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REACTION OF DIETHYLPHENYLPHOSPHINE WITH CHLORANIL

QUINONE-OXYPHOSPHONIUM BETAINES AND QUINONE-BIS-OXYPHOSPHONIUM DIBETAINES, A NEW TYPE OF STABLE PHOSPHORUS YLIDE

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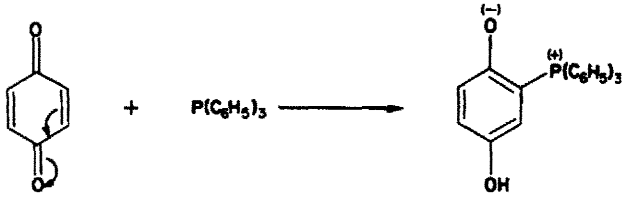
Abstract—Diethylphenylphosphine reacts with *p*-chloranil at a carbon atom and forms a trichloroquinone-C-phosphonium chloride. Triphenylphosphine reacts with chloranil at an oxygen atom and forms an O-phosphonium-phenoxide dipolar-ion. Possible reasons for this difference are discussed. The trichloroquinone-phosphonium chloride serves as starting material for a new type of stable, coloured phosphorus ylide: dichloro- and hydroxychloro-quinoneoxyphosphonium betaines and quinone-bisoxyphosphonium dibetaines. IR and UV spectra and p*K*-values are given. The P^{31} NMR shifts of these and of other stable P-ylides are given.

INTRODUCTION

THE first observable product of the reaction of triphenylphosphine with p-*benzoquinone* is the C-phosphoniumquinol betaine,[3] (I). This is formed, presumably, by a proton shift in the intermediate which results from a 1,4-addition of *phosphorus to carbon.*[3,4]



I

The reaction of triphenylphosphine with p-*chloranil* takes a different course.[3] Now, the final product is the O-phosphoniumphenoxide dipolar-Ion (II) which results from an attack by *phosphorus on oxygen.*[3]

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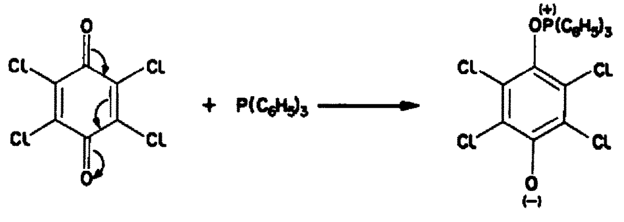
[2] Du Pont Postgraduate Teaching Assistant and U.S. Rubber Fellow at Columbia University. From part of the Ph.D. Thesis of D. R. to Columbia University, 1961.

[3] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.* **78**, 5614 (1956).

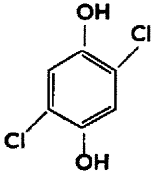
[4] A structure with P—C bond for the *p*-benzoquinone-triphenylphosphine adduct was also proposed by H. Hoffman, L. Horner and G. Hassel, *Chem. Ber.* **91**, 58 (1958), replacing the previous formulation with a P—O bond given in pp. 79 and 94 of L. Horner and K. Klupfel, *Liebigs Ann.* **591**, 69 (1955) and other Ref. therein.



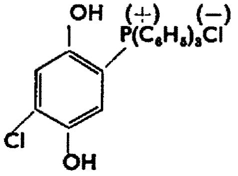
II

The reaction of chloranil with triphenylphosphine generates a red colour and an electron spin resonance spectrum during the early stages of the reaction[3,5] in certain solvents. The nature of the species responsible for these phenomena has been elucidated recently.[6]

Both, carbon-attack and oxygen-attack, were observed in the reaction of triphenylphosphine with 2,5-dichloro-*p*-benzoquinone. The solid that separated when three moles of the phosphine were added to two moles of the quinone in benzene solution had one ionic and three non-ionic chlorines.[3] This solid was converted by water into two moles of triphenylphosphine oxide and one mole each of 2,5-dichlorohydroquinone (III) and triphenyl-(2,5-dihydroxy-4-chlorophenyl) phosphonium chloride (IV).

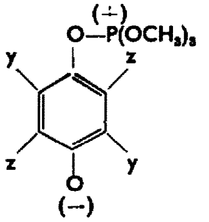


III

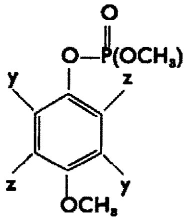


IV

In contrast with triphenylphosphine, trimethyl phosphite attacked the oxygen atom of the three *p*-quinones mentioned above.[5] The final products were methyl ethers of *p*-quinol phosphates (VI) formed, probably, from the intermediate dipolar ions (V).



V



VI

To obtain more information on the effects caused by changes in the structure of the trivalent phosphorus compound in these reactions, we have examined the behaviour of

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[5] [a] F. Ramirez and S. Dershowitz, *J. Org. Chem.* **22**, 856 (1957); [b] *Ibid.* **23**, 778 (1958); [c] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.* **81**, 587 (1959); [d] F. Ramirez, E. H. Chen and S. Dershowitz, *Ibid.* **81**, 4338 (1959).

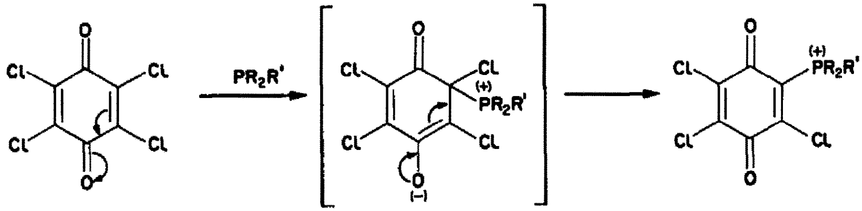
[6] F. Ramirez, V. P. Catto, D. Rhum, S. Dershowitz and E. A. C. Lucken, *Tetrahedron* (1965).

p-chloranil toward diethylphenylphosphine, a relatively strong base[7] and nucleophile.[8] The results are described in this paper.

RESULTS

Reaction of chloranil with diethylphenylphosphine

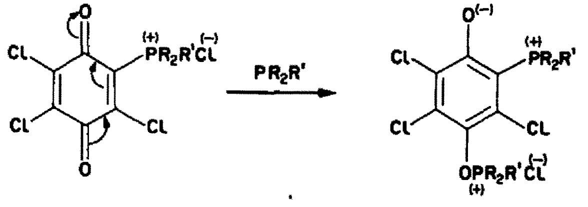
When a benzene solution of chloranil was treated, at 20°, with diethylphenylphosphine, a brown solid precipitated immediately. The formation of this solid ceased after 1·3 to 1·4 mole equivs of the phosphine had been added; any further excess of the latter remained unreacted. The precipitate was mainly 2,3,5-*trichloro*-6-(*diethylphenylphosphonium*)-p-*benzoquinone chloride* (VIII), probably formed *via* intermediate VII).



VII

VIII $\left\{ \begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array} \right.$

A minor component of the precipitate was an adduct containing one mole of the quinone, in a reduced form, and two moles of the phosphine. One of the two phosphorus atoms in this adduct was attached to carbon, since it could not be easily hydrolysed. The other phosphorus was attached to oxygen and could be removed from the adduct by treatment with cold water (*vide infra*). One of the four chlorines present was ionic. The adduct is therefore formulated as the tetrapolar-ion (IX). This could have resulted from an attack by the phosphine on one of the two oxygen atoms of the trichloroquinone-betaine (VIII), which remained in solution. The evidence does not establish which of the two oxygens in (VIII) was attacked, but structure (IX) seems to have a more favourable charge-distribution than its isomer.



