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ORGANOPHOSPHORUS COMPOUNDS—XV

THE REACTION OF TRIVALENT PHOSPHORUS WITH HALO SUBSTITUTED *p*-QUINONEIMINES

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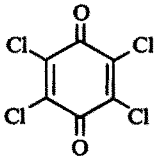
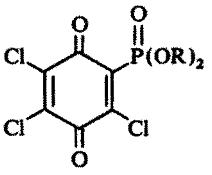
Abstract—Trimethyl and triethyl phosphites react with quinoneimine IV, in aprotic and protic solvents to produce compounds V, VI and VII. The outcome of this reaction depends on the experimental conditions. Triphenyl phosphite, triphenyl-phosphine and phosphorous acid cause the quantitative reduction of IV to VII. A mechanism for the reaction is presented which accounts for the experimental results.

Trimethyl and triethyl phosphites react with quinoneimine XI, in benzene, forming the phosphoramidates (XIIa and XIIb) respectively.

INFORMATION found in the literature regarding the behaviour of *p*-chloranil (I) towards trialkyl phosphites is not fully in agreement. Upon the authority of Ladd and Harvey,[1] dialkyl trichloro-*p*-quinone phosphonates (II) are produced. Ramirez and Dershowitz[2] are, however, of the opinion that the reaction leads to *p*-alkoxyaryl-dialkyl phosphates (III).

