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NUCLEOPHILIC 1,2-ADDITIONS TO THE CARBONYL GROUP OF *p*-QUINONES

HYDROLYSIS AND ALCOHOLYSIS OF THE PENTAOXYPHOSPHORANES DERIVED FROM THE CONDENSATION OF α-DIKETONES WITH *p*-QUINONES BY MEANS OF TRIALKYL PHOSPHITES[1]

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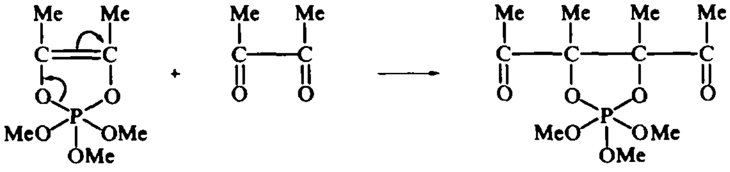
Abstract—The tendency of certain nucleophiles to perform 1,2-additions to the CO group of *p*-quinones has been demonstrated. The nucleophile was 2,2,2-trimethoxy—4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene, made from biacetyl and trimethyl phosphite. The products of the 1,2-additions to *p*-benzoquinone and to 1,4-naphthoquinone were derivatives of the 2,2-dihydro-1,3,2-dioxaphospholane ring system with pentacovalent phosphorus. These pentaoxyphosphoranes were converted by one equivalent of water into biacetyl, methanol and the phosphate ester of the corresponding hydroquinone. Methanol induced a molecular rearrangement of the pentaoxyphosphoranes; the products were methyl acetate, trimethyl phosphate and the *p*-acetyl-phenols, i.e. acetophenone and 1-hydroxy-4-acetyl-naphthalene, respectively.

INTRODUCTION

THE ability of 2,2,2-trimethoxy-4,5-dialkyl-2,2-dihydro-1,3,2-dioxaphospholenes, I, to act as nucleophiles was first reported[2] in 1962.



I: ∂P^{31} = +48·9 ppm *vs.* H_3PO_4

IIa: *cis* Me/Me; ∂P^{31} = +54·8 ppm

IIb: *trans* Me/Me; ∂P^{31} = +52·6 ppm

This discovery was a corollary of the previous observation to the effect that one mole of trialkyl phosphite caused the condensation of two moles of the α-diketone acenaphthenequinone.[3] The product of this condensation was a derivative of the 2,2-dihydro-1,3,2-dioxaphospholane ring system (V). It was reasoned that the 2:1-adduct V was formed by reaction of the 1::1-adduct, III or IV, with a second molecule of acenaphthenequinone. It was not possible to establish if the 1:1-adduct in this case was an open dipolar structure III or a cyclic pentaoxyphosphorane IV.

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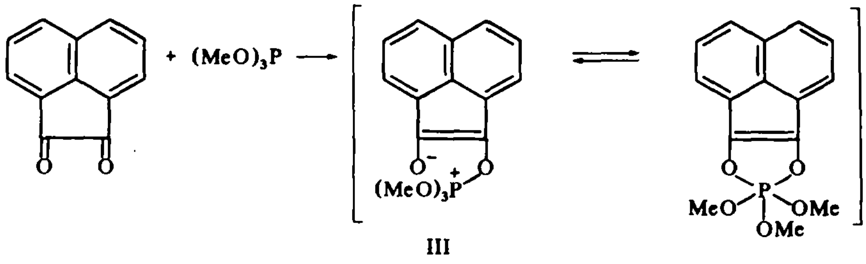
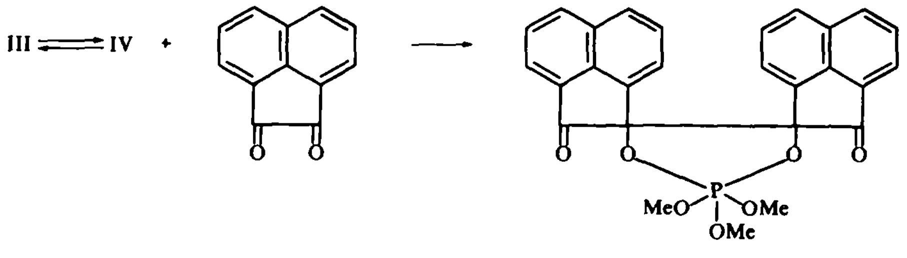
* This investigation was supported by Public Health Service Grant, CA-04769 from the National Cancer Institute.



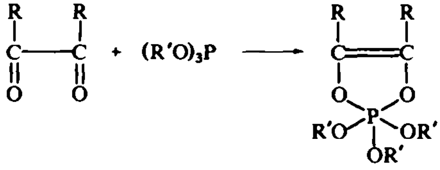
III

IV



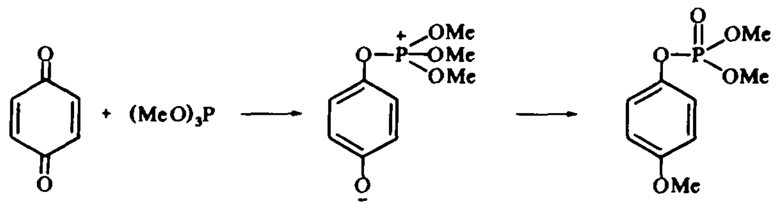
V: $\partial P^{31} = +48{\cdot}0$ ppm

The derivatives of the 2,2-dihydro-1,3,2-dioxaphospholene ring system (I) were made from the reaction of trialkyl phosphites with α-diketones and with *o*-quinones.[4] This reaction was reported independently by three different groups of investigators,[4–6] Recent work has shown the generality of the formation of phospholenes of type VI from the reaction of trialkyl phosphites with vicinal polycarbonyl compounds.[7]