VIII IX

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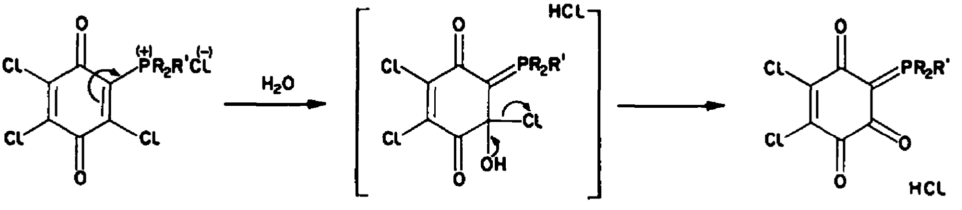
[7] The p*Ka* of dimethylphenylphosphonium chloride is 4·32 and that of dimethylphenylammonium chloride is 4·21, both in 50% ethanol. W. C. Davies and H. W. Addis, *J. Chem. Soc.* 1622 (1937). See also W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.* **82**, 5791 (1960).

[8] Diethylphenylphosphine is said to form a quaternary ethiodide 1000 times faster than diethylaniline. W. C. Davies and W. P. G. Lewis, *J. Chem. Soc.* 1599 (1934). See also W. A. Henderson and S. A. Buckler, *J. Amer. Chem. Soc.* **82**, 5794 (1960).

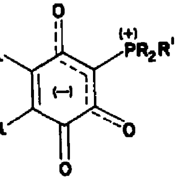
The original brown precipitate formed from diethylphenylphosphine and chloranil was hygroscopic; exposure to moisture led to evolution of hydrogen chloride and formation of a bright-red solid. Consequently, the precipitate was treated with water at 20°, and the resulting products were separated by fractional crystallization. The major product, obtained in 70–75% yield was the red ylide, 2,3-*dichloro*-5-*oxy*-6-(*diethylphenylphosphonium*)*benzoquinone betaine* (XIa). This ylide could have been formed *via* intermediate X.



VIII X XIa $\left\{\begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array}\right.$

Formula (XIa) is one of the several possible resonance structures and brings out the *triketoalkylidenephosphorane* character of the red substance.

A convenient way of representing this new type of stable phosphorus ylide is shown in formula (XI). This structure is based on the following data. The substance had molecular formula $C_{16}H_{15}PCl_2O_3$. Its IR spectrum had a band at 5·9 μ (Fig. 1), which is attributed to one of the carbonyl groups. There was a very strong band at 6·3–6·4 μ which is typical for the "enolate" carbonyl of acylphosphine-methylenes. For example, triphenylbenzoylmethylenephosphorane[9] has its carbonyl at 6·6 μ.



XI

The P^{31} NMR spectrum of the dichloro-ylide (XI) had a signal at (CH_2Cl_2) $\delta P^{31} = -25{\cdot}6$ ppm *vs* 85% H_3PO_4. The significance of this value will be discussed below.

The UV absorption spectrum of the red compound is given in Table 1. The maximum at 441 mμ could be related to an "ortho-quinone" chromophore.

The ylide (II) is a very weak base. The p*K* value for the corresponding acid-base equilibrium will be discussed below, and is consistent with the structure given.

In addition to the red ylide (XI), a colourless substance was isolated in 20% yield from the action of water on the original brown precipitate. This proved to be 2,3,5-*trichloro*-6-(*diethylphenylphosphonium*)*hydroquinone chloride* (XIII). In addition, *diethylphenylphosphine oxide* was obtained. Isolation of these substances forms the basis for structure (IX) assigned to the tetrapolar adduct.

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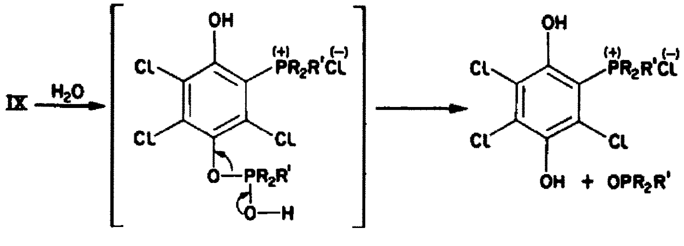
[9] [a] F. Ramirez and S. Dershowitz, *J. Org. Chem.* 22, 41 (1957); [b] F. Ramirez and Z. Hamlet, to be published.



XII XIII

The IR spectrum of this phenol is included in Fig. 1. The UV spectrum and the changes caused in it by acids and bases, are shown in Fig. 2.

Oxidation of the trichlorohydroquinonephosphonium chloride (XIII) with aqueous ferric chloride regenerated the red ylide (XI).

These experiments show that diethylphenylphosphine, unlike triphenylphosphine, tends to attack a *carbon atom* of *p*-chloranil. The dialkylarylphosphine, however, is capable of attacking the *oxygen atom* of a *p*-quinone like (VIII), in which one of the chlorine atoms has been replaced by a phosphonium group.

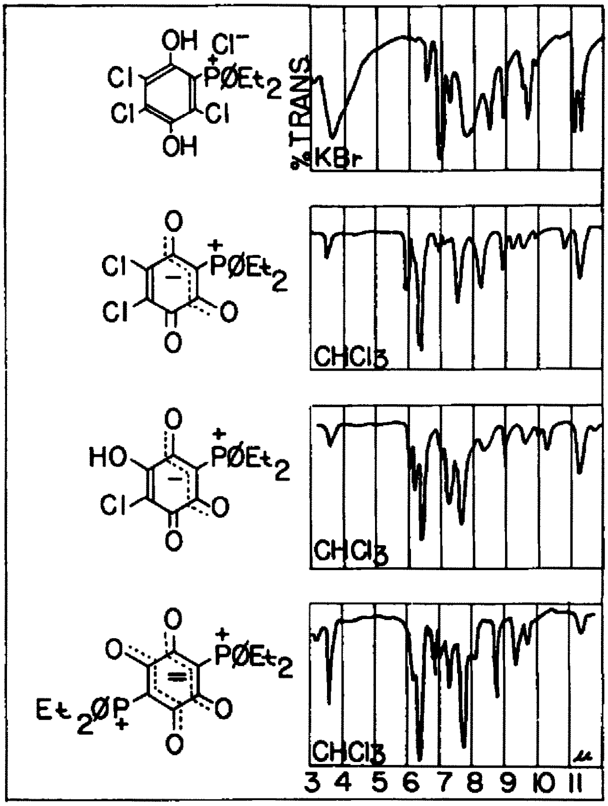


FIG. 1 Infra-red spectra of quinone-oxyphosphonium betaines and of trichlorophosphonium hydroquinone chloride.

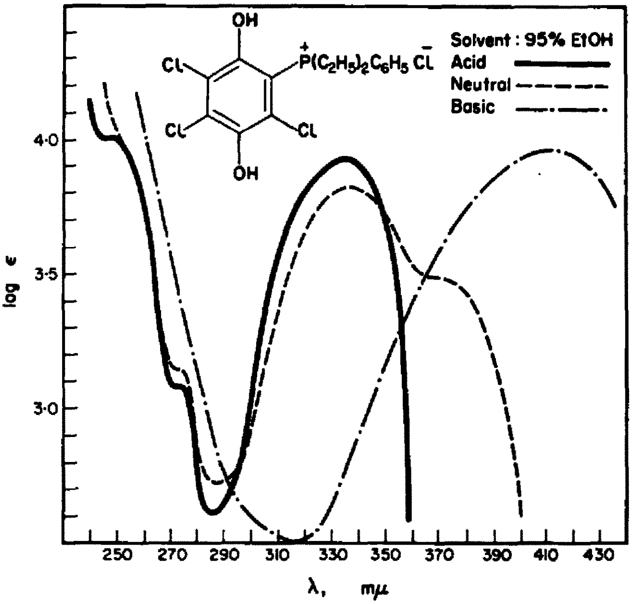
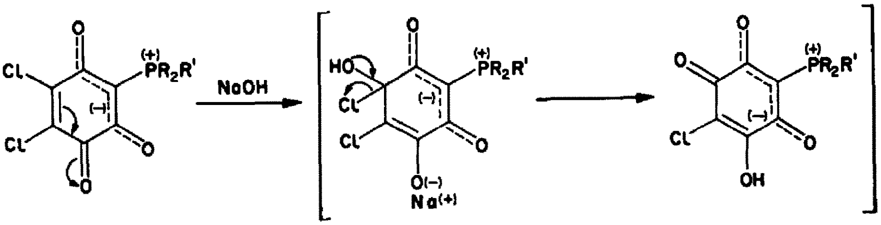


Fig. 2 UV-spectrum of trichlorophosphonium hydroquinone chloride in neutral, acidic and basic ethanol.

