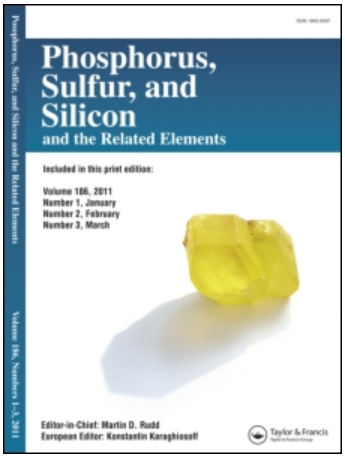

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Scope and Limitation of the Reaction of Benzocycloalkanone Oximes with Lawesson's Reagents

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SCOPE AND LIMITATION OF THE REACTION OF BENZOCYCLOALKANONE OXIMES WITH LAWESSON'S REAGENTS

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1,3,2,4-Dithiadiphosphetane-2,4-disulfide and its p-phenoxy derivatives react with 2-indanone-, 1-indanone-oxime, and tetralone oxime at different reaction temperatures to give 1,3,2-dithiaphosphetane-2-sulfide, dimeric compounds, 1-thioxo-1H-inden- phosphinodithioic acid, and 1,3,5,2-trithiaphosphorine. Compatible analytical and spectroscopic results were obtained for all the new compounds.

Keywords 2-Indanone; 1-indanone-oximes; Lawessons's and Japanese reagents; tetralone oxime

INTRODUCTION

Lawesson's reagents (LR) have now been an indispensable reagent for sulfur chemistry, particularly for converting almost all kind of oxo groups to thios thioxo groups,[1–3] which are important functional groups that can perform various organic reactions or can be used as end products in materials, medicinal, and industrial chemistry. LR are widely applied for the synthesis of heterocyclic compounds incorporating sulfur atom(s). Moreover, LR can give unexpected reactions, results of which lead to new methodologies and reactions.[3] Therefore, we investigated the reactions of Lawesson's reagents **(1a–b)** with 2-indanone-(**2**), 1-indanone-(**3a**), and tetralone-oximes (**3b**) to produce new bioactive heterocyclic thiophosphoryl compounds (Scheme 1).

RESULTS AND DISCUSSION

Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**1a**) reacts with 2-indanone oxime (**2**) in acetonitrile using 1:1 molar ratio at room temperature (25°C) to give the cyclic 2(4-methoxyphenyl)-1′,3′-dihydrospiro[1,3,2-dithia-phosphetane-4,2′-indene]2-sulfide (**5a**) as the main reaction product (78%) (Scheme 2). When the above reaction has been performed in refluxing toluene using 1 mol of LR and 1 mol of 2-indanone oxime (**2**),

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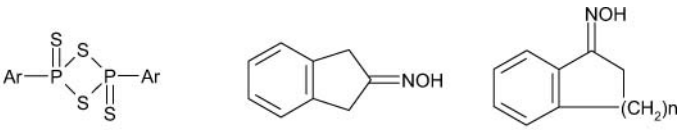


1a, Ar = 4-$H_3COC_6H_4$
b, Ar = S-C_6H_5 (also named Japanese reagent)

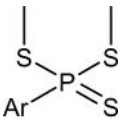
2

3a, n = 1
b, n = 2

Scheme 1

products **6** and **7** were isolated (Scheme 2). The structure of compounds **5a**, **6**, and **7** were confirmed by analytical results and spectral data (see the Experimental section).

Compound **5a**, taken as example, gave correct elemental analysis, and its IR spectrum shows peaks at 642 cm^{-1} (P═S)[4], 1178 cm^{-1} (P-C, aryl)[5]. The ^1H NMR spectrum of compound **5a** exhibits signals at 3.79 ppm (OCH_3), 3.72, 3.10 with $^4J_{HP} = 4.5$ Hz for two methylene, multiplets at 7.74–7.66 (m, 4H, Ar), 6.91–6.88 (m, 4H, Ar) ppm. The structure assigned for compound **5a** was based on ^{13}C NMR spectra, which indicates the presence of signals at $\delta = 55.9$ OCH_3, 49.8 (C-S-P, d, $^2J_{CP} = 24$ Hz), 39.5 (CH_2), 121.5 (P-C-Ph, d, $^1J_{CP} = 115.3$ Hz), 132.5 (d, $^2J_{CP} = 23.0$ Hz), 114.2 (d, $^3J_{CP} = 15.8$ Hz), and 160.7, corresponding to the carbon atoms of methoxy phenyl ring attached to phosphorus atom, 128.3, 126.2, 143.9 (C_6H_4). Product **5a** exhibits a positive phosphorus shift at $\delta =$ 44.0 (vs, 85% H_3PO_4), which is in complete accordance with shift recorded for structures incorporating the moiety "A."[6]



