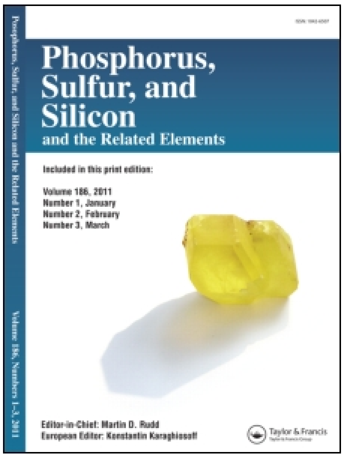

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ORGANOPHOSPHORUS COMPOUNDS, XXIX ON THE REACTION OF DIALKYL PHOSPHITES WITH p-BENZOQUINONEDIBENZENESULPHONIMIDE

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ORGANOPHOSPHORUS COMPOUNDS, XXIX† ON THE REACTION OF DIALKYL PHOSPHITES WITH p-BENZOQUINONEDIBENZENESULPHONIMIDE

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The reaction of *p*-benzoquinonedibenzenesulphonimide (1) with dialkyl phosphites (**2a-c**) to give phosphoramidate (3), phosphonate **4** and/or *p*-benzoquinonedibenzenesulphonamide (5), has been studied under different experimental conditions. The factors influencing the reaction-course are discussed.

INTRODUCTION

The first report[1] on the behaviour of *p*-quinoneimines towards alkyl phosphites has appeared from this Laboratory.‡ It showed that *p*-benzoquinonedibenzenesulphonimide (**1**) reacts with dialkyl phosphites (DAP, **2a**–**c**), in boiling benzene to give 1:1 adducts (**4a**–**c**) together with *p*-benzoquinonedibenzenesulphonamide (**5**). The latter compound constituted the main reaction product when the dialkyl phosphites used were not freshly distilled. Later, however, the reaction of dialkyl phosphites with quinoneimine (**1**) has attracted the interest of other investigators and was the subject of two subsequent publications,[3,4] In the first, Levy and Sprecher[3] claimed that they were unable to obtain reproducible results upon repeating the uncatalyzed reaction of quinoneimine (**1**) with purified dialkyl phosphites under the conditions given in our report.[1] They added that neither addition of benzoyl peroxide nor admission of air nor exposure to sunlight induced significant product-formation from dimethyl phosphite. These authors pointed out that base (NaH) catalysis, however, resulted in consistently successful reactions. Under such conditions, the reaction of quinoneimine (**1**) with dimethyl-, or diethyl phosphite yielded a mixture of phosphoramidate (**3**) ($>80\%$) and phosphonate (**4**) ($<20\%$) together with trace amounts of *p*-benzoquinonedibenzenesulphonamide (**5**). Furthermore, they reported that the catalyzed or uncatalyzed reaction of quinoneimine (**1**) with pure diisopropyl phosphite (**2c**) was unsuccessful. They claimed, however, that they obtained a 1:4 adduct (**4c**, 43%) having properties similar to those reported by us[1] only when impure diisorpopyl phosphite was refluxed with quinoneimine (**1**) in benzene for one week. Levy and Sprecher[3] concluded that despite the considerably lower P—N bond energy ($\sim$83 Kcal/mole in phosphoramidates)[3,5] and the fact that the lone electron pair on the nitrogen of quinonedisulphonimides (cf. **1**), is already involved in p_π-d_π-interaction with the sulphonyl group, dialkyl phosphites bond preferentially to the imide-nitrogen of (**1**) rather than to the ring-carbons.

