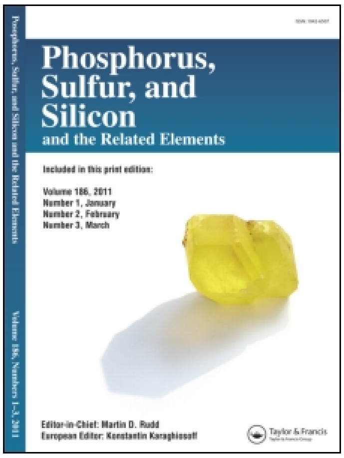

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REACTION OF 1-(DIPHENYLMETHYLENE)-2(1H)-AND 4-(DIPHENYLMETHYLENE)-1(4H)-NAPHTHALENONES WITH THIOL PHOSPHORIC ACIDS, LAWESSON REAGENT AND PHOSPHORUS PENTASULPHIDE

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REACTION OF 1-(DIPHENYLMETHYLENE)-2(1H)- AND 4-(DIPHENYLMETHYLENE)-1(4H)-NAPHTHALENONES WITH THIOL PHOSPHORIC ACIDS, LAWESSON REAGENT AND PHOSPHORUS PENTASULPHIDE

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Naphthalenone **1** reacts with thiol phosphoric acids **3** and **6** to give adducts **5** and **7**, respectively. Reaction of **1** with Lawesson reagent **8** and P_4S_{10} gives adducts **9** and **10**, respectively. On the other hand, reaction of naphthalenone **2** with reagent **3** and **6** leads to the formation of adducts **11** and **12**, respectively. Thiation of **2** with **8** or P_4S_{10} yields the dimeric adduct **14**. The identity of the new products is established from analytical and spectroscopic evidences.

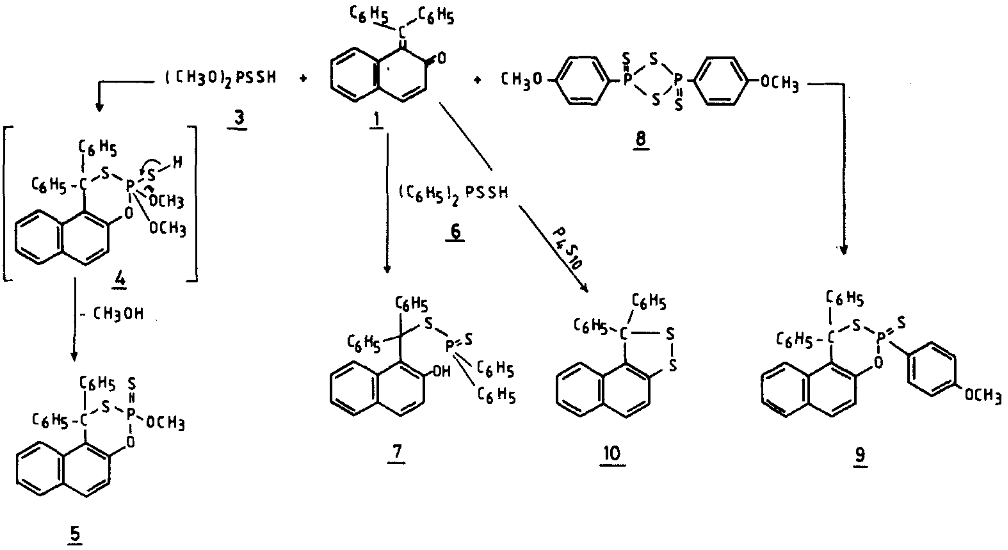
Key words: o,pi-Naphthalenones; thiol phosphoric acids; Lawesson reagent; P_4S_{10}; oxathiaphosphorine derivatives; 1,1-di[-4-(diphenylmethylene)-1,4-dihydronaphthyl]-dithietanes.