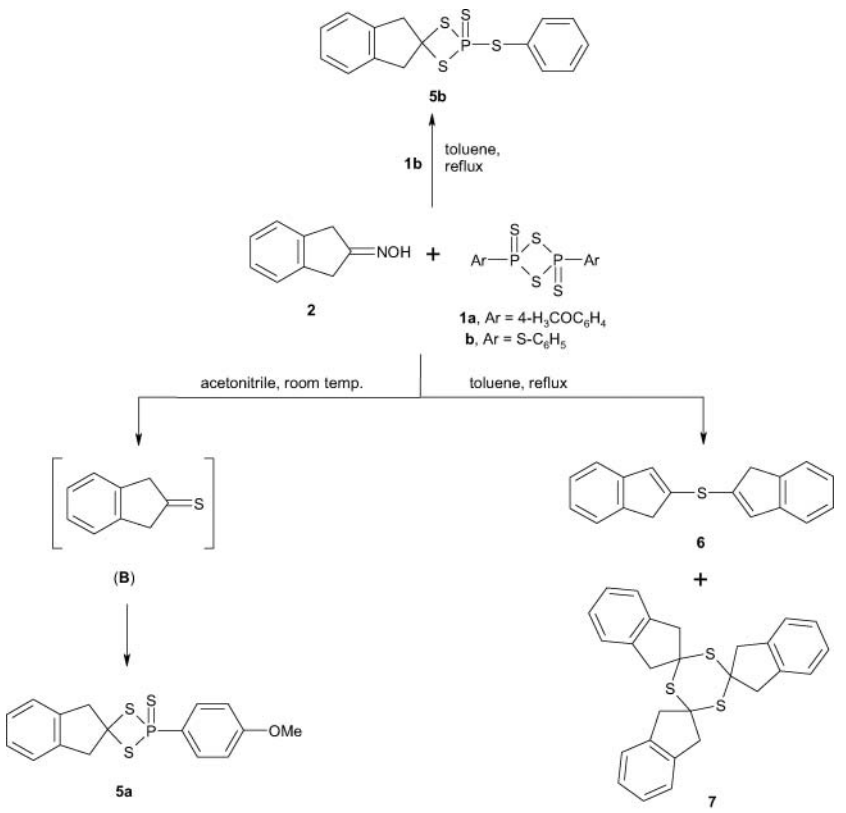
"A"

The formation of compound **5a** could be explained by assuming the formation of the unstable thionated[7] product (B) from the reaction of LR followed by addition of another molecule of LR to give the cyclic compound **5a** (Scheme 2).

Moreover, when 1 mol equivalent of compound **2** was allowed to react with 2,4-bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (**1b**) in dry refluxing toluene for 0.5 h, compound **5b** was isolated as the main reaction product in (85% yield). The structure of compound **5b** is confirmed from microanalysis, IR, ^1H, ^{13}C NMR, and mass spectral data (see the Experimental section).

When 1-indanone oxime **3a** was allowed to react with Lawesson's reagent (**1a**) (1:1 mol) using acetonitrile as solvent at room temperature for 8 h, the reaction gave compound **8** in 65% yield (Scheme 3). On the other hand, when 2,4-bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (**1b**) reacted with **3a** in refluxing toluene, product **9** was isolated in 80% yield (Scheme 3). Compounds **8** and **9** were characterized by ^1H, ^{13}C NMR, IR, MS, and elemental analysis (see the Experimental section).

