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Organophosphorus Compounds XV. The Reaction of 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent) with Aromatic Dihydroxy Compounds. Simple New Route to 1,3,2-Dioxaphospholane-2-sulfide

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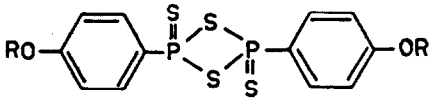
Abstract: 2,4-Bis(4-methoxypheny1)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent) and its *p*-phenoxy derivative react with *o*-dihydroxybenzene derivatives, dihydroxy naphthalene and 2,2-dihydroxybipheny1 in toluene at reflux temperature to give 1,3,2-dioxaphospholane-2-sulfide derivatives, **3a-f, 8a,b** and **11a,b** respectively.The structure of the products has established either chemically using methanolysis and methylation or spectroscopically . Also, analytical data has been used . A mechanistic considerations on the formation of the above products are discussed .

Introduction :

1,3,2-Dioxaphospholane-2-sulfide can be prepared in two or three steps by initial condensation of $[RCH(OH)]_2$ with $PSCl_3$ followed by methanolysis[1] or by phosphorochloridate to give the corresponding phosphites which were heated with sulfur to give 1,3,2-dioxaphospholane-2-sulfide.[2] The same compounds can be prepared by the reaction of 2,3-naphthalenediol with $PSCl_3$ followed by treatment with ethyl alcohol.[3] Also, different methods has been used to synthesize such compounds [4-8] which are very important as pesticides[9] or fire-proofing agents[10] but it is clear that these methods are long and give low yields .

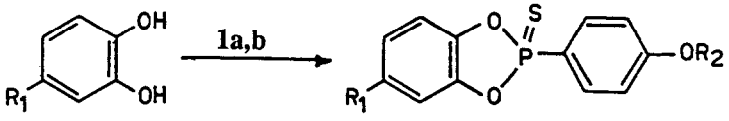
In a previous paper,[11] we succeeded in preparing these compounds using Lawesson's Reagent (LR) and aliphatic dihydric alcohols. This paper will report on the synthesis of 1,3,2-dioxaphospholane-2-sulfide from the reaction of Lawesson's Reagent (**1a**) and its *p*-phenoxy derivative **1b** with aromatic dihydroxy compounds.



1a, R = CH_3 (Lawesson's)
b, R = C_6H_5

Results and discussion :

Aromatic *o*-dihydroxybenzene derivatives **2a-c** react with Lawesson Reagent, (**1a**) and its *p*-Phenoxy derivative **1b** in toluene at reflux temperature to give benzo-1,3,2-dioxaphospholane-2-*p*-alkoxy(aryloxy)pheny1-2-sulfide (**3a-f**) as sole products in moderate to high yields.



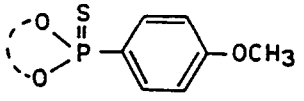
2a, R_1 = H
b, R_1 = $C(CH_3)_3$
c, R_1 = $C(Ph)_3$

3a, R_1 = H ; R_2 = CH_3
b, R_1 = $C(CH_3)_3$; R_2 = CH_3
c, R_1 = $C(Ph)_3$; R_2 = CH_3
d, R_1 = H ; R_2 = C_6H_5
e, R_1 = $C(CH_3)_3$; R_2 = C_6H_5
f, R_1 = $C(Ph)_3$; R_2 = C_6H_5

The formation of **3** are not dependent on the molar ratios of the reactant which is in contrast to the reaction of Lawesson reagent with aliphatic diols. Also, we are not able to separate or even detect the cyclic trithiopyrophosphonate which separated in case of aliphatic diol.[11]

The structure of compounds **3a-f** has been elucidated using analytical results and spectroscopic data (IR, ^1H, ^{31}P and MS). Compound **3c** (taken as representative example)

gave correct elemental analysis and its IR spectra shows peaks at 650 cm^{-1} (P=S) [12], 1025 cm^{-1} (P-O-C)[12], 1600 cm^{-1} for aromatic (C=C). The ^1H NMR of **3c** exhibits a singlet at 3.9 ppm (OCH_3), a multiplet at 6.8-7.1 for 5H (2H *meta* to phosphorus in LR part and 3H of the ring catechol), 7.1-7.4 (m,15H, CPh_3), 7.1-7.9 (m, 2H, *ortho* protons to phosphorus in LR part). Also, it lacks 2 signals at 8.80 and 8.85 ppm for the 2H of the 2 (OH) groups of the starting 1,2-dihydroxy-4(triphenylmethyl)benzene. Compound **3c** gave M^+ at m/e 520 and ^{31}P NMR at δ 109.8 ppm which is in accordence with other compounds containing the structure **3c**.[11]