In the other article, Titov and Avdeenko[4] have described the reaction of quinoneimine (**1**) with dialkyl phosphites to proceed according to the 1:6 addition mechanism yielding phosphoramidates (**3**) and/or amide (**5**) depending upon the phosphite ester used. They reported that the reaction of quinoneimine (**1**) with diisopropyl phosphite gives exclusively the 1:6 phosphoramidate adduct (**3c**), while with di-*n*-butyl-, or di-*n*-amyl-phosphite, a mixture of the corresponding phosphoramidate (**3**, R=C_4H_9-*n* or C_5H_{11}-*n*) and amide (**5**), was formed. With dimethyl- and diethyl phosphites, on the other hand, they obtained *p*-benzoquinonedibenzenesulphonamide (**5**) as the sole reaction product. Titov and Avdeenko[4] are of the opinion that phosphorylation of quinoneimine (**1**) with dialkyl phosphites is accompanied

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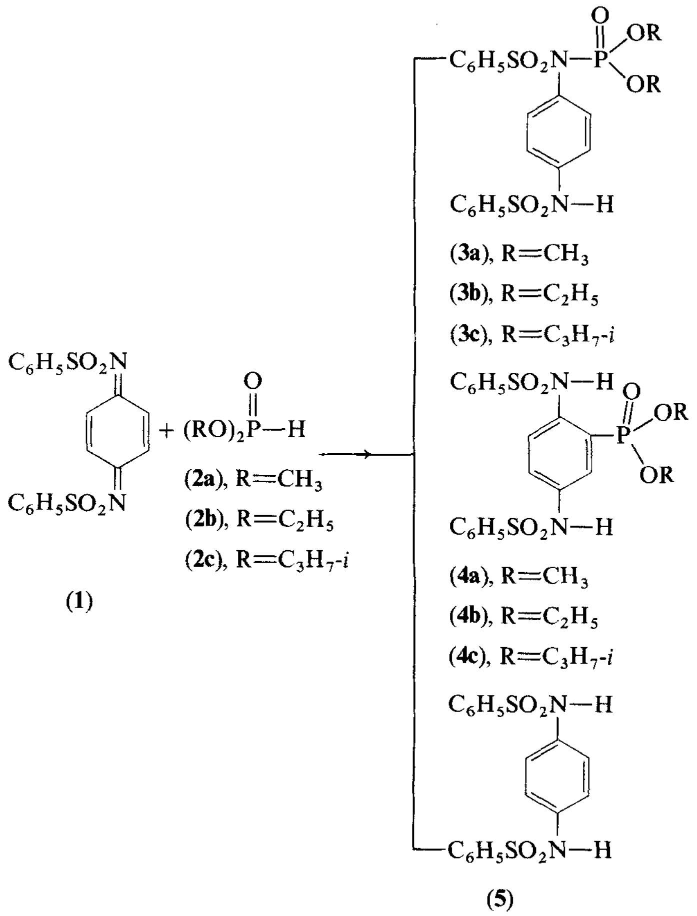
† Dedicated to Professor Dr. A. Schönberg on the occasion of his 87th birthday.

‡ For further contributions in this field, cf. Reference No. 2.



(1) + (2a), R=CH_3; (2b), R=C_2H_5; (2c), R=C_3H_7-*i* → (3a), R=CH_3; (3b), R=C_2H_5; (3c), R=C_3H_7-*i*; (4a), R=CH_3; (4b), R=C_2H_5; (4c), R=C_3H_7-*i*; (5)

by competitive oxidation-reduction process and they attributed the formation of amide (**5**) in these reactions to the high redox potential (732 eV) of quinoneimine (**1**).

From the aforementioned arguments, it can be seen that information found in the literature regarding the reaction of quinoneimine (**1**) with dialkyl phosphites is not in full agreement. Therefore, we found it desirable to re-examine this reaction, in some detail, particularly under the conditions given by Levy and Sprecher[3] as well as those given by Titov and Avdeenko,[4] in order to shed more light on the behaviour of quinoneimine (**1**) towards these phosphite esters.