Furthermore, we have found that when 1 mol equivalent of tetralone oxime **3b** was allowed to react with 1 mol equivalent of **1a** in acetonitrile at room temperature, product **10** was isolated in 76% yield (Scheme 4). When the above reaction was performed in refluxing

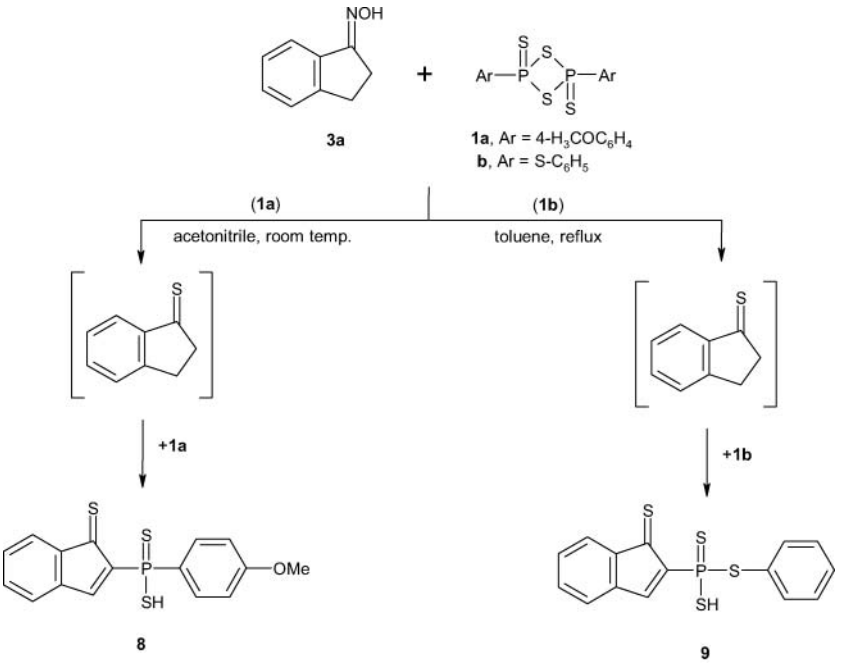


Scheme 2

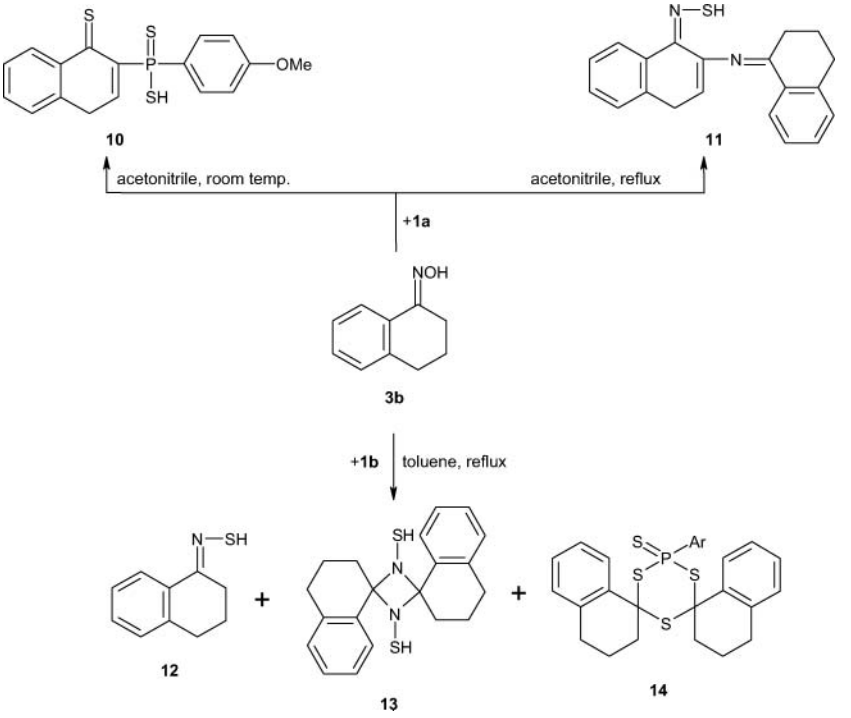
acetonitrile using 1 mol of **LR** and 1 mol of **3b**, product **11** was isolated (Scheme 4). The structure of compounds **10** and **11** was confirmed by analytical results and spectral data (see the Experimental section).

On the other hand, 2,4-bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (**1b**) (JR) reacts with **3b** in refluxing toluene to give three reaction products formulated as **12**, **13**, and **14**, respectively (Scheme 4).The identity of compounds **12**, **13**, and **14** were verified by elemental analysis and spectroscopic evidence (see the Experimental section).

