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ORGANOPHOSPHORUS COMPOUNDS XIII.+ THE REACTION OF 2,4-BIS(4-METHOXYPHENYL) -1,3,2,4-DITHIADIPHOSPHETANE -2,4-DISULFIDE (LR) WITH DIHYDRIC ALCOHOLS. A NEW ROUTE TO 1,3,2-DIOXAPHOSPHORINANE

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Abstract : 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent) and its *p*-phenoxy derivatives react with 1,2-ethanediols and 1,4-butanediol at different reaction temperatures in acetonitrile as a solvent to give 1,3,2-dioxaphosphorinane-2-sulfide, thioacetamide and cyclic trithiopyrophosphonate. Compatible analytical and spectroscopic data were obtained for all the new compounds. A mechanism is proposed to explain the formation of compounds **5**, **6**, **7**, **9** and **11**. Reaction of **5a** with LR gave 1,3,2- dithiaphosphorinane-2-sulfide.

Introduction

In 1968, Horner *et al*[1] has reacted 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (LR) with ethylene glycol in acetonitrile giving rise O-(2-hydroxyethyl)hydrogen (4-methoxyphenyl)phosphonothiolothionates (3) and O,O-(1,2-ethylene) bis(4-methoxyphenyl)-phosphorothiolothionic acid (**4**) (Scheme 1).

However, it was not possible to confirm earlier work, compounds **3** and **4** were not isolated but instead compounds **5**, **6** and **7** (Scheme 1). As a continuation of our interest- the reaction of Lawesson reagent with different types of substrates such as alcohols,[2] phenols,[2] thiols, oximes,[3] anils,[4] quinones,[5] phosphites[6] and benzene sulfenyl chlorides[7]- this paper will report on the reaction of LR with 1,2- dihydric alcohols (**2a-c**) and 1,4-butanediol (**8**) in acetonitrile as solvent.

Results and Discussion

1,3,2,4-Dithiadiphosphetane-2,4-disulfide (**1a**) reacts with ethylene glycols (**2a-c**) in acetonitrile using 1:1 molar ratio at room temperature (25°C) or at 80°C to give the cyclic 2-aryl-1,3,2-

+ For Part 12 see A.A. El- Kateb, I.T. Hennawy, R.Shabana and H.A. Abdel- Malek, Phosphorus, Sulfur and Silicon , **1991**, 63, 13 .

dioxaphospholane-2-sulfide (**5**) as the main reaction product (28-52%), cyclictrithiopyrophosphonates (**6**) (5.6-12.5%) and the thioacetamide (**7**) (Route 1, Scheme 1). When the above reaction has been performed using 0.5 mole of LR and one mole of ethylene glycol (Route 2) the products will be **5** and **7**. On the other hand, compounds **6** and **7** have been formed using 1.5 mole of LR and one mole of ethylene glycols (Route 3). The structure of compounds **5, 6** and **7** had been confirmed by analytical results and spectral data IR, NMR (^{1}H, ^{13}C, ^{31}P) and MS. Compound **5a** (taken as representative example) gave correct elemental analysis, in the IR spectra **5a** shows peaks at 642 cm^{-1} (P=S),[8] 1021 cm^{-1} (P-O-C)[8] and lacking any peak at 2450 cm^{-1} for SH which should be present if the compound is 0-(2-hydroxyethyl)hydrogen (4-methoxyphenyl)-phosphonothiolothionate (**3**) as stated earlier by Horner *et al.*[1] The ^{1}H NMR of compound **5a** exhibits a singlet at 3.85 ppm (OCH_3), multiplet at 4.20-4.70 ppm for 4H (2 OCH_2); 6.80-7.05 ppm (2H, dd) J_{PH} = 3 Hz, J_{HH} = 9 Hz (*meta* protons to P); 7.60-7.95 ppm (2 H, dd) J_{PH} = 15 Hz, J_{HH} = 9 Hz (*ortho* protons to P) . Compound **5a** gave M^+ at 230 and the ^{31}P at 106.7 ppm (Table 2).

