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The Reaction of Lawesson's Reagent with Trihydroxy Compounds*

R. Shabana, L. S. Boulos, and Y. M. Shaker

National Research Centre, Dokki, Cairo, 12622, Egypt

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ABSTRACT: *Lawesson's reagent (***1a***) reacts with pyrogallol (***2***) to give 1,3,2-benzodioxaphospholane-2-sulfide (***3***) and with 1,8,9-trihydroxyanthracene to give* **13.** *The structures of the products have been established either chemically, using methanolysis and methylation, or spectroscopically.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 25–30, 1999

INTRODUCTION

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide $(4\text{-}ROC_6H_4PS_2)_2$, R = Me, Lawesson's reagent (**1a**) reacts with aromatic monohydric alcohols at 140°C to give *O,O*-diphenyl-di(*p*-methoxyphenyl) trithiopyrophosphonate [1], while it reacts with aliphatic dihydroxy compounds in acetonitrile as the solvent giving rise to 2-aryl-1,3,2-dioxaphospholane-2-sulfides, cyclic trithio-pyrophosphonates, and thioacetamide [2]. Also, it reacts with aromatic *ortho* dihydroxy compounds in toluene at reflux temperature giving rise to 1,3,2-dioxaphospholane-2-sulfide derivatives [3]. These compounds are of interest for their insecticidal properties. As a continuation of our study of the reaction of LR with mono- and dihydroxy compounds, we report in this article on the reaction of **1a** and its phenoxy derivative (R = Ph, **1b**) with aromatic trihydroxy compounds.

Correspondence to: R. Shabana.
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RESULTS AND DISCUSSION

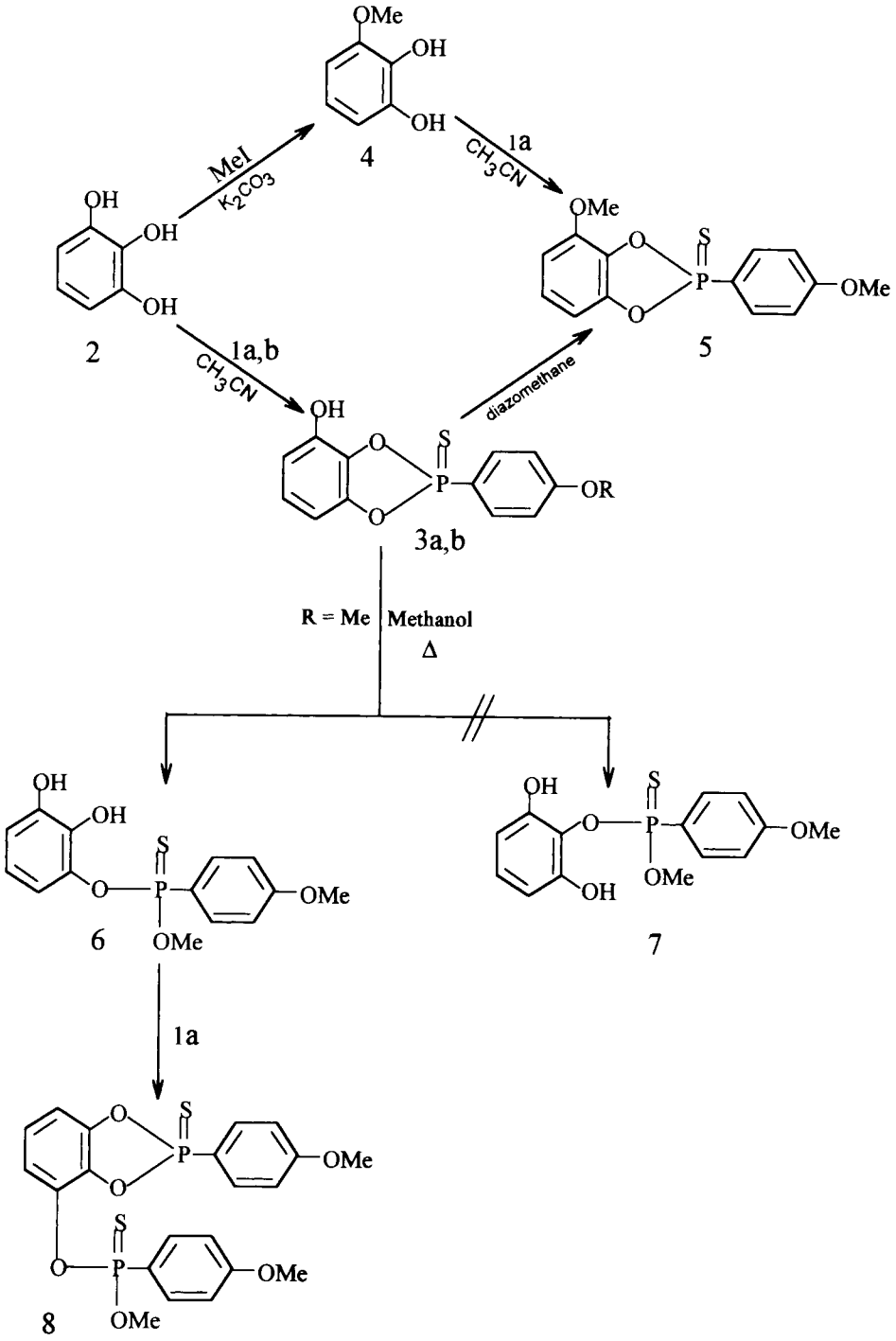
Lawesson's reagent (**1a**) and the phenoxy derivative **1b** react with pyrogallol (**2**) in dry acetonitrile as the solvent to give the heterocyclic compounds **3** (Scheme 1). The structure of compound **3a** was established by the independent synthesis of compound **5** either by methylation of **3a** using diazomethane or by reacting **2** with methyl iodide to give **4** and subsequent reaction with **1a** (Scheme 1). Also, compound **3a** has been subjected to methanolysis to give mainly compound **6** but not compound **7.** The structure of **6** has been established by reaction with **1a** to give **8.**