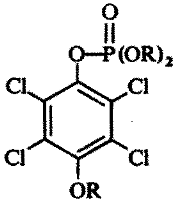


I



II

R = alkyl



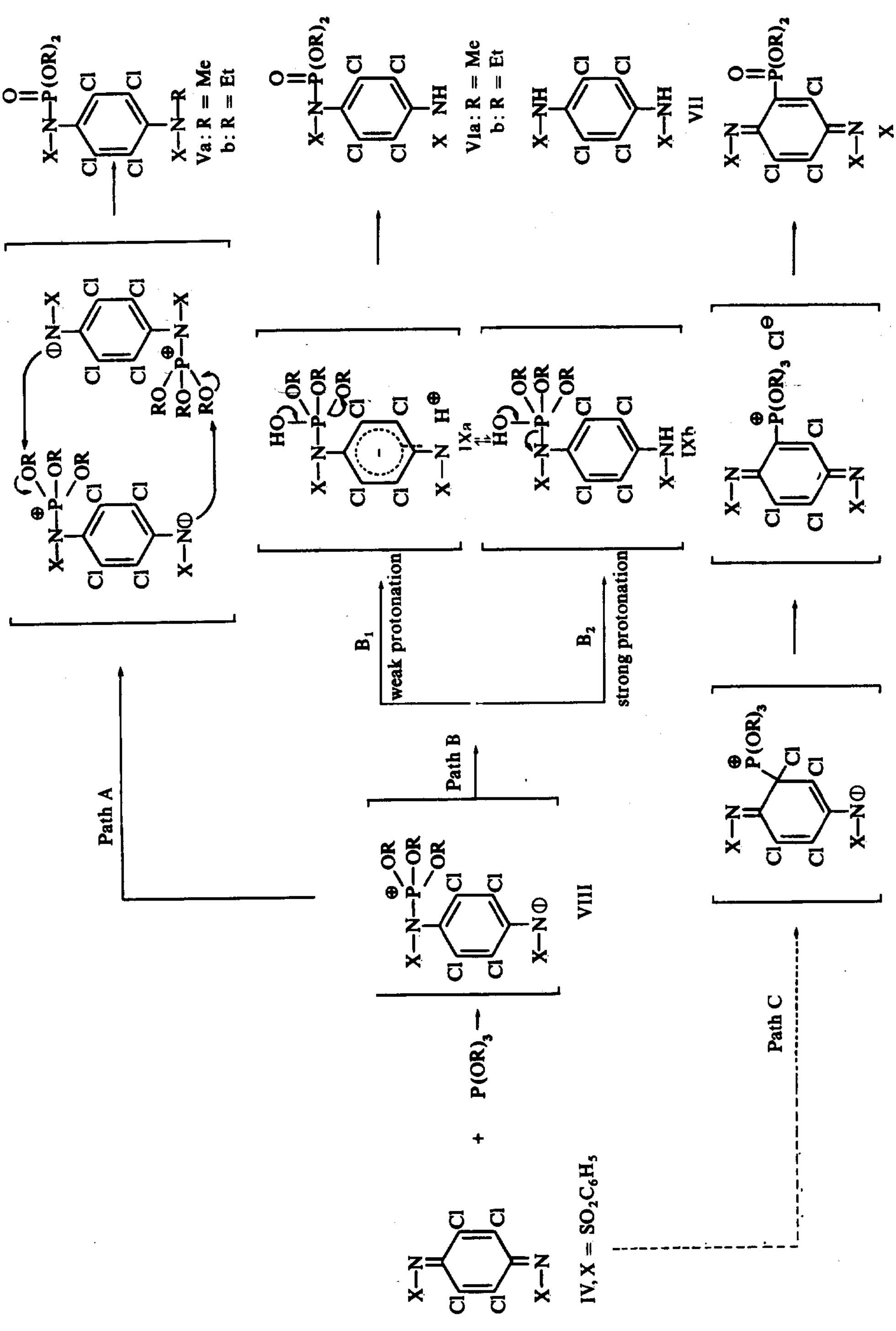
III

Since 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulphonimide (IV) bears structural resemblance to *p*-chloranil (I),[3] it appeared of interest to examine its behaviour towards these phosphite reagents to establish whether it undergoes 1,4 or 1,6 addition reaction. The study was further extended to include other tricovalent phosphorous compounds, namely, triphenyl phosphite, triphenylphosphine, and phosphorous acid. No work on IV from this standpoint has hitherto been reported.

We have found that the product of the reaction of IV with trialkyl phosphites depends on the medium in which the reaction is carried out. Thus, at room temperature, and in dry dioxane, both trimethyl-, and triethyl phosphites reacted with IV to give the colourless dialkyl[*p*-(N-alkyl-benzenesulphonamido)-2,3,5,6-tetrachlorophenyl]-(phenylsulphonyl)-phosphoramidates (Va and Vb) respectively. The same compounds were likewise formed in quantitative yields when the reaction was conducted in other

CHART 1

Mechanism for the reaction of trialkyl phosphites with 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulphonimide (IV)



aprotic solvents, e.g., benzene, acetonitrile or dimethylformamide. Raising the temperature to the b.p. of the medium and/or working with excess of the phosphite ester did not change the nature of the products. When the reaction was carried out in dioxane or benzene to which controlled quantities of water (up to 1% v/v) were added, dialkyl (4-benzenesulphonamido-2, 3, 5, 6-tetrachlorophenyl) (phenylsulphonyl)phosphoramidates (VIa and VIb) and 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulphonamide (VII) were isolated together with the main 1:1 adducts (V). The percentage of these co-products (VI and VII) depended on the solvent and/or the phosphite ester used. On the other hand, in protic solvents such as acetic acid or ethanol, compound VII represented the sole reaction product. The same was also true for dioxane-acetic acid and dioxane-ethanol mixtures.

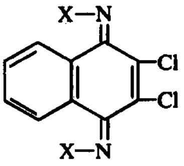
The assigned phosphoramidate structure (V) was based on the following evidence: (i) The colourless crystalline quinoneimine-triethyl phosphite adduct (Vb), taken as example, gave correct combustion values, corresponding to the formula $C_{24}H_{25}N_2O_7PS_2Cl_4$. (ii) The IR spectrum of Vb, in KBr, revealed the absence of NH absorption above 3000 cm^{-1}. Similarly, the strong C=N absorption band at 1580 cm^{-1} recorded with IV, was also absent in the spectrum of Vb. The spectrum showed also strong absorption bands at 1280 cm^{-1} (P=O),[4] and at 1035 cm^{-1} and 1175 cm^{-1} (P—O—C_2H_5).[4] (iii) The H^1 NMR spectrum of Vb showed the 10 aromatic protons as a multiplet at τ 1·75–τ 2·63. The two O—CH_2—CH_3 groups appeared as a quintet (due to P^{31} coupling) centered at τ 5·72 for the CH_2, and a triplet for the CH_3 grouping (*ca* τ 8·53). The single N—CH_2—CH_3 group gave the typical quartet, triplet pattern centered at τ 6·27 and τ 8·93 respectively. (iv) Compound Vb was found identical (comparative IR and NMR spectra) with the one prepared by the action of ethereal diazoethane on VIb. The identity of compound VIb was further verified by comparative IR spectra with a sample obtained via the action of diethyl hydrogen phosphite on quinoneimine IV either in boiling benzene or at ambient temperature when exposed to direct sunlight.[5] Compound VIb satisfied the chemical analysis and its IR spectrum showed a strong NH band at 3200 cm^{-1}. The H^1 NMR spectrum is compatible with the assigned structure VIb (Experimental).