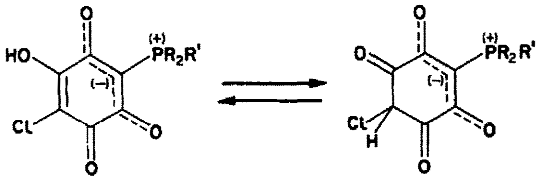
Reaction of the dichloroquinone-oxyphosphonium betaine (XI) *with alkali*

Treatment of the red ylide (XI) with aqueous sodium hydroxide resulted in the replacement of one of the two chlorine atoms by a hydroxy group. The course of this hydrolysis is shown in formulae (XIV) and (XV).



XI XIV XV

The isolated product was a yellow-orange substance, m.p. 182–183°, formulated as 2-hydroxy-3-chloro-5-oxy-6-(diethylphenylphosphonium) benzoquinone betaine (XVI); i.e., a tautomer of (XV). A third tautomer (XVII) is possible in this system.



XVI $\left\{ \begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array} \right.$ XVII

TABLE 1. ULTRA-VIOLET ABSORPTION MAXIMA OF QUINONE-OXYPHOSPHONIUM YLIDES IN CH_2Cl_2

Compound[a]	λ_{max}, mμ	$\varepsilon \times 10^{-3}$
2,3-Dichloro	266	10·7
(XI)	289	13·6
	441	1·13
2-Hydroxy-3-chloro	240	12·9
(XVI)	294	17·9
	423	0·89
2-Oxy-3-phosphonium	267	17·5
Bis-ylide	286	23·6
(XXIII)	296	25·0
	307	19·1
	370	0·51

[a] Substituents on positions 2 and 3 of a 5-oxy-6-diethylphenylphosphonium-1,4-benzoquinone betaine ring.

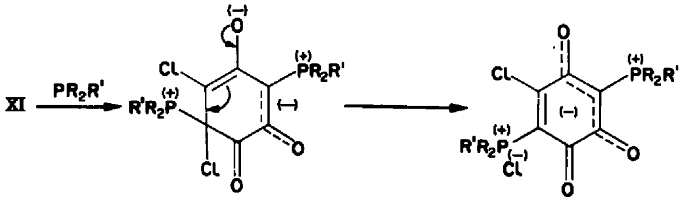
Structure (XVI), with the hydroxy *meta* to the phosphorus, is favoured over that of an isomer with the hydroxy *para* to the phosphorus, for two reasons. The IR band due to one of the carbonyls is at longer wave-length (6·0 μ) in the hydroxychloro—than in the precursor dichloro-quinone oxyphosphonium betaine, (XVI) *vs* (XI) (Fig. 1). In (XVI), but not in its isomer, the hydroxy and the carbonyl groups are conjugated, which would account for the shift to longer wave-length. Furthermore, as shown below, the hydroxychloro-betaine (XVI) was converted into a compound having two phosphorus atoms *para* to each other; therefore, the replaceable chlorine in (XVI) was also *para* to the phosphorus.

The hydroxychloro-betaine (XVI) had its "enolate" carbonyl at 6·3–6·4 μ (Fig. 1). It gave a P^{31} NMR signal at δ (CH_2Cl_2) $P^{31} = -23$ ppm *vs* 85% H_3PO_4; i.e., its nucleus is slightly more shielded by electrons than in the dichloro-betaine (XI). The conjugate acid of (XVI) was a very strong *dibasic* acid (*vide infra*), as expected from this structure.

The UV spectrum of (XVI) is summarized in Table 1.

Reaction of the dichloroquinone-oxyphosphonium betaine (XI) *with diethylphenylphosphine*

When a benzene solution of the red ylide (XI) was treated with diethylphenylphosphine, a bright red precipitate formed immediately. Again, as was the case in the original reaction of chloranil with diethylphenylphosphine, the formation of the solid

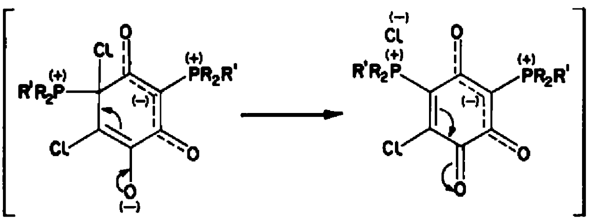


XIX

XVIII $\left\{ \begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array} \right.$

ceased after 1·3 to 1·5 moles of phosphine had been added to 1 mole of the quinone. The major component of the red precipitate was 2-*chloro*-5-*oxy*-3,6-*bis*-(*diethylphenylphosphonium*)-p-*benzoquinone betaine chloride* (XVIII). In this reaction, the chlorine atom *para* to the phosphonium group was replaced by another phosphonium group, probably *via* intermediate (XIX).

A replacement of the *meta*- chlorine in the red ylide (XI) would have resulted in the isomeric betaine chloride (XX), formed *via* intermediate (XXI).

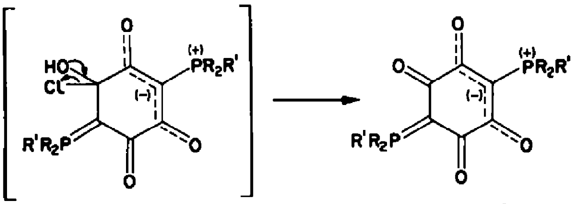


XXI Not formed XX

Structure (XX) is energetically unfavourable relative to (XVIII), as can be seen from the corresponding resonance formulae; two positive charges can be placed in adjacent positions of (XX) but not of (XVIII), which benefits also from additional phosphorane-resonance associated with the second phosphonium group.

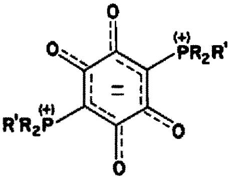
In the reaction of the dichloro-ylide (XI) with aqueous sodium hydroxide, the chlorine atom *meta* to the phosphonium group was replaced by a hydroxy group. It should be noted that the addition of a nucleophile to the *meta*-carbon of (XI) to give intermediates (XXI) or (XIV), does not disturb the extended ylide-resonance involving the phosphonium group and the two adjacent oxygen atoms; this type of addition should, therefore, be more favourable than the addition to the *para*-carbon to give intermediate (XIX). However, the phosphine reaction, unlike the hydroxide ion reaction, is probably reversible, and the less favourable path, (XI) → (XIX) → (XVIII) leading to the more stable product could be preferred over the more favourable path, (XI) → (XXI) → (XX), leading to the less stable product.

The choice of structure (XVIII) over structure (XX) for the betaine chloride is based on the results of hydrolysis experiments. The precipitate formed from diethylphenylphosphine and the dichloroquinone ylide (XI) was hygroscopic and evolved hydrogen chloride in contact with moist air. When this precipitate was treated with water two substances were isolated. The major product was the light yellow 2,5-*dioxy*-3,6-*bis*-(*diethylphenylphosphonium*)*benzoquinone bis betaine* (XXIIIa), m.p. 331–332°, resulting from (XVIII) as shown in formula (XXII).

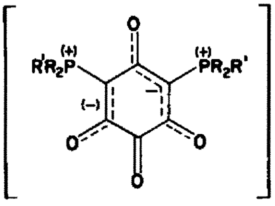


XXII XXIIIa $\left\{\begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array}\right.$

A convenient representation of the bis-oxyphosphonium betaine is (XXIII). Structure (XXIII) with *four equivalent oxygens*, rather than structure (XXIV), with three different types of oxygen-functions, is supported by the IR spectrum given in Fig. 1, which shows only one very strong carbonyl-band at 6·35 μ.