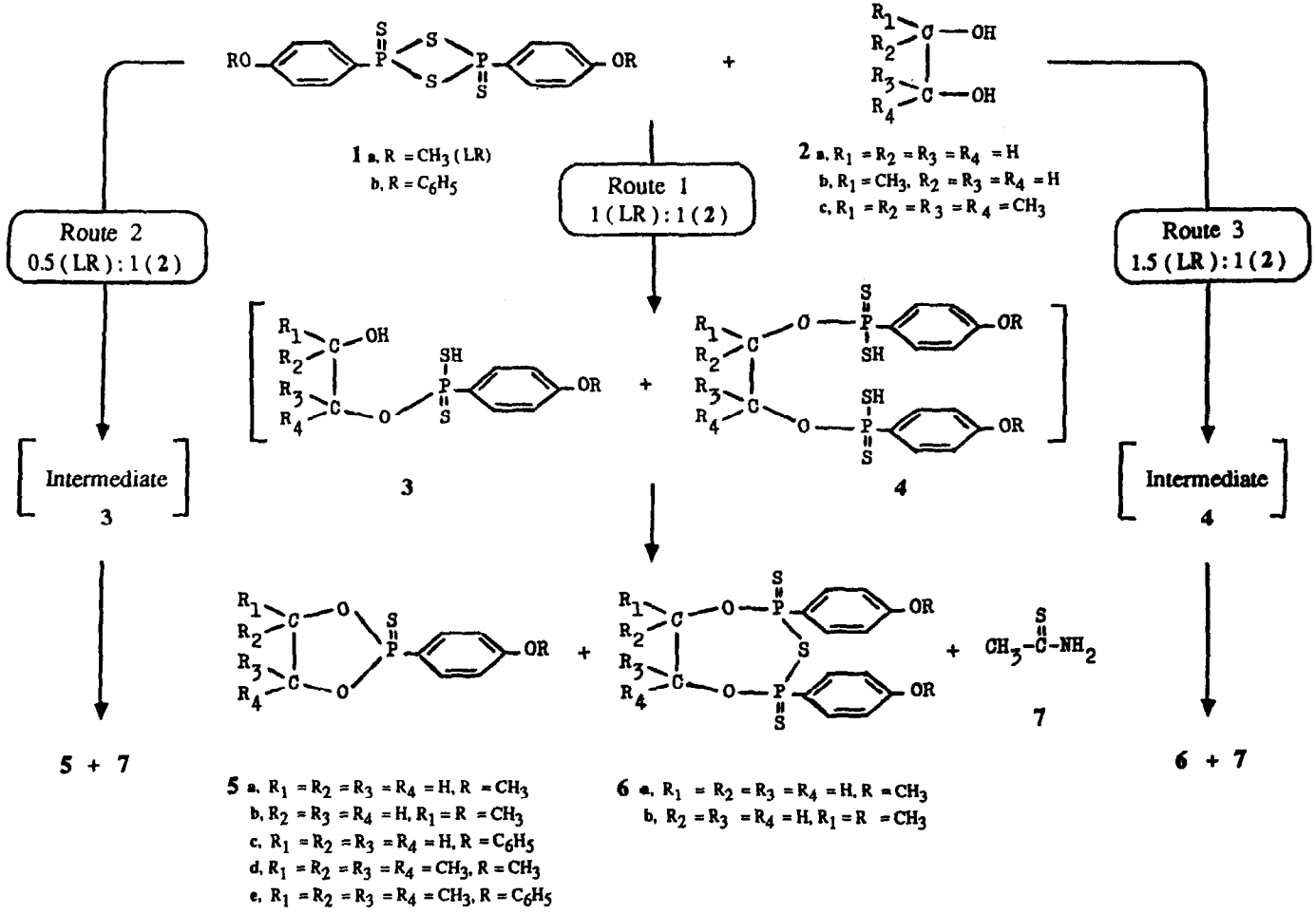
Compound **6a** gives correct combustion analysis, the IR spectrum shows absorption peaks at 452 cm^{-1} (P-S-P); 637 cm^{-1} (P=S) and 1024, 1065 cm^{-1} (P-O-C-C-). The ^{1}H NMR shows signals at 3.85 ppm as singlet for 6H (2 OCH_3); 4.00-4.50 ppm, multiplet for 2H of the ethlyene glycol; 5.00-5.45 ppm, multiplet for another 2H of the ethylene glycol probably deshielded by its vicinity to the sulfur atom so they show down field shift.[9,10] Other probability is that the first 2H is axial while the second is equatorial, 6.80-7.10 ppm, dd, 4H, *meta* protons to phosphorus; 7.90-8.25 ppm, dd, 4H, *ortho* protons to phosphorus. Compound **6a** gave M^+ 432.

Compound **7**, the thioacetamide, has been established by m.p. and mixed m.p. with authentic sample,[11] NMR (^{1}H, ^{13}C).

Table 1 : Experimental, reaction conditions and the products of the reaction of 1,3,2,4-dithiadiphosphetane- 2,4-disulfide with 2a-c and 8.