INTRODUCTION

Extending our work on the reaction of 1-(diphenylmethylene)-2(1H)-naphthalenone (**1**) and 4-(diphenylmethylene)-1(4H)-naphthalenone (**2**) with organophosphorus compounds,[1-3] we now wish to report the chemical reactivity of compounds **1** and **2** towards some thiol phosphoric acids, 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson reagent) (**8**) and phosphorus pentasulphide. Furthermore we report the synthesis of a new sulphur and phosphorus derivative of naphthalene, a number of which are important oil additives[4] and potential insecticides.[5-7]

RESULTS AND DISCUSSION

When naphthalenone **1** is allowed to react with O,O-dimethyldithiophosphoric acid (**3**) in refluxing toluene, the oxathiaphosphorine derivative **5** is obtained as a colourless crystalline adduct. The formation of adduct **5** is assumed to involve the loss of one mole of methanol from the unstable intermediate compound **4**. Structure **5** is assigned on the following evidence: (a) correct analytical values were obtained for adduct **5**; (b) the IR spectrum of **5** (in KBr) reveals the absence of the carbonyl and the C═C (conjugated with aromatic) absorption bands which were recorded in the starting naphthalenone **1** at 1630 cm^{-1} and 1625 cm^{-1} respectively, it shows an absorption band at 1055 cm^{-1} (P—O—CH_3); (c) the ^1H-NMR spectrum of **5** (in $CDCl_3$) shows a doublet centred at δ = 3.3 ppm due to the —OCH_3 protons



SCHEME I

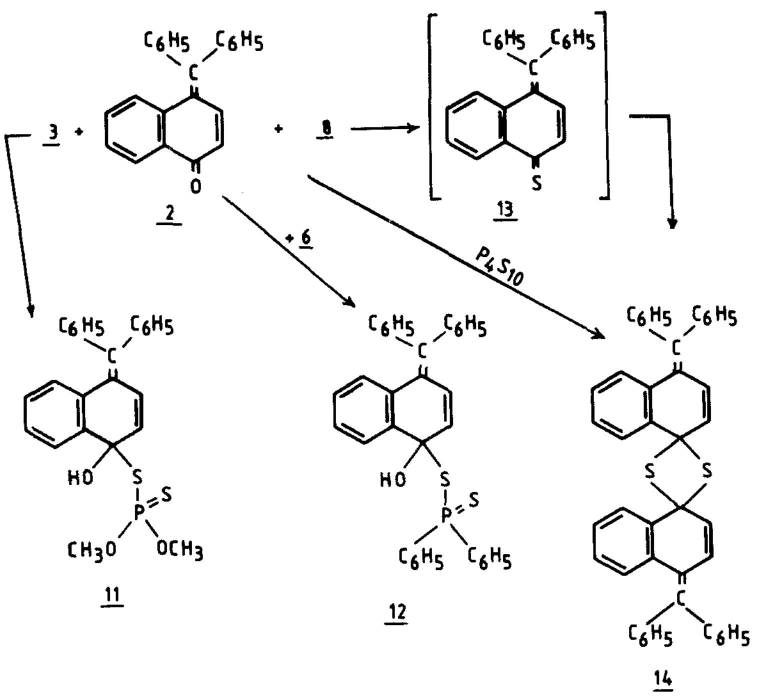
and a multiplet at $\delta = 7.00-7.90$ ppm due to the aromatic protons; (d) the molecular weight determination (MS) of **5** gives a prominent peak at *m/e* 434 (M^+, 30%). Loss of S atom from the latter ion affords the positive radical ion at *m/e* 402 (5%), further loss of S atom from the latter gives the positive radical ion at *m/e* 370 (5%). Ejection of $P(OCH_3)$ radical from the latter gives rise to the positive radical ion at *m/e* 308 (100%). The latter then fragments in a pattern similar to that observed in the case of the parent naphthalenone **1** (*m/e* 308, M^+). Thus ejection of a CO molecule from the ion at *m/e* 308 affords the positive radical ion at *m/e* 280 (5%) which suffers further loss of $C_6H_5^{\cdot}$ radical to give the cation at 203 (10%). This latter can also originate through expulsion of a $C_6H_5^{\cdot}$ radical from the ion at *m/e* 308 followed by expulsion of a CO molecule from the resulting cation at *m/e* 231 (50%).

