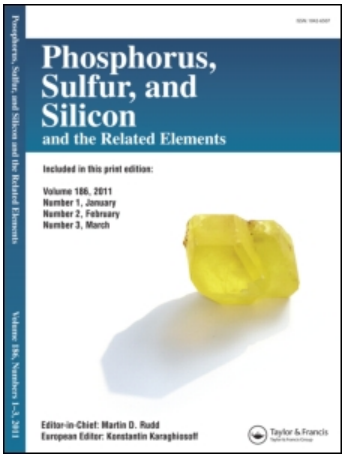

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THE REACTION OF PHOSPHITE ESTERS AND TRIS(DIMETHYLAMIN0)PHOSPHINE WITH 1,4-NAPHTHOQUINONEMONOBENZENESULFONIMINE

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THE REACTION OF PHOSPHITE ESTERS AND TRIS(DIMETHYLAMINO)PHOSPHINE WITH 1,4-NAPHTHOQUINONEMONOBENZENESULFONIMINE

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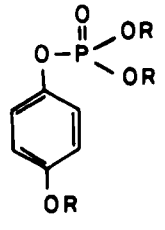
Trimethyl and triisopropyl phosphites react with quinoneimine III to give the corresponding phosphonate derivatives having structure IV) Tris(dimethylamino)phosphine, on the other hand, attacks the carbonyl oxygen of III, yielding the dipolar structure VIII. Possible reaction mechanisms are considered and the structural assignments are based on chemical and spectroscopic evidence.

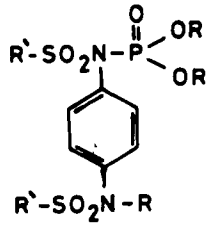
Key words: Trialkyl phosphites; 1,4-Naphthoquinone monobenzenesulfonimine III; 4-Benzosulfonylamino-1-hydroxy-2-dimethylphosphonate-1,4-hydronaphthalene IVa; 4-Methylbenzosulfonylamino-1-hydroxy-2-dimethylphosphonate-1,4-hydronaphthalene IVb; 4-Isopropylbenzosulfonylamino-1-hydroxy-2-di-isopropyl-phosphonate-1,4-hydronaphthalene IVc; and phosphate adduct VIII.

INTRODUCTION

It has been reported[1–4] that trialkyl phosphites react with p-quinones and p-quinoneimines yielding phosphates (I) and phosphoramidates (II), respectively.



I



II

R = CH_3; R′ = CH_3 or C_6H_5

R = C_2H_5; R′ = CH_3 or C_6H_5

R = C_3H_7-i; R′ = CH_3 or C_6H_5

Since 1,4-naphthoquinonemonobenzenesulfonimine (III) bears both the carbonyl and imino-functions, it appeared, therefore, of interest to examine its behaviour towards these phosphite reagents to establish whether it would undergo a preferential oxygen or nitrogen attack by phosphorus.

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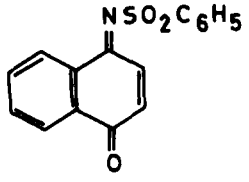
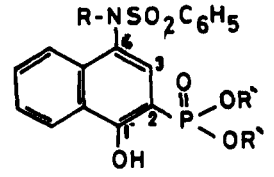
RESULTS AND DISCUSSION

We have found that the reaction of trimethyl phosphite with 1,4-naphthoquinonemonobenzenesulfonimine (III), in dry benzene, proceeds at room temperature to give two chromatographically pure 1:1 adducts formulated as IVa and IVb in 25% and 75% yield, respectively.



