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The Novel Behaviour Of Dialkyl Phosphites Toward 1,4- Benzoquinone Monoimines

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Abstract : Diethyl phosphite **2a** reacts with N-(phenylsulfonyl) - 1,4 - benzoquinone monoimine **1a** to give 1,4-diethyl { (2-hydroxy-5-[(phenylsulfonyl) amino] phenyl } bisphosphonate **3a**, diethyl { 1-hydroxy -4- [(phenylsulfonyl) imino] -2,5-cyclohexadiene) }phosphonate **3b** and amide **3c** , respectively . When quinone monoimine **1a** was reacted with dimethyl- and diisopropyl phosphites (**2b,c**), the corresponding dialkyl phosphonate adducts **3e** and **3f** were obtained . Whereas quinone monoimine **1b** is reduced mainly to amide **4b** when treated with diethyl phosphite **2a** , it reacts with dimethyl phosphite **2b** to give the dialkyl phosphonate adduct **4a** together with amide **4b** . Possible reaction mechanism are considered and the structural assignments are based on compatible analytical and spectroscopic results.

INTRODUCTION

It has been reported [1] that dialkyl phosphites react with p-benzoquinone diimines to form the corresponding phosphoramidates **a**, phosphonates **b**, and amide **c**, respectively. On the other hand, p-naphthoquinone monoimine is known [2] to react with dialkyl phosphites yielding the phosphonate adducts **d** .

Since 1,4-benzoquinone monoimines **1a,b** bear both the carbonyl and imino function , it appeared therefore of interest to examine their behaviour toward the same phosphite reagents to determine the preferential site of attack .

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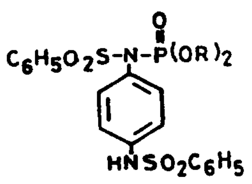
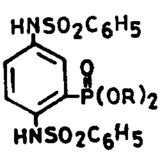

a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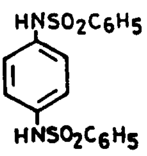
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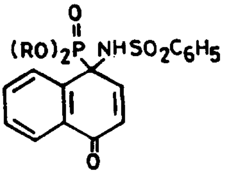

d

$R = CH_3$ or C_2H_5 or $CH(CH_3)_2$

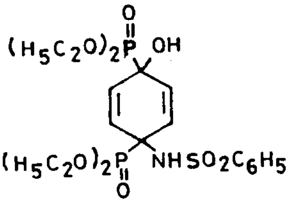
RESULTS AND DISCUSSION

When N-(phenylsulfonyl)-1,4- benzoquinone monoimine **Ia** was allowed to react with freshly distilled diethyl phosphite **2a** , in 1:15 molar ratio, in boiling benzene for 16 hrs, 1,4-diethyl {2-hydroxy-5-[(phenylsulfonyl) amino] phenyl } bisphosphonate **3a** , diethyl { 1-hydroxy-4- [(phenylsulfonyl) imino] -2,5 - cyclohexadiene} phosphonate **3b**, and 4-phenylsulfonyl -aminophenol **3c** were isolated (Scheme 1). The same compounds were likewise formed when the reaction of quinone imine **Ia** and diethyl phosphite **2a** was conducted without solvent. Structures **3a-c** are chromatographically pure and possess sharp melting points. Elemental and mass spectral analyses for compound **3a** corresponded to an empirical formula of $C_{20}H_{29}NO_9P_2S$.

The structure assigned for compound **3a** was based on the ^{31}P-NMR shifts (+18.28 ppm and + 22.30 ppm, vs. 85% H_3PO_4) which corresponds to the presence of bis (phosphonate) groups in position C-1 and C-4 respectively, with coupling constant value Jpp = 16.4 Hz . Long-range coupling between two phosphorus-nuclei in organic molecules have rarely been reported. Ernst [3] reported (3-9 Hz) J(pp) values over five to seven bonds in isomeric xylylene phosphonate. Recently, Duddeck et al.[4] reported (17-18.2 Hz , ^{4}Jpp) values for 3-substituted -l-adamantyl phosphoryl derivatives . Coupling constant value of 16.4 Hz (^{5}Jpp) in bisphosphonate **3a** can be explained in terms of dominating π - electron mechanisms.[3]

The IR spectrum of **3a** revealed the absence of C=O and C=N absorption bands recorded at 1665 and 1585 cm^{-1} , respectively , in the starting quinone imine **Ia** . The spectrum also showed strong absorption bands at 3150 (NH), 3250 (OH) , 1335 , 1183 (SO_2), 1230 (⇋ P=O, bonded) [5] , 1035 , and 1175 cm^{-1} ($P-O-C_2H_5$).[5]

