ORGANOPHOSPHORUS COMPOUNDS—XIX

THE REACTION OF TRIALKYL PHOSPHITES WITH EXTENDED *p*-QUINONES

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Abstract—Trimethyl and triethyl phosphites react with diphenoquinone **3**, yielding 4,4'-dihydroxydiphenyl **10**; 4'-alkoxy-4-biphenylyl dialkyl phosphates **5**, 4,4'-biphenylylene tetraalkyl bis(phosphates), **6**, and 4'-hydroxy-4-biphenylyl dialkyl phosphates **9** are also isolated in minor yields. The effect of temperature on the reaction is studied. A mechanism for the reaction is presented which accounts for the experimental results. The reaction of trimethyl and triethyl phosphites with quinoneimines **12** gives the corresponding phosphoramidates **13**, in quantitative yields.

In recent years, considerable interest has been focused on the reaction of trivalent phosphorus compounds with mono- and polycyclic quinones, e.g., **1** and **2**.[1,2] However, to our knowledge, there appears

1a, X = H
b, X = Cl

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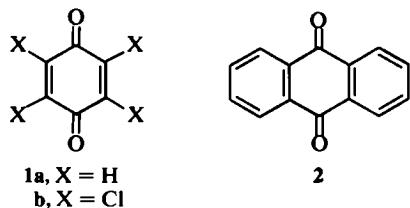
to be no information in the literature regarding the same reaction with extended *p*-quinones,[3] and we have examined, therefore, the behaviour of diphenoquinone **3** towards trialkyl phosphites.

With trimethyl phosphite, in dry benzene, no reaction was observed at room temperature even after 72 hr, and quinone **3** was recovered practically quantitatively. When the same reaction was conducted at 50° for 24 hr, a polymeric material was exclusively obtained having the same features described for the self-polymerization product of quinone **3**.[4,5] Upon raising the temperature to that of the boiling point of the solvent, the red colour of the reaction mixture faded gradually and it became colourless after 24 hr. This reaction afforded 4'-methoxy-4-biphenylyl dimethyl phosphate **5a**, 4, 4'-biphenylylene tetramethyl bis(phosphate) **6a** 4'-hydroxy-4-biphenylyl dimethyl phosphate **9a** and 4,4'-dihydroxydiphenyl **10**, accompanied by a large amount of the polymer mentioned above. Heating quinone **3** with excess trimethyl phosphite in absence of solvent for 30 min led to an increase in the yields of the phosphorus-containing compounds **5a**, **6a**, and **9a**, indicating that the rate of the phosphorylation reaction is more temperature dependent than that of self-polymerization of quinone **3**.

Triethyl phosphite reacted with **3** in an analogous manner. In all these reactions, the alkyl ethers **7a–d** could not be isolated but their presence in the reaction mixtures was revealed by direct comparison with reference samples by TLC.

The structures of the colourless crystalline compounds **5**, **6**, and **9**, were elucidated as follows: The quinone-trimethyl phosphite adduct **5a** gave correct combustion values corresponding to the formula $C_{15}H_{17}O_5P$. The IR spectrum of **5a** revealed the absence of OH absorption above $3000\,cm^{-1}$. Similarly, the strong C=O absorption band at $1626\,cm^{-1}$ recorded for quinone **3**,[6] was absent in the spectrum of **5a**. The spectrum showed, however, strong absorption bands at $1600\,cm^{-1}$ (C=C, aromatic),

$1280\,cm^{-1}$ $\left(\!\!>\!P\!=\!O\right)$,[7] and at $1050\,cm^{-1}$ (P—

O—CH₃).[7] No bands were observed in the $1450–1435\,cm^{-1}$ region characteristic of the P—Ph absorption.[7] The ¹H NMR spectrum of **5a** showed the presence of 8 aromatic protons as a multiplet centred at $\tau2.65$. The two methoxy groups attached to phosphorus appeared as a doublet centred at $\tau6.20$, with ¹HP = 11·5 c/s, and the signal at $\tau6.25$ (singlet) was due to the three protons of the OCH₃ group. Upon alkali hydrolysis, compound **5a** yielded 4-hydroxy-4'-methoxydiphenyl **7a**. 4,4'-Biphenylylene tetramethyl bis(phosphate) **6a** was identical with an authentic sample prepared by the action of dimethylchlorophosphonate on **10** (m.p., IR and ¹H NMR spectra). 4'-Hydroxy-4-biphenylyl dimethyl phosphate **9a** satisfied the chemical analyses and its IR spectrum showed a strong OH absorption band at $3250\,cm^{-1}$. The ¹H NMR spectrum of **9a** was compatible with the assigned structure. Treatment of **9a** with 10% NaOH effected its hydrolysis to 4,4'-dihydroxydiphenyl **10**.

