Heteroatom Chemistry
Volume 10, Number 6, 1999

Action of Lawesson's Reagent on Substituted 2-Amino-1,4-Naphthoquinones: Novel Synthesis of Benzodiphenoquinone-bis-1,3,2-thiazaphospholine-2-sulfide Derivatives

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Received 22 January 1999; revised 20 May 1999

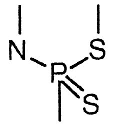
ABSTRACT: *1,3,2,4-Dithiadiphosphetane-2,4-disulfide* **1** *reacts with substituted 2-amino-1,4-naphthoquinons* **2a–d** *to give 4,5,4′,5′-benzodiphenoquinone-bis-1,3,2-thiazaphospholine-2-sulfide derivatives of type* **3**. *Compatible analytical and spectroscopic results were obtained for all the new compounds. A mechanism is proposed to explain the formation of compounds* **3**. © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 488–491, 1999

INTRODUCTION

2,4-Bis-(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (**LR**) **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]. Moreover, we have reported that Lawesson's reagent **1** reacts with *p*-quinone monoimines to give the corresponding 1,3,2-benzoxathiaphosphol-2-sulfide and 1,3,2-dithiaphosphol-2-sulfide derivatives [6]. As part of our continuing interest in organophosphorus chemistry [7–12], we describe here the reaction of Lawesson's reagent **1** with substituted 2-amino-1,4-naphthoquinones **2a-d** (Scheme 1).

RESULTS AND DISCUSSION

We have found that, when one mole of 2-methylamino-1,4-naphthoquinone (**2a**) was allowed to react with half an equivalent of **1 in refluxing toluene for 10 hrs, product 3a** and the starting quinone **2a** were isolated. Carrying out the reaction using one and a half mole of Lawesson's reagent instead of half a mole, led to the formation of product **3a** in good yields (Scheme 1). Compound **3a** is a chromatographically pure yellow crystalline compound and possesses a sharp melting point. The IR spectrum of **3a** disclosed the presence of strong absorption bands at 1627 cm^{-1} (C=O, quinone), 686 (P=S), 1592 (C=C) and at 1178 cm^{-1} (P-C, aryl) [13]. Moreover, the IR spectrum of **3a** lacks both the C=O (amide) and the -NH absorption bands appearing in the spectrum of **2a** at 1670 and 3230 cm^{-1}, respectively. Product **3a** exhibits a positive phosphorus shift at δ = 96.87 (vs, 85% H_3PO_4) which is in complete accordance with shifts recorded for structures incorporating the moiety "A" [14,15].



(A)

The ^{1}H-NMR spectrum (200 MHz) of Compound **3a** shows two doublets centered at δ 2.85 (3H, d, $^3J_{HP}$ =

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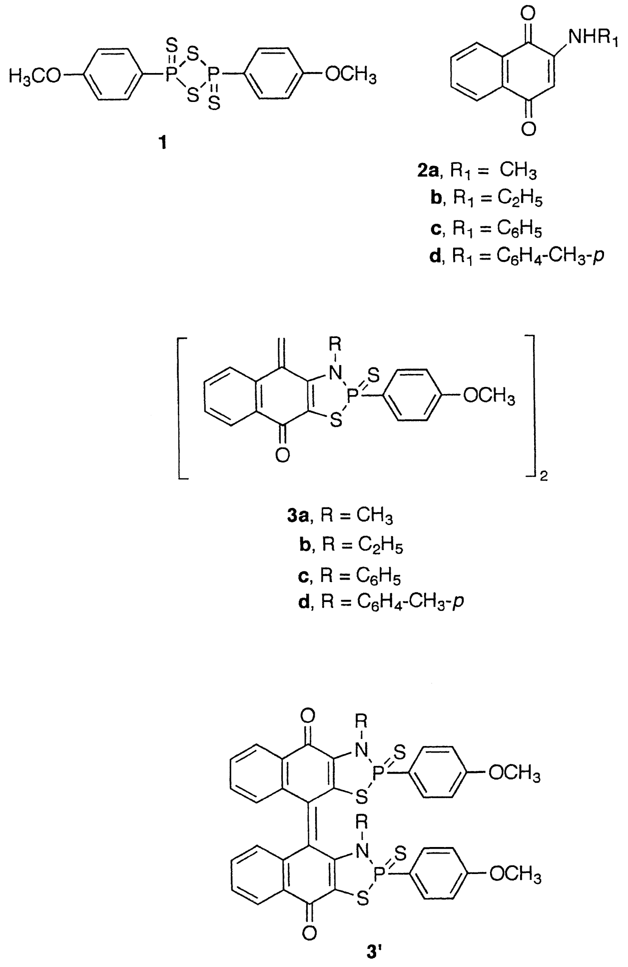
CCC 1042-7163/99/060488-04