VI

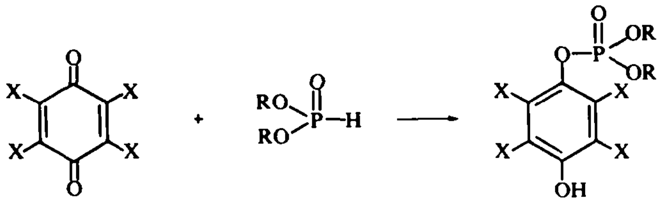
Our studies of the reactions of trialkyl phosphites with α-diketones and with *o*-quinones were suggested by the observation that the phosphorous of trialkyl phosphites attacked the CO oxygen of *p*-quinones.[8] This reaction was first described in 1957 and provided a new route to monoalkyl ethers of *p*-quinol phosphates (VIII).[8]



VII

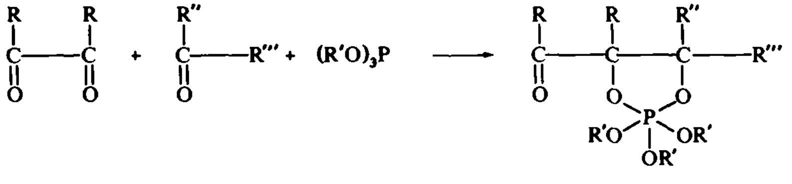
I: $\partial P^{31} = +3{\cdot}7$ ppm

The phenolic *p*-quinol phosphates (IX) were made, at about the same time, by the reaction of dialkyl phosphites (dialkyl hydrogenphosphonates) with *p*-quinones.[9]



IX

The present paper relates several of these observations and is concerned with the condensation of α-diketones with *p*-quinones by means of trialkyl phosphites. Other investigations from this laboratory[10] had shown that trialkyl phosphites could be used to condense α-diketones with a variety of monocarbonyl and of polycarbonyl compounds.



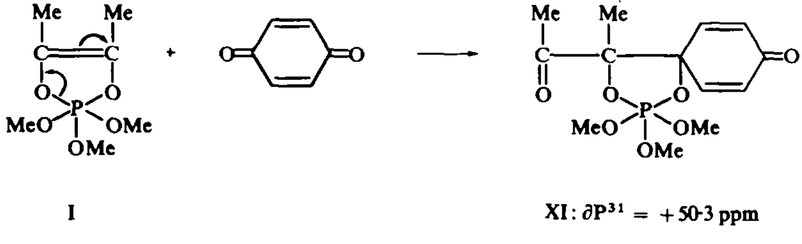
X

It seemed desirable to study the addition of phospholenes of type I to *p*-quinones because no authentic products of nucleophilic 1,2-addition to the CO carbon of *p*-quinones had been reported. Bishop *et al.*[11] provided indirect evidence that bisulfite ions and hydroxide ions were capable of performing reversible nucleophilic 1,2-additions to the CO carbon of *p*-quinones. However, the adducts could not be isolated and, therefore, their structures could not be established unequivocally.

RESULTS

Reaction of 2,2,2-*trimethoxy*-4,5-*dimethyl*-2,2-*dihydro*-1,3,2-*dioxaphospholene* (I) *with* p-*quinones*

The phospholene I added to *p*-benzoquinone at 20° in methylene chloride solution. The crystalline adduct which was isolated from this reaction in nearly quantitative yield was assigned the pentaoxyphosphorane structure XI.



I

XI: $\partial P^{31} = +50{\cdot}3$ ppm

The IR spectrum of adduct XI is reproduced in Fig. 1. The bands at 5·84, 5·98 and 6·13 μ are entirely consistent with the presence of the acetyl and the cyclohexadienone groupings. The UV spectrum had a max at 230 mμ with a relatively high extinction coefficient, ε = 9600.

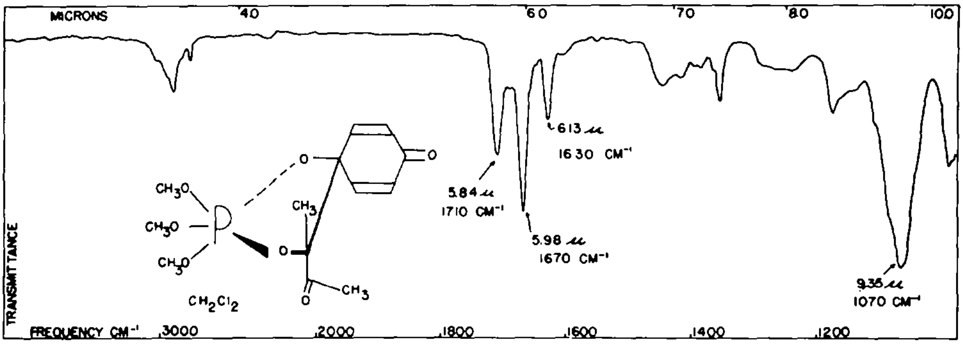


FIG. 1.