RESULTS AND DISCUSSION

When quinoneimine (**1**) was allowed to react with freshly distilled dimethyl phosphite (DMP, **2a**) in 1:15 molar ratio, at room temperature for 48 hr, a mixture of phosphoramidate (**3a**) (25 %), phosphonate (**4a**) (40 %) and amide (**5**) (30 %) was obtained. Conducting this reaction in dry benzene gave a similar result. Raising the temperature of the latter reaction to that of the boiling point of the solvent, resulted in formation of (**3a**) (20 %), (**4a**) (30 %) and amide (**5**) (45 %), after 10 hr. When the reaction of quinoneimine (**1**) and DMP (1:15, mol:mol) was performed in absence of a solvent at 110°, compound (**3a**) (10 %), (**4a**) (20 %) and amide (**5**) (65 %) were gained. Elevation of the reaction-temperature to 140° did not affect an appreciable change on the percentage yield of the final products. Compounds (**3a**) and (**4a**) were found to possess physical properties (m.p., IR and NMR spectra) similar to those of identical substances obtained in 80 % and 15 %, respectively, upon repeating the reaction of DMP with quinoneimine (**1**) in presence of a base (NaH) under the conditions given by Levy and Sprecher[3] (Experimental). Reacting quinoneimine (**1**) with DMP of

TABLE I

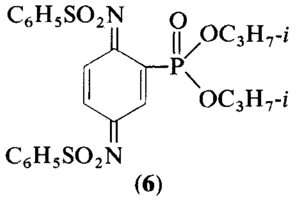
The reaction of *p*-benzoquinonedibenzenesulphonimide (**1**) with dimethyl phosphite and diethyl phosphite[a]

Exp. No.	Solvent Solvent	Reaction temp. °C	DAP (2)	Duration time/hr.	Yield % of the products[b]				
					3a	**4a**	**3b**	**4b**	**5**
1	—	25	DMP	48	25	40	—	—	30
2	Benzene	25	DMP	72	20	45	—	—	30
3	Benzene	Reflux	DMP	10	20	30	—	—	45
4	—	110	DMP	2	10	20	—	—	65
5	—	140	DMP	2	10	15	—	—	70
6	—	100	DMP[c]	3	—	—	—	—	>95
7	Benzene	Reflux	DMP[c]	6	—	—	—	—	>95
8	—	25	DEP	48	—	—	35	45	15
9	Benzene	25	DEP	72	—	—	30	45	20
10	Benzene	Reflux	DEP	10	—	—	15	45	35
11	—	110	DEP	2	—	—	20	25	50
12	—	140	DEP	2	—	—	15	20	60
13	—	100	DEP[c]	3	—	—	—	—	>95
14	Benzene	Reflux	DEP[c]	6	—	—	—	—	>95

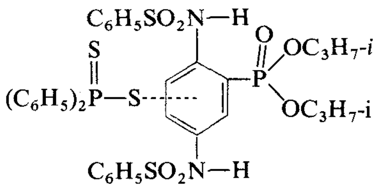
[a] Using 15 mol of phosphite/mol of quinoneimine **1**. DAP = dialkyl phosphite; DMP = dimethyl phosphite; DEP = diethyl phosphite.
[b] = The percentage yield is approximated.
[c] = The phosphite ester used was of little purity.

little purity† in refluxing benzene for 6 hr or at 100° in absence of solvent for 3 hr, afforded amide (**5**) as the sole reaction product. Parallel experiments using diethyl phosphite (DEP, **2b**) in place of DMP gave comparable results. Percentage yields of the resulting phosphoramidate (**3b**), phosphonate (**4b**) and/or amide (**5**), are given in Table I.