Compound **3a,** under electron impact, gives the molecular ion peak (294), which loses **S** to give an ion with *m/e* 262. Fission gives rise to two ions that are in agreement with the proposed cyclic structure (Scheme 2).

Additional evidence for structure **3** comes from an earlier finding [3] showing that **1a** reacts with o-dihydroxybenzene (catechol) to give 1,3,2-benzodioxaphospholane. 1,3-Dihydroxybenzene (resorcinol) in reaction with **1a** gave after methylation compound **9** in good overall yield (Scheme 3).

It is noteworthy to mention that the reaction of **1a** with hydroquinone (1,4-dihydroxybenzene) gave mainly compound **10**, which is in contrast to what Horner et al. [4] reported in 1968, namely, that compound **11** was the only compound to be isolated (Scheme 4).

The reaction of 1,8,9-trihydroxyanthracene **12** with **1a** was investigated next. We were able to isolate the dioxaphosphinane **13**.



SCHEME 1

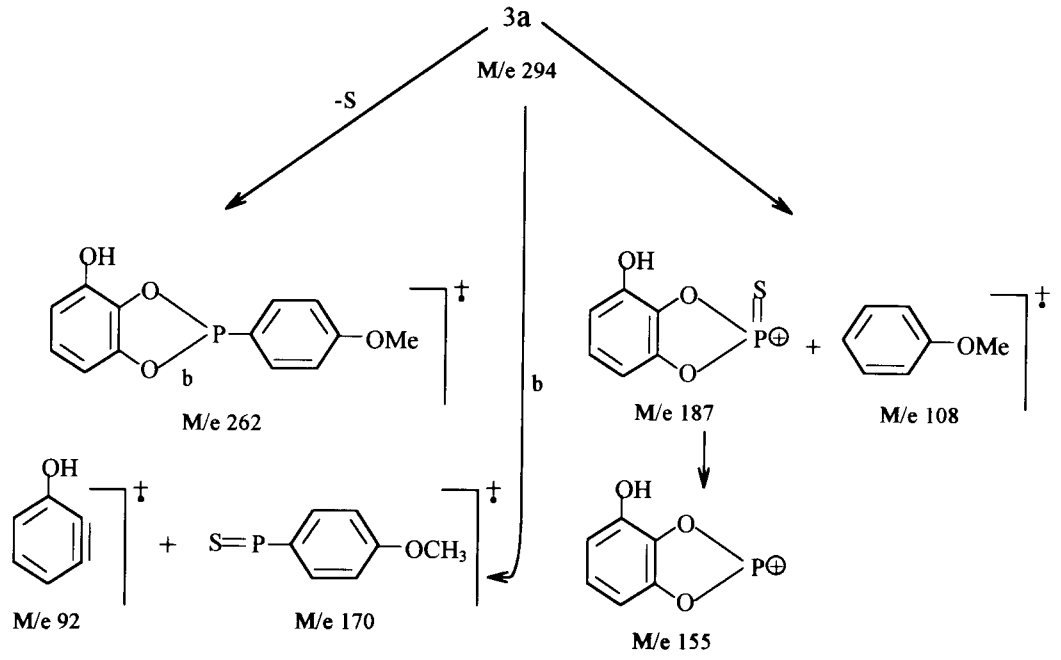
In support of the proposed structure, trials have been made to react 1,8-dihydroxyanthraquinone **14** with **1a.** We obtained compound **15,** probably through thiation of **14** and reduction to **15** [5]. It should be noted that Luskutova [6] in 1995 prepared anthradioxaphosphinin sulfide by treatment of 1-hydroxy-9-anthrone with **1a.**