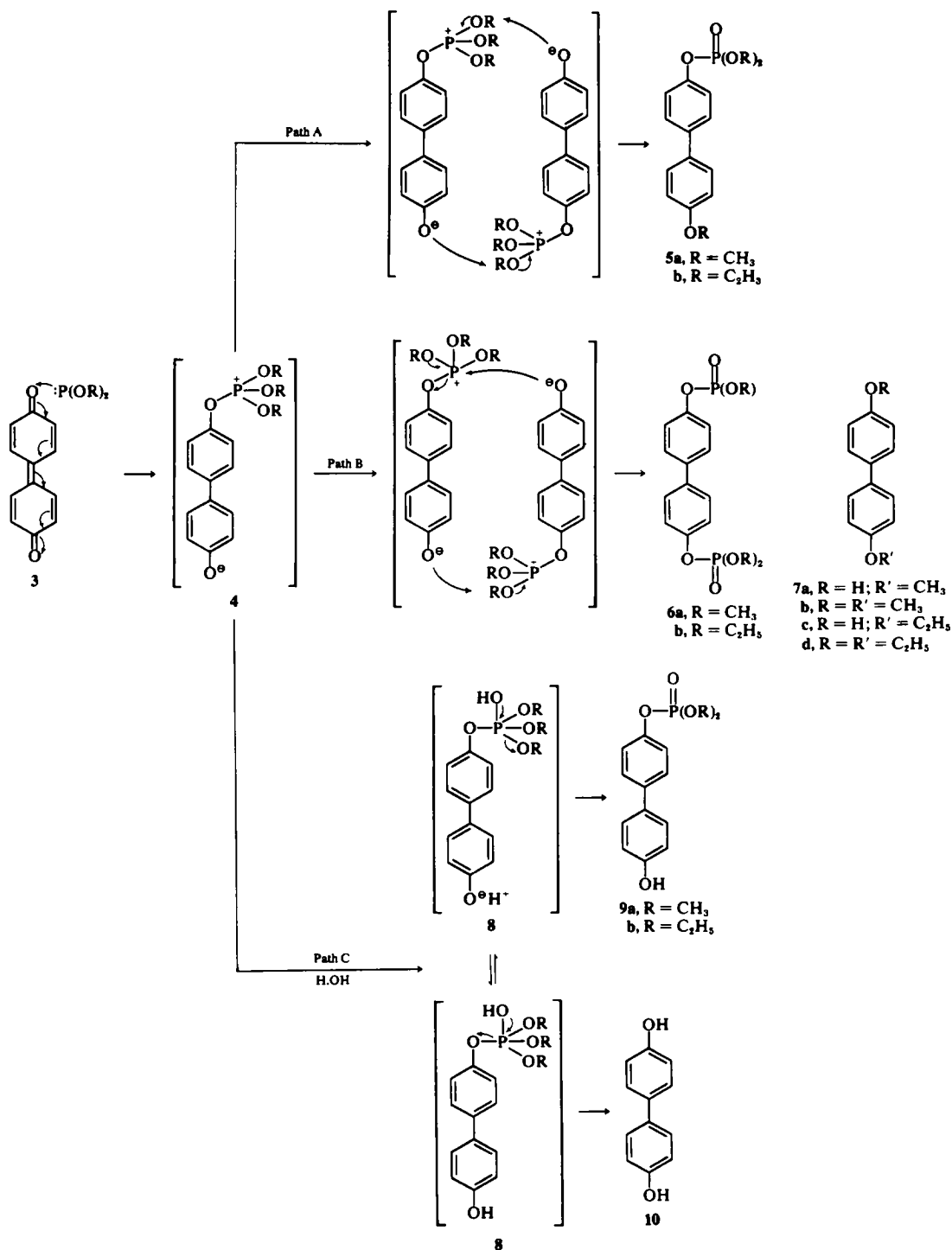Primary nucleophilic attack by the phosphite-

CHART 1. Mechanism for the treaction of trialkyl phosphites with diphenoquinone 3.

phosphorus on the carbonyl-oxygen in **3**, gives the intermediate dipolar adduct **4** which then undergoes group-translocation with the formation of the ether phosphate esters **5**. This rearrangement takes place, most probably intermolecularly, through the mutual nucleophilic attack by the phenoxide oxygen of one molecule on the alkyl residue of the other (Chart 1, Path A). The bis(phosphates) **6** could originate from adduct **4** *via* an attack on the phosphorus by the phenoxide oxygen (Chart 1, Path B), as an alternative to the predominant attack on the alkyl carbon by the phenoxide oxygen observed in the alkyl group-translocation.

