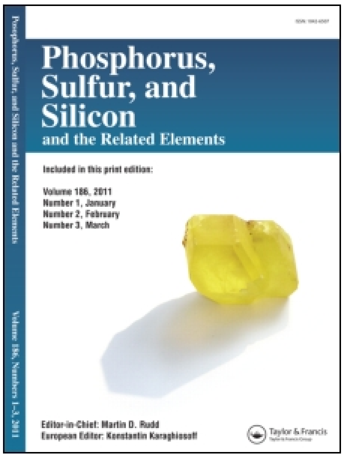

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS, PART XVI.[1] THE REACTION OF 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDE WITH BENZIL DIANILS. A NOVEL SYNTHESIS OF *2H*-1,3,6,2-THIADIAZAPHOSPHORINE-2-SULFIDE DERIVATIVES*

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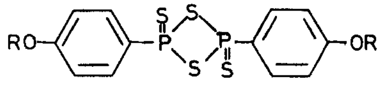
1,3,2,4-Dithiadiphosphetane-2,4-disulfide (Lawesson reagent, **1a**) and its *p*-phenoxy derivative, **1b** react with benzil dianils **2a,b** in refluxing toluene to give *2H*-1,3,6,2-thiadiazaphosphorine-2-sulfide derivatives of type **3a–c**. Compatible analytical and spectroscopic results were obtained for the new compounds. A mechanism is proposed to explain the formation of compounds **3a–c**.

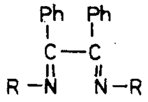
INTRODUCTION

Lawesson's reagent has been used previously as a thiating agent for different substrates.[2–11] It can be seen that it is the reagent of choice for this purpose. In some cases the monomeric part of LR can be incorporated with the substrate to give heterocyclic phosphorus compounds.[12–16] The last group meets our main interest as these products can be used as phosphorus insecticides.[17]

In a previous paper from this laboratory Lawesson's reagent has been reacted with aliphatic dihydric alcohols[18] which gives rise to 1,3,2-dioxaphosphorinane-2-sulfide together with cyclic trithiopyrophosphonate. Using aromatic diol[1] results in 1,3,2-dioxaphospholane-2-sulfide. This paper reports on the reaction of Lawesson reagent (**1a**) and its *p*-phenoxy derivative (**1b**) with benzil dianils **2a,b**.



1a, R = CH_3 (Lawesson Reagent)
1b, R = Ph



2a, R = Ph
2b, R = C_6H_4-CH_3-p

RESULTS AND DISCUSSION

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson Reagent, **1a**) react with benzil dianil **2a,b** in boling toluene, at reflux temperature to

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*Names of the compounds are in accord with IUPAC.
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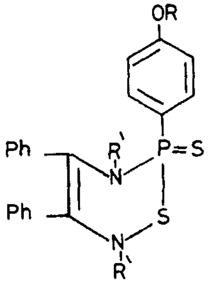
give chromatographically pure products **3a,c** in ca. 22–34% incorporating both sulfur and phosphorus (elementary analysis). These products are assigned the *2H*-



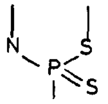
3a, R = CH_3 R' = Ph
b, R = R' = Ph
c, R = CH_3, R' = C_6H_4-CH_3-p

1,3,6,2-thiadiazaphosphorine-2-sulfide structure **3a,c** respectively for the following reasons:

(a) Correct elementary analysis and molecular weight determinations (MS) were obtained for each product.

(b) The ^1H NMR spectra of **3a**, taken as representative example, showed a singlet due to the OCH_3 protons at 3.9 ppm; a multiplet due to 22 ^1H in the region 6.70–7.40 ppm; while the other 2 aromatic protons which are ortho to phosphorus atom in the anisyl part appear in the area 7.80–8.30 ppm as double doublets with J_{PH} = 15 Hz and J_{HH} = 9 Hz.