Starting	Molar Ratio	Reaction time (h)	Reaction temp. (°C)	Reaction Products		
				5	6	7
LR + 2a	1:2	4	80	48	-	54
LR + 2a	1:1	4	80	52	5.6	37.3
LR + 2a	1:1	5	25	28	9.3	53
LR + 2a	1.5:1	12	25	-	23	20
LR + 2b	1:2	2	80	27	-	36
LR + 2b	1:1	3	80	31	12.5	41.3
LR + 2c	1:2	2	80	54	-	13
LR + 2c	1:2	5	25	30	-	34
LR + 8	1:2	4	80	26	-	24
LR + 8	1:1	4	80	43	-	20

Notes to Table 1 : **2a** = ethylene glycol; **2b** = propane 1,2-diol, **2c**= tetramethyl ethylene glycols **8**= butane 1,4- diol; yields were determined after separation on silica gel column.


Route 2
0.5 (LR) : 1 (2)
Route 1
1 (LR) : 1 (2)
Route 3
1.5 (LR) : 1 (2)
Intermediate
3
Intermediate
4
5 + 7
6 + 7
1 a, R = CH3 (LR)
b, R = C6H5
2 a, R1 = R2 = R3 = R4 = H
b, R1 = CH3, R2 = R3 = R4 = H
c, R1 = R2 = R3 = R4 = CH3
3
4
7
5 a, R1 = R2 = R3 = R4 = H, R = CH3
b, R2 = R3 = R4 = H, R1 = R = CH3
c, R1 = R2 = R3 = R4 = H, R = C6H5
d, R1 = R2 = R3 = R4 = CH3, R = CH3
e, R1 = R2 = R3 = R4 = CH3, R = C6H5
6 a, R1 = R2 = R3 = R4 = H, R = CH3
b, R2 = R3 = R4 = H, R1 = R = CH3

Scheme 1

Efforts had been devoted to optimize the yields of the different products of the reaction of Lawesson's Reagent (LR)with glycols **2a-c** and **8**. Table 1 shows that 1,3,2-dioxaphosphorinane-2-sulfide **5** is the main reaction product when using 0.5 mole of LR to one mole of glycols, and increases in yields when using 1:1 molar ratio. Also, the cyclic trithiopyrophosphonates **6** was formed only when using 1:1 moles of the reactants and in low yields, while using excess LR (1.5:1 mole) the tricyclicpyrophosphonates formed exclusively. The thioacetamide in all these reactions is formed in moderate to good yield (Table 1).

Similarly, **1a** reacts with **2b** to give **5b, 6b,** and **7** while it affords **5c** and **7** on reaction with 2c. Also, reaction of **1b** with **2a,c** gave only 1,3,2-dioxaphosphorinane-2-sulfide (**5c** and **5e**) together with the thioacetamide **7**. Table 2 contains the ^{1}H NMR spectra of all the products together with the available data of ^{31}P NMR while Table 3 the ^{13}C NMR for compounds **5d, 5e** and **9a**.

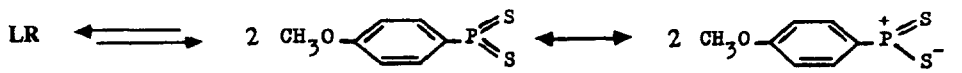
1,4-Butanediol (**8**) reacts with **1a** and **1b** in acetonitrile to give **9a,b** together with **7**.

8

9a, R = CH_3
b, R = C_6H_5

The structure elucidation of **9** has been achieved using microanalysis, IR, NMR (^{1}H, ^{13}C, ^{31}P) and mass spectra. In the ^{1}H NMR of **9a,b** it is interesting to mention that in case of **9a**, the 4H of $(CH_2)_2$ group are not equivalent and gives rise to 2H at 0.9 ppm (axial) and the other 2H at 1.3 ppm (equatorial). In case of **9b**, the 4H of $(CH_2)_2$ are all equivalent and appear at 2.0 ppm while the 4H of the 2 OCH_2 are not equivalent due to deshielding of 2H near sulfur atom (Table 2).

