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Reactions of *p*-Quinone Monoimines with Lawesson Reagent and Phosphorus Pentasulfide

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ABSTRACT

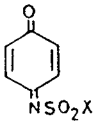
2,4-Bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide [Lawesson reagent (LR)] ***1*** *reacts with p-quinone monoimine-* ***2a*** *to give the novel benzo-1,3,2-oxathiaphosphol-5-(methanesulfonamido)-2-(4-methoxyphenyl)-2-sulfide* ***4****. On the other hand, the reaction of* ***2b*** *and* ***3*** *with LR* ***1*** *leads to the formation of the benzo- and the naphtho-1,3,2-dithiaphosphol-5 -(benzenesulfonamido)- 2- (4-methoxyphenyl) -2-sulfide* ***5,6****. Thiation of* ***2a****,* ***2b****, and* ***3*** *with P_4S_{10} yields phenoxathiin derivatives* ***8a****,* ***8b****, and* ***9****, respectively. The identity of the new products is established from analytical and spectroscopic evidence.*

INTRODUCTION

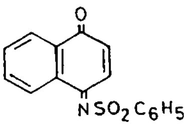
2,4-Bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **1** is a very useful and effective thiation reagent [1–3]. With *p*-quinones and *p*-quinonediimines, it gives 1,3,2-benzoxathiaphosphol-5-ol-2-sulfides and 1,3,2-benzazathiaphosphol-2-sulfides, respectively [4,5]. As a part of our continuing interest in the reaction of quinoneimines with organophosphorus reagents [6–13], we describe here the behavior of 1,4-benzoquinone- and 1,4-naphthoquinone-monoimines **2,3** toward **1** and phosphorus pentasulfide.

RESULTS AND DISCUSSION

We have found that when one mole of *N*-(methylsulfonyl)-1,4-benzoquinone monoimine **2a** was allowed to react with a half equivalent of **1** in refluxing toluene, the benzoxathiaphosphol derivative **4** is obtained as a colorless crystalline adduct. The structure of compound **4** was verified through elemental analysis and spectroscopic results.



2a, X = CH$_3$
b, X = C$_6$H$_5$



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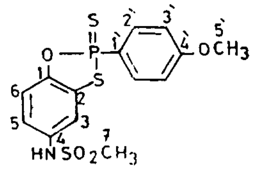

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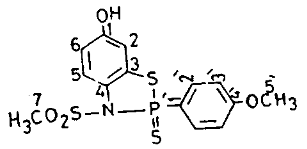

4' (not formed)

The IR spectra showed bands at 3270 cm^{-1} (NH), 710 cm^{-1} (P=S), and 1411 cm^{-1} [P–C (aryl)]. Moreover, the strong C=N and C=O absorption bands at 1585 and 1665 cm^{-1} present in the quinoneimine **2a** vanished completely in the spectrum of adduct **4**. The ^{1}H NMR spectrum of benzo-1,3,2-oxathiaphosphol- 5 -(methanesulfonamido)- 2-(4-methoxyphenyl)-2-sulfide **4** showed signals at δ = 3.05 (s, 3H, SO_2CH_3), 3.95 (s, 3H, OCH_3), 9.05 (s, 1H, NH), and 6.65–8.05 (m, 7H, Ar). The ^{31}P NMR shift recorded for the product **4** was δ = +103 which is in complete accordance with literature values [14,15]. In the mass spectrum, the m/e = 387 (M$^+$). Actually, the structure elucidation of adduct **4** is mainly based on the ["attached proton test" (APT)]

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TABLE 1 ^{13}C NMR Chemical Shifts and P–C Coupling Constants (Hz) of Compound **4** Solvent $CDCl_3$ (Internal Reference, TMS)

C		*J_{PC}* *(Hz)*	*C*		*J_{PC}* *(Hz)*
1	150.6 (d)	24	'1	128.1 (d)	123.0
2	130.7 (d)	24	'2	136.1 (d)	19.7
3	117.6 (d)	11	'3	116.1 (d)	17.0
4	134.8		'4	166.4	2.8
5	122.6		'5	57.5	
6	120.13 (d)	11			
7	45.6				

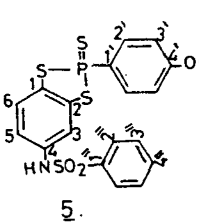
TABLE 2 ^{13}C NMR Chemical Shifts (200 MHz) and P–C Coupling Constants (Hz) of Compounds **5** and **6** Solvent DMSO (Internal Reference, TMS)