The reaction of quinoneimine (**1**) with diisopropyl phosphite (**2c**) was also reinvestigated using the latter in analytically pure and twice-distilled form. We found that this reaction yielded phosphonate (**4c**) almost exclusively, both upon conducting the reaction in absence of solvent for 24 hr at 25° and in boiling benzene for 4 hr. Structural assignments for adduct (**4c**) have been inferred from IR and NMR spectral data. In KBr, the IR spectrum of (**4c**) showed a sharp NH absorption band around 3200 cm^{-1} (in Nujol at 3210 cm^{-1}) while in $CHCl_3$ the same absorption appeared at 3350 cm^{-1}. This indicates that the NH group is involved in hydrogen bonding, in the solid state. Strong absorption bands at 1335 cm^{-1}, 1175 cm^{-1} (SO_2), 1230 cm^{-1} (⩾P=O, bonded),[6] 1050 cm^{-1} (P—O—C_3H_7-*i*)[6] and at 1440 cm^{-1} (P—Ph)[6] were also present in the IR spectrum of (**4c**), in KBr. The ^1H NMR spectrum of (**4c**) (in $CDCl_3$) showed signals at $\delta = 1.18$, $\delta = 1.02$ [two doublets, 12 H, each with J = 6.5 Hz, due to the isopropoxy-CH_3 protons coupled with phosphorus], $\delta = 4.37$ (multiplet, 2 H, for the isopropoxy-*CH* protons attached to phosphorus) and at $\delta = 7.59$ (multiplet, 13 H, for the aromatic protons). The NH protons gave two exchangeable (D_2O) singlets at $\delta = 10.20$ and 8.40. Additional evidence has been gained from oxidation of (**4c**) with leadtetraacetate followed by treatment of the resulting quinoneimine derivative (**6**) with diphenylphosphinodithioic acid [$(C_5H_5)_2P(S)SH$]. This afforded an adduct (**7**) whose combustion values agreed with an empirical formula of



(**6**)



(**7**)

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† By little purity is meant that the phosphite was either crude or purified by distillation then aged for 30 days.

$C_{36}H_{38}N_2O_7P_2S_4$. That the phosphorus-containing moiety has survived upon oxidation of (**4c**) indicates that ring attack (and not *N*-attack as suggested by Titov and Avdeenko)[4] by diisopropyl phosphite on quinoneimine (**1**), has taken place.

From the results of the present investigation, it could be noticed that the reaction between quinoneimine **1** and dialkyl phosphites (**2a–c**) depends upon several factors such as the nature and degree of purity of the phosphite reagent, the molar ratio of the reactants, and the reaction conditions. Thus, while DMP and DEP react with quinoneimine (**1**) to give a mixture of phosphoramidate (**3a** or **3b**), phosphonate (**4a** or **4b**) and amide (**5**), the reaction with diisopropyl phosphite affords phosphonate (**4c**) almost exclusively. This can be consistently and successfully achieved by using reactants of high degree of purity and by allowing quinoneimine (**1**) to react with the phosphite ester in a 1:15 molar ratio, both in absence or presence of solvent and with or without admission of a catalyst. That Levy and Sprecher[3] obtained erratic results upon repeating the uncatalyzed reaction of quinoneimine (**1**) with phosphites (**2a–c**) under the conditions given in our report,[1] is due to a typographic error in writing the molar ratio (1:1.5 instead of 1:15 mol:mol) for the quinoneimine (**1**):phosphite interaction. Moreover, we have found that when quinoneimine (**1**) was allowed to react with freshly distilled DMP (**2a**) or DEP (**2b**) in a 1:1.5 molar ratio, no reaction was observed both in absence and in presence of solvent (benzene) and quinoneimine (**1**) was recovered practically unaffected in each reaction (cf. Experimental).

Worth-mentioning is that while phosphoramidates (**3**) and phosphonates (**4**) chance to form in the reaction of quinoneimine (**1**) with DAP derived from primary alcohols (e.g. DMP and DEP), the phosphites containing secondary alkyl groups (e.g. diisopropyl phosphite) only give the phosphonate adduct (cf. **4c**). This is completely at variance with the findings of Titov and Avdeenko,[4] while in accord with some of those of Levy and Sprecher[3] but differ from them in experimentation.