The IR spectrum of compound **14** (taken as example) shows a peak at 640 cm^{-1} (P═S). The ^1H NMR spectrum of compound **14** exhibits signals at 1.37, 2.19, and 3.02 for methylene groups, multiplets at 7.37–7.29 (m, 5H, Ar), 7.43–7.38(m, 4H, Ar), and 7.55–7.45 (m,4H,Ar) ppm. The structure assigned for compound **14** was based on ^{13}C NMR spectra,[8] which indicates the presence of signals at 65.0 (S-C-S-P, d, $^2J_{CP}$ = 11.3 Hz), 27.6 (d,$^3J_{CP}$ = 4.6 Hz,CH_2), 128.2 (d, $^2J_{CP}$ = 8.4 Hz, S-Ph), and 135.7 (d,$^3J_{CP}$ = 4.6 Hz, S-Ph) ppm. Product **14** exhibits a positive phosphorus shift δ = 63.8.0 (vs, 85% H_3PO_4).[9,10] Similarly, 1,3,5,2-trithiaphosphorins were also noted to be formed in the reaction of Lawesson's reagent with cyclohexanone and cyclopentanone.[10]



Scheme 3



Scheme 4

CONCLUSION

In conclusion, the reaction of Lawesson's and Japanese reagents with indanone- and tetralone-oxime depends not only on the molar ratios of the reactants, but also on the reaction temperature. Moreover, the reaction of Lawesson's and Japanese reagents here is indicative of their broad reactions in addition to the usual thiation reactions.

EXPERIMENTAL

Melting points were determined in open glass capillaries using Electrothemal IA 9000 Series digital melting point apparatus (Electrothermal, Essex, UK) and are uncorrected. The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord Spectrophotometer Model 157 (Grating). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and d_6-DMSO as solvents on a JOEL-300 MHz Spectrometer, and the chemical shifts were recorded in δ values relative to TMS. The ^{31}P NMR spectra were taken with a Varian CFT-20 (vs. external 85% H_3PO_4 standard). The mass spectra were performed at 70 eV on a Shimadzu GCS-OP 1000 Ex Spectrometer. Elemental analyses were performed using the Elmeuter Varu EL, Germany, instrument.

Reaction of Lawesson's Reagent 1a with 2-Indanone Oxime (2)

To a solution of **2** (0.14 g, 0.001 mol) in acetonitrile (30 mL), **1a** (0.4 g, 0.001 mol) was added, and the reaction mixture was stirred at rt for 8 h. When no more starting material could be detected (TLC), the mixture was evaporated under reduced pressure. The residue was placed on a column of silica-gel using eluent solution to give adduct **5a**.

2-(4-Methoxyphenyl)-1′,3′-dihydrospiro[1,3,2-dithiaphosphetane-4,2′-indene]2-sulfide (5a). Eluent: petroleum ether:acetone (20:80, v/v). Product **5a** was separated as brown crystals, mp 237–238°C, yield (78%). Anal. Calcd. For $C_{16}H_{15}OPS_3$ (350.45): C, 54.83; H, 4.31; P, 8.84; S, 27.45. Found; C, 54.95; H, 4.40; P, 8.74; S, 27.60%. IR (KBr): 642 (P=S) cm^{-1}; 1178 (P-C-aryl) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 3.79$ (s, 3H, OCH_3), 3.72, 3.10 (d, 4H, $^{4}J_{HP} = 4.5$Hz, $2CH_2$), 7.74–7.66 (m, 4H, Ar) 6.91–6.88 (m, 4H, Ar) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 55.9$ (4-OCH_3), 49.8 (d, $^{2}J_{CP} = 24.0$ Hz, S-C-S-P), 39.5 (d, $^{3}J_{CP} = 12.0$ Hz, CH_2),121.5 (d, $^{1}J_{CP} = 115.3$ Hz, C_6H_4),132.5 (d, $^{2}J_{CP} = 23.0$ Hz, C_6H_4), 114.2 (d, $^{3}J_{CP} = 15.8$ Hz, C_6H_4), 160.7 (d, $^{4}J_{CP} = 4.5$ Hz, C_6H_4), 128.3, 126.2, 143.9, 140.6 (C_6H_4)ppm; ^{31}P NMR: $\delta = 44.0$ ppm; MS, m/z(%): 350 (80)[M^+].