The addition of diphenyldithiophosphinic acid to naphthalenone **1** is performed in refluxing toluene to give adduct **7** as orange crystals. Structure **7** is verified by correct combustion values and from spectral data (c.f. Experimental). Adduct 7 regenerates the starting material **1** upon thermolysis under reduced pressure and gives a positive ferric chloride reaction.

A cyclo addition product is obtained from the reaction of naphthalenone **1** with Lawesson reagent **8** and the oxathiaphosphorine sulfide derivative **9** is isolated as orange crystals. Structure **9** is deduced from microanalyses, IR, ^{1}H-NMR, MS and ^{31}P-NMR. The ^{31}P-NMR measurements for this adduct showed positive chemical shifts (vs. 85% H_3PO_4) around $\delta = 90.85$ ppm which supports structure **9**.[8]

Attempted thiation of naphthalenone **1** with phosphorus pentasulphide in refluxing toluene leads to the isolation of adduct **10**. Structure **10** is confirmed from microanalyses, IR and MS data (c.f. Experimental).

Next, the reaction of naphthalenone **2** with compound **3** is performed in refluxing toluene to give a yellow crystalline products assigned structure **11**. Structure **11** is



SCHEME II

deduced from correct elemental analyses IR, ^{1}H-NMR, MS and ^{31}P-NMR spectra. The ^{1}H-NMR spectrum of **11** in $CDCl_3$ shows one doublet centered at $\delta = 3.7$ (6 protons of the methoxy groups attached to the phosphorus atom) with $J_{HP} = 13.95$ Hz, a singlet at $\delta = 9.85$ (OH proton, exchangeable) and a multiplet at $\delta = 7.08$–8.35 (16H, aromatic protons). Its ^{31}P-NMR spectrum (in $CDCl_3$, vs. 85% H_3PO_4) gave a positive shift at $\delta = 93.05$ ppm, a value which falls in the range frequently recorded in the spectra of compounds incorporating the $>$C—S—P(S)$<$ moiety.[9]

In a similar manner naphthalenone **2** reacts with diphenylphosphinodithioic acid (**6**) to yield adduct **12** as a dark orange crystalline product. Structure **12** is confirmed from microanalyses, IR and molecular weight determinaton (c.f. Experimental).

The reaction between naphthalenone **2** and the effective thiation agent[10,11] **8** is undertaken in refluxing toluene to give the dimeric adduct **14**. The formation of **14** is obtained via dimerization of the unstable thiono derivative **13** which was formed from the thiation of **2** with compound **8**. Product **14** is equally obtained and identified (m.p., mixed m.ps. and comparative IR spectra) by reacting naphthalenone **2** with phosphorus pentasulphide. Structure **14** is deduced from correct microanalyses, IR and molecular weight determination (c.f. Experimental).

CONCLUSION

From the present study, it is shown that naphthalenone **1** undergoes carbophilic attack at the more reactive exocyclic C atom by the thiol phosphoric acids, **3**, **6** and Lawesson reagent **8**. Addition of **3** and **8** is followed by ring closure to give the cyclic products **4** and **9** respectively. Moreover adduct **4** is unstable which undergoes decomposition affording **5** through expulsion of methanol. This expulsion of alcohol was reported in the reaction of the same naphthalenone **1**,[1] ethylidene and benzylidene aceto acetic ester as well as ethylidene acetyl acetone with alkyl phosphites,[12-14] but it was not observed before during the reaction of thiol phosphoric acids with unsaturated carbonyl compounds. On the other hand, the same reagents, **3**, **6** and **8** attack naphthalenone **2** at the ketonic carbonyl group only.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on Perkin-Elmer Infracord spectrometer 197 (Grating) in KBr. The ^{1}H-NMR spectra were recorded on a Bruker Model WH 90 spectrometer. The chemical shifts are recorded in ppm relative to TMS. The ^{31}P spectra were taken on a Varian (FT-20, vs. 85% H_3PO_4). The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) spectrometer.