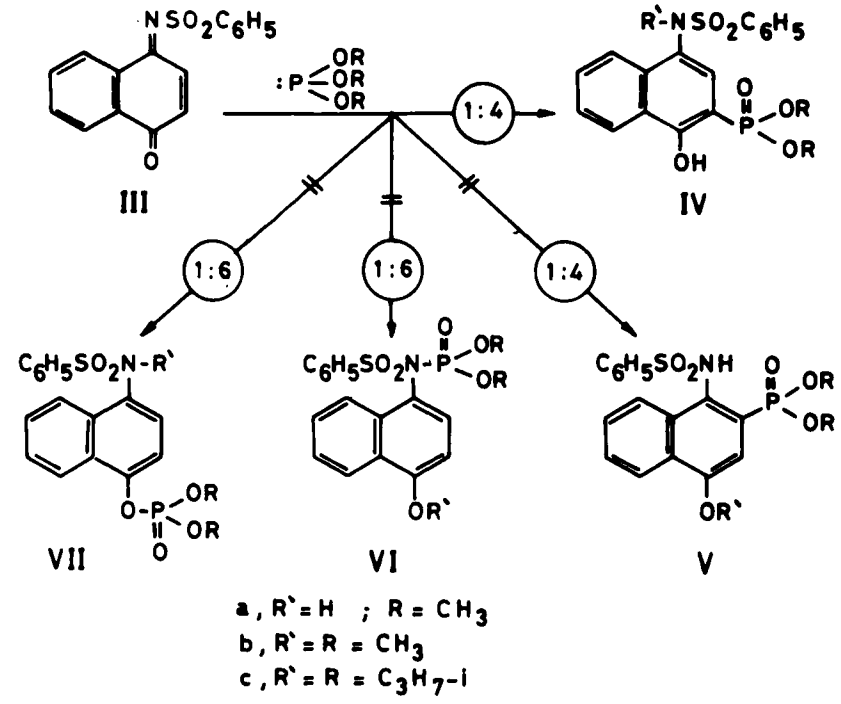
III



IV a, R = H ; R` = CH_3
b, R = R` = CH_3
c, R = R` = C_3H_7-i

Structure elucidation for 4-methylbenzosulfonylamino-1-hydroxy-2-dimethylphosphonate-1,4-hydronaphthalene (IVb), taken as example, was attested by the following evidence: (**a**) Elemental analysis and molecular weight determination (MS) for compound (IVb) corresponds to $C_{19}H_{20}NO_6PS$. (**b**) The IR spectrum of adduct (IVb), in KBr, reveals the presence of strong-OH absorption band at 3200 cm^{-1}. Moreover, its IR spectrum lacked both the carbonyl and C=N absorption bands appearing in the starting quinoneimine at 1675 and 1580 cm^{-1} respectively. The IR spectrum of adduct (IVb) exhibits strong absorption bands at 1335 cm^{-1}, 1175 cm^{-1} (SO_2), 1230 cm^{-1} ($\nearrow$P=O, bonded),[5] 1050 cm^{-1} (P—O—CH_3),[5] and at 1440 cm^{-1} (P-Ph).[6] (**c**) Compound IVb responds positively to the ferric chloride reaction and dissolves freely in 10% aqueous alkali. (**d**) The ^{1}H-NMR spectrum of compound IVb (in $CDCl_3$) disclosed the presence of a doublet centered at δ = 3.92 with J_{HP} = 11.5 Hz, due to the two OMe groups attached to phosphorus,[7] whereas the N—CH_3 group appeared as a singlet at δ = 3.65. The 5 aromatic protons of the phenylsulfonyl appeared as a multiplet at 7.30–7.53 ppm and the 4 aromatic protons of the unsubstituted ring of the naphthylene molecule appeared as a multiplet at 7.65–7.87 ppm. The ^{1}H-NMR spectrum of IVb shows a doublet centered at δ = 6.97 with J_{HP}=15.2 Hz ascribed to the C-3 proton. This doublet is attributed to the coupling of this proton with phosphorus.[8] The exchangeable (D_2O) protons (OH) appeared as broad signal at δ = 11.73. Actually, the structure assigned for compound IVa was also based on the ^{31}P-NMR shift (+25.17 ppm vs 85% H_3PO_4) which corresponds to a phosphonate (IV) and not to phosphate (VII) adducts[9,10] (Scheme I).