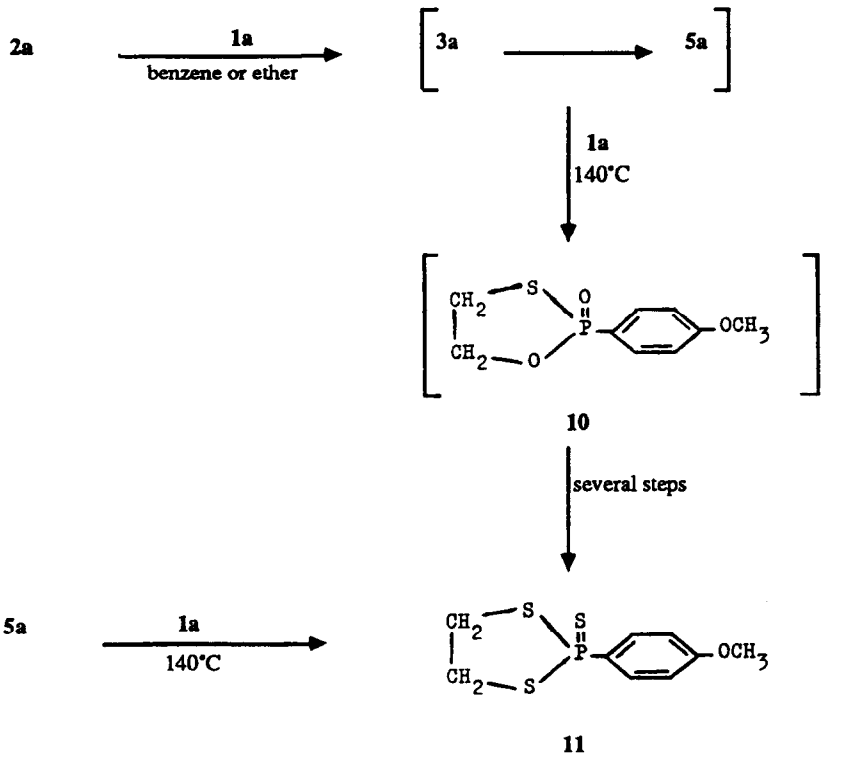
As to the mechanism, it is known that 1,3,2,4-dithiadiphosphetane-2,4-disulfide (**1a**) exist in equilibrium with the monomeric species **LR'** and **LR"**. [12-14]



LR' **LR"**

So, electrophilic attack of the species LR" on the nucleophilic oxygen of ethylene glycol will afford the intermediate **3** and/or **4** (Scheme 1). The intermediates in presence of acetonitrile afford products **5** and /or **6** together with the thioacetamide **7**. [15,16]

In order to understand more about the mechanism of the reaction, we have done the reaction of LR with ethylene glycol **2a** in benzene or diethyl ether which should give **3a**.[17,18] Heating the intermediate **3a** in presence of LR at 140°C in o-dichlorobenzene gave 1,3,2-dithiaphosphorinane-2-sulfide (**11**) probably through the intermediates **5a** and **10**. Compound **11** was prepared independently by heating **5a** with LR at 140 °C in o-dichlorobenzene (Scheme 2).



Scheme 2

As a conclusion, the reaction of Lawesson's Reagent with ethylene glycols depends not only on the molar ratios of the reactants but also on the reaction temperature. So, using 0.5 mole of LR to one mole of ethylene glycol affords only 1,3,2-dioxaphosphorinane-2-sulfide, while using 1:1 molar ratio gives rise to both the dioxaphosphorinane and the cyclic trithiopyrophosphonate. The last compound was formed exclusively by using excess of LR. At high temperature, the reaction gives rise to 1,3,2-dithiaphosphorinane-2-sulfide.

Table 2 : ^{1}H NMR and available ^{31}P *for compounds 5a-e, 6a,b, 9a,b and 11.*