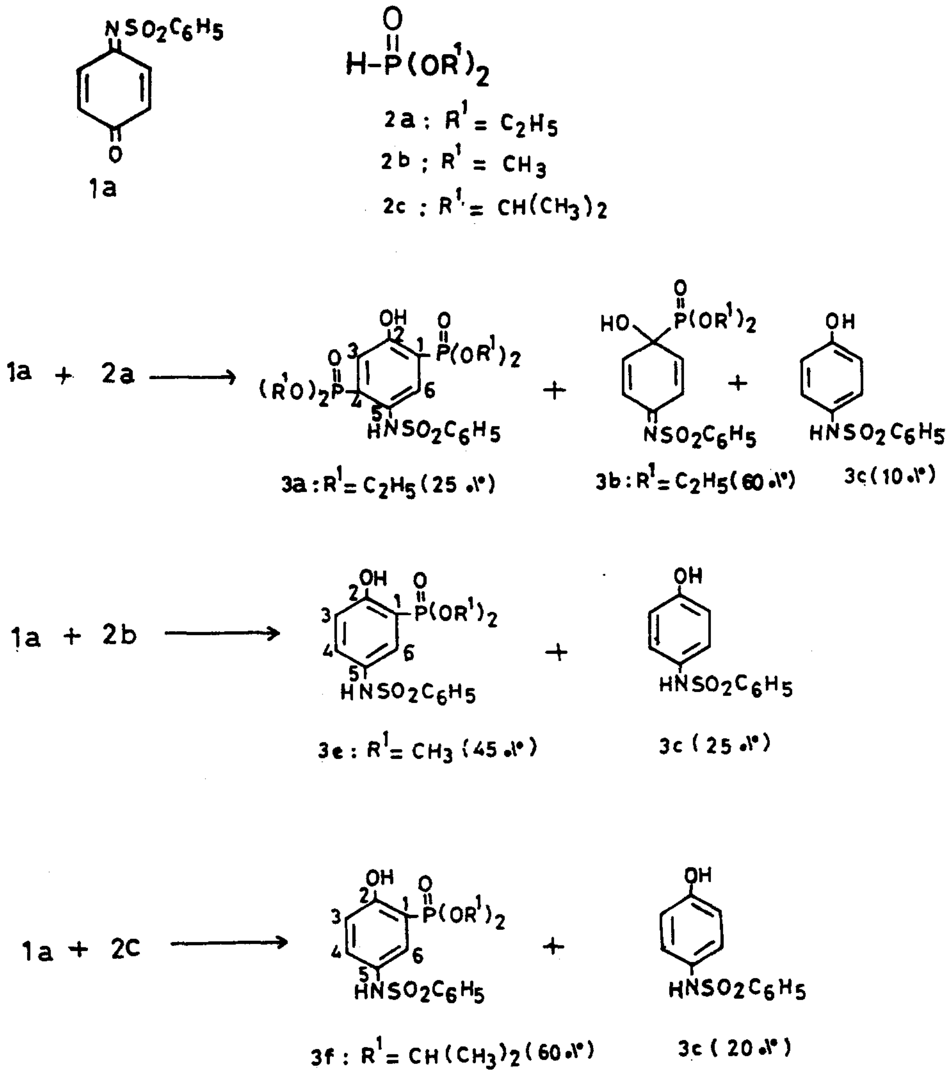
The ^1H-NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$ disclosed the presence of two exchangeable (D_2O) -NH and - OH protons appeared as two signals at 11.38 and 12.12 ppm, respectively . The four ethoxy-CH_3 protons attached to both phosporus appear as a complex pattern in the region (1.23-1.30 ppm, 12H, m). The quintets of the same ethoxy-CH_2 protons of the bisphosphontae groups appear as a complex pattern in the region 3.79-4.14 ppm (8H, m). The 5 aromatic protons of the (phenylsulfonyl) group appeared as a multiplet at 7.30-7.58 ppm. The spectrum also showed a doublet of doublets centered at 7.15 ppm with $^3J_{HP}$ = 9 Hz corresponding to the C-3 proton. C-6 proton appeared as doublet of doublets centered at 7.97 ppm with $^3J_{HP}$ = 9 Hz (cf. Scheme 1). The ^{13}C-NMR spectrum of compound **3a** furnishes strong evidence in support of the bisphosphonate structure. The ^{13}C -NMR of **3a** in $CDCl_3$ shows a doublet at 129.71 ppm with coupling constant value ^{1}Jpc= 114.28 Hz ascribed to C-1 attached to phosphorus. Another doublet at 125.66 ppm with $^1J_{PC}$ = 114.28 Hz attributed to C-4 attached to the other phosphorus atom[6]. Also, the spectrum shows signals at 62.8, 62.7 ($\geq$P-O$\underline{C}H_2$) and at 16.1, 16.05 ppm (P-O-CH_2-$\underline{C}H_3$). ^{1}H and ^{13}C-NMR of compound **3a** are in favour of the 1,4 diethylphosphonate structure which rule out the other possible alternative form **3d**.