Concurrent with group-translocation, the dipolar adduct **4**, in the presence of unavoidable moisture, can add the elements of water to furnish a transient intermediate **8** with pentacovalent phosphorus which would collapse to yield the hydroxyphosphates **9** and/or 4,4'-dihydroxydiphenyl **10** (Chart 1, Path C). Such a state of affairs can take place both in presence or absence of benzene. In fact, it was found that if the reaction of trimethyl phosphite with quinone **3** was conducted in boiling benzene containing controlled amounts of water, the only products isolated were 4,4'-dihydroxydiphenyl **10** and the polymeric product. That compound **10** was not formed *via* the hydrolysis of the hydroxyphosphates **9** was supported by the fact that **9a**, for example, was recovered almost quantitatively when boiled in benzene-water mixture for 24 hr.

Apparently, the high redox potential of quinone **3** (954 mv)[8] together with the strong reducing character of trialkyl phosphites,[9] would facilitate the reduction of the dipolar adduct **4** to **10**. Also, the effect of temperature and/or water display a definite role on the course of this reaction (*vide supra*).

From the above results, it is evident that diphenoquinone **3** behaves towards the P^{III} reagents in a manner not quite similar to that described for monocyclic p-quinones, e.g., p-benzoquinone **1a** (696 mv)[10] and chloranil **1b** (712 mv),[10] where ethers of p-quinolphosphates **11** are predominantly or exclusively formed.[11,12] This difference in behaviour towards one and the same phosphite reagent is thus in accord with that noted in other reactions, namely, the reaction of piperidine and morpholine with p-benzoquinone **1a** and diphenoquinone **3**. Whereas these nucleophilic nitrogen compounds form addition products with **1a**,[13,14] they cause the
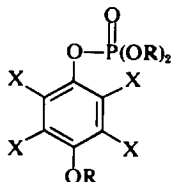
quantitative reduction of quinone **3** to 4,4'-dihydroxydiphenyl **10**.[3]
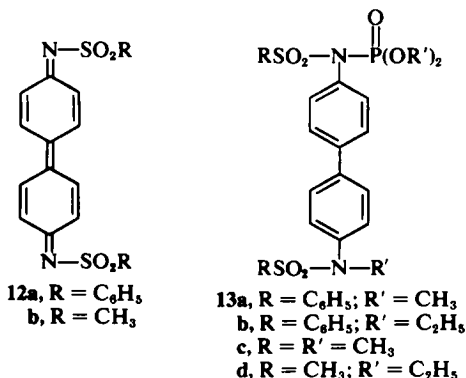
Since diphenoquinonedibenzenesulphonimide **12a** bears a structural resemblance to diphenoquinone **3**, it was also of interest to examine the reaction of **12a** with trialkyl phosphites to establish whether it would behave in a similar manner. We have found that trimethyl phosphite and triethyl phosphite react with **12a**, in boiling benzene, to give the corresponding phosphoramidates **13a** and **13b** in quantitative yields. The phosphoramidate structure **13** was based on the following evidence: (i) Elemental analysis of compound **13a**, taken as example, corresponded to an empiric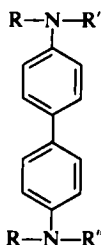al formula of $C_{27}H_{27}N_2O_7PS_2$. (ii) Strong bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(\!\!\begin{array}{c}\diagdown\\\diagup\end{array}\!\!P\!\!=\!\!O\right)^7$ and at 1050 cm^{-1} (P—O—CH$_3$)^7 were distinguishing features of its IR spectrum. Moreover, the $\begin{array}{c}\diagdown\\\diagup\end{array}$C=N absorption band at 1542 cm^{-1} recorded in the spectrum of quinoneimine **12a**,[15] was absent in the spectrum of **13a**. (iii) The ^{1}H NMR spectrum of adduct **13a** showed 18 aromatic protons as a multiplet at τ1·95–2·85. The two OCH$_3$ groups attached to phosphorus appeared as a doublet centred at τ6·16 with $^JHP = 12$ c/s, and the signal at τ6·78 (singlet) was due to the 3 protons of the N—CH$_3$ group. (iv) Adduct **13a** when treated with dilute aqueous alkali yielded **14b**. This latter reacted with methyl iodide to give compound **14c**. This compound was identical with that obtained by allowing **14a** to react with methyl iodide. When treated with concentrated sulphuric acid, **14b** afforded N-methylbenzidine. This reaction thus represents a new route for the preparation of N-alkylbenzidines when adducts **13** are subjected to hydrolysis.