EXPERIMENTAL

Melting points were determined with a MeI Temp apparatus and are uncorrected, as are the boiling points. IR spectra were recorded by use of a Unicam Sp 1100 or pu 9712 infrared spectrophotometer. The ^{1}H-NMR spectra were recorded on a Varian Gemini 200 MHz or a Bruker 270 MHz spectrometer. Chem-

ical shifts are expressed in δ relative to TMS as an internal standard in $CDCl_3$ as a solvent. ^{31}P chemical shifts were referenced to external 85% H_3PO_4. MS data were obtained on a gas chromatography/mass spectrometer EX 1000 QP Schimadzu-Japan. The reported yields refer to pure isolated materials obtained by column chromatography using silica gel 60 (Merck).

Compound **1a** (Lawesson's reagent) is commercially available and can be prepared as described earlier [7]. Compound **1b**, 2,4-bis(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, was pre-



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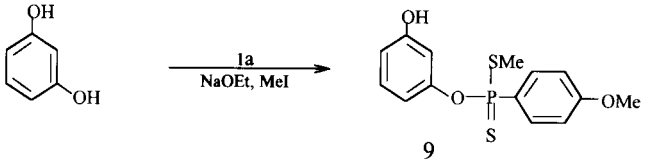
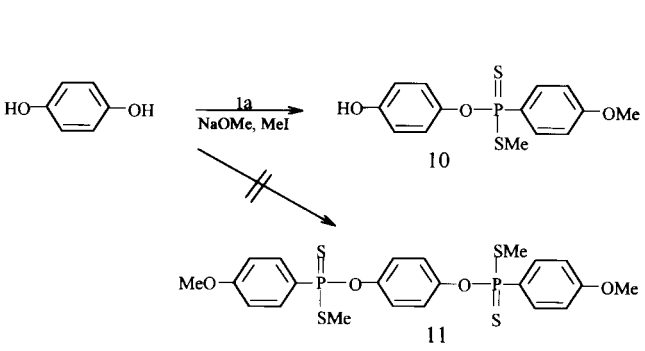
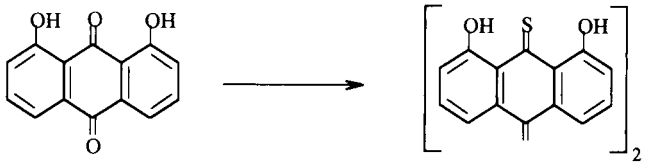


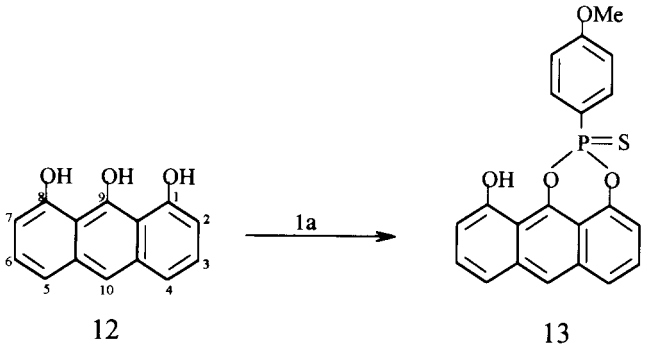
SCHEME 3



SCHEME 4



SCHEME 5



SCHEME 6

pared from P_4S_{10} and diphenyl ether by use of the same method.