3d

Actually, the mass spectrum of compound **3a** provided strong evidence in support of the bisphosphonate adduct. The mass spectrum of **3a** yielded a prominent peak for M^+ at m/e 521 (60%), (M^+-SO_2Ph) = 380 (100%). Compound **3a** responds positively to the ferric chloride test (an indication of the presence of a phenolic - OH group).

The structure of the other isolated compound **3b** is deduced from its analysis, IR, ^{1}H, ^{31}P, ^{13}C-NMR and mass spectral data. Elemental and mass spectral analyses for compound **3b** corresponded to an empirical formula of $C_{16}H_{20}NO_6PS$. Its IR spectrum, in KBr, revealed the presence of strong - OH absorption band at 3200 cm^{-1}. Moreover, its IR spectrum lacked the carbonyl absorption band at 1656 cm^{-1} recorded for quinoneimine **la**. Also, the IR spectrum of **3b** exhibits strong absorption bands at 1558 cm^{-1} (C=N), 1347 cm^{-1}, 1185 cm^{-1} (SO_2), 1230 ($>$P=O, bonded)[5], 1035, 1175 cm^{-1} ($>$P-O-C_2H_5)[5]and at 1440 (P-Ph).[6] ^{1}H-NMR spectrum (400 MHz) of diethyl {1-hydroxy-4-[(phenylsulfonyl)- imino]-2,5-cyclohexadiene} phosphonate **3b** in $CDCl_3$ disclosed the presence of a triplet centered at 1.17 ppm, due to the two ethoxy-CH_3 groups attached to phosphorus (6H, t), and a 4 H quintet centered at 3.89 ppm with J_{HP} = 12.5 Hz, due to the ethoxy-CH_2 protons attached to phosphorus.[7] It also shows doublets centered at 6.90 ppm with J_{HP} = 15.5 Hz and J_{HH} = 8.80 Hz (H-2, H-3) and another pair of doublets centered at 6.73 ppm with J_{HP} 15.5 Hz and J_{HH} = 8.80 Hz (H-3, H-2).[8] The 5 aromatic protons of the (phenylsulfonimino) appeared as a multiplet at 7.62-7.82 ppm. The ^{1}H-NMR of **3b** disclosed the presence of a signal at 9.20 ppm (-OH, s, exchangeable with D_2O). The ^{13}C-NMR spectrum of **3b** proved that C-1 appears at 69.8 ppm (d,$^1J_{CP}$ = 149.7 Hz) corresponding to the quatenary carbon atom (head bridged saturated carbon) and C-4 appears at 139.1 (C=N).[9] Also, the ^{13}C-NMR spectrum of **3b** shows signals at 62.96 ppm($>$P-O-CH_2) and at 15.98 ppm(P-O-CH_2-CH_3). The structure assigned for compound **3b** was also based on the ^{31}P-NMR shift (+18.3 ppm, vs. 85% H_3PO_4) which corresponds to a phosphonate structure.[10,11] The mass spectrum of **3b** yielded a prominent peak for M^+


1a
2a : R¹ = C₂H₅
2b ; R¹ = CH₃
2c ; R¹ = CH(CH₃)₂
1a + 2a
3a : R¹ = C₂H₅ (25 %)
3b : R¹ = C₂H₅ (60 %)
3c (10 %)
1a + 2b
3e : R¹ = CH₃ (45 %)
3c (25 %)
1a + 2c
3f : R¹ = CH(CH₃)₂ (60 %)
3c (20 %)

Scheme 1

at m/e 385 (100%) , ($M^+ - P^{\neq O}-(OC_2H_5)_2$) = 248 (22%) .

A possible explanation for the reaction of diethyl phosphite **2a** with N - (phenylsulfonyl) 1,4 - benzoquinone monoimine **1a** is shown in (Scheme 2) . Product **3a** is presumably formed via a series of 1,4 - additions and oxidations.[12] Formation of compound **3b** is explained by assuming a 1,2 - addition of diethyl phosphite to the starting quinone imine **1a** .