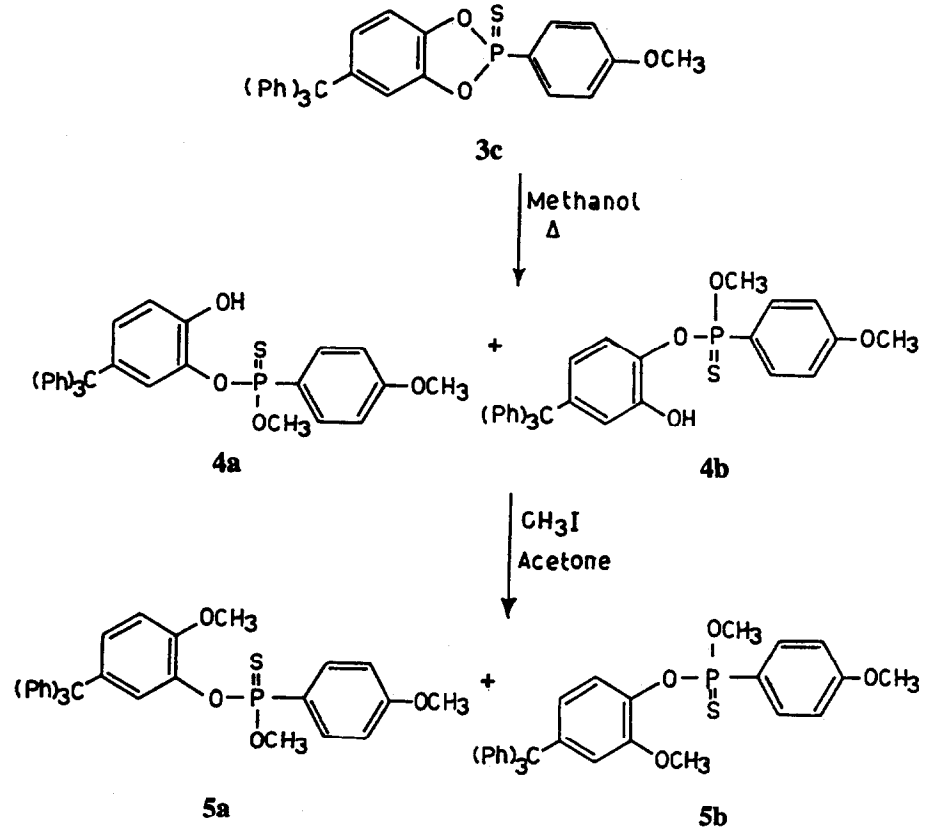


3c

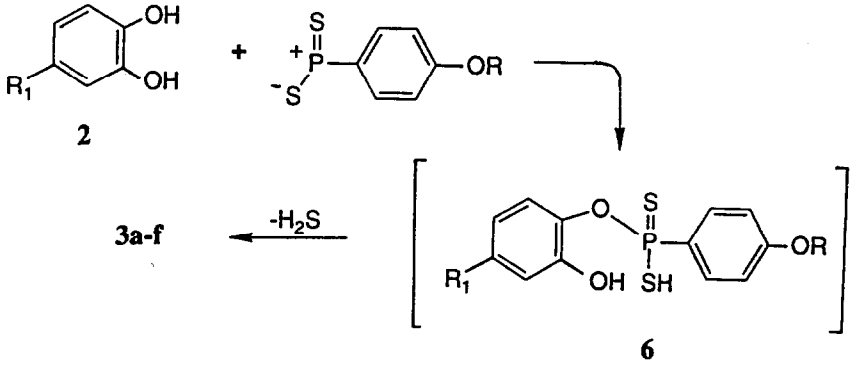
Compound **3c** was stable at high temperature (225°C) under reduced pressure (0.1 mm/Hg) but when heated for a short time in methanol, a mixture of *o*-(2-hydroxy-5-triphenylmethyl)benzene-4(methoxypheny1)phosphonothiolothionic acid (**4a**) and *o*-(2-hydroxy-4-triphenylmethyl)benzene-4-(methoxyphenyl)phosphonothiolothionic acid (**4b**) was formed (scheme 1). This was detected from the ^1H NMR spectra which shows that these two compounds exist in equal amounts. Trials has been devoted to separate **4a** and **4b** using fractional crystallization or silica gel column were unsuccessful .The methylation of the mixture **4a** and **4b** using methyl iodide in dry acetone followed by separation on column chromatography seems by far the best method for the separation of these two compounds as methyl ethers **5a** and **5b** (scheme1).