Next, diphenoquinonedimethanesulphonimide **12b** was reacted with trimethyl and triethyl phosphites in boiling benzene to give mainly 1:1-adducts **13c** and **13d**. The IR spectrum of **13c**, taken as example, revealed the absence of NH and

11, X=H or Cl and R=Alkyl

12a, R = C$_6$H$_5$
b, R = CH$_3$

13a, R = C$_6$H$_5$; R' = CH$_3$
b, R = C$_6$H$_5$; R' = C$_2$H$_5$
c, R = R' = CH$_3$
d, R = CH$_3$; R' = C$_2$H$_5$

14a, R = SO$_2$C$_6$H$_5$; R' = R" = H
   b, R = SO$_2$C$_6$H$_5$; R' = H; R" = CH$_3$
   c, R = SO$_2$C$_6$H$_5$; R' = R" = CH$_3$
   d, R = SO$_2$CH$_3$; R' = R" = H

$\diagdown$C=N$\diagup$ absorptions, and its ^{1}H NMR spectrum

showed (a) $\tau = 7\cdot10$ and $\tau = 6\cdot58$ (for protons of the SO$_2$CH$_3$ groups, 2 singlets), (b) $\tau = 6\cdot61$ (for N—CH$_3$ protons, singlet), (c) $\tau = 6\cdot10$ [for protons of P(O)(OCH$_3$)$_2$ groups, doublet with ^{1}HP = 12 c/s] and (d) $\tau = 2\cdot42$ (for aromatic protons, multiplet). The integration ratio is 6:3:6:8.

These data show that the reaction of trialkyl phosphites with the extended p-quinoneimines (**12a** and **12b**) simulates that with monocyclic p-quinoneimines, where phosphoramidates are the sole reaction products.[16-18]

EXPERIMENTAL

All m.ps are uncorrected. Benzene (thiophene-free) and pet. ether (b.p. 60–80°) were dried (Na). The trialkyl phosphites were prepared by established procedures[19,20] and were purified by treatment with Na followed by fractional distillation. IR spectra were recorded in KBr discs, with a Carl Zeiss Infracord Spectrophotometer Model UR 10. The ^{1}H NMR spectra were determined on a Varian A 60 Spectrometer using TMS as an internal standard and CDCl$_3$ as solvent. Thin layer chromatography was performed on chromatoplates (10 × 15 cm) of Silica Gel G, using benzene-ethylacetate (1:1 v/v) as the solvent system and iodine vapour as the visualizer.

Reaction of trimethyl phosphite with diphenoquinone 3 in benzene

(a) *At room temperature.* A mixture of quinone 3[21] (0·9 g; 0·005 mole), trimethyl phosphite (1·2 g; 0·01 mole) in benzene (30 ml), was kept at room temp for 72 hr. 3 (0·85 g; 95%) was recovered [m.p. and mixed m.p. 165°[21]]. (b) *At 50°.* To a suspension of quinone 3 (0·9 g) in benzene (30 ml) was added trimethyl phosphite (1·2 g) and the mixture was heated at 50° for 24 hr. After evaporation of the volatile materials, *in vacuo*, the residue was treated with hot ethanol. The brittle yellow powder (0·8 g), so formed, turned brown at 290° and did not char above 360°. Its IR spectrum was superimposable on that of the self-polymerization product of diphenoquinone 3.[4,5] The polymeric material was obtained exclusively upon heating quinone 3 in benzene, at 50° for 24 hr. (c) *At reflux temperature.* Quinone 3 (7·4 g; 0·04 mole) and trimethyl phosphite (12 g; 0·1 mole) in benzene (150 ml) were refluxed (steam-bath), whereby the red colour of the reaction medium faded gradually until it became colourless after 24 hr. After filtration (hot), the insoluble material was

twice extracted with 20 ml portions of boiling benzene, dried and treated with aq NaOH (30 ml; 10%). The alkali-insoluble residue was washed with water, then boiled with ethanol to give the polymeric material (3·5 g) (*vide supra*). After neutralization of the alkaline solution with 10% HCl, the precipitate was collected (2·6 g; 35%), recrystallized from ethanol and proved to be 4,4'-dihydroxydiphenyl 10 [m.p. and mixed m.p. 270°[22]].