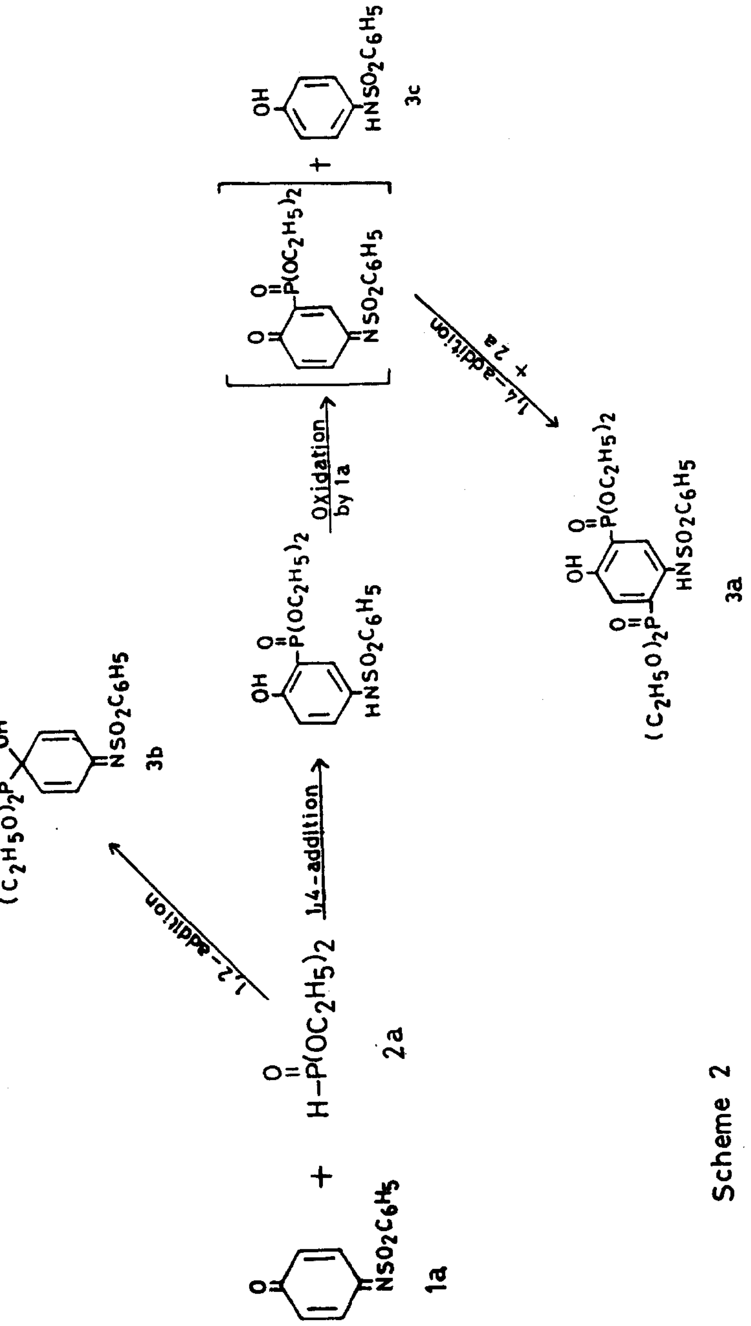
The significance of this finding is not only the discovery of an anomalous behaviour of diethyl phospite but also the demonstration of a novel route for preparing the new 1,4 - bisphosphonate adduct **3a** via diethyl phosphite .