(c) The ^{31}P NMR shift for **3a** were 91.19, 86.29 ppm in almost 1:1 ratio which are in accordance with shifts recorded for structures incorporating moiety "A."[19,20]



"A"

(d) The ^{13}C chemical shift of **3a** show two olefinic carbons as double doublets at 113 and 116 ppm due to the presence of the phosphorus atom which represent a chiral centre in the molecule. This conclusion adds a supplementary proof for the two chemical shifts in the ^{31}P NMR.

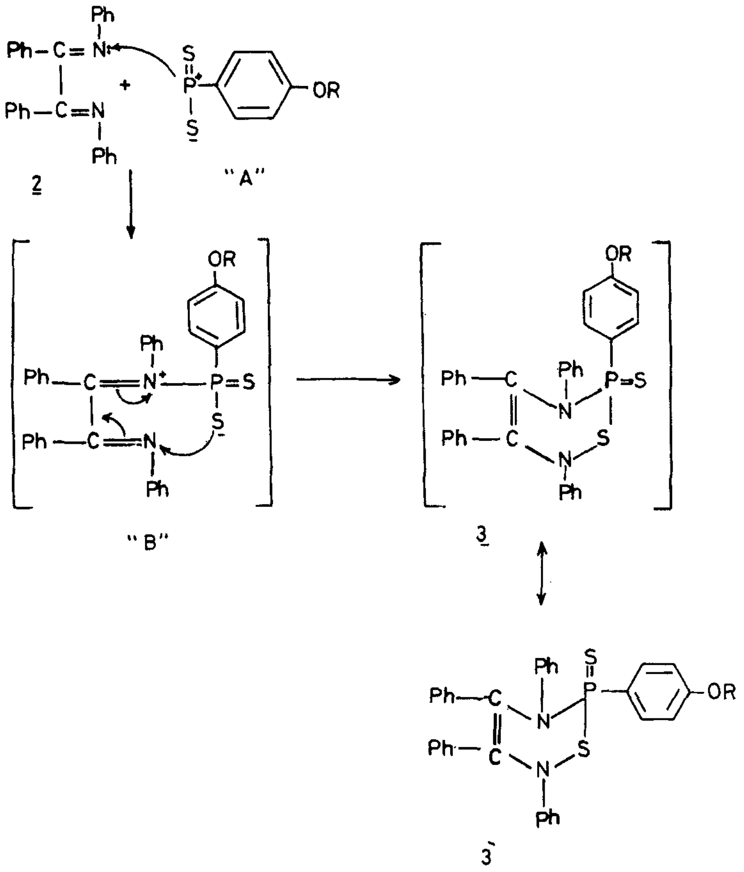
Similarly, the diphosphetane-2,4-disulfide **Ib** react with the dianil **2a** to give tetrahydro-2-(*p*-phenoxyphenyl)-3,4,5,6-tetraphenyl-*2H*-1,3,6,2-thiadiazaphosphorine 2-sulfide (**3b**). The ^1H, ^{31}P and yields for compounds **3a–c** were cited in Table I.

As to the formation of compound **3**, it is suggested that the phosphorus atom of the monomeric part of Lawesson's reagent[14] attacks the lone pair of electrons of one of the nitrogen atoms of the dianil **2** to give the intermediate "B" which cyclize to give **3** (Scheme I). Compound **3** is in equilibrium with another isomeric structure **3**, (1:1) as indicated from the ^{31}P chemical shift.

TABLE I

^1H, ^{31}P and yields for compounds **3a–c**

Comp.No.	1H NMR (ppm) (CDCI3)	^{31}p	Yield
3a	3.9 (s, OCH3) , 6.70-.7.40 (m,22H, aromatic), 7.8-8.3 (dd,2H, ortho-protons to P) with $^3J_{PH} \approx 15$; $J_{HH}=9$.	91.19 86.29	22
3b	6.7-7.4 (m, 27 H, aromatics), 7.8-8.1 (dd, 2H, ortho-proton to p)	109 104	28
3c	2.2 (s, 6H, 2CH3), 3.9 (s, OCH3), 6.7-7.3 (m, 20H, aromatics), 7.8-8.3 (dd, 2H, Ortho-protons to P).	101.46 92.48	34



SCHEME I

In conclusion, the reaction of Lawesson reagent and its *p*-phenoxy derivative with benzil dianil gives rise to the heterocyclic system assigned the structure *2H*-1,3,6,2-thiadiazaphosphorine-2-sulfide which is in contrast to the behaviour of 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Japanese reagent)[21] which yields phenyl(phenyl thio)(arylimino)methanes.