Compounds **5a** and **5b** were easily differentiated using the ^1H chemical shift of the OCH_3 *meta* or *para* to the C-trityl group. The chemical shift of 3H of OCH_3 in **5a** is sharp singlet at 3.85 ppm while in **5b** is at 3.60 ppm which is nearly compatable with methoxyl protons at the same situations in 3, 4-dimethoxytetrapheny1methane.[13]

As to the formation of compounds **3a-f,** it is suggested that nucleophilic attack of the phosphorus atom of the monomeric species[14] of LR on one of the hydroxyl group of the dihydroxy compound **2** to form the intermediate **6** followed by ring closure after elimination of H_2S (Scheme 2).

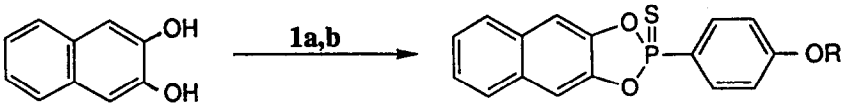


Scheme 1



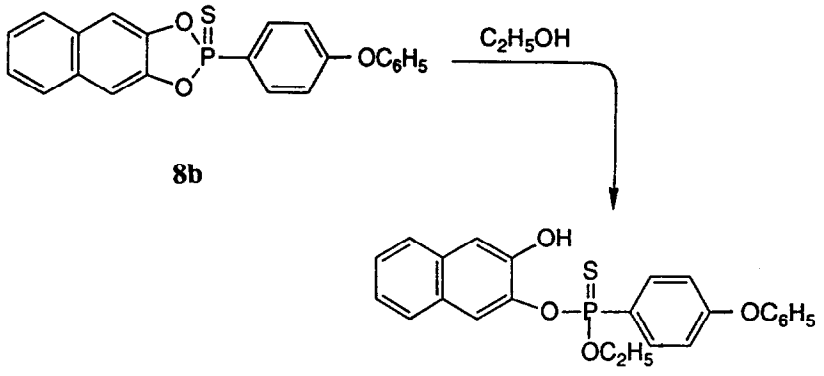
Scheme 2

2,3-Dihydroxynaphthalene (**7**) behaves similarly on reaction with **1a,b** giving rise to 1,3,2-naphthodioxaphosphole-2-*p*-alkoxy- (or aryloxy)phenyl-2- sulfide **8a** and **8b**, respectively.



7 **8a**, R = CH_3
b, R = C_6H_5

The structure of **8a,b** has been established spectroscopically (Table 1) and also using chemical evidence just by ethanolysis of **8b** to give **9** only.



8b

9

The structure of **9** has been elucidated using both analytical and spectroscopic methods (Table 1 and experimental). In the mass spectra the compound gave M^+ at m/e 436 (66.5%) which loose OC_2H_5 to give 391 (23.9%) and then hydrogen to give the base peak at 390 (100%).

Also, 2,2-dihydroxybiphenyl (**10**) react with LR and its *p*-phenoxy- derivative to give **11a,b** in high yield. The structure has been proved using microanalysis and also by spectroscopic methods (Table1).

Table 1 : ^{1}H NMR and ^{31}P for compounds **3a-f, 4a,b, 5a,b, 8a,b, 9** and **11a,b** .