After evaporation of the volatile materials from the combined benzene solutions *in vacuo*, the residual material was cooled and treated with aq NaOH (20 ml; 10%). The alkali-insoluble residue was collected, dried and extracted with boiling hexane. Colourless crystals from the cold hexane extract, were collected (2·4 g; 15%) and proved to be 4,4'-biphenylene tetramethyl bis(phosphate) **6a** [(m.p., mixed m.p. and IR and ^{1}H NMR spectra, *vide infra*)]. The hexane-insoluble fraction was recrystallized from chloroform-pet. ether to give 4'-methoxy-4-biphenylyl dimethyl phosphate **5a** (1·8 g; 15%) as colourless crystals, m.p. 152–154°. (Found: C, 58·80; H, 5·80; P, 9·98. Calcd. for C$_{15}$H$_{17}$O$_5$P: C, 58·50; H, 5·56; P, 10·06%). The IR spectrum had bands at 1600 cm^{-1} (aromatic),

1280 cm^{-1} $\left(\diagup\!\!\!\!\!\diagdown\!\!\!\!P{=}O\right)$[7] and at 1050 cm^{-1} (P—O—CH$_3$).[7] The

^{1}H NMR spectrum revealed the presence of 8 aromatic protons as a multiplet centred at $\tau2\cdot65$. The two OCH$_3$ groups attached to phosphorus appeared as a doublet centred at $\tau6\cdot20$, with ^{1}HP = 11·5 c/s, and the signal at $\tau6\cdot25$ (singlet) was due to the 3 protons of the OCH$_3$ group.

After neutralization of the alkaline solution with 10% HCl, the precipitate was filtered off, dried and extracted with boiling ligroin (b.p. 100–120°). The colourless crystals that precipitated from the cold ligroin extract, were filtered off and recrystallized from benzene to give 4'-hydroxy-4-biphenylyl dimethyl phosphate **9a** (0·8 g; 7%), m.p. 182–184°. (Found: C, 57·64; H, 4·99; P, 9·78. Calcd. for C$_{14}$H$_{15}$O$_5$P: C, 57·19; H, 5·14; P, 10·54%). The IR spectrum had bands at 3250 cm^{-1} (OH), 1600 cm^{-1}

(aromatic), 1280 cm^{-1} $\left(\diagup\!\!\!\!\!\diagdown\!\!\!\!P{=}O\right)$[7] and at 1050 cm^{-1} (P—

O—CH$_3$).[7] The ^{1}H NMR spectrum showed the 8 aromatic protons as a multiplet centred at $\tau2\cdot88$. The protons of the two OCH$_3$ groups appeared as a doublet (due to P^{31} coupling), centred at $\tau6\cdot20$, with ^{1}HP = 11·5 c/s.

The ligroin-insoluble fraction (1·1 g; 15%) was recrystallized from ethanol and proved to be 4,4'-dihydroxydiphenyl 10 (m.p., mixed m.p. and IR spectra).

(d) *In presence of water.* Quinone 3 (0·9 g), suspended in benzene (20 ml) containing 2 ml of water, was treated with trimethyl phosphite (0·6 g) and the reaction mixture was refluxed for 24 hr, then cooled. The precipitate was filtered off (filtrate "A") and treated with aq. NaOH (10 ml; 10%). The alkali-insoluble residue was filtered off (filtrate "B"), boiled with ethanol and the brittle yellow powder (0·6 g), so obtained, was proved to be the self-polymerization product of quinone 3.[4,5]

After neutralization of filtrate "B" with 10% HCl, the precipitate was collected (0·2 g; 20%), recrystallized from ethanol and proved to be 4,4'-dihydroxydiphenyl 10 (m.p. and mixed m.p.).

Adding known amounts of trimethyl phosphate[23] to a previously analyzed sample of filtrate "A" (the benzene phase), caused an increase in the corresponding GLC peak.

Reaction of trimethyl phosphite with diphenoquinone 3 in absence of solvent. A mixture of quinone 3 (7·4 g; 0·04 mole) and trimethyl phosphite (37 g; 0·3 mole) was heated at 100° (bath temperature). After 25 min, a vigorous reaction was observed which subsided within 5 min, and the red colour of the reaction medium became colourless. Boiling benzene (150 ml) was added and the reaction mixture filtered while hot. Upon working up as described in the case of boiling benzene (*vide supra*), the following products were separated and identified: (a) The self-polymerization product of quinone 3 (2 g).[4,5] (b) 4,4'-dihydroxydiphenyl 10, m.p. and mixed m.p. 270° (yield 3·3 g; 45%). (c) Compound 6a (yield 3·2 g; 20%), m.p. and mixed m.p. (*vide infra*). (d) Compound 5a (yield 2·5 g; 20%), m.p. and mixed m.p. 152–154°. (e) Compound 9a, m.p. and mixed m.p. 182–184°, (yield 1·2 g; 10%).

Action of water on 4'-hydroxy-4-biphenylyl dimethyl phosphate 9a. A mixture of compound 9a (0·5 g) and 10 ml of benzene containing 0·5 ml of water, was boiled for 24 hr. After cooling, compound 9a was recovered practically quantitatively (m.p. and mixed m.p.).