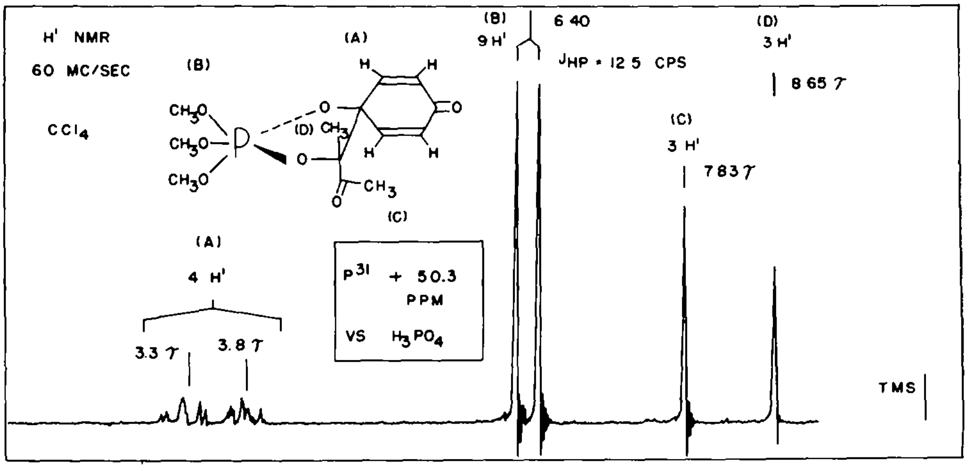
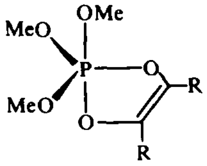


FIG. 2.

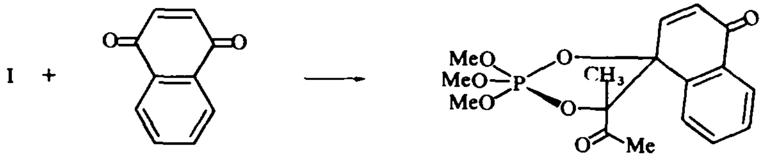
The ^{1}H NMR spectrum of the adduct is shown in Fig. 2; it is in good agreement with the proposed structure. Note the singlets due to the Ac and the Me groups attached to the phospholene ring, and the doublet due to the three magnetically equivalent or indistinguishable OMe groups attached to the phosphorus. The doublet is due to H-P coupling, and the apparent equivalence of the three OMe groups is analogous to the equivalent situation observed in a rather large number of pentaoxyphosphoranes.

The positive value of the ^{31}P NMR shift is characteristic of structures having 5 oxygens covalently bound to the phosphorus. X-ray analysis of a related pentaoxyphosphorane has shown that compounds of this type have the configuration of trigonal bipryramids, XII, in the crystalline state.[12] The phosphorus was at the center of the bipyramid and the 1,3,2-dioxaphospholene ring was situated in an apical-equatorial plane. In solution, the three OMe groups apparently underwent relatively rapid positional exchange at 20°, and even at −70°, as shown by the ^{1}H NMR spectrum.[10, 13]*



XII

The phospholene I reacted very slowly with 1,4-naphthoquinone at 0° in methylene chloride. The reaction was carried out also at 20°. It was found that the rate of formation of the adduct, XIII, was only slightly greater than the rate of its decomposition. Therefore, the reaction of the phospholene with the naphthoquinone was allowed to proceed only to 60% completion and the adduct XIII was isolated as described in the Experimental.



XIII: $\partial P^{31} = +50$ ppm

The spectral data were consistent with the pentaoxyphosphorane structure. This compound was significantly less stable than the corresponding p-benzoquinone adduct, both in solutions and in the solid state.

Two diastereomers are possible for the oxyphosphorane structure, but only one could be characterized. Its configuration was not established with certainty; however, the ^{1}H NMR spectrum suggested that the acetyl group was *cis* to the Ph ring as shown in XIII. Thus, the Ac signal was at a significantly higher magnetic field, τ 8·34, in XIII than in the p-benzoquinone analog XI, τ 7·83. On the other hand, the Me groups attached to the phospholene ring gave comparable signals in both compounds, i.e. τ 8·56 in XIII and τ 8·65 in XI. The upfield shift of the Ac signal is probably due to the shielding of the protons by the benzene ring.

Hydrolysis of the trimethyl biacetylquinone-phosphite adducts

When a 2M solution of the biacetyl-p-benzoquinone-phosphite adduct, XI, in methylene chloride was treated with *one mole equivalent* of water, methanol, biacetyl and dimethyl p-hydroxyphenyl phosphate (XIV) were produced.