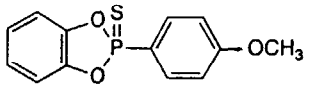
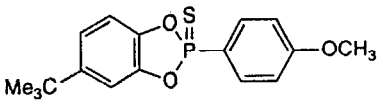
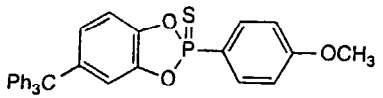
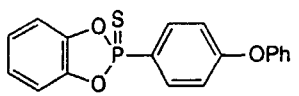
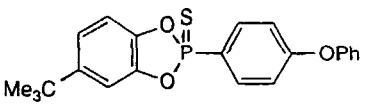
Compound	Formula	^{31}P	^{1}H NMR ($CDCl_3$) δ (ppm)
3a		108.8	3.85 (s, 3H, OCH_3), 6.9-7.0 (dd, 2H, J_{PH} = 3Hz, J_{HH}=9Hz, *meta* protons to P), 7.0-7.16(m,4H, of the ring catechol), 7.74-7.92 (dd, 2H, J_{PH} = 15Hz, J_{HH} = 9Hz, *ortho* protons to P).
3b		109.4	1.2(s,9H, *tert*-butyl),3.9(s,3H, OCH_3),6.9-7.0(dd,2H *meta* protons, to P), 7.08 (m,1H of the catechol),7.16-7.34 (m,2H, 2 *ortho* protons of the ring catechol), 7.80-7.96 (dd, 2H *meta* protons to P.).
3c		109.8	3.9(s,3H,OCH_3),6.8-7.1(m,5H, 2 protons *meta* to P in LR part + 3H of ring catechol), 7.1- 7.4(m,15H,CPh_3), 7.7-7.9 (dd, 2H, *ortho* protons to P.)
3d			6.8-7.6 (m,11H, aromatic), 7.7-8.0 (dd, 2H, *ortho* protons to phosphorus).
3e		108.2	1.4 (s,9H, *tert*-butyl), 6.98-7.46 (m, 10H, aromatic), 7.78-7.94 (dd, 2H, *ortho* protons to phosphorus).

Table 1 : (*continued*)

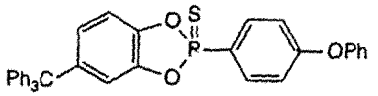
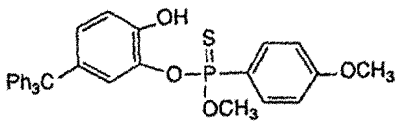
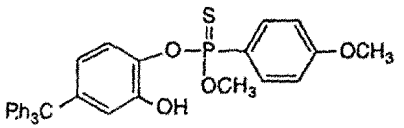
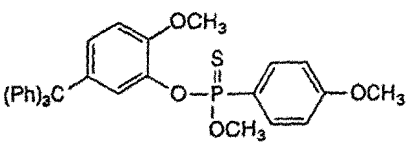
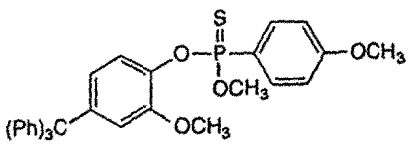
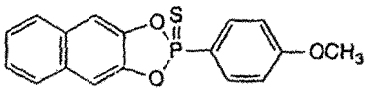
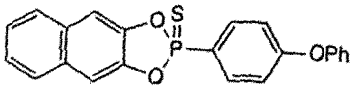
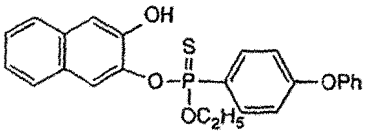
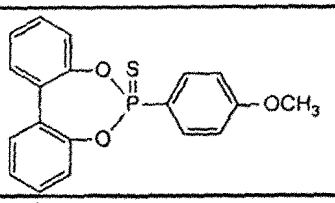
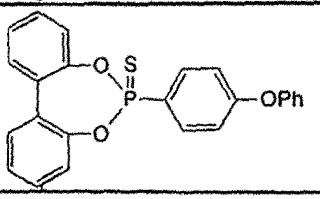
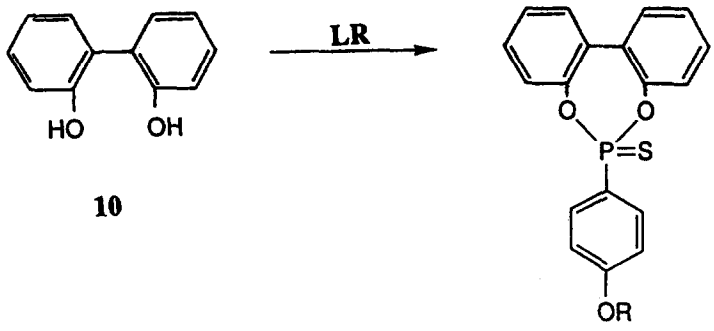
Compound	Formula	31p	^{1}H NMR ($CDCl_3$) δ (ppm)
3f		108.7	6.8-7.5 (m, 25H, aromatic), 7.70-7.95 (dd, 2H, *ortho* protons to phosphorus in LR part).
4a			two doublets centered at 3.70 and 3.85 ppm for 2 OCH_3 groups attached to P with $J_{P\text{-}C\text{-}C\text{-}H}$=14$H_Z$, 3.82 and 3.86 two singlets for 2 OCH_3 *para* to P. 6.5-7.8, (m,4OH, aromatic), 7.4-7.9 (two dd for 4H *ortho* protons to phosphorus).
4b			
5a			3.85 (d,3H, OCH_3 attached to P), 3.84 (s,3H,OCH_3 *para* to CPh_3), 3.85 (s,3H, OCH_3 of LR part), 6.65-6.90 (m, 5H, 2H *meta* to P+3H of ring catechol), 7.1-7.4 (m,15H,CPh_3), 7.90-8.00 (dd,2H *ortho* in LR part).
5b			3.70 (d, $J_{P\text{-}O\text{-}C}$=14Hz, OCH_3 attached to P,3.69 (s,3H,OCH_3 *meta* to CPh_3),3.81 (s,3H, OCH_3 of LR part), 6.70-7.00 (5H, 2H, *meta* to P in LR part + 3H in ring catechol), 7.1-7.4 (m,15H, CPh_3), 7.70-7.85 (dd, 2H *ortho* in LR part).