XXIII



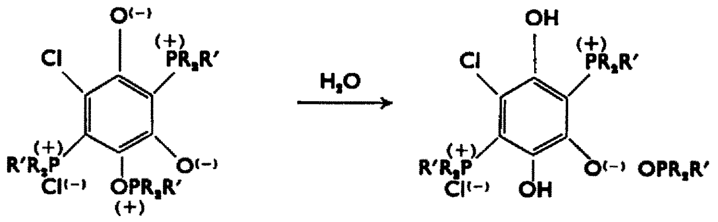
XXIV Not formed

The P^{31} NMR spectrum of the bisylide (XXIII) could be determined only in trifluoroacetic acid, where $\delta P^{31} = -26$ ppm. There appeared to be only one type of phosphorus in the molecule. The bisylide (XXIII) as discussed below, is a very weak base, therefore, the signal that was detected in the P^{31} NMR spectrum corresponds apparently to the phosphorus of the ylide and not of its conjugate acid.[10]

The pK-measurements also support structure (XXIII) for the bis-ylide. The UV spectrum of (XXIII) is summarized in Table 1.

The hydrolysis of the precipitate formed from diethylphenylphosphine and the dichloroylide, (XI) afforded small amounts of a colourless phosphonium chloride with a double m.p. 183–186° and 213–214°, probably (XXVI). This material discoloured slowly, on exposure to air. Elemental analysis showed a P/Cl ratio of 1. No definite structure is assigned to this substance, but, by analogy with the reaction of the phosphine with chloranil, the following reactions seem plausible:

$$\text{(XVIII)} + R'R_2P \longrightarrow \text{(XXV)} \xrightarrow{H_2O} \text{(XXVI)}$$



XXV XXVI

Reaction of the hydroxychloroquinone-oxyphosphonium betaine (XVI) *with diethylphenylphosphine*

The chlorine atom in this ylide should not be very reactive towards nucleophiles.

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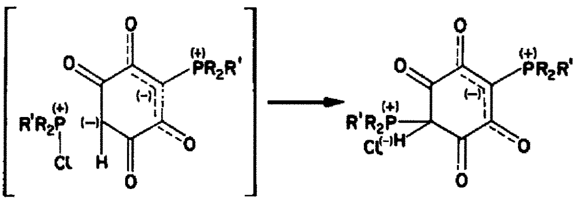
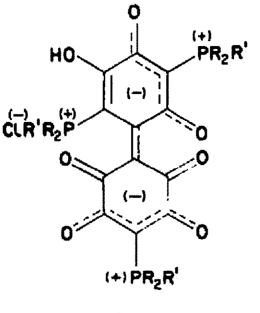
[10] However, it should be noted that among *triphenylphosphine* derivatives, the signal of the ylide is not at a much higher magnetic field than the signal of the corresponding hydrochloride. Thus: triphenylbenzoylmethylenephosphorane, $\delta P^{31} = -16{\cdot}7$ ppm; its hydrochloride, $-20{\cdot}7$ ppm, both in $CHCl_3$. (The figures for this hydrochloride and this ylide given by A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.* **85**, 2790 (1963), are in error.)

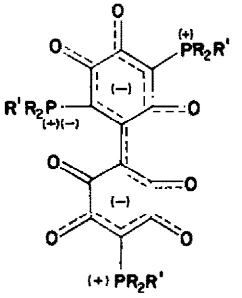
This is more clearly seen in the tautomer (XVII), in fact, the chlorine atom is probably more "positive" than "negative".

A reaction between the hydroxychloro-ylide, (XVI ⇄ XVII) and an excess of the phosphine occurred in boiling toluenne, and gave small amounts of bis-ylide (XXIII). This showed that the chlorine was *para* to the phosphorus in (XVI). A possible path is attack by phosphorus on chlorine to give (XXVII), followed by recombination to (XXVIII) and loss of HCl to bis-ylide (XXIII).

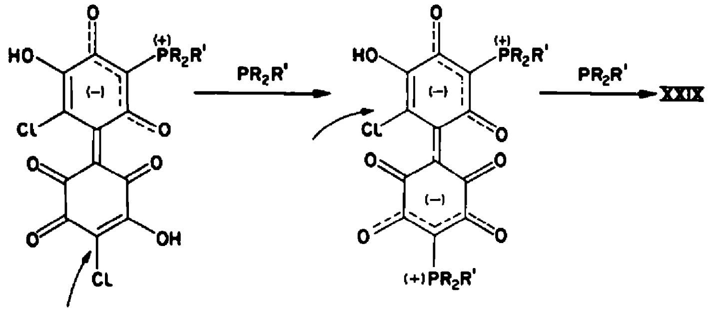

XXVII XXVIII

The major product of the reaction of hydroxychloroylide (XVI) with diethylphenylphosphine was a purple solid m.p. 251–254°. This substance turned blue in alkali and orange in acid; the colour-changes appeared to be reversible. The methylene chloride solution of the crystals had maxima at 260 mμ ($\varepsilon = 1{,}700$), 299 mμ (1,400), 378 mμ (700) and 515 *mμ* (3,000). The molecular extinction coefficients are based on formula $C_{42}H_{48}P_7P_3Cl$, established by elemental analysis and mol. wt. determination. The crystals were soluble in water and also in methylene chloride, but insoluble in acetone. Formula (XXIX) is in agreement with the available data; in particular, the shift to a blue colour in alkali is accounted for by the formation of the conjugate base, a tris-ylide (XXX).


XXIX $\left\{\begin{array}{l} R = C_2H_5 \\ R' = C_6H_5 \end{array}\right.$


XXX

The dimer (XXIX) could arise from a Wittig olefination reaction between two molecules of hydroxychloro-ylide (XVI) to give (XXXI). The latter can react with more phosphine and form the dimer bis-ylide (XXXII). Reaction of this with more phosphine results in the purple compound (XXIX). These types of reactions were observed in the simpler systems discussed earlier in this paper. Further investigation of (XXIX) is in progress.



XXXI XXXII

pK Values of the quinone-oxyphosphonium betaines

Representing the conjugate acid of the dichloro-ylide (XI) as BH^+ and the ylide itself as B, the equilibrium between the two is

$$BH^+ \rightleftarrows B + H^+$$

and

$$pKa = Ho + \log \frac{[BH^+]}{[B]}$$

where Ho is the Hammett acidity function, a measure of the proton-donor power of a medium. The base B is formally neutral, but actually it is a dipolar-ion, i.e. an ylide. The neutralization reaction, therefore, is not of the usual type in which a proton is added to a neutral base or to an anion.

The conjugate acid of the hydroxychloro-ylide (XVI) is a dibasic acid; two equilibria are involved,

$$BH_2^+ \rightleftarrows BH + H^+; \qquad BH \rightleftarrows B^- + H^+$$

The equilibria in the bis-ylide case (XXIII) are

$$BH_2^{++} \rightleftarrows BH^+ + H^+; \qquad BH^+ \rightleftarrows B + H^+$$

Here, again the bases B are dipolar or tetrapolar ions whenever they appear as formally neutral.

pK values can be readily obtained spectrophotometrically, using a graphic method, since, at the mid-point of a titration

$$[BH^+] = [B], \qquad \text{and} \qquad pKa = Ho.$$

The pK values of the ylides are of considerable interest. First, they give information concerning the structure of the compounds themselves. Second, the values can be compared among themselves and with related compounds of known acidity, like chloranilic acid (2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone) and nitranilic acid (2,5-dihydroxy-3,6-dinitro-*p*-benzoquinone). These comparisons provide a way of assessing the significance of ylide-resonance in providing stabilization to systems in which they can occur.

The p*K*'s of the hydroxychloro ylide (XVI) and of the bis-ylide (XXIII) were determined in aqueous-hydrochloric acid; however, the dichloro-ylide (XI) was not sufficiently soluble in water for this purpose. The p*K*'s of the three ylides were then measured in acetic–sulphuric acids. The data required to calculate the p*Ka*'s are given in Figs. 3 and 4 and the p*Ka* values are listed in Table 2.