The aforementioned IR and ^{1}H-NMR spectral data of IVb rule out alternative structures like Vb, VIb which would predict a singlet around 4 ppm attributable to the methoxyl protons (OCH_3). The fact that compound IVa responds positively to the ferric chloride colour reaction and is freely soluble in 10% NaOH solution are in favour of the phosphonate structure IV rather than the possible alternative formulae (V-VII), (Scheme I). Structural elucidation for the other isolated product (25%) IVa was based upon elemental and spectroscopic data (cf. Experimental). It is worthy to mention that when the reaction of trimethyl phosphite with qui-

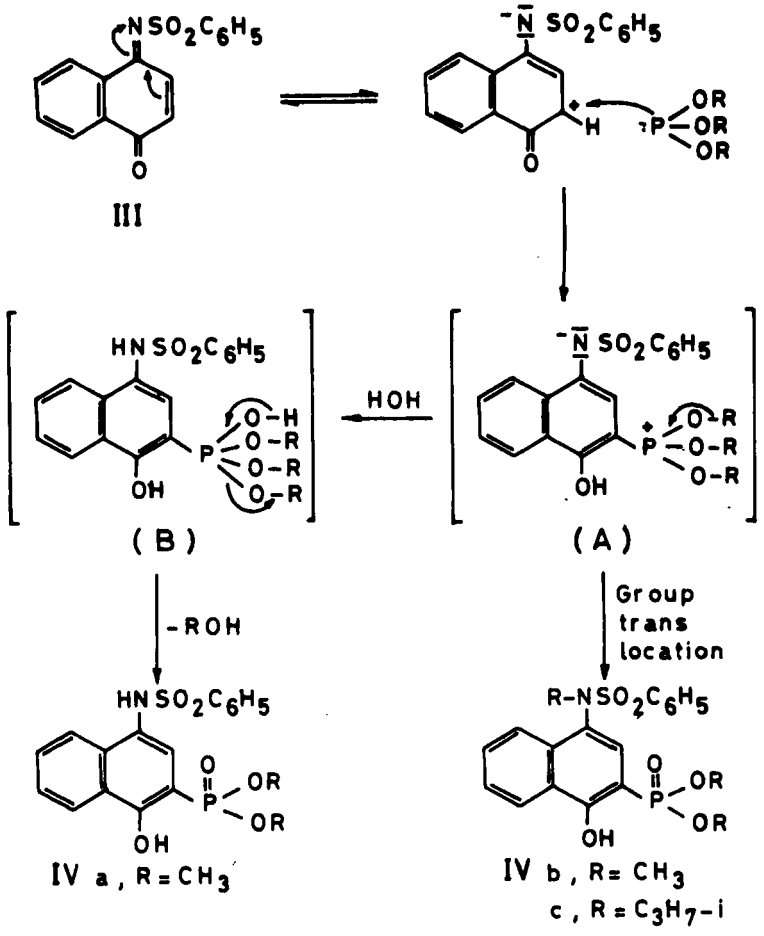


Scheme (I)

noneimine III was performed in dry benzene to which controlled amounts (ca. 5%) of water were added, it proceeded with the formation of adduct IVa as a major product besides minor quantities of adduct IVb. On the other hand, when the same reaction was performed in benzene in presence of a few drops of acetic acid, adduct IVa comprises the sole reaction product. Adduct IVa regenerated the starting quinoneimine III and the respective dialkyl hydrogen phosphite, when subjected to pyrolysis.

Similarly, the reaction of triisopropyl phosphite with quinoneimine III proceeded, in dry benzene, at room temperature, to give mainly 1:1 adduct having structure IVc. This based on analytical and spectroscopic data (IR, ^{1}H,^{31}P-NMR and MS) (cf. Experimental).

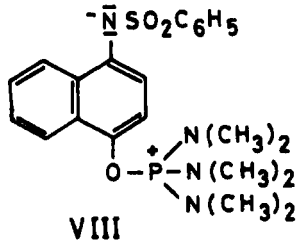
A possible explanation for the course of the reaction of trialkyl phosphites with (III) is shown in Scheme II. This involves Michaelis addition[11,12] by a tertiary phosphite ester on quinoneimine III to give 1,5-dipolar intermediate (A), which undergoes group translocation (*N*-methylation) to yield the phosphonate adducts IVb,c. Addition of elements of water (unavoidable moisture) to intermediate (A) (only in case of trimethyl phosphite) produces a transient intermediate (B) with pentacovalent phosphorus.[12-14] The latter then collapses to give the minor product (IVa). From the results of the present investigation it could be concluded that the reaction of quinoneimine III with trialkyl phosphites proceeds according to the 1,4 addition mechanism to give the phosphonate adducts IV almost exclusively. Worth-mentioning is that quinoneimine III added dialkyl phosphites in a 1,2 fashion to give phosphonate adduct.[15] The present study clearly shows that 1,4-naphthoqui-