SCHEME 1

15 Hz) and 2.93 (3H, d, $^3J_{HP}$ = 15 Hz), corresponding to the two N-Methyl groups attached to the phosphorus atoms. Moreover, the ^{1}H-NMR of **3a** consists of signals at 6.9 (2dd, 4H, $^4J_{HP}$ = 3 Hz, J_{HH} = 9 Hz, meta protons to P), two doublets of doublets centered at 7.76 (4H, $^3J_{HP}$ = 15 Hz, J_{HH} = 9 Hz), and protons *ortho* to phosphorus [2,16] at 3.85 (s, 6H, OCH_3) and 7.5–8.45 (m, 8H, Ar.). It should be noted that the presence of two doublets for the N–CH_3 groups attached to the phosphorus atoms in the ^{1}H-NMR of **3a** suggests both the *E* and *Z* isomeric forms. The mass spectrum of **3a** provides strong evidence in support of the benzodiphenoquinone-bis-1,3,2-thiazaphospholine structure. The mass spectrum of 4,5,4′,5′-benzodiphenoquinone-bis-1,3,2-thiazaphospholine-1-methyl-2-sulfide **3a** showed an ion peak at *m/z* [M$^+$, 742, 100% using CI mode]. The structure assigned for compound **3a** was based on the ^{13}C-NMR spectra, which indicates the presence of signals at δ = 180.45 (C=O, quinone), 131.56 (C–S, $^2J_{CP}$ = 24 Hz), 143.33 (C–N, $^2J_{CP}$ = 24 Hz), 148.51 (C=C), 117.32, 133.45, 124.35, 125.43, 134.25, 131.83 (C_6H_4). Moreover, the ^{13}C-NMR for compound **3a** exhibits resonances at δ = 128.73 (d, $^1J_{CP}$ = 122.15 Hz), 134.09 (d, $^2J_{CP}$ = 23.23 Hz), 114.23 (d, $^3J_{CP}$ = 15.90), and 163.98, corresponding to the carbon atoms of the methoxyl phenyl ring attached to the phosphorus atom, a doublet at 27.96 ppm with J_{PC} = 33 Hz for the N–CH_3 groups, and a singlet at 55.67 corresponding to the OCH_3 group.

It is worth mentioning that the presence of only one carbonyl absorption band at 1627 cm^{-1} (C=O, quinone) in the IR spectrum of **3a** accords with the proposed structure **3** and disqualifies alternative structure **3′**, which would predict the presence of two different carbonyl absorption bands. Moreover, from the ^{13}C-NMR of **3a**, the presence of one value for the (C=C) at 148.51 ppm supports the proposed structure **3**.

In the same way, 2-ethylamino, (**2b**) 2-anilino, (**2c**) and 2-*p*-toluidino-1,4-naphthoquinones (**2b–d**) reacted with Lawesson's reagent **1** in boiling toluene to yield the corresponding benzodiphenoquinone-bisthiazaphospholine derivatives **3b**,**3c**, and **3d**. Compatible analytical and spectral data (IR, ^{1}H-NMR, ^{31}P-NMR, and MS) were obtained for the new compounds (see Experimental section).