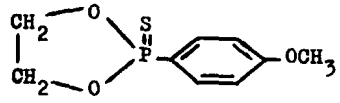
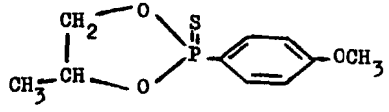
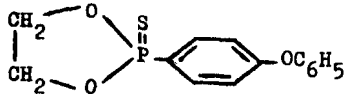
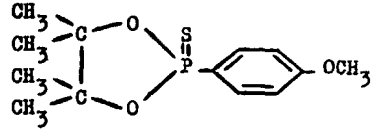
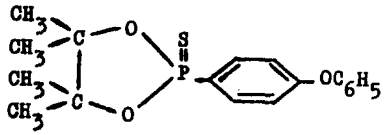
Compound	Formula	^{31}P	^{1}H NMR ($CDCl_3$), δ (ppm)
5a		106.7	3.8 (s, 3H, OCH_3), 4.2-4.7 (m, 4H, 2 CH_2, splitted by P). 6.80-7.05 (dd, 2H) J_{HH}= 3Hz, J_{HH}= 9Hz, *meta* proton to P), 7.6-7.95 (dd, 2H, J_{PH} =15Hz,J_{HH}=9_{Hz}, *ortho-* ptoton to P).
5b			1.5 (d, 3H, CH_3), 3.8(s, 3H, OCH_3), 4.3-4.8 (m, 3H, CH, CH_2), 6.80-7.05 (2H, dd, *meta* protons to P), 7.60-7.95 (dd, 2H, *ortho*-protons to P in the aromatic ring).
5c			2.2 and 2.4 (2m, 4H, 2 OCH_2) 2H axial and 2H equatorial 7.0-7.5 (m, 7H, protons of OC_6H_5 + 2H *meta* to P. 7.80-7.95 (m, 2H, *ortho-* protons to P in the aromatic ring).
5d		97.85	1.3 (s, 6H, $2CH_3$, axial); 1.6 (s, 6H, $2CH_3$, equatorial); 3.8(s, 3H, OCH_3), 6.95 (dd, 2H, *meta*-protons to P), 7.9 (dd, 2H, *ortho-* protons to P in the aromatic ring).
5e		96.9	1.4 (s, 6H, 2 CH_3, axial), 1.6 (s, 6H, 2 CH_3 equatorial), 3.8 (s, 3H, OCH_3), 6.95 (dd, 2H, *meta-* protons to P),7.9 (dd, 2H) *ortho-* protons to P in the aromatic ring).

Table 2 (*Continued*)

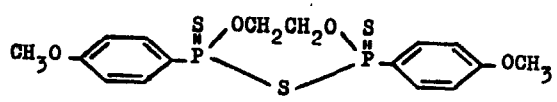
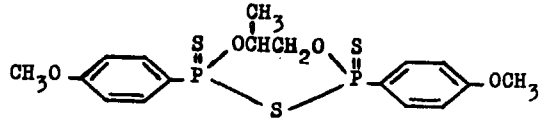
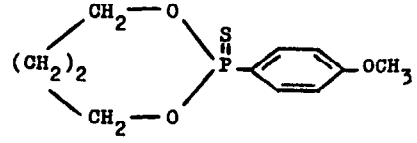
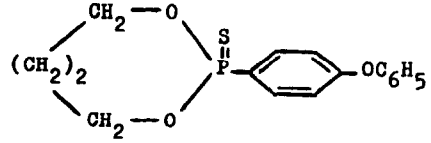
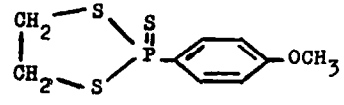
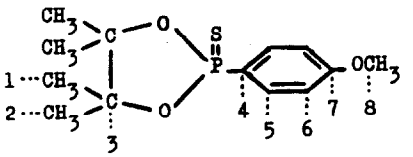
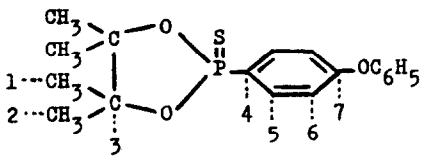
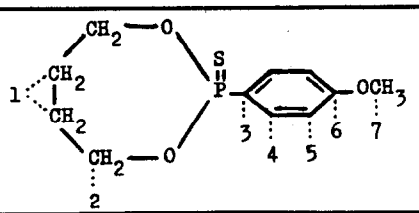
Compound	Formula	^{31}P	^1H NMR ($CDCl_3$), δ (ppm)
6a		89.9	3.85 (s, 6H, 2 OCH_3), 4.0-4.7 (m, 2H), 5.0-5.4 (m, 2H, with downfield shift due to P), 6.8-7.1 (dd, 4H, *meta*-protons to P),7.9-8.25 (dd, 4H, *ortho*- protons to P).
6b			1.4 (d, 3H, CH_3), 3.85 (s, 6H, 2 OCH_3) , 4.0-4.3 (m, 2H,OCH_2), 4.8-5.1 (m,1H, CH), 6.8-7.1 (m, 4H, *meta*- protons to P); 7.9-8.2 (m,4H, *ortho*- protons to P in the aromatic ring).
9a		89.8	0.9 (m, 2H, axial from the $(CH_2)_2$ group), 1.3 (m, 2H, equatorial of same $(CH_2)_2$ group, 3.85(s, 3H, OCH_3), 4.0-4.5(m, 4H, 2 OCH_2), 7.1,7.9 (2dd, 4H, *meta* and *ortho*- protons to P in the aromatic ring).
9b			multiplet centered at 2.0 [4H, $(CH_2)_2$], 4.1 (m, 2H, axial),4.4 (m, 2H, equatorial from the 2 OCH_2 groups. 6.95-7.5 (m,7H, OC_6H_5 protons + 2H, *meta* to P), 7.8-8.0 (dd, 2H, *ortho* to P).
11			3.6-4.0 (m, 4H, SCH_2), 3.8 (s, 3H, OCH_3), 7.0 and 8.1 are two dd, for 4H, aromatic protons *meta* and *ortho* to P.