Based upon the above results, it is safe to conclude that trialkyl phosphites, derived from primary alcohol, do not induce chlorine replacement from quinoneimine IV, at least under the experimental conditions described. The dependence of the reaction product on the nature of the medium can be tentatively explained by assuming the primary formation of intermediate VIII. This in dry aprotic solvents, would allow group-translocation with the formation of the phosphoramidate adducts (V). This rearrangement takes place, most probably intermolecularly, through the mutual nucleophilic attack of the nitrenium ion of one molecule on the alkyl rest of the other (Chart 1, Path A). Such a behaviour recalls the Arbuzov transformation proposed for esters of phosphoramidic acids, in which a N—P bond is likewise formed.[6] Concurrent with group-translocation, the dipolar adduct (VIII) can add the elements of water to yield a transient intermediate (IX) with pentacovalent phosphorus. Both the strength and availability of the free protons in solution dictate the nature of electronic interaction in the transient. When the proton is too weak to affect permanent bonding with the nitrenium ion, this latter will enter into conjugation with the benzene ring. This prevents the conjugate base (IXa) from acting as a leaving group, and favours its collapse to give VI and methanol (Chart 1, Path B_1). When, on the other hand, strong protonation takes place, charge delocalization (*cf* IXb) will lead to the rupture of the P—N bond and the production of compound VII. Apparently, when the proton availability and/or strength is intermediate between the two limiting cases, both products VI and VII are to be expected. Such a state of affairs is met with in dioxane-water or benzene-water mixtures. In the much stronger acid solutions, e.g., acetic acid or ethanol, solvolysis to the diamide VII represents the main route. That diamide VII was not formed via the hydrolysis of compound VI was supported by the fact that the latter was recovered practically unchanged when boiled in dioxane-water mixture for 4 hr.

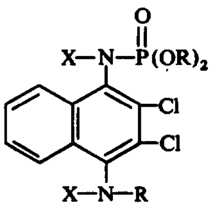
There is still a possibility that trialkyl phosphites add in a 1,4 fasion, with the elimination of chlorine from the benzene nucleus (Chart 1, Path C). The fact that—under the experimental conditions of the present study—no phosphonate derivative of the structure X was isolated, indicates that the rate of such a reaction is too low to compete with those of reactions A and B.

The reaction of triphenyl phosphite or triphenylphosphine with quinoneimine IV, in benzene, led to the quantitative formation of the colourless diamide (VII). Triphenylphosphine oxide was isolated in the case of the phosphine reagent. Group-translocation in this case is unlikely. This behaviour is not unexpected in view of the restricted phenyl group migration in the Arbusov reaction.[7] Similarly, the treatment of IV with phosphorous acid gave VII.

The reaction of trimethyl- and triethyl phosphites with 2,3-dichloro-1,4-naphthoquinonedibenzenesulphonimide (XI) was also investigated. The reaction proceeded, in dry benzene, at ambient temperature, to give mainly 1:1 adducts having structure XII. This was based on analytical data and IR and H^1 NMR spectra (*vide infra*).



XI: X = SO_2Ph



XIIa: R = Me
b: R = Et

This lends further support to the general conclusion that the reaction of trialkyl phosphites with unsubstituted-[8] or halo substituted *p*-quinoneimines proceeds through a 1,6 addition route.

EXPERIMENTAL

All m.p's are uncorrected. The trialkyl phosphites were prepared by established procedures[9,10] and were purified by drying over Na. The dialkyl hydrogen phosphites used were freshly prepared.[11,12] The benzene (thiophene-free), dioxane and light petroleum (40–60°) were dried over Na. Acetonitrile (P_2O_5) and dimethylformamide (drierite) were freshly distilled. All manipulations were carried out under N_2 atmosphere.

The IR spectra were recorded with a Carl Zeiss Infracord Spectrophotometer Model "UR 10" and the NMR spectra were performed on a Varian A-60 Spectrometer in $CDCl_3$ soln, using TMS as an internal standard.

Reaction of trialkyl phosphites with 2,3,5,6-tetrachloro-p-quinonedibenzenesulphonimide (IV) *in dry aprotic solvents.* Triethyl phosphite (1·6 g; 0·01 mole) was added dropwise at 10° during a period of 10 min to IV[13] (3·8 g; 0·01 mole) in dioxane (200 ml). The mixture was kept at room temp for 12 hr, whereby the red colour of the soln faded gradually until it became colourless. The solvent was evaporated *in vacuo*, the residual solid washed with light petroleum and recrystallized from benzene-light petroleum to give Vb (yield 95%) as colourless crystals, m.p. 188°. (Found: C, 41·80; H, 3·71; N, 4·08; P, 4·45; Cl, 20·47; $C_{24}H_{25}N_2O_7PS_2Cl_4$ requires: C, 41·72; H, 3·61; N, 4·05; P, 4·48; Cl, 20·52%). Compound Vb was also formed when the above described procedure was performed using 4 mole equivs of the phosphite reagent, and/or when the reactants were boiled for 3 hr.