Dimethyl - , and diisopropyl phosphites **2b** , **c** , on the other hand , react with N - (phenylsulfonyl) – 1,4- benzoquinone monoimine **1a** in the coventional manner to give the corresponding dialkyl phosphonate adducts **3e** and **3f** , respectively. 4 - Phenylsulfonyl aminophenol **3c** is also isolated in both reactions (Scheme 1). Structure elucidation of dimethyl { 2 - hydroxy - 5 - [(phenylsulfonyl) amino] phenyl } phosphonate **3e** was performed from the following evidence : (a) Microanalysis and molecular mass determination (MS) for compound **3e** correspond to $C_{14}H_{16}NO_6PS$. (b) The IR spectrum of adduct **3e** , in KBr , reveals the presence of strong NH , and - OH absorption bands at 3290 and 3300 cm^{-1} , respectively . Moreover , its IR spectrum lacked both the carbonyl and C=N absorption bands appearing in the starting quinone imine **1a** at 1656 and 1585 cm^{-1} , respectively. Also , the IR spectrum of **3e** exhibits strong absorption bands at 1347 cm^{-1}, 1183 cm^{-1} (SO_2) , 1230 cm^{-1} ($\geq$P=O , bonded) , 1056 cm^{-1} ($>$P-O-CH_3) and 1447 cm^{-1} ($>$P - Ph) . (c) Compound **3e** responds positively to the ferric chloride test and dissolves in aqueous alkali (due to the presence of phenolic - OH group) . The ^1H - NMR spectrum (400 MHz) of **3e** (in $CDCl_3$) disclosed the presence of a doublet centered at 3.68 ppm with J_{HP} = 11.60 Hz , ascribed to the two OMe groups attached to phosphorus.[7] It also shows a doublet of doublets centered at 7.03 with J_{HP} = 14.95 Hz and J_{HH} = 2.4 Hz ascribed to the C - 6 proton (Scheme 1). The spectrum also showed doublets at 6.87 ppm and 6.85 ppm with a coupling constant value of J_{HH} = 7.32 for (H-3, H-4)[8] , 7.43 with coupling constant value J_{HH} = 7.33 Hz for (H-4 , H-3).[8] The 5 aromatic protons of the (phenylsulfonylamino) appeared as a multiplet at 7.62 - 6.78 ppm . The exchangeable (D_2O) protons (NH) and (OH) appeared as singlets at 8.7 and 10.01 ppm , respectively . The structure assigned for compound **3e** was also based on the ^{31}P-NMR shift (+ 23.2 , vs 85% H_3PO_4) which corresponds to a phosphonate structure .[10,11] The mass spectrum of compound **3e** yielded a prominent peak for M^+ at m/e 357 (35%) , $M^{+}-P^{\neq O}-(OCH_3)_2$) = 249 (50 %) , $P^{\neq O}-(OCH_3)_2$ = 108 (100%

The ^{13}C- NMR of dimethyl { 2- hydroxy - 5 - [(phenylsulfonyl) amino] - phenyl } phosphonate **3e** in $CDCl_3$, shows a doublet at 127.30 ppm with coupling constant $^1J_{PC}$ = 91.5 Hz ascribed to C-1 attached to phosphorus . The presence of $P^{\neq O}-(OCH_3)_2$ group in **3e** was also performed from a signal at 53.139 ppm in its ^{13}C-NMR .

The identity of diisopropyl { 2 - hydroxy- 5 - [(phenylsulfonyl) amino] phenyl } phosphonate **3f** was deduced from its elemental analysis , IR , ^1H - NMR and mass spectral data (cf. Experimental) .

From the above results , it is evident that although N-(phenylsulfonyl) - 1 , 4 - benzoquinone monoimine **1a** behaves toward dimethyl and diisopropyl phosphites in a manner quite similar to that described for p-benzoquinone diimines where the phosphonate adducts **3e** , **f** are predominately or exclusively formed[1], yet the reaction of diethyl phosphite with the same quinone imine **1a** proceeds in an anomalous manner where