Percentage yield of the phosphonate structure (**4**) is noticed to be higher than the accompanying phosphoramidate form (**3**) in each reaction of quinoneimine (**1**) with DAP, in absence of a base. The reverse is the case, on the other hand, when a base (NaH) is used,[3] which seems to enhance attack by the phosphite on the quinoneimine-nitrogen rather than attack on the ring-carbon. The percentage yield of amide (**5**) depends upon the degree of purity of the phosphite ester used. Thus, it constitutes the main reaction product (>95%) when quinone imine (**1**) is treated with DAP of little purity. This might be attributable to hydrolysis of the phosphite ester, e.g. upon long storage, to give the strong reducing phosphorous acid (H_3PO_3).[7] In favour of this idea is the finding that heating of quinoneimine (**1**) with phosphorous acid, in benzene, affords amide (**5**) almost quantitatively. The yield of amide (**5**) seems also to be temperature-dependent. Thus, for example, while it reached a value of 30% when the uncatalyzed reaction of quinoneimine (**1**) with freshly distilled DMP was performed in benzene at 25°, it attained a value of 45% in boiling benzene. Moreover, this value was raised to 70% when the reactants were heated to 140°, in absence of solvent. The percentage yield of amide (**5**) may also be associated with the role that unavoidable moisture can display during the reaction course between quinoneimine (**1**) and DAP. In favour of this conclusion is the finding that amide (**5**) is formed almost exclusively when the reaction of quinoneimine (**1**) with DAP (e.g. DMP) is performed in benzene-water mixture (Experimental).

The findings of the present investigation may explain why Titov and Avdeenko[4] were not able to obtain phosphorylation products and obtained only amide (**5**) from the reaction of quinoneimine (**1**) with DMP or DEP. Meanwhile, the reaction of quinoneimine (**1**) with diisopropyl phosphite proceeds according to the 1:4 addition mechanism (and not according to the 1:6 addition pattern as suggested by Titov and Avdeenko)[4] to give phosphonate (**4c**) almost exclusively. The same structural assignment (cf. **4c**) was also postulated by Levy and Sprecher[3] for the reaction product of quinoneimine (**1**) with diisopropyl phosphite.

EXPERIMENTAL

All melting points are uncorrected. Dimethyl phosphite (**2a**) and diethyl phosphite (**2b**) were prepared according to established methods.[8,9] Diisopropyl phosphite (**2c**), provided from Koch-Light Laboratories Ltd., Colnbrook-Bucks-England, was twice distilled before use. The benzene (thiophene-free) utilized, was dried over sodium. Solvent systems of benzene-ethylacetate 2:1 and 9:1 (v/v) were used (TLC) and iodine vapour was the visualizing agent. The reaction mixtures were resolved into their individual constituents by column chromatography on Silica Gel G. [particle size 0.2–0.5 mm, 37–70 mesh

(ASTM), E. Merck, Darmstadt], through elution with cyclohexane, benzene and/or suitable combinations of both. IR spectra were recorded with Perkin-Elmer Infracords Model 137 and 237B. ^{1}H NMR spectra were run on Varian A 60 equipment, in $CDCl_3$, using TMS as internal reference. Correct combustion values (C, H, N, P & S) were obtained for all products.

The Reaction of p-benzoquinonedibenzenesulphonimide (**1**) *with dialkyl phosphites* **2a-c**.

a) At 1:1.5 molar ratio A mixture of *p*-benzoquinonedibenzenesulphonimide (**1**)[10] (0.4 g, 0.001 mol) and the phosphite ester (0.0015 mol) in dry benzene (10 ml) was kept at room temperature for 72 hr. Petroleum ether (b.r. 40–60°, 20 ml) was added and the precipitated material collected (ca. 0.38 g, 95 %), recrystallized from acetic acid to give golden yellow needles proved to be unchanged quinoneimine **1** (m.p. and mixed m.p. 179°)[10].

b) In presence of NaH A mixture of quinoneimine (**1**) (0.004 mol), DMP (**2a**, 0.04 mol) and NaH (0.001 mol) in benzene (30 ml) was refluxed for 4 hr. After cooling, the precipitated material was filtered off (*filtrate A*), washed with 2 ml. cold ethylacetate then recrystallized from acetic acid to give colourless needles (3 %) proved to be *p*-benzoquinonedibenzenesulphonamide (**5**) (m.p. and mixed m.p. 244).[11]