Similar results were obtained by allowing the reaction to proceed in benzene (yield 90%), acetonitrile (yield 95%) or dimethylformamide (yield 95%).

In a similar manner, Va was produced when IV reacted with trimethyl phosphite in dioxane. Compound Va was obtained as colourless crystals from benzene-light petroleum, m.p. 179° (yield 90%). (Found: C, 38·87; H, 3·09; N, 4·69; P, 4·72; Cl, 21·75; $C_{21}H_{19}N_2O_7PS_2Cl_4$ requires: C, 38·91; H, 2·93; N, 4·31; P, 4·77; Cl, 21·82%). The IR spectrum had bands at 1280 cm^{-1} (P=O) (4) and 1040 cm^{-1} (P—OCH_3) (4). The H^1 NMR spectrum had multiplet at τ 2·42 (aomatics), a doublet at τ 6·17 (J_{HP} = 11·4 cs, $POCH_3$) and a singlet at τ 6·9 (NCH_3).

Reaction of triethyl phosphite with quinoneimine IV *in presence of water.* Quinoneimine IV (3·8 g), suspended in dioxane (200 ml) containing 2 ml water was treated with triethyl phosphite (1·6 g). The mixture was kept for 1 hr at ambient temp and the solid material filtered off (yield 15%), crystallized from ACOH proved to be VII (m.p. and mixed m.p. 278°).[13] The filtrate was evaporated *in vacuo* and the residue was dissolved in $CHCl_3$ (50 ml). Addition of cyclohexane (50 ml) resulted in the isolation of VIb. This was recrystallized from chloroform-light petroleum (yield 10%) and proved identical with VIb obtained as described below. The filtrate was further treated with cyclohexane (50 ml) and kept in the ice-chest overnight. The colourless crystalline product formed (yielded 70%) proved to be Vb (m.p. and mixed m.p. 188°) (*vide supra*).

Reaction of trimethyl phosphite with quinoneimine IV *in presence of water.* This was carried out in the manner described above. The following products were separated and identified: (a) Compound VII, m.p. and mixed m.p. 278°[13] (yield 35%). (b) Compound VIa, m.p. and mixed m.p. 230° (yield 30%) (*vide infra*). (c) Compound Va, m.p. and mixed m.p. 179° (yield 30%).

Reaction of trialkyl phosphites with quinone IV *in acetic acid.* A mixture of IV (0·38 g), AcOH (20 ml), and triethyl phosphite (0·16 g) (or trimethyl phosphite (0·12 g)) was kept at room temp for 30 min. The crystals thus formed were recrystallized from AcOH to give VII as colourless crystals, m.p. and mixed m.p. 278°[13] (yield 96%). Similarly compound VII was obtained (yield 94%) when EtOH was used.

Reaction of dialkyl hydrogen phosphites with quinoneimine IV. A mixture of IV (0·38 g), diethyl hydrogen phosphite (0·12 g; 0·001 mole) and benzene (30 ml) was refluxed for 10 hr. The volatile materials were removed under reduced pressure and the residue was crystallized from chloroform-light petroleum to give VIb (yield 80%) as colourless crystals m.p. 203°. (Found: C, 39·85; H, 3·27; N, 4·32; P, 4·65; Cl, 21·54. $C_{22}H_{21}N_2O_7PS_2Cl_4$ requires: C, 39·98; H, 3·19; N, 4·23; P, 4·67; Cl, 21·42%). The IR spectrum had bands at 3200 cm^{-1} (NH), 1260 cm^{-1} (P=O)[4] and 1040 cm^{-1} (P—OC_2H_5).[4] The H^1 NMR spectrum had a multiplet at τ 2·22 (aromatics), a quantet at τ 5·64 (J_{HP} = 7·5 cs, P—OCH_2CH_3) and a triplet at τ 8·59 (P—OEt).

Similarly, VIa was formed by the action of dimethyl hydrogen phosphite on IV. Compound VIa was obtained from chloroform as colourless crystals, m.p. 230° (yield 70%). (Found: C, 37·85; H, 2·81; N, 4·75; P, 4·85; Cl, 22·40; $C_{20}H_{17}N_2O_7PS_2Cl_4$ requires: C,37·92; H, 2·70; N, 4·73; P, 4·88; Cl, 22·36%). The IR spectrum had bands at 3210 cm^{-1} (NH), 1280 cm^{-1} (P=O)[4] and 1040 cm^{-1} (P—OCH_3).[4] The H^1 NMR spectrum had a multiplet at τ 2·17 (aromatics) and a doublet at τ 6·02 (J_{HP} = 11·4 cs, $POCH_3$).