Reaction of naphthalenone **1** *with O,O-dimethyldithiophosphoric acid* (**3**). *General procedure:* A mixture of naphthalenone **1**[15] (0.6 gm, 0.002 mole) and thiol **3**[16] (0.32 gm, 0.002 mol) in 40 c.c. dry toluene was refluxed for 5 hrs and then toluene removed under reduced pressure. The residue was chromatographed on a column of silica-gel and eluted with a mixture of methylene chloride-petroleum ether (1:4) to give 1,2-dihydro-2-methoxy-1,1-diphenyl naphth[1,2d][1,2]-oxathiaphosphorine-sulphide (**5**) which was crystallized from chloroform to give colourless crystals with m.p. 220°C in 65% yield. Anal. Calcd. for $C_{24}H_{19}O_2PS_2$ (434.528), C, 66.33; H, 4.40; P, 7.10; S, 14.76%. Found: C, 66.26; H, 4.38; P, 7.06; S, 14.79%.

Reaction of **1** *with diphenylphosphinodithioic acid* (**6**). In a similar manner **1** reacts with **6**, the reaction time is 50 hrs. Elution was done with a mixture of acetone-petroleum ether (1:4) to give diphenyl-1-S-[-1-(diphenylmethylene)-1,2-dihydro-2-hydroxynaphthyl]-dithiophosphinic acid ester (**7**) which was crystallized from benzene to give orange crystals m.p. 138°C in 60% yield. Anal. Calcd. for $C_{35}H_{27}OPS_2$ (558.713), C, 75.24; H, 4.87; P, 5.54; S, 11.47%. Found: C, 75.20; H, 4.85; P, 5.60; S, 11.42%. IR (expressed in cm^{-1}) lacks, the C=O and C=C (conjugated with aromatic) absorptions, it shows bands at 3250 (OH), 1430 (P—C—aryl). The ^{1}H-NMR spectrum of **7** (in $CDCl_3$, expressed in δ scale), 9.35 (1H, broad singlet, OH), 7.05–8.24 (26H, multiplet, aromatics).

Action of heat on adduct **7**. Adduct **7** (0.3 gm) was heated in a cold Finger Sublimator at 145°C (bath temperature for about 30 minutes under reduced pressure (0.6 mmHg). The residue was boiled in petroleum ether (40–60). The remaining solid was crystallized from acetic acid to give the starting compound **1** as proved from m.p., mixed m.ps. and comparative IR spectra).[15]

Reaction of **1** *with Lawesson reagent* **8**. To a solution of **1** (0.6 gm, 0.002 mol) in dry toluene (40 ml) was added freshly prepared Lawesson reagent **8**.[17] The mixture was stirred for 30 min at room temperature, then refluxed for 5 hrs, and the solvent removed under reduced pressure. The residue was placed on a column of silica-gel and eluted with ether-petroleum ether (1:1) to give 1,2-dihyro-2-p-methoxyphenyl-1,1-diphenylnaphth[1,2d][1,2]-oxathiaphosphorine-sulphide (**9**), which was crystallized from benzene/petroleum ether to give pale orange crystals m.p. 212°C (70%). Anal. Calcd. for $C_{30}H_{23}O_2PS_2$ (510.626), C, 70.56; H, 4.54; P, 6.06; S, 12.55%. Found: C, 70.50; H, 4.59; P, 6.10; S, 12.51% Mol. wt. (MS) = 510. IR, absence of CO and C=C (conjugated with aromatic), 1440 (P—C—aryl), 1560, 1580 (C=C aromatics). ^{1}H-NMR δ = 3.8 singlet (3H, OCH_3), δ = 7.10–7.95 multiplet (20H, aromatic protons).