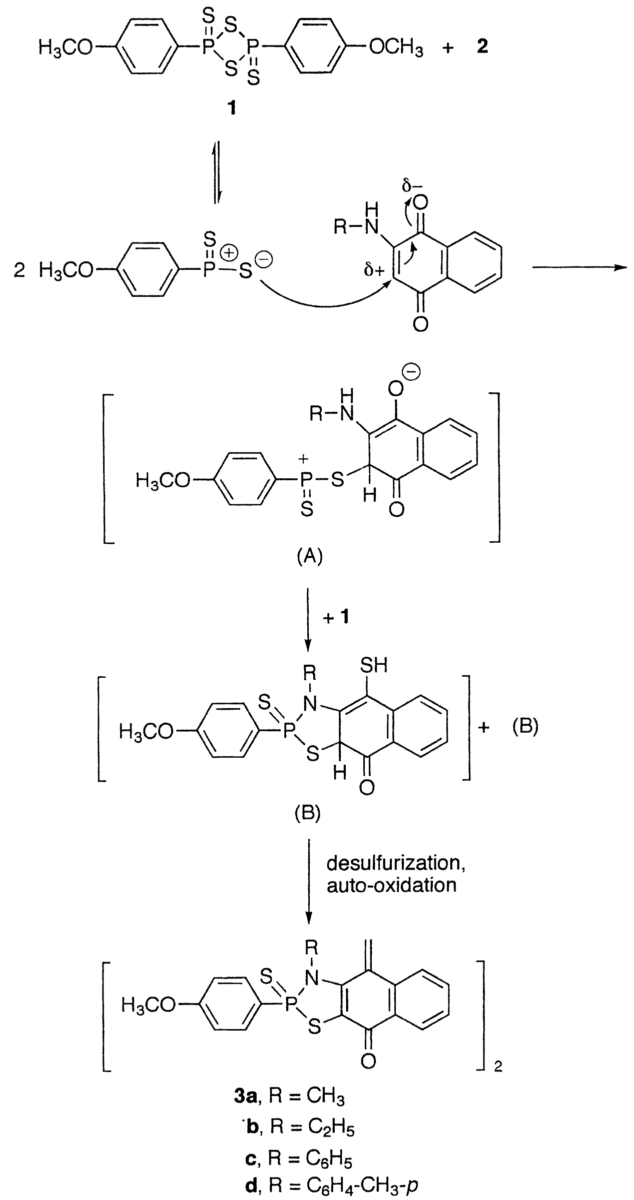
A possible explanation for the formation of products **3** is illustrated in Scheme 2. Quinones **2a–d** react with Lawesson's reagent **1** to give the intermediate addition product (B) (via addition followed by thiation), which reacts with another molecule of (B) to afford the dimeric thiazaphospholine derivative **3**, possibly through desulfurization followed by autooxidation to attain the aromaticity (this being the driving force) [12].

CONCLUSION

Significantly, the reaction of Lawesson's reagent here is indicative of its broad reaction spectrum in addition to the usual thiation reactions. Moreover, the present study clearly shows that Lawesson's reagent reacts with 2-amino-1,4-naphthoquinones **2a–d** in a manner rather different from that already known of quinones [4–6]. Also, this discovery, which represents a novel route to **3**, is a supplement to the expanded utility of reagent **1** for the new synthesis of bisthiazophospholine derivatives **3a–d**.

EXPERIMENTAL

Melting points were determined with a MeI Temp. apparatus and are uncorrected. The IR spectra were recorded by using a Unicamp 1100 or PU 9712 infrared spectrometer. The ^{1}H-NMR spectra were re-



SCHEME 2

corded on a Varian Gemini 200 (200 MHz) or Bruker 250 M Hz spectrometer in $CDCl_3$. ^1H- and ^{31}P-chemical shifts are relative to tetramethyl silane (TMS) as an internal standard and to 85% H_3PO_4 as an external standard. ^{13}C-NMR spectra were taken in $CDCl_3$ on a Varian spectrometer at 200 MHz. Mass spectroscopy data were obtained on a gas chromatography/mass spectrometer (GC/MS) EX 1000, QP Shimadzu-Japan. The reported yields are of pure isolated materials obtained by column chromatography using silica gel 60 (Merck).

Lawesson's reagent is commercially available and can also be prepared as described previously [17].

Reaction of Lawesson's Reagent (**1**) *with 2-Methylamino-1,4-naphthoquinone* (**2a**)

A mixture of **2a** (0.18 g, 0.001 mol) and **LR** (0.6 g, 0.0015 mol) in 25 mL of dry toluene was stirred magnetically at the reflux temperature until no more of the starting quinone **2a** could be detected by thin-layer chromatography (TLC) (10 hours). The reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column using ethyl acetate/*n*-hexane mixtures as the eluent (starting from 2% up to 20% ethyl acetate) to give **3a** in 70% yield as yellow crystals with m.p. 143–144°C. Anal. calcd. for $C_{36}H_{28}N_2O_4P_2S_4$ (742.012): C, 58.22; H, 3.79; N, 3.77; P, 8.32; S, 17.3%. Found: C, 58.13; H, 3.82; N, 3.73; P, 8.30; S, 17.29%. MS: *m*/*e* (%, rel. int.) 742 (M^+, 100) using CI mode, ^{31}P-NMR δ = 96.87. IR, ^1H-NMR, ^{13}C-NMR were mentioned in the text.