The volatile materials were evaporated from the benzene filtrate (*filtrate A*), *in a vacuo*, and the residual substance dissolved in a suitable amount of dry chloroform ($CaCl_2$). Silica Gel G. (particle size 0.2–0.5 mm, E. Merck) (10 g) was added to the chloroform solution and the solvent then allowed to evaporate till dryness at 50° (bath temperature). The reaction mixture thus adsorbed on the Gel support, was then introduced to a colomn (3 cm × 120 cm) charged with a slurry of Silica Gel G., (ca. 80 g) in cyclohexane. Phosphonate (**4a**) and phosphoramidate (**3a**) were respectively isolated upon elution with cyclohexane followed by benzene-cyclohexane (2:8 or 1:1 V/V).

Phosphonate (**4a**) (15 %) was obtained as colourless needles from benzene-petroleum ether (b.r. 40–60°), m.p. 80–82°. IR (KBr): bands at 3240, 3130 cm^{-1} (NH), 1250 cm^{-1} ($\geqslant$P=O, bonded) and 1030 cm^{-1} (P—O—CH_3).[6] ^{1}H NMR: Signals at $\delta = 3.50$ (doublet, 6 H, ^{J}HH = 11.5 Hz, for the methoxyl group protons attached to phosphorus) and at $\delta = 7.1$–7.92 (multiplet, 13 H, for the aromatic protons). The NH protons gave two exchangeable broad singlets at $\delta = 10.70$ and $\delta = 10.92$.

Phosphoramidate (**3a**) (80 %) gave colourless crystals (from methanol), m.p. 174–176°. IR (KBr): 3100 cm^{-1} (NH), 1310 cm^{-1} ($\geqslant$P=O, free)[6] and at 1030 cm^{-1} (P—O—CH_3).[6] ^{1}H NMR: signals at $\delta = 3.50$ (doublet, 6 H, ^{J}HH = 11.5 Hz, for the methoxyl group protons attached to phosphorus), $\delta = 6.75$ (singlet, 4 H, for protons of the —N—C_6H_4—N— grouping), $\delta = 7.32$–7.84 (multiplet, 10 protons, for protons of both C_6H_5—SO_2—N— groupings) and at $\delta = 8.60$ (singlet, 1 H, for the NH proton, exchangeable).

In a similar manner, the reaction of quinoneimine (**1**) (0.004 mol), DEP (**2b**, 0.04 mol) and NaH (0.001 mol) in benzene (25 ml) afforded amide (**5**) (1 %), phosphonate (**4b**) (20 %) and phosphoramidate (**3b**) (75 %).

Phosphonate (**4b**) was obtained as colourless crystals (from cyclohexane), m.p. 170–172° (dec.). IR (KBr): 3240 cm^{-1} 3140 cm^{-1} (NH), 1255 cm^{-1} ($\geqslant$P=O, bonded) and at 1040 cm^{-1} (P—O—C_2H_5).[6] ^{1}H NMR: signals at $\delta = 1.15$ (triplet, 6 H, ^{J}HH = 7 Hz, for the ethoxy-CH_3 protons attached to phosphorus), $\delta = 7.80$ (multiplet, 4 H, for the ethoxy-CH_2 protons attached to phosphorus) and $\delta = 7.10$–8.20 (multiplet, 13 H, aromatics).