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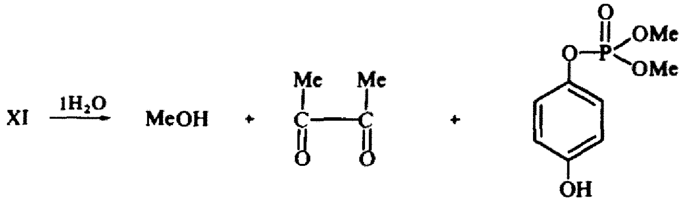
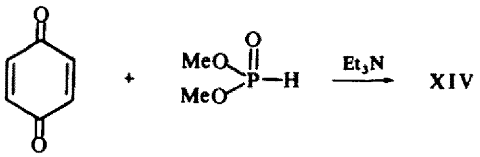
[*] Apparently, cyclic tetraoxyalkylphosphoranes, unlike cyclic pentaoxyphosphoranes, showed magnetic non-equivalency of the three OMe groups at −67°, but not at 20°.[13]

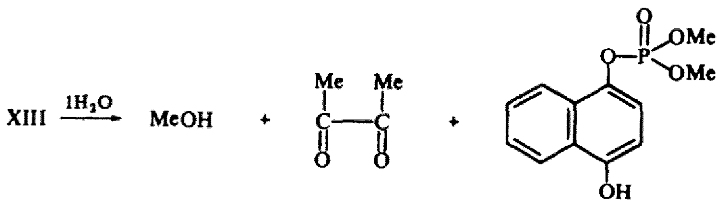


XIV: $\partial P^{31} = +4{\cdot}1$ ppm

The three substances were formed in equimolar amounts and in nearly quantitative yields. The *p*-quinol phosphate, XIV, was made, independently, from *p*-benzoquinone and dimethyl phosphite.[9,14,15]



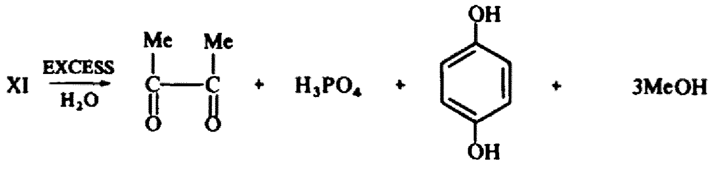
Hydrolysis of the biacetyl-1,4-naphthoquinone-phosphite adduct with *one mole equivalent* of water in benzene solution gave methanol, biacetyl, and dimethyl 4-hydroxy-1-naphthylphosphate (XV).



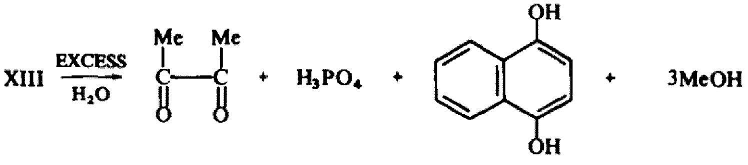
XV

The addition of a *large excess of water* to the benzene solutions of the pentaoxyphosphoranes, XI and XIII, gave different products than those obtained in the hydrolyses with one mole equivalent of water.

With excess of water the products were biacetyl, phosphoric acid and the corresponding *p*-quinols, i.e. hydroquinone (XIV) and 1,4-dihydroxynaphthalene (XVII). It was independently shown that the phosphate esters XIV and XV derived from hydroquinone and 1,4-dihydroxynaphthalene, respectively, did not undergo hydrolysis under the conditions of these experiments. Therefore, the mechanisms of the hydrolyses of the pentaoxyphosphoranes were significantly different when one mole equivalent of water and when an excess of water were used. Possible mechanisms are proposed in the Discussion.



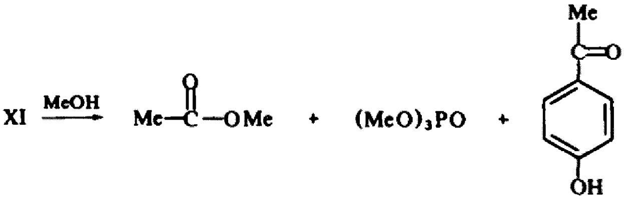
XVI



XVII

Methanolysis of the trimethyl biacetylquinonephosphite adducts

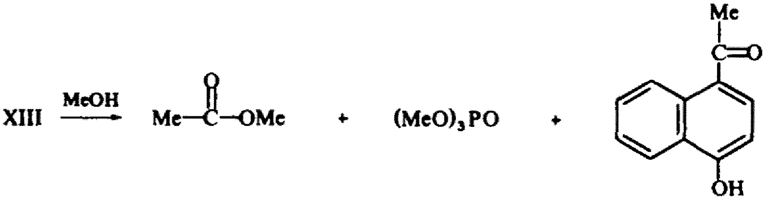
An exothermic reaction was observed when the *p*-benzoquinone-adduct, XI, was treated with an excess of methanol at 20°. The products were methyl acetate, trimethyl phosphate and *p*-hydroxyacetophenone, XVIII.



XVIII

This interesting molecular rearrangement was significantly faster in methanol than in ethanol. The reaction was quite slow in t-butyl alcohol; in this solvent, no visible reaction occurred up to 80°, when the mixture turned dark brown. The formation of about 20% of t-butyl acetate was demonstrated, but no other crystalline products were isolated.

Methanolysis of the naphthoquinone adduct gave methyl acetate, trimethyl phosphate and 4-hydroxy-1-acetyl-naphthalene (XIX).