Table 3 : ^{13}C NMR spectra of compounds 5d, 5e and 9a

Compound	Formula	C No.	δ (ppm)	J_{PC}
5d		1	24.23	4.0
		2	25.02	3.5
		3	89.44	2.0
		4	128.94	115.0
		5	132.00	11.0
		6	113.74	12.5
		7	162.26	3.0
		8	55.21	- - -
5e		1	24.18	3.8
		2	24.95	3.5
		3	89.62	2.0
		4	131.10	114.0
		5	131.92	10.5
		6	117.23	12.5
		7	162.65	3.0
9a		1	28.72	- - -
		2	67.17	6.5
		3	124.86	124.0
		4	132.24	15.0
		5	113.90	16.0
		6	162.29	2.6
		7	55.30	- - -

Experimental

Melting points were determined with Mel Temp apparatus and are uncorrected, as are the boiling points. IR spectra were recorded by using a Unicam SP, 1100 or PU 9712 Infrared spectrometers. The ^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Bruker 250 MHz spectrometers. Chemical shifts are expressed in δ relative to TMS as internal standard . ^{13}C NMR spectra in $CDCl_3$ - taken at 62.5 MHz. ^{31}P NMR 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 to pure isolated material from column chromatography using silica gel 60 (Merck).

Compound **1a** (Lawesson's Reagent, LR) is commercially available and can be prepared as described earlier.[19] Compound **1b**, 2,4-Bis(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, was prepared by using the above method from P_4S_{10} and diphenyl ether . The starting, ethylene glycol (2a), propane-1,2-diol (2b), tetramethyl ethylene glycol (2c) , and butane-1,4- diol (8) were commercially available

1- Reaction of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (LR, 1a) with ethylene glycol (2a) using 1:1 molar ratio (preparation of compounds 5a, 6a, 7) (Route 1). 0.32 g (5 mmole) of ethylene glycol (**2a**) was treated with 2.02 g (5 mmole) of LR in 20 ml anhydrous acetonitrile as a solvent. The reaction mixture was stirred magnetically at reflux temperature (80°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 applied to silica gel column using ethyl acetate / pet. ether (90-100) as eluent to give :-

a) Fraction 1 : 2,4-Bis(4-methoxyphenyl)-2,4-dithiono-1,5-dioxa-3-thio-2,4-diphosphetane (6a) : 0.06 g (5.6%), m.p. 122-4 °C., Anal. Calcd. for $C_{16}H_{18}O_4P_2S_3$ (432.44). C, 44.44; H, 4.19; P,14.32; S, 22.24 %. Found : C, 44.28, H, 4.25; P,14.18; S, 22.15. IR ($\bar{\nu}$, cm^{-1}, group) : 452 (P-S-P); 637 (P=S); 1024, 1065 (P-O-C-C), 1594 (C=C, aromatic). MS : m/e (% , rel. int.) : 432 (M^+, 12); 336 ($C_{16}H_{18}O_4P_2$, 20.1); 285 (11.9); 246 (21.1); 230 (100, base peak); 187 (63.3) ; 169 (52.7); 139 (39.5); 108 (20); 91 (32); 69 (67.3).

b) Fraction 2 : 1,3,2- Dioxaphosphorinane-2- sulfide-2 (4-methoxyphenyl) (5a) : 0.3g (52%), m.p.76 °C. Anal. Calcd. for $C_9H_{11}O_3PS$ (230.22). C, 46.96; H, 4.82; P, 13.45; S, 13.92 %. Found: C, 47.07; H, 4.71; P, 13.25; S, 13.96. IR ($\bar{\nu}$, cm^{-1}, group): 642 (P=S); 1021 (P-O-C-C); 1593 (C=C, aromatic). MS: 230 (M^+, 100, base peak); 197(8.4); 187 (46.3); 171 (12.5); 150 (6); 108 (6); 91 (11.8) .

c) Fraction 3 : Thioacetamide (7) 0.28 g (37.3%). m.p. 112 °C.