Compound 5			*Compound 6*		
C		J_{PC} *(Hz)*	*C*		J_{PC} *(Hz)*
1	129.0	13.8	1	129.0	12.4
2	134.0	13.8	2	132.3	12.4
3	132.0	15.6	3	123.0	14.5
4	136.0		4	133.0	
5	119.0		5	126.0	
6	131.0		6	129.0	
'1	126.0	120.0	7	123.0	
'2	139.8	12.5	8	132.0	
'3	118.5	15.1	9	129.0	
'4	160.0	2.1	10	139.0	
'5	56.8		'1	128.0	9.5
"1	140.5		'2	133.0	13.8
"2	124.3		'3	113.0	15.2
"3	127.0		'4	161.0	
"4	130.9		'5	55.3	

^{13}C NMR spectroscopy (200 MHz), and the data are given in Table 1. They exclude structure **4'**, which would predict a singlet for C_1 at $\delta = 150$, a doublet for C_4 with $J_{PC} = 24$ Hz at $\delta = 132$, a doublet for C_2 with $J_{PC} = 11$ Hz at $\delta = 117$, and a doublet for C_3 with $J_{PC} = 24$ Hz at $\delta = 129$.

As to the formation of adduct **4**, it is suggested [4] that nucleophilic attack of the carbonyl oxygen on phosphorus of **1** is followed by the nucleophilic attack of a sulfur atom on the carbon atom in the ortho-position and a proton shift from this position to nitrogen [16,17].

When one mole equivalent of *N*-(phenylsulfonyl)-1,4-benzoquinone monoimine **2b** and/or *N*-(phenylsulfonyl)-1,4-naphthoquinone monoimine **3** was allowed to react with a half-mole equivalent of **1** in dry toluene at reflux temperature, crystalline adducts **5** and **6**, respectively, were produced in low yields (ca. 25%). However, when an excess amount of **1** was used (3 mole equivalents), compounds **5** and **6** were produced in quantitative yield. In both reactions, a crystalline phosphorus compound was also isolated and proved to be the trimeric 4-methoxyphenylthionophosphine oxide **7** (comparative study with an authentic sample) [18,19].



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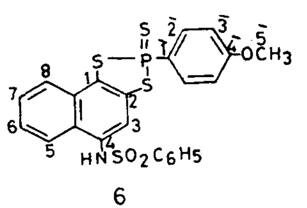
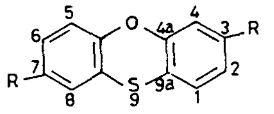


6

On the basis of IR, ^1H NMR, ^{31}P NMR, ^{13}C NMR, MS, and elemental analyses, the structures of compounds **5** and **6** were deduced. The IR spectrum of benzo-1,3,2-dithiaphosphol-5-(benzenesulfonamido)-2-(4-methoxyphenyl)-2-sulfide **5** showed bands at 3300 cm^{-1} (NH), 721 cm^{-1} (P=S), 1449 cm^{-1} (P-aryl), and 1183 cm^{-1} (SO_2). In the ^1H NMR spectrum of **5**, signals appeared at $\delta = 3.68$ (3H, OCH_3, s), 6.85–7.65 (12H, Ar, m), and 9.3 (1H, NH, s). Supplementary evidence for the assigned structure **5** has been gained from its ^{31}P NMR spectrum, and it gave a signal at $\delta = 62$, a value that falls in the range frequently recorded for this class of compound [2]. The ^{13}C NMR spectrum offered strong evidence in support of structure **5** (cf. Table 2). The mass spectrum showed the ion peak at *m/e* 465 (M^+).

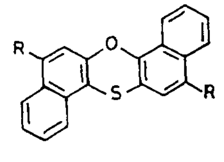
The structure of naphtho-1,3,2,-dithiaphosphol- 5-(benzenesulfonamido)- 2-(4 -methoxyphenyl)-2-sulfide **6** was proven from analytical and spectroscopic data. The IR spectrum showed bands at 3290 cm^{-1} (NH), 750 cm^{-1} (P=S), and 1450 cm^{-1} [P–C (aryl)]. In the ^1H NMR spectrum of **6**, signals appeared at $\delta = 3.95$ (3H, OCH_3, s), 7.7–8 (Ar, 14H, m), and 9.2 (1H, NH, s). The dithiaphosphol structure **6** gave rise to a signal at $\delta = +44$ in its ^{31}P NMR spectrum. Moreover, ^{13}C NMR data can positively confirm the assigned structure **6** (cf. Table 2). In the mass spectrum of **6**, the $m/e = 515$ (M^+). Compounds **5** and **6** might be formed by initial thiation [2] of **2b** and **3** followed by addition of **1**.