Scheme (II)

nonemonoimine (III) behaves in a different manner to that reaction of p-benzoquinonedimine with trialkyl phosphites where 1,6 addition takes place to form the phosphoramidates.[3,4]

Further, this study was extended to include the reaction of hexamethylphosphorustriamide (HMPT) with quinoneimine III in order to determine the mode of addition, as HMPT possesses a greater order of nucleophilicity in comparison to trialkyl phosphites.[16,17] When quinoneimine III was allowed to react with HMPT in dry benzene, it yielded a colourless crystalline adduct assigned structure VIII



VIII

due to the following reasons: (i) Correct elemental analysis and molecular weight determination (MS) corresponded to $C_{22}H_{29}NO_3P$. (ii) The IR spectrum of VIII in KBr, showed a band at 1460 cm^{-1} which is ascribed to the enolate carbonyl.[18] (iii) Its ^{1}H-NMR spectrum (in $CDCl_3$) disclosed the presence of three doublets centered at δ = 2.58 (18H, J_{HP}12 Hz) due to the N—CH_3 protons. The two protons α and β to the carbonyl group appeared as two doublets centered at 6.65 and 8.26 ppm. The ^{1}H-NMR spectrum of VIII disclosed the presence of a multiplet centered at δ = 7.26 and 7.60 ppm due to the 9 aromatic protons. (iv) The ^{31}P-NMR spectrum of VIII gave a signal at +59.84 ppm. This value is in complete accordance with the assigned dipolar structure.[19,20]

EXPERIMENTAL

All melting points are uncorrected. Trialkyl phosphites[21,22] were purified by treatment with Na followed by fractional distillation. Tris(dimethylamino)phosphine[23] is freshly distilled and 1,4-naphthoquinone-monobenzenesulfonimide[24] was recrystallized and dried before use. The benzene (thiophene-free) and petroleum ether (40–60°C) utilized were dried over sodium. The IR spectra (KBr) were recorded with Perkin-Elmer Spectrophotometer 157-G. The ^{1}H-NMR spectra were run in $CDCl_3$ in Varian Spectrometers at 90 MHz, using TMS as an external reference. The ^{31}P-NMR spectra were taken in $CDCl_3$ (vs. H_3PO_4 as external standard) on Varian CFT 20, 32 MHz Spectrometer. The mass spectra were run at 70 eV on Kratos MS 50 equipment and/or Varian MAT 711 spectrometer.

Reaction of trimethyl phosphite with quinoneimine III. To a solution of III (0.3 g; 0.001 mole) in dry benzene (10 ml) was added trimethyl phosphite (0.013 g; 0.001 mole) and the reaction mixture was left at room temperature for 24 hr. The colourless precipitate that formed (0.1 g; 25% yield) was filtered off, washed with benzene and recrystallized from benzene to give 4-benzosulfonylamino-1-hydroxy-2-dimethylphosphonate-1,4-hydronaphthalene (IV), m.p. 205°C. Anal. Calcd. for $C_{18}H_{18}NO_6PS$ (407.17) C, 53.05; H, 4.45; N, 3.44; P, 7.61; S, 7.86. Found: C, 53,23; H, 4.51; N, 3.37; p, 7.50; S, 7.91%, Mol. Wt. (MS = 407. IR bands at 3290 (NH), 3300 (OH), 1335, 1175 (SO_2), 1230 (P=O bonded), 1050 (P—O—CH_3), and at 1440 cm^{-1} (P-ph).

