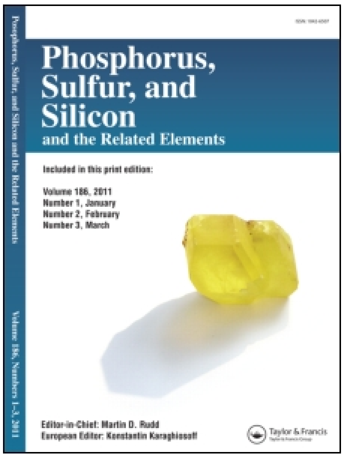

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THE BEHAVIOUR OF *p*-QUINONEDIIMINES TOWARDS 2,4-BIS-(4-METHOXYPHENYL)-1,3,2,4- DITHIADIPHOSPHETANE-2,4-DISULFIDE

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THE BEHAVIOUR OF *p*-QUINONEDIIMINES TOWARDS 2,4-BIS-(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDE

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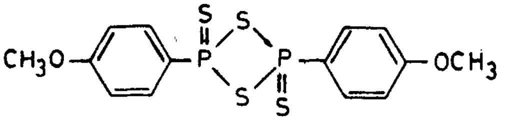
p-Benzoquinonediimines (**IIIa–c**) react with 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**I**) to produce compounds Va-c. *p*-Naphthoquinonediimines (**IVa,b**) react with the same reagent to produce compounds **Xa,b**.

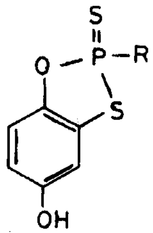
Key words: *p*-Benzoquinonedibenzenesulfoimine **IIIa**; *p*-benzoquinonedimethanesulfonimine **IIIb**; *p*-benzoquinonedibenzimide **IIIc**; 1,4-naphthoquinonedibenzenesulfonimine **IVa**; 1,4-naphthoquinonedimethanesulfonimine **IVb**; 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson Reagent) (**I**); 1,3,2-benzoazathiaphosphole-2-sulfides (**V**); 1,3,2-naphthoazathiaphosphole-2-sulfides (**X**).

INTRODUCTION

It is widely realized that 2,4-bis-(4-methoxyphenyl)-1,3,2,4-diphosphetane-2,4-disulfide (**I**) is a most effective thiating agent for ketones[1] and imides.[2] However, this reagent was known to react with *p*-quinones to give the corresponding 1,3,2-benzoxathiaphosphol-5-ol-2-sulfide derivatives (**II**).[3]



I (Lawesson Reagent)

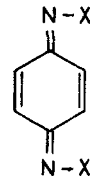


II, R = $C_6H_4OCH_3$-p ; $C_6H_4OC_6H_5$-p

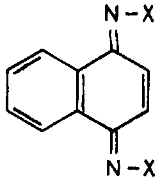
The present work reports on the reaction of *p*-benzoquinonediimines (**IIIa–c**) and *p*-naphthoquinonediimines (**IVa,b**) with Lawesson Reagent (LR) (**I**) in continuation of our work on the behaviour of *p*-quinonemonoimines[4,5] and *p*-quinonediimines[6,7] towards alkyl phosphites and phosphines.

RESULTS AND DISCUSSIONS

We have found that when 1 mole equivalent of *p*-benzoquinonedibenzenesulfonimine (**IIIa**) and/or *p*-benzoquinonedimethanesulfonimine (**IIIb**) was allowed to

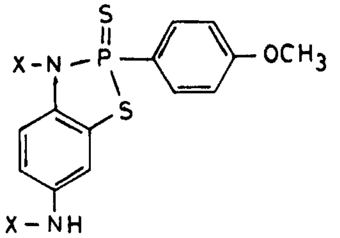


III a, X = $SO_2C_6H_5$
b, X = SO_2CH_3
c, X = COC_6H_5



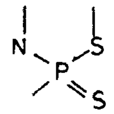
IV (a, b as in III)

react with $\frac{1}{2}$ mole equivalent of LR (I) in dry toluene at reflux, crystalline adducts **Va** and **Vb** were produced, respectively, in quantitative yields. These adducts are chromatographically pure and possess sharp melting points. The assigned structures are based on the following:

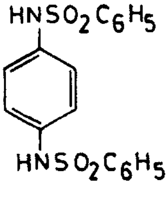


V a, X = $SO_2C_6H_5$
b, X = SO_2CH_3
c, X = CSC_6H_5

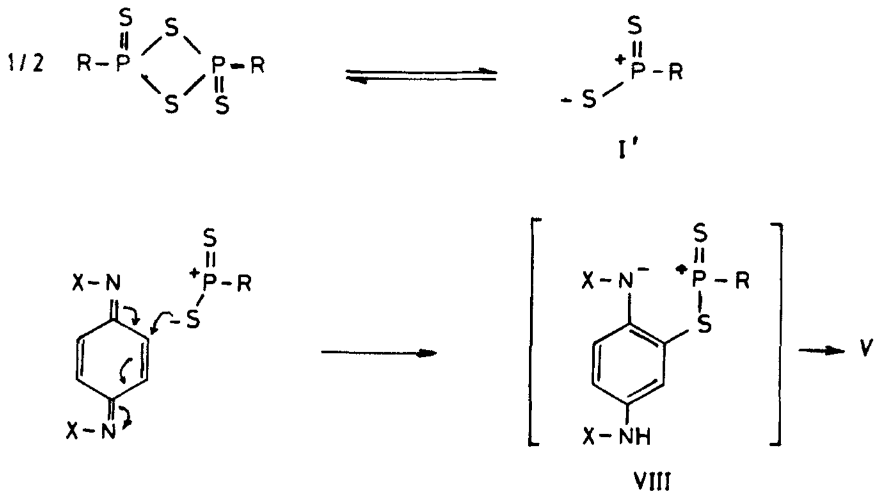
(1) Satisfactory microanalysis (C, H, N, P, S) were obtained for the two compounds. (2) The IR spectrum of **Va**, taken as an example showed bands at 3215 cm^{-1} (NH), 1440 cm^{-1} [P—C (aryl)], 820 cm^{-1} (P—N) and at 790 cm^{-1} (P═S). Moreover, the strong C═N absorption band appearing at 1580 cm^{-1} with quinoneimine **IIIa**, vanished completely in the spectrum of **Va**. (3) The MS of compound **Va** showed peaks at 588 (M$^+$), 556 (M$^+$—S) and 386 (M$^+$—$\frac{1}{2}$ LR). (4) The ^{31}P NMR chemical shift for compound **Va** was 85.40 ppm which is in complete accordance with shifts recorded[8,9] for the structure encorporating moiety **VI**. (5) The ^{1}H NMR spectrum of **Va** showed a singlet due to OCH_3 protons at δ = 3.75 ppm, doublet of doublets due to the two protons ortho to phosphorus in the area 6.73–6.88 ppm with JHP = 18 Hz and JHH = 10 Hz, a multiplet due to 15 aromatic protons at 7.057.70 ppm and a singlet at 9.50 ppm due to the NH proton. (6) Adduct **Va** when treated with alcoholic alkali yielded *p*-phenylenedibenzenesulfonamide (**VII**).



VI



VII

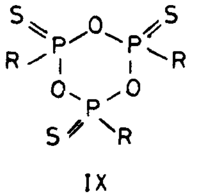


SCHEME I

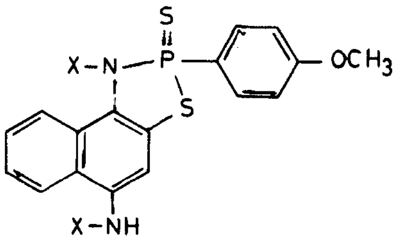
From the above data, it appears that adducts **Va,b** bear the new 1,3,2-benzoazathiaphosphole-2-sulfide structure. A mechanism accounting for the formation of these compounds is depicted in Scheme I. It is based on the assumption of the addition of the monomeric species (**I′**), existing in equilibrium with **I**,[10,12] to *p*-quinonediimine **III** in a 1,4 fashion yielding intermediate **VIII** which collapses to produce **V**.