Table 1 : (*continued*)

Compound	Formula	31P	^{1}H NMR ($CDCl_3$) δ (ppm)
8a		108.5	3.8(s, 3H, OCH_3) ,7.00-8.10 (m,10H, aromatic)
8b		107.4 108.5	6.80-7.10 (m, 4H, 2H *ortho* to O in the Naphthalene ring+ 2H *meta* to P in the LR part). 7.20-7.60 (m, 7H,3H of the OPh ring + 4H of ring naphthol), 7.7-8.0 [m,4H (2H *ortho* to P and 2H *ortho* to oxygen in OPh)].
9		87.3	1.2(t, 3H, CH_3 of the ethoxy group), 4.3 (m., 2H,CH_2 of the ethoxy group),7.00-7.80 (m, 13H, aromatic); 8.00 (dd, 2H, *ortho* protons to phosphorus), 10.2 (s.,OH group) .
11a		101.0	3.85(S, 3H, OCH_3), 6.80(dd, 2H, *meta* protons to P), 7.00(dd, 2H, *ortho* protons to O) 7.3 (m, 4H, aromatic), 7.6 (dd, 2H, aromatic, *meta* to oxygen, 7.8 (dd, 2H, *ortho* proton to P).
11b			6.8-7.6 (m, 15H, aromatic) 7.70-7.90 (dd, 2H *ortho* protons to P in the ring anisole)



10

11a, R = CH_3
b, R = C_6H_5

Conclusion

The reaction of Lawesson's reagent (LR) with aromatic dihyroxy compounds affords a new and versitile method for preparing a very important class of compounds namely 1,3,2-dioxaphospolane-2-(*p*-methoxyphenyl)-2-sulfide. The yields of these compounds are independent on the molar ratios of the reactants which is in contrast to the compounds formed from aliphatic diol. Also we are not able to separate or even detect the cyclic trithiopyrophosphonate separated with aliphatic diols.[11]

Experimental

Melting points were determined with MeI Temp apparatus and are uncorrected, as are the boiling points. IR spectra were recorded by using a unicam SP 1100 or PU 9712 infrared spectrophotometers. The ^1H NMR spectra were recorded on a Varian Gemini 200 MHz or Bruker 270 MHz spectrometers. Chemical shifts are expressed in δ relative to TMS as internal standard in $CDCl_3$ as a solvent. ^{31}P were referenced to external 85% H_3PO_4. MS data were obtained on a gas chromatography/mass spectrometer EX1000 QP Schimadzu-Japan. The reported yields to pure isolated materials from column chromatography using silica gel 60 (Merck).

Reaction of 2,4-bis(4-methoxyphenyl)-1, 3, 2, 4-dithiadiphosphetane-2,4-disulfide (LR, 1a) with catechol (2a) using 0.5 : 1 molar ratio. Preparation of 3a.

A mixture of 1.1 g catechol (10 mmole) and 2.02 g (5 mmole) of the title compound (LR)[15] in 25 ml anhydrous toluene as a solvent was stirred magnetically at reflux temperature (110°C) untill no more of the starting material could be detected (TLC), (5 hrs). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to silica gel

column 20% diethyl ether/pet. ether (60-80) up to 50% ether-pet. ether to give 0.9 g (32%) of benzo-1,3,2-dioxaphosphole-2-(*p*-methoxyphenyl)-2-sulfide (**3a**), m.p. 55°C, Anal. Calcd. for $C_{13}H_{11}O_3PS$ (278). C, 56.12; H, 3.98; P, 11.13; S, 11.52. Found : C, 56.08; H, 4.05; P, 11.00; S, 11.34%. IR ($\bar{\nu}$, cm^{-1}, group). 650 (P=S); 1190 (P-O-C), 1600 (C=C, aromatic) the compound lacks bands at 3400 for OH groups. MS : m/e (% rel. int.) 278 (M^+, 70), 262 (15), 245 (8), 155 (47), 139 (100, base peak), 92 (18), 77 (9).