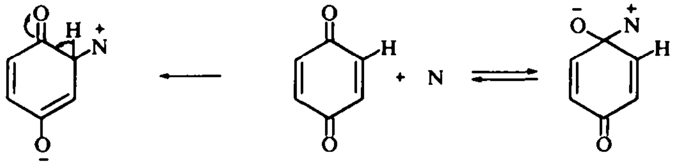


XIX

DISCUSSION

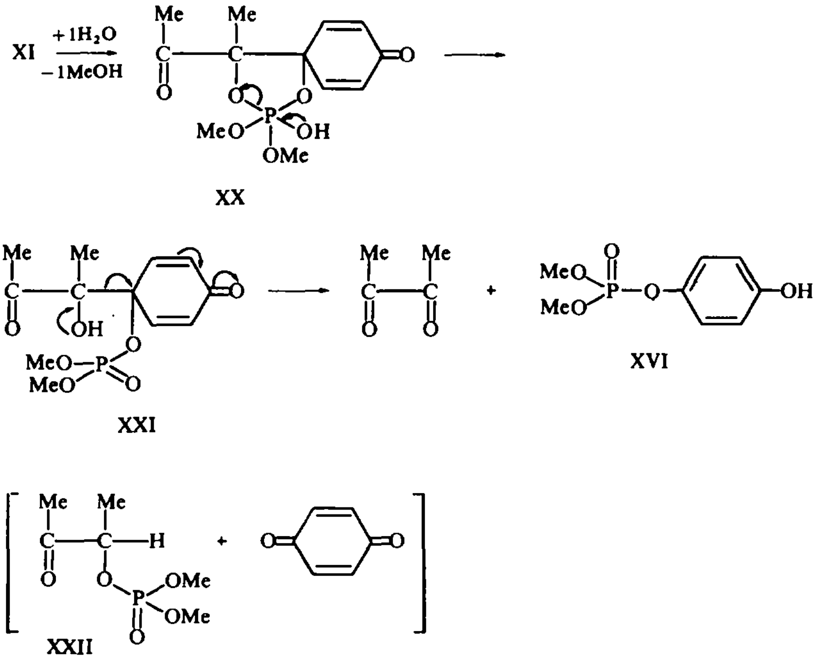
This investigation showed that nucleophiles can, indeed, add to the CO group of *p*-quinones to form relatively stable products of 1,2-additions.[11, 16] The 2,2-dihydro-

1,3,2-dioxaphospho*lene* system is particularly suitable for the demonstration of this phenomenon because the products of the 1,2-carbonyl additions are stabilized in the form of the 2,2-dihydro- 1,3,2-dioxaphospho*lane* system. It may be that many nucleophiles, N, add *reversibly* to the CO of *p*-quinones but end up finally as the more stable products of the 1,4-additions of the nucleophile to the carbon of the quinone, i.e. 1,4-addition.



The results of the hydrolyses and of the methanolysis of the pentaoxyphosphorane were of considerable interest. The following mechanisms explain our results satisfactorily.[17]

The nucleophilic attack by one equivalent of water on the cyclic pentaoxyphosphorane in solvents of low polarity should lead to a cyclic hydroxytetraalkoxyphosphorane XX. The latter should collapse to the observed products, biacetyl and dimethyl *p*-hydroxyphenylphosphate (XIV) as shown. The intermediate, XXI, is a quinonoid α,β-dihydroxyketone and should decompose rapidly to the observed products, i.e. the diketone and the *p*-quinol phosphate. The hydrolysis may be a concerted process not involving XXI as an *intermediate* at all. The alternate mode of cleavage of the phosphorane XX to quinone and dimethyl phosphoacetoin (XXII) is, evidently, a less favorable reaction.



XX

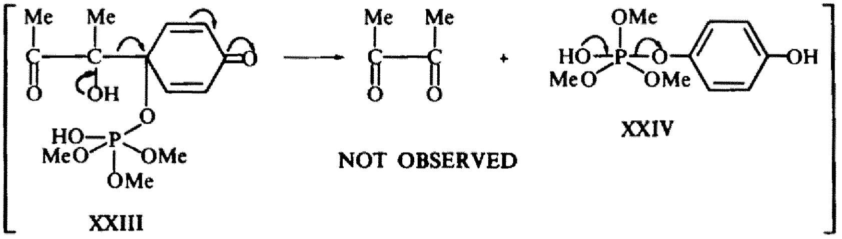
XXI

XVI

XXII

NOT OBSERVED

Note that the 5-membered ring of the pentaoxyphosphorane, XI, did not open during the replacement of the OMe group by water.[*] If this had happened, the product would have been the open-chain hydroxytetraalkoxyphosphorane, XXIII. The latter should collapse to biacetyl and the phosphorane XXIV. Since hydroquinone is a stronger acid than methanol, the phenoxide anion is a better "leaving group" than methoxide and, consequently, the phosphorane XXIV should collapse to trimethyl phosphate and hydroquinone, which is contrary to the facts.



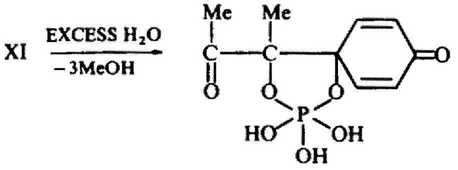
XXIII

NOT OBSERVED

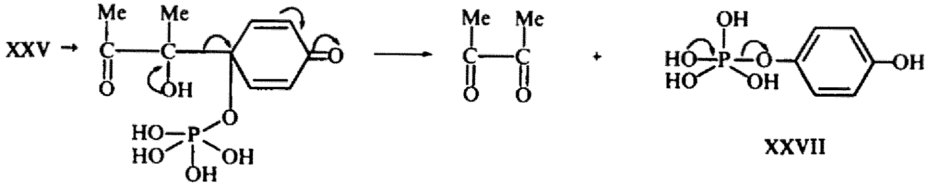
XXIV

It is known that the reaction of trimethyl phosphite with *p*-benzoquinone gave, *in the presence of water*, trimethyl phosphate and hydroquinone. This is to be expected from the hydrolysis of intermediate VII previously shown. The latter becomes XXIV on addition of water.