Evidently, the Ho scale cannot be extended to the acetic acid–sulphuric acid system in the particular case of the ylides since the *p*Ka*'s thus obtained were not identical with the p*Ka*'s obtained in water. The *p*Ka*'s in acetic acid serve, however, to correlate the acidity of the three ylides. It can be seen that the bis-ylide (XXIII) forms the strongest acid and the hydroxychloroylide (XVI) the weakest.

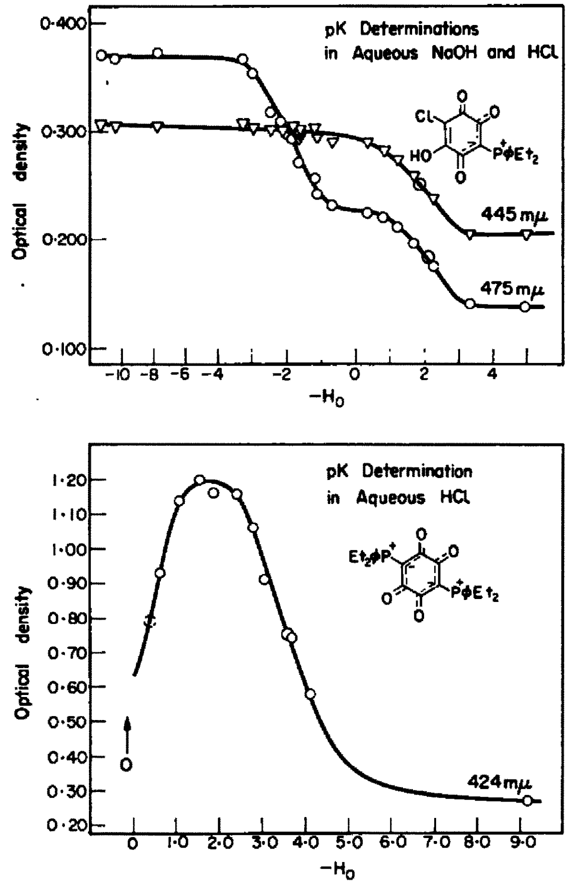


Fig. 3 p*K* Determinations of betaines. Optical density *vs* —Ho. In water.

The p*Ka*1 values for the ionization of the *first proton* in the bis-ylide acid and in the hydroxychloro-ylide acid were accurately determined in water, since both the diprotonated and the monoprotonated forms were sufficiently soluble in water. These acids are quite strong; in fact one of them is even stronger than nitranilic acid (Table 2).

The p*Ka*2 value for the ionization of the *second proton* in the hydroxychloro-ylide

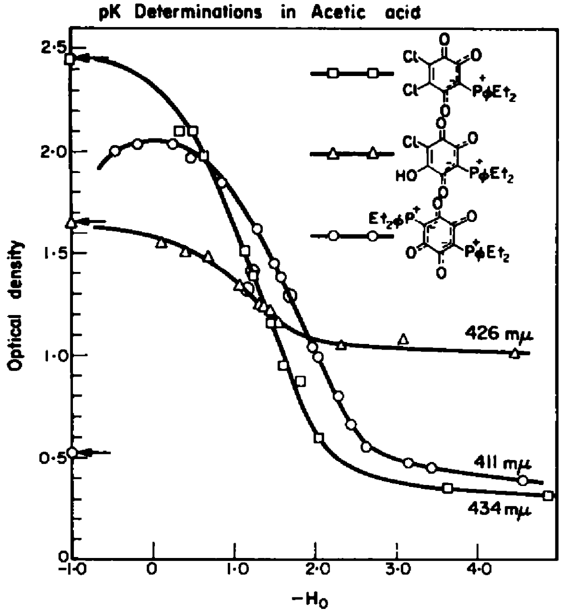


FIG. 4 Optical density *vs* —Ho for quinone-oxyphosphonium betaines in acetic acid-sulfuric acid.

TABLE 2. p*Ka* OF HYDROXYPHOSPHONIUMQUINONES (CONJUGATE ACIDS OF QUINONEOXYPHOSPHONIUM YLIDES) AND OF NITROHYDROXY- AND CHLOROHYDROXYQUINONES

Compound	In H_2O—HCl		In AcOH—H_2SO_4
	p*Ka*1	p*Ka*2	*p*Ka*1
2,3-Dichloro, (XI)	ca. −2·2	—	−1·23
2-Hydroxy-3-chloro, (XVI)	−1·99	+1·94	−1·16
2-Oxy-3-phosphonium (XXIII)	−3·55	ca. −0·4	−1·69
2,5-Dihydroxy-3,6-dinitro[a]	−3·0	−0·5	
2,5-Dihydroxy-3,6-dichloro[a]	+0·85	+3·18	
2,5-Dihydroxy[a]	+2·73	+5·18	

[a] G. Schwarzenbach and H. Suter, *Helv. Chim. Acta* **24**, 617 (1941). See also, J. N. Phillips, *Austr. J. Chem.* **14**, 183 (1961).

(XVI) was also measured with precision, because both species in the equilibrium were water-soluble. The second proton is also fairly strong as an acid. The p*Ka*2 for the bis-ylide acid was estimated only approximately, since the bis-ylide itself was insoluble in water.

The very weak basicity of the ylides shows the stability which is conferred to a molecule by the presence of a phosphonium ion and a highly delocalized negative charge. Part of this stability is undoubtedly due to some phosphorane contribution to the resonance hybrid, but the p*K* values give no information on the extent of this p–d π-bonding in the ylides.

P^{31} *NMR shifts of stable ylides*

The P^{31} chemical shifts of the three ylides are given in Table 3. This table includes also other stable ylides prepared and measured in this laboratory. The shifts are listed in the order of increasing magnetic field, i.e., in the order of increasing shielding of the P^{31} nucleus by electrons.

Ylides derived from trimethyl phosphite ($\delta P^{31} = -140{\cdot}0$ ppm) and from ethyl diphenylphosphinite ($\delta P^{31} = -109{\cdot}8$ ppm) have chemical shifts at much lower magnetic fields than those derived from tri-n-butylphosphine ($\delta P^{31} = +32$ ppm) and triphenylphosphine ($\delta P^{31} = +5{\cdot}7$ ppm). In the first group, the ylides are at higher fields than the corresponding trivalent phosphorus compounds. In the second group, the ylides are at lower fields than the corresponding trivalent phosphorus compound. These trends in the *ylides* parallel those found for the corresponding *oxides*:

$$(CH_3O)_3P{=}O,\ -2{\cdot}5;\quad (C_2H_5O)(C_6H_5)_2P{=}O,\ -31{\cdot}1;$$

$$(n\text{-}C_4H_9)_3P{=}O,\ -43;\quad (C_6H_5)_3P{=}O,\ -26{\cdot}5,\ \text{ppm}$$

P^{31} NMR SHIFTS OF STABLE PHOSPHORUS YLIDES; IN PPM *vs* 85% H_3PO_4·At 40·5 Mc/s

No.	Compound	δP^{31}	Ref.
1	Trimethoxy-benzoylphenacyl-methylenephosphorane	−56·2	11, 13
2	Ethoxydiphenyl-benzoylphenacyl-methylenephosphorane	−54·2	12, 13
3	Quinone-bis-oxyphosphonium ylide	−25·7	*
4	Dichloroquinone-oxyphosphonium ylide	−25·6	*
5	Bromomethylide-bis-triphenyl-phosphonium bromide	−24·7	14
6	Hydroxychloroquinone-oxyphosphonium ylide	−23	*
7	Tri-n-butyl-benzoylphenacyl-methylenephosphorane	−21·3	13
8	Methylide-bis-triphenylphosphonium bromide	−20·4	14
9	Triphenyl-carbethoxy-phenyl-methylenephosphorane	−19·2	9
10	Triphenyl-2-oxocyclohexylidenephosphorane	−17·6	9
11	Triphenyl-carbethoxy-methylenephosphorane	−17·3	9
12	Triphenyl-benzoylphenacyl-methylenephosphorane	−16·9	13
13	Triphenyl-benzoyl-methylenephosphorane	−16·7	9
14	Triphenyl-acetyl-methylenephosphorane	−14·1	9
15	Triphenylphosphoniumcyclopentadienylide	−12·9	15
16	Carbodi-triphenylphosphorane	0	14

* This paper.