Compound **Vc**, on the other hand, was produced in a low yield (ca 10%) when *p*-benzoquinonedibenzimide (**IIIc**) was treated with LR under the same experimental condition. However, when an excess amount of LR was used (3 mole equivalents), compound **Vc** was produced in quantitative yield. Besides, a crystalline phosphorus compound was isolated and proved to be trimeric thionophosphine oxide (**IX**). This was proved by comparative study with an authentic sample.[13,14] The structure of compound **Vc** was elucidated by analytical and spectroscopic data (cf. experimental). Compound **Vc** might be formed by initial thiation[2] of **IIIc** followed by addition of **I′**.

The reaction of LR (**I**) with 1,4-naphthoquinonedibenzenesulfonimine (**IVa**) and/or 1,4-naphthoquinonedimethanesulfonimine (**IVb**) was also investigated. The reaction proceeded in dry toluene at reflux to give mainly adducts having structure **Xa,b** respectively.



IX



X a, X = $SO_2C_6H_5$
b, X = SO_2CH_3

The identity of compounds **Xa,b** was verified by analytical and spectroscopic evidences (cf. experimental).

EXPERIMENTAL

All melting points were uncorrected. Toluene and light petroleum (40–60°C) were dried over Na. *p*-Quinonediimines **IIIa**,[15,16] **IIIb**,[15] **IIIc**[17] and **IV**[18] were recrystallized and dried before use. 2,4-Bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson Reagent) (**I**) was prepared according to an established procedure.[1,19] All manipulations were carried out under a nitrogen atmosphere.

The IR spectra (KBr) were recorded with Perkin-Elmer spectrophotometer 157 G. The ^1H NMR spectra were run in $CDCl_3$ on a Varian spectrometer at 90 MHz using TMS as an internal reference. The ^{31}P NMR spectra were taken in $CDCl_3$ (vs. H_3PO_4 as external standard) on a Varian CFT 20, 32 MHz spectrometer. The mass spectra were performed at 70 eV using a Varian MAT 112 mass spectometer.

Reaction of p-quinonediimine **III** *with Lawesson Reagent* (**I**): To a suspension of **IIIa** (0.38 g; 0.001 mole) in dry toluene (30 ml) was added **Ia** (0.2 g; 0.0005 mole). The reaction mixture was refluxed for 1 hour. The solvent was evaporated. The oil that was left behind was applied to a column prepared by packing a slurry of silica gel (30 g) in light petroleum. Toluene-light petroleum (1:8) eluted 1,3,2-benzoazathiaphosphol-1,5-bis(benzenesulfonamido)-2(4-methoxyphenyl)-2-sulfide (**Va**) as colorless crystals (0.5 g), m.p. 127°C, recrystallized from a chloroform-light petroleum mixture. Anal. Calcd. for $C_{25}H_{21}N_2O_5PS_4$ (588.666) C, 51.01; H, 3.59; N, 4.75; P, 5.26; S, 21.78. Found: C, 50.95; H, 3.55; N, 4.75; P, 5.30; S, 21.80%.

Similarly **IIIb** (0.26 g; 0.001 mole) reacted with **I** (0.2 g; 0.0005 mole) to produce 1,3,2-benzoazathiaphosphol-1,5-bis(methanesulfonamido)-2(4-methoxyphenyl)-2-sulfide (**Vb**) (eluent: toluene-light petroleum 1:6), yield 0.4 g, recrystallized from a chloroform-light petroleum mixture, m.p. 178°C. Anal. Calcd. for $C_{15}N_{17}N_2O_5PS_4$ (464.524) C, 38.78; H, 3.68; N, 6.03; P, 6.66; S, 27.60. Found: C, 38.70; H, 3.65; N, 6.09; P, 6.60; S, 27.58%. IR: bands at 3210 cm^{-1} (NH), 825 cm^{-1} (P—N) and 795 cm^{-1} (P═S). MS: m/e 464 (M^+), 432 (M^+—S), 262 M^+—$\frac{1}{2}$ LR). ^{31}P NMR: 88.30 ppm. ^1H NMR: signals at δ = 2.56 ppm (SO_2CH_3, s), 2.95 (SO_2CH_3, s), 3.84 ppm (OCH_3, s), 6.90–7.10 ppm (2H, dd), 7.15–7.80 ppm (5H, m), 9.60 (NH, s).