Reaction of Lawesson's Reagent (LR) with 4-*tert*-butylcatechol. Preparation of 5-*tert*-butylbenzo-1,3, 2-dioxaphospholane-2-(*p*-methoxyphenyl)-2-suflide (3b) .

A mixture of 0.83 g (5 mmole) of 4-*tert*-butylcatechol and 1.01 g (2.5 mmole) of LR in 25 ml dry toluene was heated under reflux for 8 hrs. The reaction mixture was evaporated on silica gel and applied to silica gel column using 25% ether/pet. ether up to 50% ether-pet. ether to give 0.8 g (48%) of the title compound, m.p. 65°C. Anal. Calcd. for $C_{17}H_{19}O_3PS$ (**3b**) (334). C, 61.09; H, 5.68; P, 9.26; S, 9.59. Found: C, 61.00; H 5.54, P, 9.30; S, 9.39%. IR ($\bar{\nu}$, cm^{-1} group) 650 (P=S), 1180 (P-O-C), 1600 (C=C, aromatic). Compound **3b** lacks bands in the region 3400 for OH group. MS: m/e (% rel. int.) 334 (M^+, 100, base peak); 319 (M^+ -CH_3, 80), 287 ($C_{16}H_{16}O_3P$, 15) 211 (60), 179 (22), 155 (25), 139 (24), 105 (20), 91 (18), 77 (35).

Reaction of Lawesson Reagent with 4-triphenylmethyl-1,2-dihydroxybenzene. Preparation of 5-triphenylmethylbenzo-1,3,2-dioxaphospholane-2-(*p*-methoxyphenyl)-2-sulfide (3c).

Heating a mixture of 1.36 g (4 mmole) of 4-tripenylmethyl-1,2-dihydroxybenzene (**2c**) and 0.89 g (2 mmole) of LR in 25 ml anhydrous toluene as a solvent gave after heating under reflux with stirring, worked out by column chromatography using 25% ether-pet. ether 1 g (49%) of 4-tripenylmethylbenzo-1,3,2,-dioxaphospholane-2-(*p*-methoxyphenyl)-2-sulfide (**3c**) m.p 190°C. Anal. Calcd. for $C_{32}H_{25}O_3PS$ (520) C, 73.85; H, 4.81; P, 5.95; S, 6.16. Found: C, 73.65, H, 4.80; P, 5.95; S, 6.17 %. IR ($\bar{\nu}$, cm^{-1}, group) 700 (P=S), 1190 (P-O-C), 1600(C=C, aromatic). Compound **3c** lacks any band in region 3400 which corresponds to OH group. MS : m/e (% rel. int.) 520 (M^+, 2), 443 (5), 244 (35), 243 (12), 191 (8), 167 (25), 165 (25), 152 (10) 142 (12), 119 (25).

Reaction of 2,4-bis(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (1b) with catechol (2a). Preparation of benzo-1,3,2-dioxaphospholane-2-(*p*-phenoxyphenyl)-2-sulfide (3d) .

To 0.66 g (6 mmole) of Catechol (**2a**) was added 1.58 g (3 mmole) of **1b** in 25 ml of toluene as a solvent and the mixture was refluxed for 4 hrs. After evaporation of the solvent and puri-

fication of the product on silica gel column using 40% $CHCl_3$/pet. ether as eluent gave 0.21 g (10.3%) of **3d**, oil. Anal. Calcd. for $C_{18}H_{13}O_3PS$ (340). C, 63.54; H, 3.82; P, 9.10; S, 9.42. Found: C, 63.34, H, 3.75; P, 8.85; S, 9.32%. MS : m/e (% rel. int.). 340 (M^+, 69), 315 (10), 199 (11.6), 155 (11.6), 139 (100), 115 (11.7), 77 (24).