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 spectrometer. The ^{1}H 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, and $CDCl_3$ as a solvent. ^{31}P NMR were referenced to external 85% H_3PO_4. MS data were obtained on gas chromatography/mass spect. EX 1000, QP Schinadzu Japan. The reported yields to pure isolated material from column chromatography using silica gel 60 (Merck).

Compound **Ia**: (Lawesson's Reagent) is commercially available and can be prepared as described earlier.[22]

Compound **Ib**: 2,4-Bis(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, was prepared using the same method from P_4S_{10} and diphenyl ether.

The starting benzil dianil has been prepared from benzil and the corresponding amine.[23]

General Procedure for the Reaction of Benzil Dianil with 1,3,2,4-Dithiadiphosphetane-2,4-Disulfide. A mixture of 0.004 mole of benzil dianils (**2a,b**) and 0.004 mole of 1,3,2,4-dithiadiphosphetane 2,4-disulfide (**Ia,b**) was heated in toluene (25 ml) under reflux with stirring until no more of the starting materials 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 with the reaction condition and yields. The spectroscopic data (^{1}H, ^{31}P) were cited in Table I.

Compound **3a**: *Tetrahydro-2-(p-methoxyphenyl)-3,4,5,6-tetraphenyl-2H-1,3,6,2-thiadiazaphosphorine-2-sulfide.* Reaction temperature 110°C, reaction time 4 hrs, eluent, ether/light petroleum (1:10, V:V), 0.5 g, (22%) M.P. 187°C, MS (%, rel. int.): 471 (M^+-C_7H_7, 5), 455 (M^+-C_7H_7O, 50), 181 (C_6H_5 CH=N—C_6H_5, 10); 180 (C_6H_5—C—N^+—C_6H_5, 100, base peak), 77(C_6H_5, 32). Anal. Calcd. for $C_{33}H_{27}N_2OPS_2$ (562.4). C, 70.47; H, 4.80; N, 4.98; P, 5.51; S, 11.40%. Found: C, 69.70; H, 4.71; N, 4.72; P, 5.29; S, 10.85%.

Compound **3b**: *Tetrahydro-2-(p-phenoxyphenyl)-3,4,5,6-tetraphenyl-2H-1,3,6,2-thiadiazaphosphorine-2-sulfide.* Reaction temperature 110°C, reaction time, 2 hrs, eluent ether/light petroleum (20:80, V:V); 0.7 g (28%), m.p. 143°C. MS: m/e (%, rel. int) 558(80), 486(60), 470(M^+-2C_6H_5, 80); 194(100, base peak). Anal. Calcd. for $C_{38}H_{29}OPS_2$ (624.5), C, 73.08; H, 4.64; N, 4.49; P, 4.96; S, 10.27%; Found, C, 72.8; H, 4.57; N, 4.31; P, 4.87; S, 10.08%.

Compound **3c**: *Tetrahydro-2-(p-methoxyphenyl)-4,5-diphenyl-3,6-di-p-*tolyl-2H-1,3,6,2-thiadiazaphosphorine-2-sulfide. Reaction temperature 110°C, reaction time 2 hrs, eluent ether/light petroleum 10–25% mixtures. Yield 0.8 g (34%); m.p. 128–30°C MS: m/e (%, rel. int) 558(M^+-S, 2); 485 (M^+-C_7H_7N, 8), 196 (100, base peak), 194 (30). Anal. Calcd for $C_{35}H_{31}N_2OPS_2$ (590.5) C, 71.19, H, 5.25, N, 4.74, P, 5.25, S, 10.86% Found: C, 71.00; H, 5.19; N, 4.79; S, 10.69%, P, 5.09.

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