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[11] F. Ramirez and O. P. Madan, *Abstracts of the Division of Organic Chemistry*, 148*th National Meeting of the American Chemical Society* p. 13-S, Chicago, Illinois, September (1964).

[12] F. Ramirez, O. P. Madan and C. P. Smith, *J. Amer. Chem. Soc.* **86**, 5339 (1964).

[13] F. Ramirez, O. P. Madan and C. P. Smith, *Tetrahedron Letters* No. 3, 201 (1965).

[14] [a] F. Ramirez, N. B. Desai, B. Hansen and N. McKelvie, *J. Amer. Chem. Soc.* **83**, 3539 (1961); [b] F. Ramirez, N. B. Desai and N. McKelvie, *Ibid.*, **84**, 1745 (1962).

[15] [a] F. Ramirez and S. Levy, *J. Amer. Chem. Soc.* **79**, 67 (1957); [b] *Ibid.* **79**, 6167 (1957); [c] F. Ramirez and S. Levy, *J. Org. Chem.* **23**, 2035 (1958).

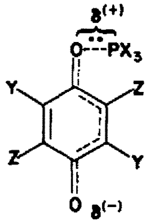
For the same carbon compound, the ylide with three alkyl groups on phosphorus is only at a slightly lower field than the ylide with three phenyl rings on the phosphorus. Therefore, rough comparisons between triphenyl-ylides and diethylphenyl-ylides can be made. The quinone-oxyphosphonium betaines fall toward the more negative or low-field end of the group of phosphine-derived ylides while carbodiphosphorane and triphenylphosphoniumcyclopentadienylide are in the less negative or high-field end.

Although several factors enter into these n.m.r. shifts, the general trend is in the direction to be expected from a relatively low contribution of phosphorane structures i.e. of p-d π-bonding in the quinone-oxyphosphonium betaines.

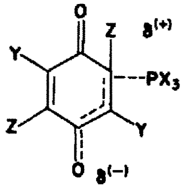
DISCUSSION

The course of the reactions of trivalent phosphorus compounds, PX_3, with complex carbonyl compounds like *o*-quinones,[3,5] *o*-qunions,[16] α-diketones,[16] or α,β-unsaturated ketones,[11–13] will vary with the electronic and the steric characteristics of *both* reactants. In this paper we are concerned only with the reactions of three *p*-quinones (*p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone and *p*-chloranil) with two types of phosphorus compounds: tertiary phosphines and trialkyl phosphites. Several facts must be explained. (1) The phosphorus of trimethyl phosphite attacked the *oxygen* atom of the three *p*-quinones.[5] (2) Triphenylphosphine attacked the *oxygen* of *p*-chloranil,[3] but it attacked the *carbon* of *p*-benzoquinone[3] and of 2,5-dichloro-*p*-benzoquinone.[3] (3) Diethylphenylphosphine attacked the *carbon* of *p*-chloranil.

The transition states for the attack by phosphorus on oxygen and on carbon can be represented by formulae (XXXIII) and (XXXIV), respectively.[17]



XXXIII



XXXIV

Considering first the quinone portion, it can be seen that an attack on oxygen (XXXIII) is favoured by the incipient aromatization, but is, perhaps, discouraged by the larger charge-separation which is generated in the transition state.

Considering, next, the nature of the phosphorus compound, several effects may be operating. Variations in the nature of the substituent X in PX_3 can affect the reactions

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[16] Lit. reviewed by F. Ramirez, *Pure and Applied Chemistry* **9**, 337 (1964).

[17] Transition states (XXXIII) and (XXXIV) could be called *oxophilic* and *carbophilic*, respectively, to emphasize the nature of the atom which is being attacked by the phosphorus. The term *biphilic* transition state has been used by Shaw and his co-workers in an explanation of the direct oxygen transfer from dimethyl sulphoxide to trivalent phosphorus compounds. This would be comparable to the quinone case (XXXIII) if an intermediate were involved in the sulphoxide case. See E. H. Amonoc-Neizer, S. R. Ray, R. A. Shaw and B. C. Smith, *J. Chem. Soc.* (1965). The nature of the chemical bonding in organophosphorus compounds has been disscused by R. F. Hudson, *Pure and Applied Chem.* **9**, 371 (1964) and in Refs. therein.

of PX_3 in several ways,[17] some of which are undoubtedly, interrelated. (a) The nucleophilicity and the basicity of PX_3 will change. (b) The hybridization of the phosphorus will change, both in the ground state of PX_3, and in the transition state of its reaction at oxygen (XXXIII), and at carbon (XXXIV), of the *p*-quinone. The transition state for oxygen-attack (XXXIII) would be favoured to the extent that there is p–d π-bonding involving the phosphorus and the unshared electrons on the oxygen which is being attacked. The extent of this electron delocalization is, in turn, affected by the nature of the substituent X on the phosphorus. This leads to a predominance of oxygen attack (XXXIII) by trimethyl phosphite ($X = OCH_3$) in all the *p*-quinones, since the tetraoxyphosphonium cation, $[\text{—O—}\overset{(+)}{(P)}(OCH_3)_3]$ represents a situation most favourable for p–d π-bonding. The tendency for oxygen-attack diminishes in the case of triphenylphosphine ($X = C_6H_5$) which reacts at oxygen only in the case of *p*-chloranil. This result may be due, in part, to a reluctance of the large phosphine to attach itself to a carbon carrying a chlorine and flanked by another, as in (XXXIV); (note attack on carbon in 2,5-dichloro-*p*-benzoquinone). Finally, diethylphenylphosphine attacks the carbon of *p*-chloranil (XXXIV) probably because of a smaller size and a greater nucleophilicity, i.e. a greater tendency to share the electron-pair on phosphorus with a *carbon* atom.

The three ylides reported in this paper (XI, XVI and XXIII), and the yields previously reported[9,11–15] from this laboratory and listed in Table 3, illustrate various ways in which negative charge can be accommodated in a molecule which carries also a phosphonium cation.

Much work has been reported in recent years on *stable triphenylalkylidenephosphoranes*[18–21] and on the less known *trialkylalkylidenephosphoranes*.[22–29] There are also scattered examples of *trialkoxyalkylidenephosphoranes*.[30,31] Some measurements on P^{31} NMR spectra of ylides have been reported.[32,33]

EXPERIMENTAL

2,3-*Dichloro-5-oxy-6-(diethylphenylphosphonium)benzo-quinone betaine* (XI) *and* 2,3,5-*trichloro-6-(diethylphenyl-phosphonium)hydroquinone chloride* (XIII)

Procedure A. Diethylphenylphosphine (0·251 mole) in benzene (400 ml) was added dropwise at a rapid rate, to a stirred saturated solution of chloranil (0·167 mole; recrystallized) in benzene. A

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[18] D. B. Denney and S. T. Ross, *J. Org. Chem.* **27**, 998 (1962).

[19] A. V. Dombrovsky and M. I. Shevchuk, *J. Gen. Chem., U.S.S.R.* **33**, 1235 (1963).

[20] J. S. Discoll, D. W. Grisley, Jr., J. V. Prustinger, J. E. Harris and C. N. Matthews, *J. Org. Chem.* **29**, 2427 (1964).

[21] S. Trippett, *Quart. Rev.* **17**, 406 (1963).

[22] A. W. Johnson and R. B. LaCount, *Tetrahedron* **9**, 130 (1960).

[23] [a] G. Wittig and H. Laib, *Liebigs Ann.* **580**, 57 (1953); [b] G. Wittig, *Angew. Chem.* **68**, 505 (1956).

[24] S. Trippett and D. M. Walker, *J. Chem. Soc.* 1266, 2130 (1961).