Reaction of 1b with 4-*tert*-butylcatechol. Preparation of 5-*tert*-butylbenzo-1,3,2-dioxaphospholane-2-(*p*-phenoxyphenyl)-2-sulfide (3e) :

A mixture of 1.66 g (10 mmole) of 4-*tert*-butylcatechol (**2b**), 2.64 g (5 mmole) of **1b** in 25 ml anhydrous toluene was relfuxed for 4 hrs with stirring. Evaporation of the solvent under reduced pressure and separation of the product on silica gel column using 10% up to 50% ethyl acetate/pet. ether as eluent to give 0.6 g (15.1 %) of **3e**, m.p. 110°C. Anal. Calcd. for $C_{22}H_{21}O_3PS$ (396) C, 66.51; H, 5.53; P, 7.79; S, 8.06. Found: C, 66.80; H, 5.45; P, 7.71; S, 8.00 %. IR ($\tilde{\gamma}$, cm^{-1}, group) 695, 720 (P=S), 1200 (P-O-C aromatic); 1590, 1610 (C=C, aromatic). No bands were observed in the region of 3400 cm^{-1} characterstic for OH, MS : m/e (% ret. int.) 369 (M^+, 51), 381 (M^+ -CH_3, 100), 211 (12), 190 (13.6), 176 (7.4), 77 (11.4), 28 (24).

Reaction of 1b with 4-triphenylmethyl-1,2-dihydroxybenzene (2c). Preparation of 5-triphenylmethylbenzo-1, 3, 2-dioxaphopolane-2-(*p*-phenoxyphenyl)-2-sulfide (3f).

A mixture of 2.11 g (6 mmole) of 4-triphenylmethyl-1,2-dihydroxybenzene (**2c**) and 1.5 g (3 mmole) of **1b** was heated under reflux in 25 ml anhydrous toluene untill no more of the starting material could be detected (TLC) (5 hrs), the solvent was stripped off and the residue was applied to silica gel column using 10% up to 30% ethyl acetate/pet. ether as eluent to give 0.77 g (22%) of **3f**, m.p. 212°C. Anal. Calcd. for $C_{37}H_{27}O_3PS$ (582). C, 76.16; H, 4.8; P, 5.31; S, 5.49. Found: C, 76.05; H, 4.52; P, 5.20; S, 5.65%. IR ($\tilde{\gamma}$ cm^{-1}, group) 720 (P=S), 1200 (P-O-C-aromatic), 1600 (C=C, aromatic) No bands were observed in the region 3500 for OH groups. MS : m/e (% rel. int.) : 582 (M^+, 50), 505 ($C_{31}H_{22}O_3PS$ 100, base peak), 427 (7), 335 (35), 285 (20), 259 (40), 169 (55), 149 (20), 85 (30), 71 (48), 57 (55), 43 (85).

Pyrolysis of 3c

0.1 g of **3c** was heated to 225°C in a pyrolysis tube under vacuum (0.1 mm/Hg) for 2 hrs. After working up of the residue, it gave the starting **3c** (m.p. and mixed m.p. 190°C).

Methanolysis of 3c

0.52 g of the title compound was heated in methanol (20 ml) under reflux for 1/2 hr to give after evaporation of the solvent 0.46 g (83% yield) of a mixture of **4a** and **4b.**

Methylation of 4a, 4b

0.46 g of a mixture of **4a, 4b** in 20 ml dry acetone was treated with 0.14 g (1 mmole) of CH_3I in presence of anhydrous K_2CO_3 and heated on water bath for 6 hrs. Evaporation of the solvent under reduced pressure and separation of the products on silica gel column using 10 % ether/pet. ether to give :

5a : 0.05 g (8.8%), oil. Anal. Calcd. for $C_{34}H_{31}O_4PS$ (566.6) C, 72.07; H, 5.51; P, 5.46; S, 5.66. Found: C, 71.89; H, 5.45; P, 5.36; S, 5.55%.

5b: 0.12g (21. 2%), m.p. 195°C. Anal. Calcd. for $C_{34}H_{31}O_4PS$ (566.6). C, 72. 07; H, 5.51; P, 5.46; S, 5.66. Found : C, 72.17; H, 5.47; P, 5.32; S. 5.60%.

Reaction of Lawesson Reagent (1a) with 2, 3-dihydroxynaphthalene (7) . Preparation of naphtho-1,3, 2- dioxaphospholane-2 (*p*-methoxypheny1)-2-sulfide (8a) .