2- Reaction of Lawesson Reagent with propane-1,2-diol using 1:1 molar ratio (preparation of 5b, 6b, and 7) : A mixture of 0.76 g (10 mmole) of propane-1,2-diol (**2b**) and 4.04 g (10 mmole) of LR in 25 ml acetonitrile was refluxed under stirring for 3 hrs. Evaporation of the solvent under reduced pressure and purification of the products on silica gel column using ethyl acetate / pet. ether mixtures (starting from 5%-20%) gave :-

Fraction 1 : 2,4-Bis(4-methoxyphenyl)-2,4-dithiono-1,5-dioxa-3-thio-6-methyl-2,4- diphosphetane (6b) : 0.28 g (12.5 %) oil, Anal. Calcd. for $C_{17}H_{20}O_4P_2S_5$ (446.47). C, 45.73; H, 4.51; P, 13.87; S, 21.54%. Found: C, 45.51: H, 4.62; P, 13.61; S, 21.35. MS : 431 ($M^+ - CH_3$, 33.3); 358 (60.2), 278 (37.3), 261 (24.9); 245 (67.5); 187 (100, base peak); 171 (12.2); 149 (98); 139 (97); 108 (45.8); 63 (95.6).

Fraction 2 : 1,3,2-Dioxaphosphorinane-2-sulfide-2(4-methoxyphenyl)-4-methyl (5b) : 0.38g (31.1%), oil, Anal. Calcd. for $C_{10}H_{13}O_3PS$ (244.24). C, 49.18; H, 5.36; P, 12.68; S, 13.13%. Found: C, 49.05; H, 5.40; P, 12.50; S, 12.92. IR : 461 (P-S-P); 645 (P=S); 1064 (P-O-C-C); 1594 (C=C, aromatic). MS : 245 (M^+ +1, 41); 229 (10) ; 212 (10); 187 (25); 139 (27).

Fraction 3 : Thioacetamide (7): 0.31 g (41.3%).

3- General Procedure for the reaction of LR with dihydric alcohols (2a-c) using 0.5 :1 molar ratio at reflux temperature. (preparation of 5a, 5b and 5d) (Route 2).

Dihydric alcohol (10 mmole) and LR (5 mmole) were heated in 20 ml anhydrous acetonitrile (80°C), until no more of the starting material could be detected (TLC). After cooling to room temperature the reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column using the eluent stated below. The reaction conditions (°C, hr) and the physical, spectroscopic and analytical data are given below.

Compound 5a : (From ethylene glycol + LR)

8 hrs, eluent 25-60% ethyl acetate - pet. ether 40-60), 1.11 g (48.2%), m.p.76°C. Anal. correct for $C_9H_{11}O_3PS$. Spectroscopic data (^1H NMR) is cited in Table 2. IR and MS as in experiment 1. Thioacetamide, 0.41 g (54.66%).

Compound 5b : (From propane -1,2- diol + LR)

2 hrs, eluent used is first 100% $CHCl_3$ then 25-75% ether / pet. ether (40-60) to give 0.67 g (27.4%), oil, Anal. correct for $C_{10}H_{13}O_3PS$. Spectroscopic data: ^1H NMR Table 2, MS and IR, experiment 2. Thioacetamide, 0.27 g (36%).

Compound 5d : 2(4-methoxyphenyl)-1,3,2-dioxaphosphorinane-2-sulfide. (from tetramethyl ethylene glycol + LR)

4 hrs, eluent used 20-40% ether- pet. ether (60-80) to give 1.46 g (54.5%), m.p. 83°C. Anal. Calcd. for $C_{13}H_{19}O_3PS$ (286.3), C, 54.53; H, 6.69; P, 10.82; S, 11.2%. Found : C,54.31; H, 6.60; P, 10.90; S, 11.00. IR : 706 (P=S), 1028 (P-O-C-C), 1643 (C=C, aromatic). MS: 286 ($(M^+$, 58.5); 204 (100), 171 (68.7), 83 (54.2), 55 (29.4), 28 (24.5). Thioacetamide, 0.05 g (13.3%).