Reaction of **1a** *with Pyrogallol* (**2**) *Using a 0.5:1 Molar Ratio: Preparation of* **3**

A mixture of 1.26 g of pyrogallol (10 mmol) and 2.02 g (0.5 mmol) of **1a** in 25 mL of anhydrous acetonitrile as the solvent was stirred magnetically at reflux temperature (80°C) until no more of the starting material could be detected (TLC) (5 h). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica-gel column with 30% diethyl ether/petroleum (60–80) up to 70% ether/petroleum ether as the eluent to give 1.8 g (61.2%) of 2-(4-methoxy-phenyl) 1,3,2-benzodioxaphospholane-2-sulfide (**3a**), mp 130°C. Anal. calcd for $C_{13}H_{11}O_4PS$ (294): C, 53.06; H, 3.76; P, 10.52; S, 10.89%. Found: C, 52.89; H, 3.60; P, 10.50; S, 10.76%. IR (u, cm^{-1}; group) [8] 650 (P = S), 1190 (P-O-C), 1600 (C = C, aromatic), 3400 (OH). MS: *m/e* (% rel.int.) 294 (M^+, 100, base peak), 262 ($M^+ - S$,27), 170 ($M^+ - C_6H_4O_3$, 39), 155 ($M^+ - C_7H_7OS$, 62), 108 ($M^+ - C_6H_4O_3PS$, 21), 92 ($M^+ - C_7H_7O_3PS$, 17). ^1H NMR ($CDCl_3$), δ = 3.85 (s, 3H, OCH_3), 6.1 (br., 1H, OH), 6.9 (dd, 2H, $^4J_{PH}$ = 3 Hz, J_{HH} = 9 Hz, meta protons to P), 7.7–7.9 (dd, 2H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz, ortho protons to P) [9,10]. ^{31}P NMR, δ = 108.

Methylation of **3***: Preparation of 4-Methoxy-2-*(*4-methoxyphenyl*)*-1,3,2-benzodioxaphospholane-2-sulfide* (**5**)

Exactly 1 g of **3a** was added to an ether solution of diazomethane (30 mL) at room temperature. Nitrogen gas was evolved, and the reaction mixture was left at room temperature until no more of the starting material could be detected (TLC) (2 h). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica-gel column with 10% ethyl acetate /*n*-hexane up to 25% ethyl acetate/*n*-hexane as eluent to give 0.45 g (43.2%) of **5**, mp 110°C. Anal. calcd for $C_{14}H_{13}O_4PS$ (308): C, 54.54; H, 4.28; P, 10.04; S, 10.39%. Found: C, 54.35; H, 4.08; P, 10.00; S, 10.29%. IR (u, cm^{-1}, group) 670 (P=S), 1190 (P-O-C), 1600 (C=C), aromatic, the compound lacks bands at 3400 for OH group. Ms:*m/e* (% rel. int.) 308 (M^+, 100, base peak), 201 (30), 169 ($M^+ - C_7H_7OS$, 23), 139 (8), 95 (5), 77.1 (3). ^1H NMR ($CDCl_3$), δ = 3.9 (two s, 6H, 2 OCH_3), 6.7–6.9 (dd, 2H, $^4J_{PH}$ = 3 Hz, J_{HH} = 9 Hz, meta protons to P), 7.4 (m, 3H, pyrogallol ring), 7.7–7.9 (dd, 2H, $^3J_{PH}$ = 15 HzJ_{HH} = 9 Hz, ortho protons to P).

Reaction of **1a** *with 3-Methoxycatechol: An Independent Synthesis of* **5**

A mixture of 1.4 g of 3-methoxycatechol [11] (10 mmol) and 2.02 g (5 mmol) of **1a** in 25 mL of anhydrous acetonitrile was stirred magnetically at reflux temperature (80°C) until no more of the starting material could be detected (TLC) (5 h). The reaction mixture was worked up as described earlier, 10% ethyl acetate/pet. ether up to 20% ethylacetate/pet. ether being used as eluent to give 0.9 g (29%) of **5**, mp 110°C. Found: C, 54.40; H, 4.15; P, 9.85; S, 10.25%.