Reaction of LR with **2b**

The same method as described for **3a** was used to give **3b** in 65% yield, as yellow crystals with m.p. 122–123°C. Anal. calcd. for $C_{38}H_{32}N_2O_4P_2S_4$ (770.04): C, 59.21; H, 4.18; N, 3.63; P, 8.04; S, 16.60%. Found: C, 59.17; H, 4.21; N, 3.65; P, 8.01; S, 16.35%. IR (ν, cm^{-1}, group): 1627 (C=O, quinone), 684 (P=S), 1592 (C=C), 1178 (P-C-aryl). ^1H-NMR: two multiplets centered at 0.95, 1.15 ppm (6H, 2-N-CH_2-$\mathit{C}H_3$), multiplets centered at 3.23, 3.35 (4H, 2N-$\mathit{C}H_2$-CH_3) corresponding to the two N-$\mathit{C}H_2$ groups attached to phosphorus atoms, 3.82 (s, $2OCH_3$), 6.85 (2dd, 4H, $^4J_{PH}$ = 3 Hz, J_{HH} = 9 Hz, *meta* protons to P), two doublet of doublets centered at 8.10 ppm (4H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz) *ortho* protons to P, 7.15–8.45 (8H, m, Ar.). MS: *m*/*e* (%, rel. int.) 770 (M^+, 100) using CI mode. ^{31}P-NMR = 94.53.

Reaction of **LR** (**1**) *with Anilino-1,4-naphthoquinone* (**2c**)

As described for **3a**, to give **3c** in 60% yield as yellow crystals with m.p. 135–136°C. Anal. calcd. for $C_{46}H_{32}N_2O_4P_2S_4$ (866.04): C, 63.73; H, 3.72; N, 3.23; P, 7.15; S, 14.76%. Found: C, 63.70; H, 3.76; N, 3.15; P, 7.20; S, 14.71%. IR (ν, cm^{-1}, group): 1627 (C=O), 690 (P=S), 1592 (C=C), 1178 (P–C-aryl). ^1H-NMR: 3.85 (s, $2OCH_3$), 6.85 (2 dd, 8H, $^4J_{PH}$ = 3 Hz, J_{HH} = 9 Hz, *meta* protons to P), 8.05 (2 dd, 8H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz) corresponding to the four methoxy phenyl protons *ortho* to the phosphorus atom and the four protons of the anilino ring *ortho* to phosphorus atoms, 7.15–8.45 (8H, Ar.). MS: *m/e* (%, rel. int.) 866 (M^+, 100) using CI mode. ^{31}P-NMR = +96.76.

Reaction of **LR** *with 2-p-toluidino-1,4-naphthoquinone* (**2d**)

Similarly, **3d** was obtained in 60% yield as yellow crystals with m.p. 145–146°C. Anal. calcd. for $C_{48}H_{36}N_2O_4P_2S_4$ (894.07): C, 64.42; H, 4.05; N, 3.13; P, 6.92; S, 14.30%. Found: C, 64.36; H, 4.12; N, 3.10; P, 6.87; S, 14.32%. IR (v, cm^{-1}, group): 1627 (C=O), 680 (P=S), 1592 (C=C), 1178 (P-C-aryl). ^{1}H-NMR: 2.35 (6H, two singlets, Ph-CH_3), 3.85 (broad s, 6H, 2OCH_3), 6.92 (2dd, 8H, $^4J_{HP}$ = 3 Hz, J_{HH} = 9 Hz, meta protons to P), 8.05 (2dd, 8H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz) corresponding to the four methoxy phenyl protons *ortho* to phosphorus atom and the four protons of the *p*-toluidino-ring *ortho* to P, 7.15–8.43 (m, 8H, Ar.). MS: *m/e* (%, rel. int.) 894 (M^+, 100) using CI mode. ^{31}P-NMR = +69.56.

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