Reaction of triethyl phosphite with diphenoquinone 3 in boiling benzene. Quinone 3 (7·4 g; 0·04 mole) and triethyl phosphite (16 g; 0·1 mole) in benzene (150 ml) were refluxed (steam bath) for 24 hr. Upon working up in the same manner as described in the case of trimethyl phosphite, *vide supra*, the following products were isolated: (a) The polymeric material (4·5 g), (b) 4,4'-dihydroxydiphenyl 9 (3·6 g; 50%), (c) 4,4'-biphenylylene tetraethyl bis(phosphate) 6b (2·7 g; 15%), (d) 4'-ethoxy-4-biphenylyl diethyl phosphate 5b (2·4 g; 17%), and (e) 4'-hydroxy-4-biphenylyl diethyl phosphate 9a (0·6 g; 5%). The polymeric material was identified by comparison of its properties with that of an authentic specimen.[4,5] Compound 10 was identified by m.p. and mixed m.p. with a reference sample.[22] Compound 6b was identical (m.p., mixed m.p. and IR spectra) with an unequivocally prepared specimen (*vide infra*). Colourless crystals of compound 5b were obtained from benzene-pet. ether, m.p. 142–144°. (Found: C, 62·01; H, 6·88; P, 6·65. Calcd. for $C_{18}H_{23}O_5P$: C, 61·77; H, 6·62; P, 8·85%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1280 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1020 cm^{-1} (P—O—C_2H_5).[7] Compound 9b was obtained from ligroin (b.p. 100–120°) as colourless crystals, m.p. 172–174°. (Found: C, 59·88; H, 6·16; P, 9·03. Calcd. for $C_{16}H_{19}O_5P$: C, 59·69; H, 5·95; P, 9·62%). The IR spectrum had bands at 3230 cm^{-1} (OH), 1600 cm^{-1} (aromatic), 1280 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1020 cm^{-1} (P—O—C_2H_5).[7] The ^{1}H NMR spectrum had a 6H triplet centred at $\tau 8·65$ (for protons of the two ethoxy-CH_3 groups attached to phosphorus), a 4H quintet centred at $\tau 5·82$ (due to the ethoxy-CH_2 protons) and a 8H multiplet centred at $\tau 2·80$ (for the aromatic protons).

When quinone 3 (0·04 mole) and triethyl phosphite (0·3 mole) were heated in absence of solvent at 100° (bath temperature) for 30 min, comparable results were obtained.

4,4'-Biphenylylene tetramethyl bis(phosphate) 6a. A mixture of 4,4'-dihydroxydiphenyl 10 (1·9 g; 0·01 mole), anhydrous K_2CO_3 (10 g) and dimethylchlorophosphonate[24] (7·2 g; 0·05 mole) in dry acetone (200 ml), was refluxed for 24 hr. After removal of the inorganic residue, the volatile materials were evaporated, *in vacuo*. The residue was recrystallized from hexane to give 6a as colour-

less crystals (3·6 g; 90%), m.p. 97–99°. (Found: C, 48·55; H, 5·11; P, 15·61. Calcd. for $C_{16}H_{20}O_8P_2$: C, 47·81; H, 5·02; P, 15·42%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1060 cm^{-1} (P—O—CH_3).[7] The ^{1}H NMR spectrum had a 12H doublet centred at $\tau 6·10$ with $^3HP = 12$ c/s [due to protons of the —P(O)(OCH_3)$_2$ groups] and a 8H multiplet centred at $\tau 2·55$ (for the aromatic protons).

Similarly, compound 10 reacted with diethylchlorophosphonate[25] to give 4,4'-biphenylylene tetraethyl bis(phosphate) 6b as colourless crystals (yield 85%), from hexane, m.p. 72–74°. (Found: C, 52·81; H, 6·37; P, 13·99. Calcd. for $C_{20}H_{28}O_8P_2$: C, 52·44; H, 6·16; P, 13·53%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1040 cm^{-1} (P—O—C_2H_5).[7]

Action of alkali on 5a and 9a. A mixture of 5a (0·5 g) and aq NaOH (20 ml; 10%) was refluxed for 2 hr. After acidification with 10% HCl, the precipitate was collected (0·29 g; 90%), recrystallized from water giving 4-hydroxy-4'-methoxydiphenyl 7a (m.p. and mixed m.p. 183°[26]).

Similarly, 4,4'-dihydroxydiphenyl 10 was obtained (yield 90%) and identified (m.p. and mixed m.p.), upon alkali hydrolysis of compound 9a.