To 1.6 g (10 mmole) of 2,3-dihydroxynaphthalene was added 2.02 g (5 mmole) of LR in toluene (25 ml) and the mixture was refluxed for 2 hrs untill the starting material has been consumed (TLC). Evaporation of the solvent under reduced pressure and purification of the product on silica gel column using 15% up to 30% ethyl acetate-pet. ether mixtures to give 0.6 g (18%) of **8a**, m.p. 118°C. Anal. Calcd. for $C_{17}H_{13}O_3PS$ (328.23). C, 62.21; H, 3.96; P, 9.44; S, 9.77. Found: C, 62.00; H, 3.91; P, 9.60; S, 9.55%. MS: m/e (% rel . int.). 328 (M^+, 60), 189 (17.7), 160 (100, base peak), 114 (37.6), 28 (53.9), 18 (50.6). IR ($\bar{\gamma}$, cm^{-1} group). No bands were observed in the region of 3400 cm^{-1} characterstic for OH group, 1600 (C=C, aromatic), 1240 (P-O-C, aromatic), 720 (P=S).

Reaction of 1b with 2,3-dihydroxynaphthalene. Preparation of naphtho-1,3,2- dioxaphospholane-2- (*p*-phenoxypheny1)-2- sulfide (8b) .

1.85 g (3.5 mmole) of **1b** was added to 1.12 g (7 mmole) of 2,3-dihydroxynaphthalene in 25 ml anhydrous toluene as a solvent, and the reaction mixture was heated under reflux for 3 hrs to give after purification on silica gel column using 40% ether-pet. ether mixture 0.9 g (33%) of the title compound, m.p. 77°C. Anal.Calcd. for $C_{22}H_{15}O_3PS$ (390). C, 67.70; H, 3.85 ; P, 7.94; S, 8.21. Found: C, 67.45; H, 3.80; P, 7.75; S, 8.00%. IR ($\bar{\gamma}$ cm^{-1}, group), 710 (P=S), 1150 (P-O-C). No bands were detected in the region 3400 cm^{-1} which correspond to OH group. MS: m/e (%, rel. int.) 390 (M^+, 100, base peak), 205 (5), 195 (7), 189(21), 28 (37).

Ethanolysis of 8b. Preparation of compound 9.

0.39 g (1 mmole) of **8b** was heated in ethyl alcohol 20 ml for 2 hrs. Evaporation of the solvent under reduced pressure and purifying the product on silica gel column to give 0.32 g (73.4%) of **9**, m.p. 83°C. Anal. Calcd. for $C_{24}H_{21}O_4PS$ (436.3), C, 66.07; H, 4.81; P, 7.10; S, 7.35.

Found: C, 65.85; H, 4.80; P, 7.00; S, 7. 25%. The ^{1}H NMR spectrum of compound **9** shows a singlet at 10.2 ppm corresponds to OH group MS: m/e (% rel. int.) . 436 (M^+, 89.6), 390 (100, base peak), 277 (19), 249 (30).

Reaction of Lawesson's Reagent with 2,2̂-dihydroxybiphenyl. Preparation of bipheny1-1,3,2-dioxaphospholane-2-(*p*-methoxypheny1)-2-sulfide (11a).

A mixture of 0. 93 g (5 mmole) of 2, 2̂-dihydroxybipheny1 1.01 g (2.5 mmole) of LR and 25 ml acetonitrile was heated under reflux untill the starting material could not be detected (TLC) (2 hrs). Evaporation of the solvent and purifying the product on column chromatography using ethyl acetate/ pet. ether mixture (20%) as eluent to give 0.2 g (11.3%) of **11a**, m.p. 115°C. Anal. Calcd. for $C_{19}H_{15}O_3PS$ (354). C, 64.42; H, 4.24; P, 8.74; S, 9.05. Found: C, 64.29; H, 4.15; P, 8.67; S, 9.00%. MS: m/e (% rel. int.) 354 (M^+, 8), 215 (10), 184 (75), 139 (5).

Reaction of 1b with 2,2̂-dihydroxybiphenyl. Preparation of biphenyl-1,3,2- dioxaphospholane-2-(*p*-phenoxyphenyl)-2-sulfide (11b).

By using the same experimental procedure as in **11a**, 0.74 g (4 mmole) of 2,2-dihydroxybiphenyl was treated with 1.05 g (2 mmole) of **1b** to give 0.5 g (30%) of **11b**, oil. Anal. Calcd. for $C_{24}H_{17}O_3PS$ (418) C, 69.24; H, 4.09; P, 7.44; S, 7.70. Found : C, 69.00; H, 4.15; P, 7.25; S, 7.50%. MS: m/e (% rel. int.) 417 (25), 264 (10), 185 (75).

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