1a
2a
1,2-addition
1,4-addition
Oxidation by 1a
1,4-addition + 2a
3a
3b
3c

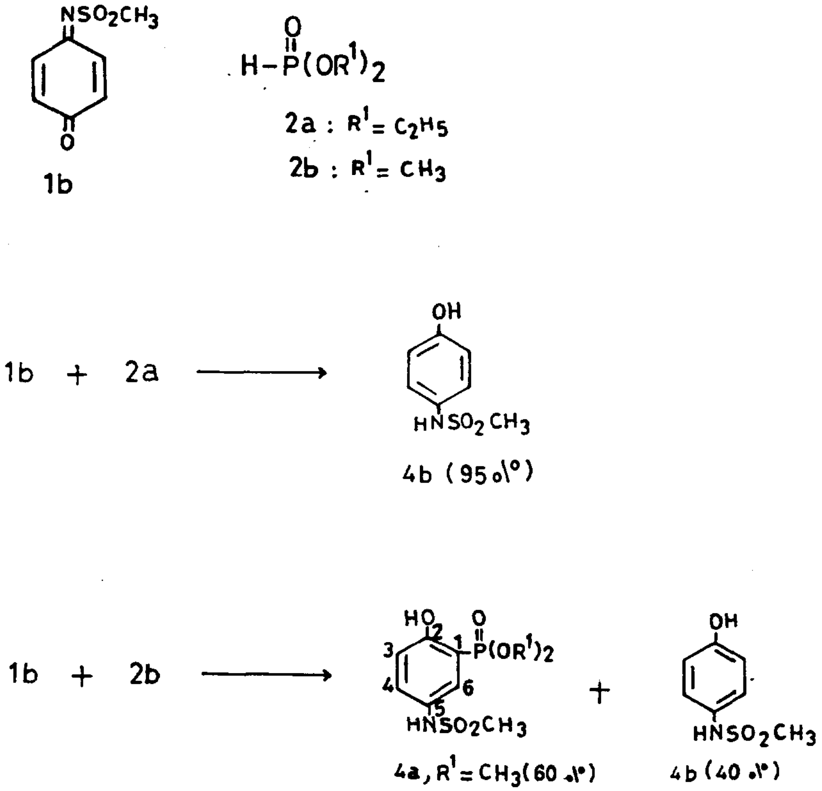
Scheme 2

1,4 - diethyl bisphosphonate and 1 - diethyl phosphonate adducts 3a and 3b are formed, respectively.

Further, this study was extended to include the reaction of N-(methylsulfonyl) - 1,4- benzoquinone monoimime 1b with the same phosphite reagents to establish whether it would behave in a similar manner.

We have found that the reaction of dimethyl phosphite 2b with p-quinone imine 1b, in boiling benzene, proceeds according to a 1,4 addition mechanism to give mainly the phosphonate adduct 4a in (60%) and the correspoonding amide 4b in 40% yield (Scheme 3).

The structure of dimethyl { 2 - hydroxy - 5 - [(methylsulfonyl) - amino] phenyl } phosphonate 4a was elucidated as follows : Compound **4a** gave correct combustion values corresponding to the formula $C_9H_{14}NO_6PS$. The structure assigned for compound **4a** was also based on ^{31}P-NMR shift (+ 20.7 ppm, 85% H_3PO_4) which corresponds to a phosphonate and not to phosphate adduct.[10,11] The IR spectrum of **4a** revealed the absence of C=O and C=N absorption bands at 1656 and 1587 cm^{-1} recorded for quinone imine **1b**. The spectrum showed, however, strong absorption bands at 1280 cm^{-1} ($\gtrdot$P=O), at 1050 cm^{-1} (P-O-CH_3), at 3320 (OH) and at 3200 (NH).



Scheme 3

The ^{1}H-NMR spectrum of **4a** showed signals at 3.82 (6H , P ($OCH_3)_2$, d , J_{HP}= 11.55 Hz), 3 ppm ($NSO_2\underline{CH}_3$, 3H , s) , 7.1 (d with J_{HP} = 14.2 , J_{HH} = 2.3 Hz) ascribed for C-6 proton , 6.9 (d with $J_{3,4}$ = 7. 3 Hz) , 7.45 (d, with $J_{4,3}$ = 7.3 Hz). The exchangeable (D_2O) protons (OH) and (NH) appeared as two signals at 10.05 and 7.48 ppm , respectively. The mass spectrum of **4a** yielded a prominent peak for M^+ at m/e 295 (93%), $M^{\pm}$NSO$_2$ CH$_3$ = 216 (90%) , $M^+ - P^{\not=O}$ $(OCH_3)_2$ = 186 (100%).

The fact that compound **4a** responds positively to the ferric chloride test and dissolve in aqueous alkali (an indication for the presence of phenolic -OH group) provided strong evidence in support of the phosphonate structure **4a** .

Quinone monoimine **Ib** is reduced mainly to amide **4b** when treated with diethyl phosphite under similar conditions. This disparity in behaviour of quinone imine **1a** , on one hand and **Ib** on the other towards dialkyl phosphites is in accord with the difference in their behaviour towards trialkyl phosphites.[13] Whereas trialkyl phosphites react with **1a** to give the corresponding phosphate adducts, the same reagents react with quinone imine **1b** to give only the alkylated products.[13]

EXPERIMENTAL SECTION

All melting points are uncorrected. Benzene (thiophene-free) and petroleum ether (boiling range, 60-80 C) were dried over sodium. The dialkyl phosphites [14,15] were prepared by established procedures and were purified by fractional distillation . The IR spectra were measured in KBr , on Perkin Elmer Infracord Spectrophotometer Model 157 (Grating) . The ^{1}H-NMR spectra were recorded in $CDCl_3$ on JNM-GX-400 Fa Jeol , Tokyo Spectrometer . The ^{31}P-NMR spectra were recorded in $CDCl_3$ (vs . H_3PO_4 as external standard) on JNM - PS - 100 Fa , Spectrometer . ^{13}C-NMR spectra were taken in $CDCl_3$ on JNM-PS-100 Fa and JNM-GX-400 Fa Spectrometer . The mass spectra were run at 70 eV on Kratos MS equipment and / or varian MAT 311 A Spectrometer .