Reaction of **1** *with phosphorus pentasulphide.* Compound **1** reacts with phosphorus pentasulphide according to the general procedure described before. After elution with a mixture of ethyl acetate-petroleum ether (1:4), 1,2-dihydro-1,1-diphenylnapth[1,2d][1,2]-dithiole (**10**) is obtained which was crystallized from petroleum ether to give yellow crystals m.p. 190°C (60%). Anal. Calcd. for $C_{23}H_{16}S_2$ (276.253), C, 77.48; H, 4.52; S, 17.98%. Found: C, 77.44; H, 4.50; S, 17.93%. The molecular weight determination (MS) gave a prominent peak at *m/e* 356 (M$^+$ 80%), *m/e* 324 (356-S, 25%), *m/e* 292 (324-

S, 100%), *m/e* 215 (292-C_6H_5, 30%), *m/e* 279 (356—C_6H_5, 90%). The IR spectrum revealed the absense of >C=O and C=C (conjugated with aromatic) absorptions.

Reaction of naphthalenone **2** with thiols **3**, **6**, Lawesson reagent and P_4S_{10} were carried out according to the general procedure described before.

Reaction of **2** *with reagent* **3**. Reaction time is 5 hrs, elution solvents are a mixture of methylene chloride-petroleum ether (1:4). After crystallization from benzene, dimethyl-1-S-[-4-(diphenylmethylene)-1,4-dihydro-1-hydroxynaphthyl]-dithiophosphoric acid ester (**11**) is isolated as yellow crystals m.p. 142° (67%). Anal. Calcd. for $C_{25}H_{23}O_3PS_2$ (466.571), C, 64.35; H, 4.96; P, 6.63; S, 13.74%. Found: C, 64.28; H, 4.92; P, 6.60; S, 13.81%. Mol. wt. (MS) = 466. IR, 1625 (C=C, conjugated with aromatic), 1040 (P—O—CH_3), 3200 (OH) and absence of >C=O absorption.

Reaction of **2** *with thiol* **6**. Reaction time is 50 hrs, elution with ethyl acetate-petroleum ether (1:4) and crystallization from benzene gives diphenyl-1-S-[-4-(diphenylmethylene)-1,4-dihydro-1-hydroxynaphthyl]-dithiophosphinic acid ester (**12**) as dark orange crystals m.p. 145°C (65%). Anal. Calcd. for $C_{35}H_{27}OPS_2$ (558.713), C, 75.24; H, 4.87; P, 5.54; S, 11.47%. Found: C, 75.20; H, 4.85; P, 5.56; S, 11.44%. Mol. wt. (MS) = 558. IR, 3200 (OH), 1625 (>C=C, conjugated with aromatic), 1450 (P—C—aryl).

Reaction of **2** *with* **8**. Reaction time is 7 hrs, elution with a mixture of chloroform-petroleum ether and crystallization from chloroform-petroleum ether gives 1,1^1-di[-4-(diphenylmethylene)-1,4-dihydroaphthyl]-dithietanes (**14**) as pale yellow crystals m.p. 140°C (58%). Anal. Calcd. for $C_{46}H_{32}S_2$ (648.894), C, 85.14; H, 4.97; S, 9.88. Found: C, 85.06; H, 4.99; S, 9.84%. Mol. wt. (MS) = 648. IR, 1625 (C=C, conjugated with aromatic), absence of C=O absorption. The same adduct **14** (m.p., mixed m.ps. and comparative IR spectra) is obtained in a similar manner from the reaction of **2** with P_4S_{10}, reaction time is 12 hrs. (50%).

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