[25] [a] H. J. Bestmann and O. Kratzer, *Chem. Ber.* **95**, 1894 (1962); [b] H. J. Bestmann, O. Kratzer and H. Simon, *Ibid.* **95**, 2750 (1962); [c] H. J. Bestmann and B. Arnason, *Ibid.* **95**, 1513 (1962).

[26] A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.* **85**, 1888 (1963).

[27] A. Blade-Font, C. A. Vander Werf and W. A. McEwen, *J. Amer. Chem. Soc.* **83**, 2396, 2646 (1960).

[28] M. Schlosser, *Angew. Chem.* **74**, 291 (1962).

[29] J. A. Ford, Jr. and C. V. Wilson, *J. Org. Chem.* **26**, 1433 (1961).

[30] G. H. Birum, U.S. Patent, 3,058,876 (1962).

[31] W. J. Middleton, U.S. Patent, 3,067,223 (1962).

[32] H. Tolkmith, *J. Amer. Chem. Soc.* **85**, 3246 (1963).

[33] A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.* **85**, 2790 (1963). The value for triphenylbenzoylmethylenephosphorane given by these authors is in error.

brown precipitate immediately separated. *The solid* (VIII + IX) was filtered 30 min after completion of the reaction and was washed with benzene and triturated with 10 ml water. HCl was evolved. The new solid was filtered off with the aid of more water and was then treated with methylene chloride.

(a) The red methylene chloride solution was percolated through a column of alumina. Elution with more solvent gave 21·5 g red *dichloro-oxyphosphonium betaine* (XI) m.p. 191–192°; after recrystallization from benzene–cyclohexane. (Found: C, 54·0; H, 4·3; Cl, 19·7; P, 8·8; M.W. 370 (Rast). $C_{16}H_{15}Cl_2O_3P$ requires: C, 53·8; H, 4·2; Cl, 19·8; P, 8·7%; M.W., 357.) IR bands (in μ): 3·30 m, 5·90 m, 6·1 w, 6·26 vs, 6·33 vs, 6·95 w, 7·50 s, 8·25 s, 8·90 m, 11·38 m, (in $CHCl_3$). UV absorption maxima at 266 mμ, log ε 4·070; 289 mμ, log ε 4·133; 441 mμ, log ε 3·054, (in CH_2Cl_2).

(b) The white methylene chloride-insoluble solid (3·36 g, m.p. 187–190°) was recrystallized from methanol–ethyl acetate affording the *trichlorohydroquinone phosphonium chloride* (XIII), m.p. 187–190°. (Found: C, 46·4; H, 4·1; Cl, 34·1; P, 7·6. $C_{16}H_{17}Cl_4O_2P$ requires: C, 46·4; H, 4·1; Cl, 34·2; P, 7·5%.) IR bands (in μ): 3·3 (very broad, 6·6 w, 6·95 s, 7·2 w, 7·85, 8·0 s, 8·4 m, 8·95 m, 9·6 m, 11·1 s, 11·3 s (in KBr). UV maxima at 273 mμ, log ε 3·143; 337 mμ, log ε 3·822; 365–370 mμ, log ε 3·494 (in neutral EtOH).

Procedure B. Diethylphenylphosphine (11 mmoles) in 50 ml of benzene was added *slowly* (30 min) to a stirred suspension of chloranil (10 mmoles; Eastman Kodak as received) in benzene (100 ml). After 1 hr at 40°, the mixture was treated with 10 ml water and stirred for 2 hr. The solvents were removed *in vacuo* and the residue was treated with methylene chloride and filtered from 1 g of insoluble material. The solution was evaporated and the red residue (3·3 g, m.p. 155–160°) was recrystallized from benzene giving 2·72 g (76%) of (XI), m.p. 182–185°.

Oxidation of trichlorohydroquinonephosphonium chloride (XIII) *to dichloroquinone-oxyphosphonium betaine* (XI)

Phosphonium salt (414 mg; 1 mmole) was dissolved in 5 ml MeOH and 10 ml water. A solution of 0·600 g $FeCl_3 \cdot 6H_2O$ (2·14 mmoles) in dil. HCl was added. A red precipitate appeared quickly. After 30 min it was filtered off and washed with several small portions of water and 1 : 1 MeOH–water, yield 291 mg, m.p. 190–191°. Upon warming the filtrate on the steam bath another 36 mg of red solid, m.p. 190–192°, was obtained for a total yield of 91%. The IR spectrum of the red compound was identical to that of (XI).

2,5-*Dioxy*-3,6-*bis*-(*diethylphenylphosphonium*)*benzoquinone bisbetaine*, (XXIII) *and* 2-*chloro*-3,6-*di*(*diethylphenylphosphonium*)-5-*oxy-hydroquinone betaine chloride* (XXVI)

Diethylphenylphosphine (28·0 mmole) in benzene (200 ml) was added, dropwise, to a stirred solution of (XI) (14·0 mmole) in 1 l. benzene. A reddish-brown precipitate formed; this was stirred for 30 min, filtered and washed with benzene.

(a) *The solid* (XVIII + XXV) was stirred with 20 ml 1 : 1 MeOH–water (1 hr). The mixture was concentrated *in vacuo* to $\frac{2}{3}$ of its original volume and then filtered. This first crop of yellow *bisylide* (XXIII), m.p. 330–334°, amounted to 2·8 g. A second crop (0·3 g) was obtained by partial evaporation of the aqueous MeOH.

(b) *The original benzene filtrate* underwent some hydrolysis on exposure to moist air; it was concentrated to 20 ml and filtered. The solid was recrystallized from MeOH and gave a third crop (0·2 g, m.p. 330–336°) of yellow bis-ylide (XXIII). The total yield of (XXIII) was 3·3 g (50%); analytic sample: m.p. 331–334° from MeOH. (Found: C, 66·3; H, 6·3; P, 13·0. $C_{26}H_{30}O_4P_2$ requires: C, 66·6; H, 6·4; P, 13·2%.) IR bands (in μ): 3·30 s, 6·17 m, 6·38 vs, 6·84 w, 6·95 m, 7·1 w, 7·40 m, 7·80 vs, 8·90 s, 9·55 m, 9·9 w, (in $CHCl_3$). UV maxima at 267 mμ, log ε 4·242; 286 mμ, log ε 4·372; 296 mμ, log ε 4·399; 307 mμ, log ε 4·281; 370 mμ, log ε 2·702 (in CH_2Cl_2).

(c) *The aqueous*-MeOH *filtrate* was evaporated to a sirup, diluted with 70 ml of CH_2Cl_2, dried over $MgSO_4$ and concentrated to 30 ml. On cooling, 1·54 g of solid *betaine-chloride*, (XXVI), m.p. 175–185°, separated. This material was water-soluble; the aqueous solution gave an immediate precipitate of AgCl with $AgNO_3$. The betaine-chloride, (XXVI), was recrystallized several times from MeOH–ethyl acetate, the m.p. was 183–186° or 213–214°, depending apparently on the temp of crystallization. The two forms had identical IR spectra. (Found: C, 61·1; H, 6·8; Cl, 12·8; P, 11·3. $C_{26}H_{32}O_3P_2Cl_2$ requires: C, 59·5; H, 6·1; Cl, 13·5; P, 11·8%.)

Preparation of quinone-bis oxyphosphonium betaine (XXIII) *from chloranil*

Diethylphenylphosphine (2·2 mmoles) in benzene (20 ml) was added, during 30 min, to a suspension of chloranil (2 mmoles; Eastman Kodak Co., as received) in benzene (40 ml). The mixture was kept 16 hr at 20° and then was hydrolysed with 3 ml H_2O. The solvents were completely removed *in vacuo* and the red crude product (ca. 0·8 g) was dissolved in CH_2Cl_2 (20 ml). The solution was filtered and the filtrate was freed from solvent. The residue (0·56 g, ca. 80% of XI) was suspended in benzene (40 ml) and treated with more diethylphenylphosphine (1·8 mmoles) in benzene (20 ml) during 30 min. The mixture was kept 19 hr at 20° and then was hydrolysed (5 ml H_2O). The solvents were removed and the residue was crystallized from MeOH giving 0·43 g of (XXIII) m.p. 337–340° (45% yield based on chloranil).