If the hydrolyses are carried out using an excess of water, all the OMe groups should be rapidly replaced, leading first to the formation of a cyclic trihydroxydialkoxyphosphorane XXV and then to an open tetrahydroxyalkoxyphosphorane, XXVI. The latter should collapse to the observed phosphoric acid and hydroquinone.



XXV



XXVI

XXVII

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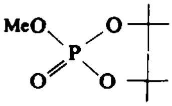
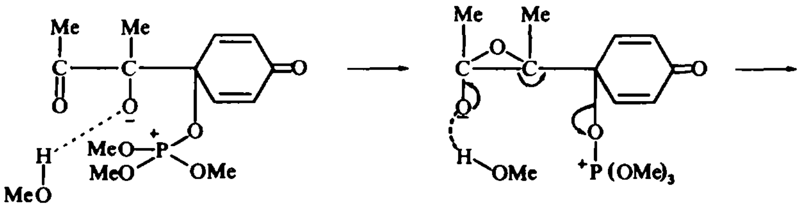
[*] *Note added in Proof.* A possible explanation is as follows. The phosphorane XI is probably a trigonal bipyramid like XII. Water can attack XI at the triangular plane defined by the three CH_3O-groups. This attack would produce the phosphorane XX, with the hydroxy at the optical position (compare with XII). If this hydrolytic mechanism is to result in the open phosphorane XXIII, compression of the 90° O—P—O angle in the phospholene ring would be required in the transition state and/or intermediate for the conversion of XI to XXIII.

The cyclic hydroxytetraalkoxyphosphorane, XX, can collapse with retention of the ring to yield the cyclic phosphotriester XXVIII. This has been observed in a number of related cyclic oxyphosphoranes, for example II.[17] However, it is known[18,19] that the reactivity of 5-membered cyclic phosphate esters toward nucleophiles is extraordinarily high. Therefore, rapid methanolysis of XXVIII to the open phosphotriester XXI would be expected. This methanolysis probably involves an addition of methanol to the phosphoryl group with formation of the common intermediate XX having pentavelent phosphorus.[20]

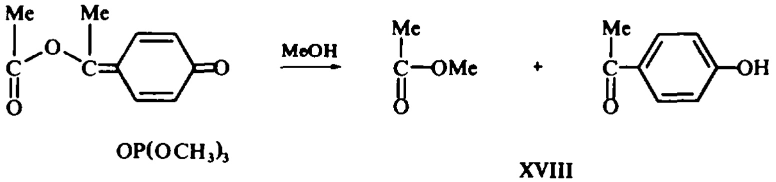


XXVIII

A solvent with a relatively large dielectric constant like methanol, capable also of hydrogen-bonding to the phosphorane, could induce the series of changes shown in formulas XXIX → XXXX → XXXI. Methanolysis of the enol-acetate XXXI should give the observed products, methyl acetate and *p*-hydroxyacetophenone (XVIII).



XXIX XXX

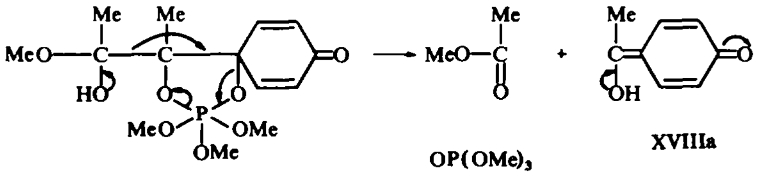


XXXI XVIII

The driving force for this rearrangement is the ejection of a molecule of the stable trimethyl phosphate.

A structure very similar to XXX was suggested by Kuart[21] to explain the formation of an anhydride from the reaction of a peroxyanion with an α-diketone.

Another mechanism for the formation of *p*-hydroxyacetophenone, trimethyl phosphate and methyl acetate from the methanolysis of the oxyphosphorane is shown in formula XXXII.



XVIIIa

XXXII

This involves addition of methanol to the keto group, followed by cleavage of a C—O bond. This mechanism would not involve the formation of an enolacetate intermediate. It was shown that the methanolysis of the pentaoxyphosphorane V made from acenaphthenequinone and trimethyl phosphite gave an enol lactone.[3] This rearrangement is strikingly similar to that observed in the quinone-diketone adducts, XI and XIII. Therefore, the former mechanism, proceeding *via* the enol acetate XXXI is favored.

EXPERIMENTAL

Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. ^{31}P NMR shifts were measured at 40·5 Mc/s; they are given in ppm *vs* H_3PO_4 as zero. ^{1}H NMR were measured at 60 Mc/s; they are given in ppm *vs* TMS = 10 (τ values).

2,2,2-Trimethoxy-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholene (I). Freshly distilled biacetyl was added dropwise, under N_2, to 1·1 mole-equivts of anhyd trimethyl phosphite held at 0–5°. The mixture was allowed to reach 20°, kept there overnight, and then distilled. The colorless phospholene I, n_D^{25} 1·4385, b.p. 45° (0·2 mm) was obtained in 95% yield. It must be protected against moisture and oxygen.