The colourless crystals of phosphoramidate (**3b**) were obtained from ethanol, m.p. 145–147°. IR (KBr): bands at 3150 cm^{-1} (NH), 1340 cm^{-1} ($\geqslant$P=O, free) and at 1045 cm^{-1} (P—O—C_2H_5). ^{1}H NMR spectrum: signals at $\delta = 1.35$ (triplet, 6 H, ^{J}HH = 7 Hz, for the ethoxy-CH_3 protons attached to phosphorus), $\delta = 4.40$ (multiplet, 4 H, for the ethoxy-CH_2 protons), $\delta = 6.80$ (singlet, 4 H, for protons of the —N—C_6H_4—N— grouping), $\delta = 7.30$–7.80 (multiplet, 10 H, for the aromatic protons) and at $\delta = 8.20$ (broad signal, NH):

c) In absence of NaH Quinoneimine (**1**) (0.8 g, 0.002 mol) was allowed to react with the phosphite ester (**2a** or **2b**) under the conditions cited in Table I, *vide infra*. The course of reaction was followed by TCL till no appreciable change was noticed on the composition of the reaction mixture. The volatile materials were evaporated, in *a vacuo*, and the residual substance introduced to a column (3 cm × 120 cm) charged with a slurry of Silica Gel G. (ca. 50 g) in cyclohexane, as described before, *vide supra*. Amide (**5**), phosphonate (**4**) and phosphoramidate (**3**) were respectively isolated upon elution with cyclohexane followed by benzene cyclohexane (2:8 v/v) mixture and finally with benzene alone.

The identity of each reaction product was established by m.p. and mixed m.p. determination with identical substance, *vide supra*, as well as by comparative IR and NMR spectra.

d) In presence of water A mixture of quinoneimine (**1**) (0.8 g, 0.002 mol) and DAP (**2a,b** and/or **c**) (0.03 mol) in benzene (30 ml) containing 0.5 ml of water, was refluxed for 2 hr. After cooling, the precipitated material (ca. 0.78 g, 98 %) was collected and recrystallized from acetic acid to give colourless needles proved to be amide (**5**) (m.p. and mixed m.p. 243°).[11]

Reaction of quinoneimine **1** *with phosphorous acid.*

A mixture of quinoneimine (**1**) (0.8 g) and phosphorous acid (0.2 g) in benzene (30 ml) was boiled under reflux for 6 hr. After cooling, the precipitated material was filtered off (>95 %), washed with water, dried then recrystallized from acetic acid to give colourless needles proved to be *p*-benzoquinonedibenzenesulphonamide (**5**) (m.p. and mixed m.p. 243°).[11]

The reaction of quinoneimine **1** *with diisopropyl phosphite* (**2c**)[1].

A mixture of quinoneimine (**1**) (0.8 g, 0.002 mol), diisopropyl phosphite (5 g, 0.03 mol) and benzene (30 ml) was refluxed under nitrogen for 4 hr. The yellow colour of the solution faded gradually and became colourless at the end of the reaction. The volatile materials were removed, *in a vacuo*, and the oily residue, thus obtained, was triturated with petroleum ether (b.r. 40–60°). The solid formed was collected (1.1 g, 95 %) and recrystallized from benzene to give phosphonate (**4c**) as colourless crystals, m.p. 180–182.

Oxidation of **4c** A solution of (**4c**) (0.5 g) in dry chloroform (50 ml) was treated with dry lead-tetraacetate (0.45 g). The solution became orange at once and it was then heated for 15 min at 50° with shaking. The insoluble residue was filtered off and the solution evaporated till dryness then treated with petroleum ether (b.r. 40–60°) but no crystals separated upon cooling in the ice-chest, even after chilling in dry ice-methanol bath. Petroleum ether was then evaporated, *in a vacuo*, and the oily residue dissolved in dry benzene and used as such in the following reaction (preparation of adduct **7**):

Preparation of adduct 7

The benzene solution obtained from the above-described procedure (containing quinoneimine derivative **6**) was treated with diphenylphosphinodithioic acid[12] (0.7 g). The mixture was refluxed for 1 hr whereby the colour of the solution faded till it became colourless. After cooling, the solution was treated with petroleum ether (b.r. 40–60°). The precipitated material was collected (80%, based on diphenylphosphinodithioic acid) and recrystallized from cyclohexane to give compound (**7**) as colourless crystals, m.p. 95–97°.

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