Reaction of trialkyl phosphites with diphenoquinone-dibenzenesulphonimide 12a. A mixture of quinoneimine 12a[15] (1·1 g; 0·0025 mole) and trimethyl phosphite (0·6 g; 0·005 mole) in benzene (30 ml) was refluxed (steam bath) for 30 min. After evaporation of the volatile materials *in vacuo*, the residue was treated with pet. ether then left to cool. The solid product was collected (1·3 g; 90%) and recrystallized from benzene-pet. ether to give dimethyl [4'-(N-methylbenzenesulphonamido)-4-biphenylyl] phenylsulphonyl) phosphoramidate 13a, as colourless crystals, m.p. 132–134°. (Found: C, 55·97; H, 4·76; N, 4·78; P, 5·31; S, 10·63. Calc. for $C_{27}H_{27}N_2O_7PS_2$: C, 55·26; H, 4·64; N, 4·77; P, 5·28; S, 10·93%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1050 cm^{-1} (P—O—CH_3).[7] The ^{1}H NMR spectrum showed 18 aromatic protons as a multiplet at $\tau 1·95$–$2·85$. The protons of the two OCH_3 groups attached to phosphorus appeared as a doublet centred at $\tau 6·16$, with $^3HP = 12$ c/s, and the signal at $\tau 6·78$ (singlet) was due to the 3 protons of the N—CH_3 group.

Similarly, triethyl phosphite reacted with quinoneimine 12a to give diethyl [4'-(N-ethylbenzenesulphonamido)-4-biphenylyl] (phenylsulphonyl)phosphoramidate 13b, as colourless crystals (yield 90%) from chloroform-pet. ether, m.p. 103–105°. (Found: C, 57·54; H, 5·65; N, 4·87; P, 5·05; S, 10·68. Calcd. for $C_{30}H_{33}N_2O_7PS_2$: C, 57·31; H, 5·28; N, 4·45; P, 4·92; S, 10·20%). The IR spectrum showed bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(\gtrdot P\!\!=\!\!O\right)^7$ and at 1050 cm^{-1} (P—O—C_2H_5).[7] No bands were observed in the regions characteristic for the NH and $\gtrdot C\!\!=\!\!N$ group absorptions.

Alkali hydrolysis of dimethyl [4'-(N-methyl-benzenesulphonamido)-4-biphenylyl] (phenylsulphonyl) phosphoramidate 13a. Compound 13a (0·6 g) was boiled with aq NaOH (20 ml; 10%) for 6 hr. After cooling and acidification with 10% HCl, the precipitate was filtered off and recrystallized from ethanol to give N-methyl-4',4'''-

bi[benzenesulphonanilide] **14b** as pale yellow needles (0·3 g; 70%), m.p. 280–282° (dec.). (Found: C, 62·34; H, 4·88; N, 5·64; S, 13·67. Calcd. for $C_{25}H_{22}N_2O_4S_2$: C, 62·69; H, 4·63; N, 5·85; S, 13·39%). [IR: 3200 cm^{-1} (NH)].

Acid hydrolysis of N-*methyl*-4,'4"-*bis*(*benzenesulphon-anilide*) **14b**. A mixture of **14b** (0·5 g) and 10 ml conc H_2SO_4 was heated at 100° (bath temperature) for 4 hr. The resulting solution was cooled, made alkaline with 20% aq NaOH, and extracted with two 50 ml portions of ether. The combined extracts were dried over $MgSO_4$ (anhydrous) and evaporated to dryness. The oily residue was crystallized from pet. ether to give colourless crystals (0·2 g; 85%) of N-methylbenzidine (m.p. and mixed m.p. 83°²⁷).

N,N'-*Dimethyl*-4', 4"-*bis*((*benzenesulphonanilide*) **14c**. A mixture of compound **14b** (0·5 g), anhydrous K_2CO_3 (5 g) and methyl iodide (10 g) in dry acetone (100 ml), was refluxed for 12 hr. After removal of the inorganic residue, the volatile materials were evaporated, *in vacuo*. The residue (0·4 g; 80%) was recrystallized from ethanol to give **14c** as colourless crystals, m.p. 180–182°. Compound **14c** was identical (m.p., mixed m.p. and IR), with that obtained by the following procedure: A mixture of benzidine N,N'-dibenzenesulphonamide **14a**[15] (1·2 g), anhydrous K_2CO_3 (7 g), methyl iodide (20 g) in dry acetone (150 ml) was refluxed for 24 hr, and the mixture was worked up as described above. Compound **14c** (1 g; 80%) was obtained as colourless crystals, m.p. 180–182°. (Found: C, 63·30; H, 4·93; N, 5·98; S, 12·96. Calc for $C_{26}H_{24}N_2O_4S_2$: C, 63·33; H, 4·91; N, 5·68; S, 13·01%). The IR spectrum had bands at 1600 cm^{-1} (aromatic) and at 1180 cm^{-1} ($-SO_2N<$).