The same reaction was carried out in dry toluene (30 mL) and was refluxed for 2 h. The reaction mixture was evaporated under reduced pressure, and the residue was placed on a column of silica-gel using eluent solution to yield adducts **6** and **7**.

Di(1*H*-inden-2-yl)sulfane 6. Eluent: petroleum ether:ethyl acetate (80:20,v/v). Product **6** was separated as white crystals, mp 130–132°C, yield (40%). Anal. Calcd. For $C_{18}H_{14}S$(262.37): C, 82.40; H, 5.38; S, 12.22. Found; C, 82.56; H, 5.20; S, 12.08%. ^{1}H NMR ($CDCl_3$): $\delta = 3.22$ (s, 4H, $2CH_2$), 6.20 (s, 2H, CH=C−S), 7.01–7.18 (m, 4H, Ar) and 7.28–7.30 (m, 4H, Ar) ppm. MS, m/z (%): 262 (60) [M^+].

Trimeric-2-indane-thione 7. Eluent: petroleum ether:ethyl acetate (15:85, v/v). Product **7** was separated as brown crystals, mp 350–352°C, yield (45%). Anal. Calcd. For $C_{27}H_{24}S_3$ (444.10): C, 72.93; H, 5.44; S, 21.63. Found; C, 72.79; H, 5.62; S, 21.50%.^{1}H NMR(DMSO): $\delta = 3.54$–3.62 (b, 12H, $6CH_2$), 7.01–7.25 (m, 4H, Ar) 7.43–7.56 (m, 4H, Ar) and 7.27–7.79 (m, 4H, Ar) ppm. MS, m/z (%): 444 (20)[M^+].

Reaction of 2,4-Bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (1b) with Oxime 2

A mixture of **2** (0.14 g, 0.001 mol) and **1b** (0.4 g, 0.001 mol) in dry toluene (30 mL) was refluxed for 0.5 h. When no more starting material could be detected (TLC), the mixture was evaporated under reduced pressure. The residue was placed on a column of silica-gel and using eluent solution to give adduct **5b**.

2-(Phenylsulfonyl)-1′,3′-dihydrospiro[1,3,2-dithiaphosphetane-4,2′-indene]2-sulfide (5b). Eluent: petroleum ether:ethyl acetate (20:80, v/v). Product **5b** was separated as green crystals, mp 230–231°C, yield (85%). Anal. Calcd. For $C_{15}H_{13}PS_4$ (352.5): C, 51.11; H, 3.72; P, 8.79; S, 36.39. Found; C, 51.25; H, 3.80; P, 8.64; S, 36.50%. IR (KBr): 710 (P=S) cm^{-1}. ^{1}H NMR (DMSO): $\delta = 3.27$, 3.01 (d, 4H, $^4J_{HP} = 4.12$ Hz, $2CH_2$), 7.64–7.56 (m, 4H, Ar), 7.02–6.98 (m, 4H, Ar) ppm; ^{13}C-NMR (DMSO): $\delta = 42.8$ (d, $^2J_{CP} = 22.8$ Hz, S-C-S-P), 45.2 (d, $^3J_{CP} = 12.8$ Hz, CH_2),135.5 (d, $^2J_{CP} = 25.3$ Hz, C_6H_5), 132.5 (d, $^3J_{CP} = 13.0$ Hz, C_6H_5), 124.2, 128.3, 126.2, 143.0 (C_6H_4) ppm; MS, m/z (%): 351 (100) [M^+], 243[M^+-109], 109 (S-Ph).

The Reaction of 1-Indanoneoxime (3a) with Lawesson's Reagent (1a)

To a suspension of **3a** (0.14 g, 0.001 mol) in acetonitrile (30 mL), **1a** (0.4 g, 0.001 mol) was added. The reaction mixture was stirred at rt for 6–8 h, and the solvent was removed under pressure. The residue was placed on a column of silica-gel and using eluent solution to give adduct 8.