Methanolysis of **3a***: Preparation of* **6**

A 1.47 g amount (5 mmol) of **3a** was heated in methanol (20 mL) under reflux until no more of the starting material could be detected (TLC) (0.5 h). The reaction was worked up as described earlier using 10% ethyl acetate/pet.ether up to 30% ethyl acetate/pet. ether as eluent to give 1.4 g (85.8%) of **6**, as on oil. Anal. calcd for $C_{14}H_{15}O_5$ PS (326): C, 51.53; H, 4.63; P, 9.49; S, 9.83%. Found: C, 51.41; H, 4.53; P, 9.55; S, 9.75%. IR (u, cm^{-1}, group) 700 (P=S), 1200 (P-O-C), 1600 (C=C, aromatic), 3400 (OH). MS:*m/e* (% rel. int.) 326 (M^+, 100, base peak), 293 (75), 201 (94), 185 (45), 169 (40), 154 (56), 139 (58), 77 (15). ^1H NMR ($CDCl_3$), δ = 3.9 (s, 3H, OCH_3, para to P), 3.8 (3H, d, OCH_3 attached to phosphorus atom with $^3J_{PH}$ = 15 Hz), 6.8 (dd, 2H, $^4J_{PH}$ = 3 Hz, J_{HH} = 9 Hz, meta protons to P), 7.0 (m, 3H of pyrogallol ring), 7.9–8.1 (dd, 2H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz, ortho protons to P). ^{31}P NMR, δ = 98.

Reaction of **6** *with* **1a***: Preparation* **8**

A mixture of 1.63 g (5 mmol) of **6**, 1.01 g (2.5 mmol) of **1a**, and 25 mL of anhydrous acetonitrile as the solvent was heated for 2 hours and purified by column chromatography using 5% ethyl acetate/pet. ether as eluent to give 1.2 g (48.5%) of **8**, as an oil. Anal. calcd for $C_{21}H_{20}O_6P_2S_2$ (494): C, 51.01; H, 4.07; P, 12.52; S, 12.96%. Found: C, 50.71; H, 4.20; P, 12.36; S, 12.78%. IR (u, cm^{-1}, group) 650 (P=S), 1180 (P-O-C), 1600 (C=C, aromatic). The compound lacks bands at 3400 for OH groups. MS: *m/e* (% rel. int.) 494 (M^+, 86.8), 324 (9.5), 308 (18), 294 (75), 264 (45), 201 (100, base peak), 185 (49), 169 (38), 139 (43), 77 (14). ^1H NMR ($CDCl_3$), δ = 3.8 (9H, 3 OCH_3; 2 OCH_3, para to P and one OCH_3, d, attached to P), 6.7–7.1 (m, 7H; 4H meta to P + 3H of pyrogallol ring), 7.7–8.0 (2 dd, 4 H, ortho protons to P). ^{31}P NMR, δ = 88.79.

Reaction of **1a** *with Resorcinol: Preparation of* **9**

A mixture of 0.28 g (2.5 mmol) of resorcinol and 1.01 g (2.5 mmol) of **1a** in 25 mL of dry toluene was heated for 3 hours at reflux temperature. A 0.2 g amount of sodium ethoxide was added to the reaction mixture, and refluxing continued for 1 hour. After that, 1.5 mL of methyl iodide was added dropwise, and the mixture was refluxed for one more hour. The reaction mixture was purified on a silica-gel column using 3% ethyl acetate/pet. ether as eluent to give 0.15 g (18.5%) of **9**, oil. Anal. calcd for $C_{14}H_{15}O_3PS_2$ (326): C, 51.52; H, 4.63; P, 9.49; S, 19.46%. Found: C, 51.37; H; 4.45; P, 9.29; S, 19.75%. IR (u, cm^{-1}, group) 710 (P=S), 1190 (P-O-C), 1600 (C=C, aromatic), 3400 (OH). MS: *m/e* (% rel. int.) 326 (M^+, 36), 279 ($M^+ - C_6H_5O_2$, 25), 217 (100, base peak), 201 (53), 139 (70), 108 (30), 63 (79). ^{1}H NMR ($CDCl_3$), δ = 2.25 (d, 3H, SCH_3), 3.9 (s, 3H, OCH_3), 4.5 (br., OH), 6.7–7.3 (m, 6 H, 2H meta to P + 4 H of the ring resorcinol), 8.0 (dd, 2H, ortho to P). ^{31}P NMR, δ = 100.