Reaction of the phospholene I *with* p-*benzoquinone*

A soln of 30·4 g (0·280 moles) *p*-benzoquinone in 150 ml CH_2Cl_2 was added over a 10 min period to a soln of 59·0 g (0·280 moles) of the phospholene in 150 ml CH_2Cl_2 at 0°. The soln was stirred for 2 hr at 0°. The solvent was evaporated at 20° (20 mm). The residue was a thick glass which crystallized when kept at −15°. Recrystallization from hexane afforded XI, m.p. 65°, in 90% yield. (Found: C, 48·8; H, 6·3; P, 9·5. $C_{13}H_{19}O_7P$ requires: C, 49·0; H, 6·0; P, 9·7%.) The ^{1}H NMR spectrum had the following signals: multiplets at τ 3·3 and 3·8 (4H), doublet at τ 6·64, J_{HP} = 12·5 c/s (9H), singlet at τ 7·83 (3H), singlet at τ 8·65 (3H). J_P^{31} = +50·3 ppm (in CH_2Cl_2). The IR spectrum had main bands at 5·84 (Ac), 5·98 (dienone C═O), 6·13 (C═C) and 9·35 ($POCH_3$) μ (in CH_2Cl_2). The UV spectrum had λ_{max} = 230 mμ, ε = 9600.

Reaction of the phospholene I *with* 1,4-*naphthoquinone*

A soln of 16·6 g (0·014 moles) 1,4-naphthoquinone in 100 ml CH_2Cl_2 was added all at once to a soln of 22·0 g (0·104 moles) of the phospholene in 100 ml CH_2Cl_2 at 20° with stirring. The soln was stirred 24 hr at 20° and was kept an additional 24 hr at 0°. The solvent was removed in an ice bath at 10 mm press and the residue was immediately treated with 80 ml MeOH, previously cooled to −15°. The mixture was vigorously shaken for a few sec and *immediately* filtered through a coarse synthered glass filter. The colorless crystalline material was quickly washed with two 30 ml portions hexane and dried in a dry N_2 atm (the rate of the reaction of the phospholane with MeOH is sufficiently slow to permit this method of purification). Compound XIII was obtained in 50% yield (19 g). The phospholane underwent rapid decomposition at 20° in the solid state and therefore, it was not submitted to analysis. However, the spectral data disclosed its identity. The H^2 NMR spectrum had the following signals: multiplets at τ 1·84 and 3·62 (6H), doublet at τ 6·25, J_{HP} = 12·0 c/s (9H), singlet at τ 8·34 (3H), and singlet at τ 8·56 (3H). J_P^{31} = +50 ppm. The IR spectrum had main bands at 5·85 (Ac), 5·98 (dienone C═O), and 9·36 ($POCH_3$), μ (in CH_2Cl_2).

*Reaction of the trimethyl biacetyl-*p-*benzoquinonephosphite adduct* (XI) *with one mole-equivalent of water*

Water (1·96 ml) was added, all at once, to a soln of 34·7 g of adduct in 240 ml of benzene at 20°, with stirring. The reaction was exothermic and the soln temp rose 45° within 15 min. Quantitative VPC of the soln showed the formation of equimolar amounts of biacetyl and MeOH in the amounts expected from the complete hydrolysis of XI. The standard for the VPC was made from authentic biacetyl and MeOH in benzene at the concentrations expected. The bulk of the reaction mixture was concentrated at 20° (20 mm) and the residue was recrystallized at −15° from benzene–hexane. Compound XIV was obtained in nearly quantitative yield. The sample had m.p. 71–72° and its spectral characteristics were identical with those of a sample made from *p*-benzoquinone and dimethyl phosphite.

Reaction of the trimethyl biacetyl 1,4-naphthoquinonephosphite adduct (XIII) *with one mole-equivalent of water*

Water (1 mole equiv) was added to a soln of 7·5 g adduct in 80 ml benzene at 20°. Crystals began to separate after 15 min. The soln was submitted to VPC after 45 min; the chromatogram showed the presence of 50–55% of the theoretically expected amount of biacetyl. The soln was filtered and the 3·5 g (50% yield) of XV thus obtained was recrystallized from hexane–ethanol. (Found: C, 53·7; H, 4·8; P, 11·6. $C_{12}H_{13}O_5P$ requires: C, 53·8; H, 4·9; P, %.)

*Reaction of the trimethyl biacetyl-*p*-benzoquinoneophosphite adduct* (XI) *with excess water*

A soln of 14·1 g (0·044 moles) of adduct in 50 ml CH_2Cl_2 was treated with 50 ml water at 20°. The soln was stirred vigorously for 1 hr and was then refluxed for 24 hr. The 2 layers were separated; the water layer was extracted twice with 30 ml CH_2Cl_2, and added to the first CH_2Cl_2 layer. The combined CH_2Cl_2 soln was subjected to VPC, IR, and H^2 NMR analysis, and was shown to contain 90% of the theoretically expected amounts of biacetyl and MeOH. This was done by comparison with CH_2Cl_2 solns containing biacetyl and MeOH in the expected amounts. The water soln was extracted 6 times with 60 ml ether. The ether was evaporated at 20° (20 mm). The residue was a crystalline material which was identified by H^2 NMR spectrometry as hydroquinone. The identify was confirmed by comparison with an authentic sample. The hydroquinone was obtained in 78% of the expected amounts. The remaining water soln was analyzed by means of P^{31} NMR spectroscopy and was found to contain phosphoric acid.