Attempted thiation of *p*-quinone monoimines **2a,b** and **3** with phosphorus pentasulfide (P_4S_{10}) in refluxing toluene led to the isolation of colorless compounds formulated as **8a**, **8b**, and **9**, respectively.



8a, R = $NHSO_2CH_3$

b, R = $NHSO_2C_6H_5$



9, R = $NHSO_2C_6H_5$

Compounds **8a**, **8b**, and **9** are chromatographically pure and possess sharp melting points. Their structures are confirmed from microanalysis, IR, ^{1}H NMR, and mass spectroscopic data. IR spectra revealed the presence of absorption bands around 3350 cm^{-1} (NH), 1610 (C=C, Ar). Moreover, the C=O and C=N absorption bands recorded at 1665 and 1585 for the starting quinone monoimines are absent in the spectra of **8**, **9**. However, compounds **8a**, **8b**, and **9** were unambiguously confirmed by high resolution proton NMR spectroscopy (cf. Table 3).

As a model example, the ^{13}C NMR spectroscopy of 3,7-bis-*N*-(benzenesulfonamido)-2-phenoxathiin **8b** has been studied (cf. Table 4).

These data are in complete accordance with ^{13}C NMR data recorded for the parent phenoxathiin compound [20].

The ^{1}H NMR spectrum of compound **9** (Acetone-d6) showed 6 of the 10 protons of the naphthalene moiety as signals at δ = 8.24 (d, 2H) and 8.56 (d, 4H), while the signals of the remaining 4 protons are obscured by the multiplet in the region 7.35–7.84 (m, 14H) due to the SO_2Ph protons. Moreover, the ^{1}H NMR spectrum of **9** revealed the presence of two signals at δ = 9 (s, NH) and 9.2 (S, NH). The mass spectra of adducts **8a**, **8b**, and **9** by the field ionization method yielded a prominent ion peak M$^+$ that is consistent with these structures.

CONCLUSIONS

These findings clearly indicate that the Lawesson reagent and phosphorus pentasulfide preferentially attack the carbonyl oxygen of *p*-quinone monoimines **2a,b** and **3** rather than the imino groups.

EXPERIMENTAL

All melting points are uncorrected. Toluene and petroleum ether (boiling range, 60–80°C) were dried over sodium. **1** was prepared according to an established procedure [21,22]. The IR spectra were measured in KBr, on a Perkin Elmer Infracord Spectrophotometer Model 157 (Grating). The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Spectrometer at 200 MHz. The ^{31}P NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on a JNM-PS-100 Fa Spectrometer. ^{13}C NMR spectra were taken in $CDCl_3$ on a Varian Spectrometer at 200 MHz. The mass spectra were run at 70 eV on a Kratos MS instrument and/or on a Varian MAT 311 A Spectrometer.

Reaction of N-(methylsulfonyl)-1,4-benzoquinone Monoimine **2a** *with* **1**

To a suspension of **2a** (0.36 g, 0.002 mol) [23] in dry toluene (30 mL) was added **1** (0.4 g, 0.001 mol). The reaction mixture was refluxed with stirring. When no more of the starting material could be detected (TLC), the mixture was allowed to cool to room temperature and was then evaporated under reduced pressure. The residue was placed on a column of silica-gel and eluted with ethyl acetate–petroleum ether (40:60) to give 1,3,2-benzoxathiaphosphol- 5-(methanesulfonamido)- 2-(4 -methoxyphenyl)-2-sulfide **4** as colorless crystals, mp 165–167°C (80%). Anal. calcd for $C_{14}H_{14}NO_4PS_3$ (387.49): C, 43.39; H, 3.64; N, 3.61; P, 7.99; S, 24.83. Found: C, 43.42; H, 3.66; N, 3.63; P, 7.95; S, 24.80. MS = 387 (M$^+$).

Reaction of N-(phenylsulfonyl)-1,4-benzoquinone Monoimine **2b** *with* **1**

To a suspension of **2b** (0.24 g, 0.001 mol) in dry toluene (30 mL) was added **1** (1.2 g, 0.003 mol). The reaction mixture was refluxed for 3 hours and the solvent removed under reduced pressure. The residue was placed on a column of silica-gel and eluted with ethyl acetate–methanol (98:2) to give 1,3,2-benzodithiaphosphol-5-(benze-

TABLE 3 ^{1}H NMR Data for Compound **8a,b** *J* (Hz)