Reaction of **1a** *with Hydroquinone: Preparation of* **10**

A mixture of 0.55 g (5 mmol) of hydroquinone and 2.02 g (5 mmol) of **1a** in 25 mL anhydrous acetonitrile was heated at reflux temperature for 3 hours, then 0.3 g sodium ethoxide was added. After the mixture had been heated for one more hour, 2 mL of methyl iodide was added dropwise, and refluxing was continued for 1 hour. The reaction mixture was purified as described earlier, using 3% ethyl acetate/pet. ether as eluent to give 0.81 g of compound **10** (50%). Anal. calcd for $C_{14}H_{15}O_3PS_2$ (326): C, 51.52; H, 4.63; P, 9.49; S, 19.64. Found: C, 51.31; H, 4.55; P, 9.55; S, 19.50%. IR (u, cm^{-1}, group) 650 (P=S), 1200 (P-O-C), 1600 (C=C, aromatic), 3400 (OH). MS: *m/e* (% rel. int.) 326 (M^+, 68), 217 ($M^+ - C_6H_5O_2$, 100, basepeak), 201 (58), 169 (30), 109 (19). ^{1}H NMR ($CDCl_3$), δ = 2.25 (d, 3H, SCH_3), 3.9 (s, 3H, OCH_3), 4.9–5.1 (br., 1H, OH), 6.7–7.2 (m, 6H; 4H of the ring hydroquinone + 2H meta to P), 8.0 (2dd, 2H, ortho protons to P).

Reaction of **1b** *with Pyrogallol* **2***: Preparation of 2(4-Phenoxyphenyl)1,3,2-benzodioxaphospholane-2-sulfide* (**3b**)

A mixture of 0.63 g (5 mmol) of pyrogallol and 1.32 g (2.5 mmol) of **1b** in 25 mL of xylene was heated at reflux temperature for 3 hours. The product was purified by column chromatography using 5% ethyl acetate/pet. ether as eluent to give 0.2 g of 2-(4-phenoxyphenyl)benzodioxaphospholane-2-sulfide (**3b**) (11.2%), oil. Anal. calcd for $C_{18}H_{13}O_4PS$ (356): C, 60.67; H, 3.67; P, 8.69; S, 8.99%. Found: C, 60.35; H, 3.60; P, 8.52; S, 9.20%. IR (u, cm-1, group) 670 (P=S), 1200 (P-O-C), 1600 (C=C, aromatic), 3400 (OH). MS: *m/e* (% rel. int.) 357 (M^{+1}, 7), 295 (11), 267 (8), 234 (15), 149 (50), 126 (100, base peak), 108 (33), 80 (45). ^{1}H NMR ($CDCl_3$), δ = 4.0–4.5 (br, 1H, OH), 6.6–7.5 (m, 10 H, 5H of the phenyl ring + 2H meta to P + 3H of the ring pyrogallol), 7.7–7.9 (dd, 2H, ortho protons to P).

Reaction of 1,8,9-Trihydroxy Anthracene (**12**) *with* **1a***: Preparation of* **13**

A mixture of 0.452 (2 mmol) of **12** and 0.404 g (1 mmol) of **1a** in 25 mL of anhydrous acetonitrile was stirred magnetically at reflux temperature (80°C) until no more of the starting material could be detected (TLC) (5 h). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica-gel column (10% methylene chloride/pet. ether), up to 50% being used to elute 0.2 g (25.3%) of **13**. Anal. calcd for $C_{21}H_{15}O_4PS$ (394): C, 63.95; H, 3.63; P, 7.85; S, 8.12%. Found: C, 63.78; H, 3.72; P, 7.90; S, 8.25%. IR (u, cm^{-1}, group) 650 (P=S), 1180 (P-O-C), 1600 (C=C, aromatic), 3400 (OH). MS: *m/e* (% rel. int.) 394 (100, base peak), 240 (29), 211 (14), 139 (9), 108 (2), 63 (3). ^{1}H NMR ($CDCl_3$), δ = 3.85 (s, 3H, OCH_3), 6.8–8.3 (m, 12H, aromatics + OH groups).

Reaction of 1,8-Dihydroxy Anthraquinone (**14**) *with* **1a***: Preparation of* **15**

A mixture of 1.2 g (5 mmol) of **14** and 2.02 g (5 mmol) of **1a** in 25 mL of anhydrous toluene as a solvent was stirred magnetically at reflux temperature (110°C), for 5 hours. The reaction mixture was purified using a silica-gel column (10% ethyl acetate/pet. ether) to give 0.56 g (30%) of **15**.

IR (u, cm^{-1}, group) 1600 (C=C, aromatic), 1620 (C=S), 3400 (OH). MS: *m/e* (% rel. int.), 240 (1.02), 226 (100, bare peak), 197 (30), 180 (13), 152 (24). ^{1}H NMR ($CDCl_3$), δ 6.8–7.0 (2d, 8H; 4H, d, ortho to hydroxy groups + 4H, d, para to hydroxy groups). 7.6 (t, 4H, meta to hydroxy groups), 4.4 (s, 4H, the four hydroxy groups).

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