 (9, M^{2+}); λ_{max}/nm 230infl (log ε 4.16), 249 (4.67), 275infl (4.36), 335 (3.56), and 358infl (3.32); ν_{max}/cm^{-1} 3440 (phenolic OH), 1601 and 1583 (aromatic C=C), 768 (3 adjacent ArH), and 748 (4 adjacent ArH); δ_H [$(CD_3)_2CO$] 6.79–7.04 (3H, m, ArH), 7.61–7.86 (4H, m, ArH), 7.97–8.09 (1H, m, 8-H), 8.65–8.87 (3H, m, 1-, 4-, and 5-H), and 9.04 (1H, brs, ArOH).

2. With Resorcinol (45.5 mmol) to Give 18 and with Hydroquinone (36.36 mmol) to Give 19

The molten product from a similar reaction using resorcinol in place of catechol was poured into chloroform and washed with 2M-sodium hydroxide solution. Acidification of the latter and subsequent PLC gave the furanol **18** (624 mg, 2.20 mmol, 45.7%). Hydroquinone gave the furanol **19** (771 mg, 2.7 mmol, 56.5%)

REACTIONS OF OTHER DIKETONES WITH P_4S_{10}

1. With Acenaphthenequinone to Give 33

P_4S_{10} (1.2 g, 2.70 mmol) was added slowly to a stirred mixture of acenaphthenequinone (1 g, 5.49 mmol) and phenol (4 g, 42.55 mmol) at 160°C under nitrogen. Treatment as in the reactions with phenanthrenequinone gave a neutral fraction which afforded di-1,2-acenaphthenothiophene **33** (20 mg, 0.06 mmol, 2.2%) m.p. 278–280°C (lit.,[29] 279–280°C) (Found: M^+, 332.0661. Calc. for $C_{24}H_{12}S$: *M*, 332.0659) identical with an authentic specimen.

2. With *o*-Chloranil to Give 34

A similar reaction between *o*-chloranil (1.23 g, 5.0 mmol) and P_4S_{10} (0.23 g, 0.52 mmol) gave 1,2,3,5,6,7,8-heptachlorodibenzothiophen-4-ol **34** (30 mg, 0.07 mmol, 3.3%) m.p. >350°C (Found: M^+, 437.7518. $C_{12}H^{35}Cl_7OS$ requires: *M*, 437.7568); *m/z* 438 (46%, M^+), and 375 (15, M-CO-Cl): λ_{max}/nm 245 (log ε 4.32), 305 (3.49), and 349infl (2.77); ν_{max}/cm^{-1} (Nujol) 3440 (phenolic OH), and 1630 (aromatic C=C); δ_H [$(CD_3)_2CO$] No signal. The acetate m.p. 226–228°C crystallized from acetone-methanol (Found: M^+, 479.7677. $C_{14}H_3{}^{35}Cl_7\ O_2S$ requires: *M*, 479.7674); *m/z* 480 (6%, M^+), and 438 (46, M-CH_2CO); λ_{max}/nm 227 (log ε 4.61), 242infl (4.70), 249 (4.75) and 314 (3.62); ν_{max}/·cm^{-1} 1762 (aryl acetate CO), 1610 and 1597 (aromatic C=C); δ_H 243 (s, $MeCO_2Ar$).

3. With Anthraquinone to Give Anthracene

The neutral fraction from the reaction between P_4S_{10} (2.05 g, 4.62 mmol), anthraquinone (1.9 g, 9.13 mmol), and phenol (4 g, 42.55 mmol) at 160°C after PLC and crystallization from chloroform gave anthracene (1.25 g, 7.02 mmol, 76.9%) m.p. and mixture m.p. 215–216°C (lit.,[30] 216–216.5°C).

Benzo[*b*]phenanthro[9,10-*d*]furan 16

This[10] had λ_{max}/nm 242infl (log ε 4.38), 265.5 (4.69), 281 (4.26), 295 (4.24), 307 (4.38), 320 (4.43), 341 (3.60), and 358 (3.60).

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