Compound	*H-1*	*H-2*	*H-4*	*H-5*	*H-6*	*H-8*	*–NH*	*SO_2CH_3*	*Aromatic*
8a	6.95 (d, 1H, $J_{1,2}$ = 7.6)	6.75 (dd, 1H, $J_{2,1}$ = 7.6, $J_{2,4}$ = 1.6)	7.6 (d, 1H, $J_{4,2}$ = 1.6)	7.4 (d, 1H, $J_{5,6}$ = 8.1)	7.25 (dd, 1H, $J_{6,5}$ = 8.1, $J_{6,8}$ = 1.6)	7.1 (d, 1H, $J_{8,6}$ = 1.6)	7.9 (s, 1H), 8 (s, 1H)	2.9 (s, 3H), 2.95 (s, 3H)	—
8b	6.88 (d, 1H, $J_{1,2}$ = 8)	6.7 (dd, 1H, $J_{2,1}$ = 8, $J_{2,4}$ = 1.8)	7.91 (d, 1H, $J_{4,2}$ = 1.8)	7.7 (d, 1H, $J_{5,6}$ = 8)	7.85 (dd, 1H, $J_{6,5}$ = 8, $J_{6,8}$ = 1.8)	7.44 (d, 1H, $J_{8,6}$ = 1.8)	8.3 (s, 1H), 8.56 (s, 1H)	—	(7.5–7.6 m, 10H)

TABLE 4 ^{13}C NMR Chemical Shifts of **8b** Solvent DMSO (Internal Reference, TMS)

Benzo	**1**	127.40
	2	124.09
	3	140.90
	4	114.14
	4a	155.09
	9a	115.60
Phenyl	**1**	145.98
	2	125.30
	3	128.50
	4	131.09

nesulfonamido)-2-(4-methoxyphenyl)-2-sulfide 5 as colorless crystals, mp 210–212°C (80%). Anal. calcd for $C_{19}H_{16}NO_3PS_4$ (465.57): C, 49.01; H, 3.46; N, 3.00; P, 6.65; S, 27.54. Found: C, 49.07; H, 3.48; N, 3.06; P, 6.68; S, 27.58. MS = 465 (M^+).

Similarly, *N*-(phenylsulfonyl)-1,4-naphthoquinone monoimine **3** (0.29 g, 0.001 mol) [24] reacted with **1** (1.2 g, 0.003 mol) in 30 mL of toluene to give 1, 3, 2-naphthodithiaphosphol-5 -(benzenesulfonamido)-2-(4-methoxyphenyl)-2-sulfide **6** (eluent: diethyl ether–petroleum ether, 3:2), yield (75%), recrystallized from chloroform, mp 215–216°C. Anal. calcd for $C_{23}H_{18}NO_3PS_4$ (515.65); C, 53.57; H, 3.51; N, 2.71; P, 6.01; S, 24.87. Found: C, 53.59; H, 3.55; N, 2.73; P, 6.05; S, 24.89. MS: 515 (M^+).

Reaction of Phosphorus Pentasulfide with N-(methylsulfonyl)-1,4-benzoquinone Monoimine **2a**

To a suspension of *p*-quinone monoimine **2a** (0.18 g, 0.001 mol) in dry toluene (30 mL) was added P_4S_{10} (0.2 g, 0.001 mol). The reaction mixture was refluxed for 10 hours. After evaporation of the volatile materials, the residual product was applied to a column of silica-gel and eluted with acetone petroleum ether (60:40) to give colorless crystals. **8a**, mp 80–83°C in 85% yield. Anal. calcd for $C_{14}H_{14}N_2O_5S_3$ (386.47): C, 43.5; H, 3.65; N, 7.25; S, 24.89. Found: C, 43.55; H, 3.68; N, 7.28; S, 24.86. MS = 386.

Similarly, *N*-(phenylsulfonyl)-1,4-benzoquinone monoimine **2b** reacted with P_4S_{10} to give adduct **8b** (eluent: acetone–petroleum ether, 70:30), yield 80%, colorless crystals, mp 225°C. Anal. calcd for $C_{24}H_{18}N_2O_5S_3$ (510.6): C, 56.45; H, 3.55; N, 5.48; S, 18.8. Found: C, 56.40; H, 3.56; N, 5.49; S, 18.83. MS = 510 (M^+).

Under similar conditions, *N*-(phenylsulfonyl)-1,4-naphthoquinone monoimine reacted with P_4S_{10} to give colorless crystals **9**, mp 210°C (eluent: ethyl acetate–petroleum ether, 30:70), yield (80%). Anal. calcd for $C_{32}H_{22}N_2O_5S_3$ (610.72): C, 62.93; H, 3.63; N, 4.58; S, 15.75. Found: C, 62.90; H, 3.65; N, 4.59; S, 15.72, MS = 610 (M^+).

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