p-Quinonedibenzimide (**IIIc**) (0.31 g; 0.001 mole) reacted with **Ia** (1.2 g; 0.003 mole) to produce 1,3,2-benzoazathiaphosphol-1,5-bis(thiobenzoylamido)-2(4-methoxyphenyl)-2-sulfide (**Vc**) (eluent: toluene-light petroleum 1:10), yield 0.46 g, recrystallized from a chloroform-light petroleum mixture, m.p. 85–87°C. Anal. Calcd. for $C_{27}H_{21}N_2OPS_4$ (548.692) C, 59.10; H, 3.85; N, 5.10; P, 5.64; S, 23.37. Found: C, 59.15; H, 3.90; N, 5.10; P, 5.60; S, 23.30%. IR: bands at 3230 cm^{-1} (NH), 820 cm^{-1} (P—N), 790 cm^{-1} (P═S), no C═O band. MS: m/e 548 (M^+). ^{31}P NMR: 84.12 ppm. ^1H NMR: signals at δ = 3.85 ppm (OCH_3, s), 6.8–7.0 ppm (2H, dd), 7.3–8.2 ppm (15 H, m), 10.4 ppm (NH, s).

Reaction of 1,4-Naphthoquinonedisulfonimine **IV** *with Lawesson Reagent* (**I**): To a suspension of **IVa** (0.43 g; 0.001 mole) in dry toluene (30 ml) was added **I** (0.2 g; 0.0005 mole) The reaction mixture was refluxed for 1 hour. After cooling to room temperature, the colorless crystals of 1,3,2-naphthoazathiaphosphol-1,5-bis(benzenesulfonamido)-2(4-methoxyphenyl)-2-sulfide (**Xa**) were separated, filtered off (0.5 g), and recrystallized from benzene, m.p. 162°C Anal. Calcd. for $C_{29}H_{23}N_2O_5PS_4$ (638.726) C, 54.53; H, 3.63; N, 4.38; P, 4.85; S, 20.07. Found: C, 54.50; H, 3.60; N, 4.30; P, 4.80; S, 20.01%. IR: bands at 3215 cm^{-1} (NH), 820 cm^{-1} (P—N) and 790 cm^{-1} (P═S). MS: 638 (M^+). ^1H NMR: signals at 3.70 ppm. (OCH_3, s), 6.90–7.15 ppm. (5 H, m), 7.20–8.05 ppm (14 H, m) and at 10.4 ppm (NH, s).

Similarly **IVb** (0.31 g; 0.001 mole) reacted with **I** (0.2 g; 0.0005 mole) in dry toluene (30 ml) to produce 1,3,2-naphthoazathiaphosphol-1,5-bis(methanesulfonamido)-2(4-methoxyphenyl)-2-sulfide (**Xb**) (0.46 g) recrystallized from benzene as colorless crystals, m.p. 180°C. Anal. Calcd. for $C_{19}H_{19}N_2O_5PS_4$ (514.584) C, 44.34; H, 3.72; N, 5.44; P, 6.02; S, 24.92. Found: C, 44.30; H, 3.70; N, 5.40; P, 6.05; S, 24.90%. IR: bands at 3230 cm^{-1} (NH), 825 cm^{-1} (P—N) and 795 cm^{-1} (P═S). MS: m/e 514 (M^+). ^1H NMR: signals at 2.83 ppm (CH_3SO_2, s), 2.90 ppm (CH_3SO_2, s), 3.72 ppm (OCH_3, s), 6.90–7.15 ppm (5 H, m), 7.60–8.10 ppm (4 H, m) and at 10.4 ppm (NH, s).

Action of alkali on **Va**: Compound **Va** (0.1 g) was treated with 10% alcoholic NaOH (10 ml) and the mixture was refluxed for 1 hour. Alcohol was evaporated and the mixture was cooled and acidified with 10% aq. HCl. The precipitate was filtered off and crystallized from ethanol to give **VII** as colorless crystals, m.p. 243°C, yield 80%. Compound **VII** proved to be identical (mixed m.p.) with an authentic sample.[15]

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