^{1}H-NMR (in $CDCl_3$ and expressed in δ-scale ppm): Signals at 3.94 (6H, OCH_3, d) with J_{HP} = 11.5 Hz, 6.87 (1 H, d) with J_{HP} = 15.2 Hz for C-3 proton, 7.3–7.87 (9H, aromatic, m). The exchangeable D_2O protons (NH) and (OH) appear as two broad singlets at 8.7 and 11.73 ppm, respectively. ^{31}PNMR (in $CDCl_3$, vs. H_3PO_4): + 25.13 ppm. The filterate was treated with petroleum ether whereby a white precipitate was obtained (0.3 g; 75% yield), filtered off, washed with petroleum ether and recrystallized from benzene-petroleum ether to give 4-methylbenzosulfonylamlino-1-hydroxy-2-dihmethyl-phosphonate-1,4-hydronaphthalene IVb, m.p. 95°C. Anal. Calcd. for $C_{19}H_{20}NO_6PS$ (421.38) C, 54.16; H, 4.78; N, 3.32; P, 7.35; S, 7.61. Found: C, 54.20; H, 4.75; N, 3.30; P, 7.30; S, 7.65%, Mol. Wt. (MS) = 421.

Pyrolysis of compound IVa. Compound IVa, (0.5 g) was heated under reduced pressure (0.5 mm/Hg) in an apparatus equipped for fractional distillation. The drops that were collected at 40° gave the violet colour reaction described for dimethyl hydrogen phosphite.[25] The solid product (ca. 0.35 g; 70% yield) was recrystallized from chloroform-cyclohexane and proved to be 1,4-naphthoquinonemono-benzenesulfonimine III (m.p. and mixed m.p.).[24]

Reaction of triisopropylphosphite with quinoneimine III. To a solution of III (0.3 g, 0.001 mole), in dry benzene (10 ml), was added triisopropyl phosphite (0.22 g; 0.001 mole) and the reaction mixture was left at room temperature for 24 hr.

Petroleum ether was added whereby a white precipitate (0.45 g, 95% yield) was isolated, filtered off, washed with petroleum ether to give 4-isopropylbenzosulfonylamino-1-hydroxy-2-diisopropylphos-phonate-1,4-hydronaphthalene IVc as white crystals, m.p. 92°C. Anal. Calcd. for $C_{25}H_{32}NO_6PS$ (505.53), C, 59.40; H, 6.37; N, 2.77; P, 6.13; S, 6.34. Found: C, 59.38; H, 6.35; N, 2.75; P, 6.10; S, 6.30%, Mol. Wt. (MS) = 505.

IR in KBr: bands at 3230 (OH), 1330, 1175 (SO_2), 1235 (P=O, bonded), 1055 (P—O—CH_3) and at 1445 cm^{-1} (P-ph).

^{1}H-NMR (in $CDCl_3$ and expressed in δ scale): Signals at 1.25 (12 H, d, J_{HH} = 7 Hz, isopropyloxy CH_3 protons), 4.75 (2 H, m, isopropyloxy C*H* protons), 1.05 $\left(6\text{ H, d, } J_{HH} = 7\text{ Hz, N—CH}\begin{matrix}CH_3\\CH_3\end{matrix}\right)$,

4.45 ($\left(1\text{ H, m, N}-\begin{matrix}\text{CH}_3\\\text{CH}_3\end{matrix}\right)$, 6.87 (1 H, J_{HP} = 15.2 Hz for the C-3 proton), 7.75–7.9 (9H, m, aromatic) and 12 ppm (exchangeable 0 H, 1 H, s).

^{31}P-NMR (in $CDCl_3$, vs. H_3PO_4): + 20.18 ppm.

Reaction of tris(dimethylamino)phosphine with quinoneimine III. Tris(dimethylamino)phosphine (0.3 g, 0.001 mole) in benzene (10 ml) was treated with (0.17 g, 0.001 mole) of III in 10 ml benzene, whereby brown crystals were precipitated in 5 minutes (0.4 g ≃ 90% yield). These crystals were filtered off, washed with benzene and recrystallized from benzene to give VIII, m.p. 150°C. Anal. Calcd. for $C_{22}H_{29}N_4O_3PS$ (460.50), C, 57.38; H, 6.34; N, 12.17; P, 6.73; S, 6.98. Found: C, 57.42; H, 6.30; N, 12.15; P, 6.70; S, 6.90%, Mol. Wt. (MS) = 460.

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