Compound 9a : (From butane -1,4- diol + LR)

4 hrs, eluent used 20-60% ether- pet. ether (40-60) to give 0.67 g (26%), m.p. 48-50°C. Anal. Calcd. for $C_{11}H_{15}O_3PS$ (258.2), C, 51.16; H, 5.85; P, 11.99; S, 12.41%. Found: C, 51.00; H, 5.75; P, 12.05; S, 12.27. IR :(ν, cm^{-1}, group) 628 (P=S), 1045 (P-O-C-C), 1599 (C=C, aromatic). MS: m/e (%, rel. int.); 259 (M^+, 69.3), 204 (40.7), 171 (100. base peak), 108 (27), 71 (31), 57 (39.7), 55 (67.2). Thioacetamide, 0.14g (18.6%).

4- Reaction of 2,4-Bis(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide with dihydroxy alcohols using 0.5 : 1 molar ratio (Preparation of compounds 5c, 5e and 9b).

The same method as in 3 except using 1b instead of LR and reactions has been made at room temperature to give :-

Compound 5c : (From ethylene glycol + 1b)

4 hrs, eluent used 20-60% CH_2Cl_2- pet. ether (60-80), to give 0.36 g (12.3%), m.p. 76°C. Analysis calcd for $C_{14}H_{13}O_3PS$ (292.29).C, 57.53; H, 4.48; P, 10.6; S, 10.97%. Found : C, 57.37: H, 4.35; P, 10.51; S, 10.85. MS: m /e (%, rel. int.) 292 (M^+, 71.2), 249 (64.6); 233 (24); 170 (36); 115 (14.4); 91 (100, base peak); Thioacetamide, 0.48 (53.3%).

Compound 5e : (From tetramethyl ethylene glycol + 1b)

4 hrs, eluent used 30-60 % ether - pet . ether (90-100) to give 1.4 g (41.6%), m.p. 95-97°C. Anal. Calcd. for $C_{18}H_{21}O_3PS$ (348.39).C, 62.06; H, 6.08; P, 8.89; S, 9.20%. Found : C, 62.00; H, 5.98;

P, 8.90; S, 9.11%. IR ($\bar{\nu}$, cm^{-1}, group): 650 (P=S), 1065 (P-O-C-C-), 1594 (C=C, aromatic). MS:, m/e (%, rel. int.) 348 (M^+, 46.8), 267 (40.6); 266 (100, base peak); 233 (49.6), 83 (53.8), 55 (33); Thioacetamide, 0.2 g (35.3%).

Compound 9b : (From Butane-1,4- diol + **1b**)

2 hrs at reflux , eluent used 20% up to 60% ether- pet. ether (90-100), to give 0.26g (8.13%) m.p. 79-80°C. Anal. Calcd. for $C_{16}H_{17}O_3PS$ (320.3). C, 59.99; H, 5.35, P, 9.67; S, 10.00%, Found :C, 59.78; H, 5.28; P, 9.60; S, 9.87. MS : m/e (%, rel. int.) 320 (M^+, 13.1), 266 (11), 233 (30); 77 (6.8); 55 (100, base peak). Thioacetamide, 0.22 g (29.3%).

5- Reaction of Lawesson Reagent with ethylene glycol (2a) using 1.5:1 molar ratio (Route 3) :

A mixture of 0.06 g (15 mmole) of LR and 0.64 g (10 mmole) of ethylene glycol (**2a**) in 25 ml acetonitrile was stirred at room temperature (25°C) for 12 hrs. Evaporation of the solvent under reduced pressure and the residue was applied to silica gel column chromatography using ethyl acetate / pet. ether mixtures (starting from 5% to 20%) to give 1.0 g (23%) of **6a** and 0.15 g (20%) of the thioacetamide (7).

6- Reaction of ethylene glycol with LR in diethyl ether Preparation of 1,3,2,- dithiaphosporinane-2- sulfide-2 (4- methoxyphenyl) (11).

A mixture of 2.02 g (5 mmole) of LR and 0.32 g (5 mmole) of **2a** in diethyl ether (25 ml) was stirred at room temperature (25°C) for 4 hrs. Evaporation of the solvent and heating the residue in o-dichlorobenzene at 140°C for 2 hrs. Evaporation of the solvent and purification of the product on silica gel column using ethyl acetate - pet. ether to give 0.34 g (27.6%), m.p. 81°C.

Similarly, the same compound **11** has been prepared using dry benzene instead of diethyl ether to give 35% yield of **11**. MS : 262 (M^+, 100, base peak).

7- Preparation of 11 from 5a

A mixture of **5a** (0.23 g, 1 mmole) and LR (0.4 g, 1 mmole) in o-dichlorobenzene as solvent (10 ml) was heated at 140°C for 10 hrs to give after purification compound **11** (20% yield): m.p. and mixed m.p. with compound separated from experiment 5.

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