Reaction of trimethyl biacetyl-1,4-naphthoquinonephosphite adduct (XIII) *with excess water*

A soln of 3 g (0·0102 moles) of XIII, in 10 ml CH_2Cl_2 was treated with 20 mole-equivs water. After 10 min crystals had separated out of the stirred soln. Mixed m.p. with authentic 1,4-dihydroxynaphthalene showed no depression.

*Reaction of the trimethyl biacetyl-*p*-benzoquinonephosphite adduct* (XI) *with methanol*

A suspension of 10·9 g (0·034 moles) of adduct in 50 ml MeOH was stirred at 20°. A vigorous exothermic reaction was noted within 15 min; at this point the flask was immersed in an ice bath for 30 min. Finally, the mixture was kept 15 min at 60°. VPC of the MeOH soln showed the formation of MeOAc in nearly quantitative yield; this ester was also characterized by IR analysis. The MeOH was removed at 20° (20 mm) and the residue was seeded with crystals of *p*-hydroxyacetophenone. The mixture was allowed to crystallize giving after filtration 1 g of *p*-hydroxyacetophenone. Short path distillation afforded 3·2 g of trimethyl phosphate and a residue consisting of another 3·15 g of *p*-hydroxyacetophenone. These materials were identified by comparison with authentic samples. The yields of trimethyl phosphate and *p*-hydroxyacetophenone were 93 and 90% respectively.

*Reaction of the trimethyl biacetyl-*p*-benzoquinoneophosphite adduct* (XI) *with ethanol*

A mixture of 19·3 g (0·062 moles) phospholane and 80 ml EtOH were stirred at 20°. In this case, unlike the situation that was observed with MeOH, no exothermic step could be detected. The mixture was stirred for 36 hr. IR spectra and VPC disclosed the formation of biacetyl and EtOAc in about 35% of the expected amounts respectively. The soln was evaporated at 45° (20 mm) and the residue was submitted to short path distillation to remove trimethyl phosphate. The residue was seeded with crystals of *p*-hydroxyacetophenone. The *p*-hydroxyacetophenone was isolated in 40% of the theoretical amount (3 g). The trimethyl phosphate was isolated in 30% yield (3 g).

Reaction of the trimethyl biacetyl-1,4-naphthoquinonephosphite adduct, (XIII) *with methanol*

A suspension of 9·2 g (0·028 moles) phospholane in 30 ml MeOH was stirred at room temp. An exothermic reaction was noted after 5 min at which point the reaction flask was immersed in an ice bath for 30 min. VPC of the MeOH soln showed the formation of MeOAc in 75% of the theoretically expected amount. The solvent was evaporated at 20° (20 mm) and the residue, a thick oil, crystallized when kept at −1° for a few hr. Filtration afforded 3·6 g of 1-hydroxy-4-acetylnaphthalene in 78% yield. The structure of this material was established by comparison of the spectral properties and a mixed m.p. determination with an authentic sample. The trimethyl phosphate was obtained in 85% yield (3·2 g).

Reaction of p*-benzoquinone with dimethyl phosphite (dimethyl hydrogenphosphonate)*

(a) A soln of 7·85 g *p*-benzoquinone in 60 ml benzene was added dropwise, over a 1 hr period, to a soln of 8·6 g (1·1 mole equivs) dimethyl phosphite, $(CH_3O)\,P(O)H$, in 20 ml benzene, containing 5 drops of Et_3N, maintained at reflux temp. The light brown soln was kept an additional hr at reflux and was then evaporated at 20° and 25 mm (finally at 0·1 mm). The spectral properties of the crude crystalline residue

(16 g) were very similar to those of the material obtained after recrystallization from $CHCl_3$-hexane. Pure XIV had m.p. 72–73°. (Found: C, 44·2; H, 5·3. $C_8H_{11}O_5P$ requires: C, 44·9; H, 5·3%.) The ^1H NMR spectrum in $CDCl_3$ had a singlet at τ 1·5 (1H), a multiplet at τ 3·2 (4H) and a doublet at τ 6·20, J_{HP} = 11·5 c/s (6H). $\delta P^{31} = +4{\cdot}1$ ppm. The IR spectrum had bands at: 2·80 (w), 3·10 (m), 6·23 (vw), 6·62 (s), 6·90 (m), 7·8–8·1 (m), 8130 (ms), 9·50 (vs), 10·40 (vs), 11·60 (s) and 11·90 (s).

(b) Quinol phosphate, XIV, of high purity was obtained in high yield when solid *p*-benzoquinone (5·5 g) was added in very small portions to dimethyl phosphite (5·5 g; 1 mole equiv) containing 5 drops Et_3N, at 0°. About one quarter of the quinone was added within 1 hr; the resulting solid mixture was diluted with 20 ml of CH_2Cl_2 and the rest of the quinone (dissolved in 25 ml of CH_2Cl_2) was added dropwise at 0°. The mixture was kept 10 hr at 20°, and was then evaporated yielding 11 g of dimethyl *p*-hydroxyphenyl phosphate melting at 55–65°. Recrystallization gave 8 g of m.p. 72–73° ($CHCl_3$-cyclohexane).

(c) In the absence of Et_3N, a mixture of *p*-benzoquinone (24 g) and dimethyl phosphite (7·4 g), kept 72 hr at 20°, contained a relatively large amount of unreacted quinone. Quinone was still present even after 3 hr at 100° and 20 hr at 20°, in the absence of the amine.

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