Photochemical reaction between diethyl hydrogen phosphite and quinoneimine IV. A mixture of IV (0·38 g), freshly distilled diethyl hydrogen phosphite (0·2 g) and benzene (30 ml) was placed in a Schlenk tube of Pyrex glass. The air was displaced by dry N_2 and the tube sealed and exposed to sunlight for 40 hr (March). The colourless crystals thus formed were filtered, washed with benzene, crystallized from chloroform-light petroleum and was proved to be VIb (85%) (m.p. and mixed m.p. 203°). A parallel experiment, carried out in the dark, gave VIb (40%) and the starting IV (60%).

Action of water on VIb. A mixture of VIb (0·5 g) and 10 ml dioxane containing 0·5 ml water was boiled for 4 hr. After cooling, VIb was recovered practically unchanged (m.p. and mixed m.p. 203°).

Action of diazoethane on VIb. To a suspension of VIb (0·3 g) in dry ether (20 ml) was added an ethereal soln of diazoethane (from 3 g nitrosoethylurea) and the mixture was then kept at 5° for 24 hr. The solvent was evaporated *in vacuo* and the residual ~~solid~~ (0·3 g) was washed with light petroleum, recrystallized from chloroform-light petroleum and proved to be Vb (m.p. and mixed m.p. 188°).

Reaction of quinoneimine IV *with triphenyl phosphite.* A suspension of IV (0·38 g) in benzene (30 ml) was treated with freshly distilled triphenyl phosphite[14] (0·31 g). After standing for 1 hr at room temp, the solid formed was extracted with 3% NaOH aq (20 ml). Acidification with 5% HCl afforded 0·36 g of VII, as proved by comparison of its m.p. and IR spectrum with an authentic specimen.[13]

Reaction of quinoneimine IV *with triphenylphosphine.* When a suspension of IV (0·38 g) in dry benzene (10 ml) was treated with triphenylphosphine[15] (0·26 g), colourless crystals were formed after standing for 30 min. These were filtered off, washed with benzene, recrystallized from AcOH and proved to be VII (yield 96%) (m.p. and mixed m.p. 278°).[13]

The filtrate and washings were freed from the solvent *in vacuo*, and the residue then recrystallized from benzene–light petroleum to give triphenylphosphine oxide (m.p. and mixed m.p. 154°).[16]

Reduction of quinoneimine IV *with phosphorous acid.* A mixture of IV (0·38 g), benzene (30 ml) and phosphorous acid (0·1 g) was heated (steam-bath) for 6 hr. The colourless product was filtered off and recrystallized from AcOH to give VII (m.p. and mixed m.p. 278°).[13]

Reaction of trialkyl phosphites with 2,3-*dichloro*-1,4-*naphthoquinonedibenzenesulphonimide* (XI). A mixture of XI[17] (0·57 g; 0·001 mole), trimethyl phosphite (0·13 g; 0·001 mole) and benzene (10 ml) was kept at room temp for 2 hr. After addition of light petroleum, the crystalline material (95%) was recrystallized from benzene–light petroleum to give XIIa as colourless crystals, m.p. 105°. (Found: C, 47·64; H, 3·71; N, 4·51; P, 4·85; S, 10·15; Cl, 11·38. $C_{25}H_{23}N_2O_7PS_2Cl_2$ requires: C, 47·70; H, 3·68; N, 4·45; P, 4·91; S, 10·18; Cl, 11·26%). The IR spectrum had bands at 1280 cm^{-1} (P=O)[4] and 1040 cm^{-1} ($P—OCH_3$).[4] The H^1 NMR spectrum had multiplet at τ2·15 (aromatics), a singlet at τ6·05 (NCH_3) and a doublet at τ6·57 (J_{HP} = 11·4 c/s, $POCH_3$).

In a similar manner, XIIb was obtained when triethyl phosphite reacted with XI. Compound XIIb was recrystallized from benzene–light petroleum, m.p. 120° (yield 98%). (Found: C, 49·92; H, 4·34; N, 4·28; P, 4·66; S, 9·61; Cl, 10·58. $C_{28}H_{29}N_2O_7PS_2Cl_2$ requires: C, 50·08; H, 4·35; N, 4·17; P, 4·60; S, 9·55; Cl, 10·52%). The IR spectrum had bands at 1265 cm^{-1} (P=O)[4] and at 1035 cm^{-1} ($P—OC_2H_5$).[4]

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