4-Methoxyphenyl-1-thioxo-1*H*-inden-2-yl)phosphinodithioic acid (8). Eluent: petroleum ether:ethyl acetate (95:5,v/v). Product **8** was separated as white crystals, mp 173–174°C, yield (65%). Anal. Calcd. For $C_{16}H_{13}OPS_3$ (348.44): C, 55.15;H, 3.76; P, 8.89; S, 27.61. Found; C, 55.32; H, 3.87; P, 8.74; S, 27.74%. IR (KBr): 2928 (SH) cm^{-1}, 1230 (C=S) cm^{-1}, 686 (P=S) cm^{-1}, 1178 (P-C, Aryl)cm^{-1}. ^{1}H- NMR (DMSO): $\delta = 3.79$ (s, 3H, OCH_3), 6.86 (d, 1H, $^3J = 3.7$ Hz, CH=C−P), 6.89–6.87 (2dd, $J_{HH} = 9$Hz, $J_{HH} = 3$Hz, Ar), 7.59–7.51 (2dd, 4H, $J_{HH} = 9$Hz, $J_{HH} = 3$Hz, Ar), 9.26 (b,1H, SH, exchangeable D_2O) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 203.9$(d, $^2J_{CP} = 16.8$ Hz, S=C−C−P), 54.8 ($OCH_{3-}4$), 135.1(d, $^1J_{CP} = 120.7$ Hz, C=C−P), 134.0 (d, $^2J_{CP} = 20.4$ Hz, C=C−P),126.0 (d,$^1J_{CP} = 121.0$ Hz, C_6H_4), 132.8 (d, $^2J_{CP} = 15.6$ Hz, C_6H_4), 113.0 (d,$^3J_{CP} = 12.5$ Hz, C_6H_4), 160.2(d, $^4J_{CP} = 4.5$ Hz, C_6H_4), 130.4, 128.4,139.7, 127.6,125.2,147.2 (C_6H_4) ppm. MS; m/z (%): 348 (40) [M^+].

Reaction of 2,4-Bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (1b) with 1-Indanonoxime (3a)

A mixture of oxime **3a** (0.16 g, 0.001 mol) and **1b** (0.4 g, 0.001 mol) in dry toluene (30 mL) was refluxed for 0.5 h. After cooling, the solvent was evaporated under reduced pressure. The residue was applied to column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give adduct 9.

Phenyl Hydrogen 1-Thioxo-1*H*-inden-2-yl-phosphonotrithioate (9). Eluent: petroleum ether:ethyl acetate (20:80, v/v). Product **9** was separated as green crystals, m.p 250–251°C, yield (80%). Anal. Calcd. For $C_{15}H_{11}PS_4$ (350.48): C, 51.40; H, 3.16; P, 8.84; S, 36.60. Found; C, 51.65; H, 3.30; P, 8.70; S, 36.48%. IR (KBr): 689 (P=S) cm^{-1}. ^{1}H NMR (DMSO):$\delta = 6.40$ (d, 2H, $^3J_{HP} = 4.9$ Hz,CH_2), 7.49–7.64 (m, 3H, Ar), 7.70 (d,

2H, J_{HH} = 8.7 Hz, Ar), 7.93 (d, 2H, J_{HH} = 8.7 Hz, Ar), 8.26 (d, 2H, J_{HH} = 8.1 Hz, Ar), and 10.7 (bs, 1H, SH, exchangeable with D_2O) ppm; ^{13}C NMR (DMSO): δ = 203.8 (d, $^2J_{CP}$ = 20.8 Hz, C=S), 135.1 (d, $^1J_{CP}$ = 123.7 Hz, C=C−P), 134.0 (d, $^2J_{CP}$ = 22.4 Hz, C=C−P), 135.5 (d, $^2J_{CP}$ = 25.1 Hz, C-Ph), 132.5 (d, $^3J_{CP}$ = 13.0 Hz,C-Ph), 127.2, 132.3, 126.2, 143.0 (C_6H_4) ppm; MS, m/z (%): 350 (100) [M^+], 109 (S-Ph).

The Reaction of 1-Tetraloneoxime 3b with Lawesson's Reagent 1a

To a suspension of **3b** (0.16 g, 0.001 mol) in acetonitrile (30 mL), **1a** (0.4 g, 0.001 mol) was added. The reaction mixture was stirred at rt for 8–10 h, and the solvent was removed under pressure. The residue was placed on a column of silica-gel using eluent solution to give adduct **10**.