Reaction of diethyl phosphite 2a with N-(phenylsulfonyl)-p-benzoquinone monoimine 1a

To a solution of quinone imine **1a** (0.48 g ; 0.002 mol) in dry benzene (20 ml) , was added diethyl phosphite **2a** (0.03 mol) and the reaction mixture was refluxed for 16 hrs . After evaporation of the volatile materials under reduced pressure , the residue was applied to silica gel column using the eluent stated below. The melting points and yields are also given .

Compound **3a** : 1,4-diethyl { 2-hydroxy - 5 -[(phenylsulfonyl) - amino] phenyl } bisphosphonate : eluent ethyl acetate/petroleum ether (15:85 , v:v) yield 25% , mp 113°C . Anal . Calc . For $C_{20}H_{29}NO_9P_2S$ (521.64) C, 46.06; H, 5.60; N, 2.68; P, 11.87; S, 6.14. Found : C, 46.03 ; H , 5.70 ; N, 2.64 ; P, 11.90 ; S, 6.32% (MS) : 521 , ^{1}H-NMR : two signals at 11.38 ppm, 12.12 ppm (s , -NH , -OH , exchangeable with D_2O) , 1.23-1.30 ppm (m , 12H , 2 [P ($OCH_2\underline{CH}_3$) $_2$]) , 3.79-4.14 ppm (m . 8H , 2 [P (OCH_2CH_3) $_2$] , 7.30-7.58 ppm (m , 5H , Ar) , 7.15 ppm (dd , 1H , $^3J_{HP}$ = 9 Hz , C-3) and 7.97 ppm (dd , ^{1}H , $^3J_{HP}$ = 9 Hz , C-6) . ^{31}P -NMR: + 18.28 ppm (C-1, Jpp = 16.4 Hz) , + 22.30 (C-4 , Jpp=16.4 Hz) . ^{13}C - NMR : signals at 129.71 ppm (d , $^1J_{PC}$=114.28 Hz , C-1) , 125.66 ppm (d, $^1J_{PC}$= 114.28 Hz , C-4) , 62.8 , 62.7 (s , P-O-$\underline{C}H_2$) and 16.1 , 16.05 ppm (s , P-O-CH_2-$\underline{C}H_3$) .

Compound **3b** : eluent : ethyl acetate/petroleum ether (30:70 , v:v) colourless crystals from benzene , mp . 128°C , yield 60% . Anal . Calcd for $C_{16}H_{20}NO_6PS$ (385.352) C, 49.87 ; H , 5.23 ; N , 3.64 ; P , 8.04 ; S ; 8.30 . Found : C , 49.80 ; H, 5.25 ; N , 3.65 ; P , 8.07 ; S , 8.33 (MS) = 385 . ^{1}H-NMR : signals at 1.17 ppm (6H , t , P ($OCH_2\underline{CH}_3$) $_2$) , 3.89 (4H , q , J_{HP}= 12.5 Hz , P($O\underline{CH}_2CH_3$) $_2$) . 6.90 (d , H-2,3, J_{HP} = 15.5 Hz , J_{HH}=8.80 HZ),6.73 (d , H - 3 , 2 , J_{HP} = 15.5 Hz , J_{HH} = 8.80 Hz) , 7.62-7.82 (m , 5H) and 9.20 ppm (s , OH exchangeable with D_2O) . ^{31}P-NMR : signal at 18.3 ppm . ^{13}C-NMR : signals at 62.69 ppm (P-O-$\underline{C}H_2$) , 15.98 ppm (P-$OCH_2\underline{C}H_3$) , 69.8 ppm (d, $^1J_{CP}$ = 149.7 Hz , C-1) and 139.1 ppm (C=N) , C-4)

Compound **3c** : (10%) was also isolated and proved to be the amide (mixed mp and comparative IR spectera with authentic sample).[16]