Benzidine N,N'-*dimethanesulphonamide* **14d**. To a solution of benzidine (18·4 g; 0·1 mole) in dry pyridine (100 ml) was added methanesulphonyl chloride (23 g; 0·2 mole) and the mixture heated at 100° (bath temperature) for 12 hr. The solid product obtained upon pouring the reaction mixture onto crushed ice, was collected, washed with boiling 3N aq HCl then with water, dried and recrystallized from dimethylformamide to give **14d** as colourless crystals (30 g; 90%), m.p. 330–332° (dec). (Found: C, 49·82; H, 4·94; N, 8·68; S, 19·27. Calc for $C_{14}H_{16}N_2O_4S_2$: C, 49·46; H, 4·74; N, 8·24; S, 18·86%). The IR spectrum showed bands at 3230 cm^{-1} (NH), 1600 cm^{-1} (aromatic) and at 1180 cm^{-1} ($-SO_2N<$).

Diphenoquinonedimethanesulphonimide **12b**. A stirred suspension of compound **14d** (10 g; 0·03 mole) in glacial acetic acid (200 ml), was treated with freshly crystallized lead tetraacetate (10 g) and stirring was continued for 12 hr, at room temp. The solid product was collected, stirred with glacial acetic acid (100 ml) then with ethylene glycol (10 ml). It was then stirred with water (300 ml) for 1 hr, and finally with acetone (300 ml) for 2 hr, collected and dried to give **12b** (7·5 g; 75%). The dark red crystals of quinoneimine **12b** decomposed at 240° without melting. Decomposition also occurred when recrystallization of **12b** was attempted in chloroform, acetone or dichloroethane. (Found: C, 49·51; H, 4·29; N, 8·56; S, 18·57. Calc for $C_{14}H_{14}N_2O_4S_2$: C, 49·76; H, 4·18; N, 8·29; S, 18·98%). The IR spectrum had bands at 1600 cm^{-1} (aromatic, 1550 cm^{-1} ($>C=N-$) and at 1180 cm^{-1} ($-SO_2N<$).

Reaction of trialkyl phosphites with diphenoquinone-dimethanesulphonimide **12b**. A mixture of quinoneimine **12b** (1 g; 0·003 mole), trimethyl phosphite (1·2 g; 0·01 mole) in benzene (30 ml) was refluxed (steam bath) for 30 min. After evaporation of the volatile materials, *in vacuo*, the residue was treated with pet. ether and left to cool. The solid product was collected (1·4 g; 85%) and recrystallized from chloroform-pet. ether to give dimethyl [4'-(N-methylmethanesulphonamido)-4-biphenylyl] methylsulphonyl) phosphoramidate **13c** as colourless crystals, m.p. 155–157°. (Found: C, 44·06; H, 5·16; N, 6·48; P, 6·49; S, 13·96. Calc for $C_{17}H_{23}N_2O_7PS_2$: C, 44·10; H, 5·01; N, 6·05; P, 6·70; S, 13·85%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(>P=O\right)$[7] and at 1050 cm^{-1} (P—O—CH$_3$).[7] The ^{1}H NMR spectrum showed (a) $\tau = 7·10$ and $\tau = 6·58$ (for protons of the SO$_2$CH$_3$ groups, 2 singlets), (b) $\tau = 6·61$ (for the N—CH$_3$ protons, singlet), (c) $\tau = 6·10$ [for protons of the P(O) OCH$_3$)$_2$ groups, doublet with ^{3}HP = 12 c/s] and (d) τ 2·42 (for the aromatic protons, multiplet). The integration ratio is 6:3:6:8.

Similarly, triethyl phosphite reacted with quinoneimine **12b** to give diethyl [4'-(N-ethylmethanesulphonamido)-4-biphenylyl] (methylsulphonyl) phosphoramidate **13d**, colourless crystals (yield 85%) from benzene-pet. ether, m.p. 79–81°. (Found: C, 47·68; H, 5·43; N, 5·32; P, 6·53; S, 13·13. Calc for $C_{20}H_{29}N_2O_7PS_2$: C, 47·56; H, 5·79; N, 5·55; P, 6·13; S, 12·70%). The IR spectrum had bands at 1600 cm^{-1} (aromatic), 1290 cm^{-1} $\left(>P=O\right)$[7] and at 1050 cm^{-1} (P—O—C$_2$H$_5$).[7]

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