(4-Methoxyphenyl)(1-thioxo-1,4-dihydronaphthalen-2-yl) phosphinodithioic acid (10). Eluent: petroleum ether:ethyl acetate (85:15, v/v). Product **10** was separated as white crystals, mp 183–184°C, yield (76%). Anal. Calcd. For $C_{17}H_{15}OPS_3$ (362.47): C, 56.33; H, 4.17; P, 8.55; S, 26.54. Found; C, 56.20; H, 4.30; P, 8.43; S, 26.40%. IR (KBr): 2930 (SH) cm^{-1}, 1232 (C=S) cm^{-1}, 720 (P=S) cm^{-1}, 1178 (P-C, Aryl) cm^{-1}; ^{1}H- NMR(DMSO): δ = 3.60 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 6.80 (d,1H, $^2J_{HP}$ = 8.9 Hz, CH=C−P), 6.84–6.92 (m, 4H, Ar), 7.49–7.61 (m, 4H, Ar), 9.26 (b,1H, SH, exchangeable D_2O) ppm;^{13}C NMR (DMSO): δ = 203.1 (d, $^2J_{CP}$ = 18.8 Hz, S=C−C−P), 160.2 (OCH_3-4), 145.1(d,$^1J_{CP}$ = 123.1 Hz, C=C−P), 140.0 (d, $^2J_{CP}$ = 20.8 Hz, C=C−P), 32.4 (CH_2),125.0 (d, $^1J_{CP}$ = 120.0 Hz, P-C-Ph), 132.1 (d,$^2J_{CP}$ = 18.6 Hz, P-C-Ph), 113.0 (d, $^3J_{CP}$ = 12.5Hz, P-C-Ph), 130.4, 128.4, 139.2, 127.6, 124.2, 146.2 ppm; MS; m/z(%): 362 (30) [M^+].

The same reaction was carried out in acetonitrile (30 mL) and refluxed for 2 h. The reaction mixture was evaporated under reduced pressure, the residue was placed on a column of silica-gel, and eluent solution was used to yield adduct **11**.

2-(3,4-Dihydronaphthalen-1(2*H*)-ylideneamino)naphthalene-1(4*H*)-one thioxime (11). Eluent: petroleum ether:acetone (40:60, v/v). Product **11** was separated as violet crystals, mp 217–220°C, yield (60%). Anal. Calcd. For $C_{20}H_{18}N_2S$ (318.43): C, 75.44; H, 5.70; N, 8.80; S, 10.07. Found; C, 75.60; H, 5.52; N, 8.68; S, 10.16%. IR (KBr):2925 (SH) cm^{-1},1589 (N=C) cm $^{-1}$, 1660 (C=C) cm^{-1}; ^{1}H- NMR($CDCl_3$): δ = 1.68 (s, 1H, SH exchangeable with D_2O), 2.15 (2t, 4H, $2CH_2$), 2.20 (m, 2H, CH_2), 6.84 (t, 1H, J_{HH} = 7.5 Hz, CH=C-), 7.37–7.34 (d, 1H, J_{HH} = 9Hz, Ar), 7.74–7.72 (m, 4H, Ar), 7.79–7.76 (d, 1H, J_{HH} = 9 Hz, Ar), 9.10–9.07 (2d, 2H, J_{HH} = 9 Hz, Ar) ppm; MS; m/z (%): 318 (20) [M^+],

Reaction of 2,4-Bis(thiophenoxy)-1,3,2,4-dithiaphosphetane-2,4-disulfide (1b) with Tetralonoxime (3b)

To a suspension of oxime **3b** (0.16 g; 0.001 mol) in dry toluene (30mL), reagent **1b** (0.4 g, 0.001 mol) was added. The reaction mixture was refluxed for 0.5 h. After cooling, the solvent was evaporated under reduced pressure. The residue was separated to its components by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to give adducts **12**, **13**, and **14**.

3,4-Dihydro-*N*-mercaptonaphthalen-1(2*H*)-imine (12). Eluent: petroleum ether:ethyl acetate (98:2, v/v). Product **12** was separated as colorless crystals, mp 130–132°C, yield (40%). Anal.Calcd. For $C_{10}H_{11}NS$ (177.27): C, 67.76; H, 6.25; N, 7.90;

S, 18.09. Found: C, 67.60; H, 6.37; N, 7.79; S, 18.18%. IR (KBr): 2968 (SH) cm^{-1},1568 (C=N) cm^{-1}, 1600 (C=C) cm^{-1}; ^{1}H- NMR($CDCl_3$): δ = 2.34 (t, 2H, CH_2), 2.81 (m, 4H, 2 CH_2), 7.05–7.02 (d, 1H, J = 9.0 Hz, Ar), 7.29–7.27 (m, 3H, Ar), 9.56 (s, 1H, SH, exchangeable with D_2O) ppm. MS; m/z(%):177 (100)[M^+], 144 (80)[M^+-SH]