Reaction of dimethyl phosphite 2b with quinone imine 1a

A mixture of **1a** (0.48 g ; 0.002 mol) , dimethyl phosphite **2b** (1.1 ml ; 0.01 mol) and dry benzene (30 ml) was refluxed for 16 hrs . The volatile materials were evaporated under reduced pressure and the residual substance applied to silica gel column using eluent (ethyl actate/petroleum ether 60 : 40 , v : v) to give **3e** as colourless crystals , mp 172°C , yield (45%) . Anal . Calc . For $C_{14}H_{16}NO_6PS$ (357.298) C , 47.06 ; H , 4.51 ; N , 3.92 P , 8.67 , S , 8.95 . Found : C , 47.03 ; H , 4.58 ; N , 3.93 ; P , 8.69 ; S , 8.99% (MS) = 357. ^{1}H-NMR : signals at 3.68 ppm (d , 6H , , J_{HP} = 11.60 Hz , P (OCH_3) $_2$) , 7.03 (d , 1H , J_{HP}=14.95 Hz , J_{HH}=2.4 Hz , C-6) , 6.87 (d , J_{HH}=7.32 Hz , 3-H) , 6.85 ppm (d , J_{HH}=7.32 Hz , 4-H),7.43 ppm (d , J_{HH}=7.33 Hz , 4-H , 3-H) , 7.62-6.78 ppm (m, 5H) , 8.7 ppm (s , NH exchangeable with D_2O) and 10.01 ppm (s , OH exchangeable with D_2O) . ^{31}P-NMR : signal at + 23.2 . ^{13}C-NMR : δ = 127.30 (d , $^1J_{PC}$=91.5 Hz , C-1) and signal at 53.139 ppm (d , $P\overset{O}{=}\!-$ (OCH_3) $_2$) . Compound **3c** was also isolated (25%) and proved to be the corresponding amide (mixed mp and comparative IR spectra) .

Reaction of diisopropyl phosphite 2c with N- (phenylsulfonyl) - 1,4- benzoquinone monoimime 1a

Amixture of diisopropyl phosphite **2c** (2 ml) and quinone imine **1a** (0.48 g) was refluxed on water bath for 2 hrs. The volatile material was then evaporated under reduced pressure , the residue applied to silica gel column using chloroform/petroleum ether (60:30 , v:v) as eluent to give **3f** as colourless crystals mp 144° , yield 60%) . Anal . Calcd For ; $C_{18}H_{24}NO_6PS$ (413.428) C , 52.29 ; H , 5.85 ; N , 3.38 ; P , 7.49 ; S , 7.75. Found : C , 52.26 ; H , 5.83 ; N , 3.36 ; P , 7.46 ; S , 7.73% MS = 413. IR: 3250 cm^{-1} (OH) , 3150 cm^{-1} (NH). ^{1}H-NMR : δ=1.25 (d , 12H , J_{HH}=7 Hz, isopropyloxy – CH_3) , 4.6 ppm (m, 2H , isopropyloxy CH).

Reaction of diethyl phosphite 2a with N-(methylsulfonyl) - 1,4 - benzoquinone monoimime 1b

A mixture of **1b** (0.36 g , 0.002 mol) , diethyl phosphite **2a** (0.03 mol) and dry benzene (30 ml) was refluxed for 16 hrs . The volatile material was evaported in vacuo . The residual substance was crystallized from ethyl acetate and proved to be **4b** (yield 95%) (mp. and mixed mp. 154°C) .

Reaction of dimethyl phosphite 2b with N-(methylsulfonyl) - 1,4 - benzoquinone monoimine 1b

A mixture of **1b** (0.001 mol) , dimethyl phosphite **2b** (0.03 mol) , and dry benzene (30 ml) was refluxed for 16 hrs.The volatile material was evaporated in vacuo and the residual substance applied to silica gel column using acetone/petroleum ether (10:90 v:v) as eluent to give **4a** as colourless crystals , mp 120°C , yield 60%. Anal. Calcd. For $C_9H_{14}NO_6PS$ (295.249) C , 36.6 ; H , 4.77 ; N , 4.74 ; P , 10.49 ; S , 10.85

Found : C , 36.56 ; H , 4.70 ; N , 4.70 ; P , 10.5 ; S , 10.8 . (MS) = 295. ^{1}H-NMR : signals at 3.82 (d , 6H , J_{HP}=11.55 Hz , P($OCH_3)_2$) , 3 ppm (s , 3H , NSO_2CH_3) , 7.1 (d , J_{HP}=14.2 Hz , J_{HH}= 2.3 Hz C-6), 6.9 (d , $J_{3,4}$=7.3 Hz) , 7.45 (d , $J_{4,3}$=7.3 Hz) , 10.05 ppm (s , OH , exchangeable with D_2O) , 7.48 ppm (s , NH) . ^{31}P-NMR : signal at + 20.7 . The amide **4b** was also isolated in 40% and identified (mixed mp and comparative IR spectra) .

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