Compound 13. Eluent: petroleum ether:ethyl acetate (94:6, v/v). Product **13** was separated as colorless crystals, mp 154–156°C, yield (40%). Anal. Calcd. For $C_{20}H_{22}N_2S_2$ (354.53): C, 67.76; H, 6.25; N, 7.90; S, 18.09. Found: C, 67.60; H, 6.37; N, 7.79; S, 18.18%. IR (KBr): 2922, 2852 (SH) cm^{-1}, 1564 (C=N) cm^{-1},1600 (C=C) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ = 2.64 (m, 4H, 2CH_2), 2.91 (t, 4H, 2CH_2), 2.75 (t, 4H, 2CH_2), 7.46, 7.43 (s, 2H, 2SH, exchangeable with D_2O), 7.72–7.60 (m, 4H, Ar), 8.10–8.25 (m, 4H, Ar) ppm. MS; m/z(%): 354 (100)[M^+], 288 (80)[M^+- 2SH].

Compound 14. Eluent: petroleum ether:ethyl acetate (95:5, v/v). Product **14** was separated as colorless crystals, mp 193–194°C, yield (40%). Anal. Calcd. For $C_{26}H_{25}PS_5$ (528.78): C, 59.06; H, 4.77; P, 5.86; S, 30.32. Found; C, 59.18; H, 4.63; P, 5.67; S, 30.48%. IR(KBr): 640 (P=S) cm^{-1}, 1602 (C=C)cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.37(m, 4H, 2CH_2), 2.19 (t, 4H, 2CH_2), 3.02 (t, 4H, 2CH_2), 7.37–7.29 (m, 5H, Ar), 7.43–7.38 (m, 4H, Ar), 7.55–7.45 (m, 4H, Ar) ppm; ^{13}CNMR($CDCl_3$): δ = 65.0 (d, $^2J_{CP}$ = 11.3 Hz, S-CS), 27.6 (d, $^3J_{CP}$ = 4.6 Hz,CH_2), 32.7 (CH_2),128.2 (d, $^2J_{CP}$ = 8.4 Hz, S-Ph), 135.7 (d,$^3J_{CP}$ = 4.6 Hz, S-Ph), 136.0 (d, $^4J_{CP}$ = 3.5 Hz,-S-Ph), 128.5, 127.6, 124.3, 119.9 (C_6H_4), 129.8 (d,$^4J_{CP}$ = 3.5 Hz,), 131.1(d, $^3J_{CP}$ = 3.6 Hz) ppm; ^{31}P NMR: δ = 63.8 ppm; MS: m/z(%) 528 (25)[M^+].

REFERENCES

1. R. Shabana, J. B. Rasmussen, S. O. Olesen, and S. O. Lawesson, *Tetrahedron*, **36,** 3047 (1980).
2. R. Shabana, S. Scheiby, K. Clausen, S. O. Olesen, and S. O. Lawesson, *New J. Chem.*, **4,** 47 (1980).
3. K. A. Rufanov, A. S. Stepanov, D. A. Lemenouskii, and A. V. Churakov, *Heteroatom Chem.*, **10**(5), 36 (1999).
4. L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Wiley, New York, 1964), p. 311.
5. M. Hesse, M. Meier, and B. Zeeh, *Spektroskopische Methoden in der Organischem Chemie* (Thieme Verlag, Stuttgart, Germany, 1991), chap. 2.1, p. 64.
6. A. A. El-Barbary, S. Scheiby, S.O. Lawesson, and H. Fritz, *Acta Chem. Scand. B*, **34,** 597 (1980).
7. A. A. El-Barbary, R. Shabana, and S. O. Lawesson, *Phosphorus, Sulfur, and Silicon*, **21,** 375 (1985).
8. E. Pretsch, J. Seibl, and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds* (Springer-Verlag, Berlin, 1983).
9. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, In *Topics in Phosphorus Chemistry*, M. Graysor and E. J. Griffith, Eds. (Interscience Publishers, New York, 1967), vol. 5, p. 227.
10. S. Scheiby, R. Shabana, S. O. Lawesson, and C. Romming, *Tetrahedron*, **38,** 993 (1982).