2-Hydroxy-3-chloro-5-oxy-6-(diethylphenylphosphonium) benzoquinone betaine (XVI)

Aqueous NaOH (250 ml of 0·374 N) was added to a solution of (XI) (15 g, 42 mmoles) in boiling MeOH (500 ml). After several min, the solution was made strongly acid with conc. HCl. On cooling, 12·4 g of the yellow-orange *hydroxychloroquinone-oxyphosphonium betaine*, (XVI) m.p. 180–183° crystallized out. Concentration of the filtrate gave more (XVI), (1·51 g). The yield was 97%. The analytical sample had m.p. 182–183° from benzene–cyclohexane. (Found: C, 56·5; H, 4·9; Cl, 10·3; P, 9·2. $C_{16}H_{16}O_4ClP$ requires: C, 56·7; H, 4·7; Cl, 10·4; P, 9·1%.)

The IR spectrum is given in Fig. 1. The UV-maxima are listed in Table 1.

Reaction of diethylphenylphosphine with the hydroxy-chloroquinone-oxyphosphonium betaine (XVI)

Procedure A. A mixture of (XVI) (3·00 g, 8·75 mmole) and the phosphine (2·90 g, 17·5 mmole) was heated to reflux for 48 hr in 1,2-dimethoxyethane (100 ml). The violet solution was decanted from a solid. The latter was stirred with water and filtered. The insoluble material was only 0·26 g of *bisylide*, (XXIII), m.p. 330–337°.

Procedure B. A mixture of (XVI) (14·9 mmoles) and diethylphenylphosphine (29 8·mmoles) was refluxed in toluene (350 ml) for 4 hr. The toluene was decanted from a deep purple-black solid (5·69 g). This was dissolved in water (100 ml). The solution was filtered and exhaustively extracted with CH_2Cl_2. The violet organic layer was dried, concentrated and treated with acetone while boiling. On cooling, violet crystals, (XXVIII; 1·3 g; m.p. 247–251°) separated. These were recrystallized from CH_2Cl_2–acetone to constant m.p. of 251–254°. (Found: C, 62·6; H, 6·8; P, 11·4; Cl, 4·4; m.w. 787 (isothermal distillation.) $C_{42}H_{46}O_7P_3Cl$ requires: C, 63·7; H, 5·8; P, 11·7; Cl, 4·4% m.w. 791.) UV spectrum in CH_2Cl_2: λ_{max} 260 mμ ($\varepsilon = 1{,}700$); 299 mμ (1,400); 378 mμ (700); 515 mμ (3,000).

The violet compound (XXVIII) underwent a reversible colour change with base to a brilliant blue and with acid to deep orange.

pK *Determinations in water.* Optical densities were measured in the Beckmann DU spectrophotometer. A stock solution of quinone-*bisoxyphosphonium* bisbetaine (XXIII), was made from 133·6 mg of betaine and 25 ml of 1 N HCl. One ml-aliquots were treated with various amounts of conc. HCl and the solutions were then diluted to 10 ml with distilled water. Optical densities at 424 mμ were measured. The acid-concentrations were determined by titration of one ml-aliquots with standard NaOH. The acid-concentrations were converted, graphically, to Ho values as given by Paul and Long.[34] A typical point in Fig. 3 was: vol. of HCl, 9 ml; O.D. 0·58; ml of 0·2393 N NaOH, 47·10; molarity of HCl, 11·26; Ho = −4·10. The last point in Fig. 3 was obtained by addition of 9 ml H_2SO_4, the molarity estimated as 15 M, the Ho at ca. −9·2; the O.D. was 0·27. The p*Ka* is given in Table 2.

A saturated solution of the sparingly soluble (XVI) was made by boiling an excess of the compound with water, cooling to 20° and filtering. Five ml-aliquots were mixed with various amounts of acid or of base; the solutions were diluted to 10 ml with water. Optical densities were measured at 475 mμ and also at 445 mμ. Acidities in the positive pH region were measured with a Beckmann pH meter. Acidities in the negative pH regions were determined by titration as before.

The technique was checked with 4-chloro-2-nitroaniline.

pK *Measurements in acetic acid–sulphuric acid.* Acetic acid of m.p. 16·3° was made by fractional distillations and freezings. 100% H_2SO_4 was made by addition of fuming H_2SO_4 (15–18% SO_3

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[34] M. A. Paul and F. A. Long, *Chem. Rev.* 57, 1 (1957).

assay) to conc. H_2SO_4 (96·4% assay) until a mixture with maximum m.p. was obtained (Beckmann freezing point apparatus).

Various amounts of H_2SO_4 were weighed into volumetric flasks (10 ml, 25 ml). Aliquots (2 ml, 5 ml respectively) of the stock solutions containing the betaines in acetic acid were introduced. The solutions were diluted to the mark with acetic acid. Optical densities were measured. When required, a 2 ml-aliquot of stock solution was introduced in a 100 ml volumetric flask and the optical density was measured in a cell of 10 cm-path. The Ho values corresponding to the H_2SO_4 concentrations were determined graphically from data by Hall and Spengeman[35] using the new "best" values of the pK's of the Hammett indicators given by Paul and Long.[34] A correction of $-0·11$ Ho units was applied to the calculated Ho values to bring the latter into agreement with values of Ho found in a check-determination using 4-chloro-2-nitroaniline. For example, 1·0666 g H_2SO_4 in a 10 ml-vol. flask was mixed with a 2 ml-aliquot of a stock solution containing 328·7 mg of *bisbetaine* in 100 ml of acetic acid. After dilution to the mark with acetic acid the O.D. was found to be 0·475 at 411 mμ. The molarity of H_2SO_4 being 1·09, the corrected Ho = $-3·15$. The data is shown in Fig. 4 and the pK values are listed in Table 2.

The technique was checked by finding Ho values in the acetic acid–H_2SO_4 system using *p*-chloro-*o*-nitroaniline, employing the "best" value of the pK of this indicator and the equation $\text{Ho} = \text{p}K - \log (\text{OD}_\text{B}—\text{OD})/(\text{OD}·\text{OD}_{\text{BH}^+})$. The found Ho (for example $-0·98$) was compared with the Ho value (for example $-0·87$) obtained from the data by Hall and Spengeman.[35]

SUMMARY AND CONCLUSIONS

The phosphorus of diethylphenylphosphine attacks the carbon and not the oxygen of *p*-chloranil. A trichloroquinonephosphonium chloride is formed as a result of the chlorine displacement. The chlorine adjacent to the phosphorus in this quinone is easily replaced by a hydroxyl from water, resulting (after loss of hydrogen chloride) in a new type of stable phosphorus-ylide, a red dichloroquinoneoxyphosphonium betaine $\delta P^{31} = -25·6$ ppm *vs.* 85% H_3PO_4 (in CH_2Cl_2).

The chlorine atom *para* to the phosphorus in the red betaine is replaced by diethylphenylphosphine. After hydrolysis and subsequent loss of hydrogen chloride, a new ylide, m.p. 331°, is formed. This is a yellow quinone—bisoxyphosphonium betaine, $\delta P^{31} = -25·7$ ppm (in $CF_3·COOH$).

The chlorine atom *meta* to the phosphorus in the red betaine is replaced by a hydroxy group upon treatment with alkali. The product is a stable, orange hydroxy-chloroquinone—oxyphosphonium betaine, m.p. 182°, $\delta P^{31} = -23$ ppm.

The three ylides are very weak bases. The p*Ka*'s were measured in aqueous hydrochloric acid. They were measured also in acetic acid–sulphuric acid and it was shown that in these compounds an extension of the Ho function to acetic acid is not feasible.

The reactions of *p*-quinones with trimethyl phosphite, with triphenylphosphine and with diethylphenylphosphine are discussed in terms of: (i) the electronic and steric characteristics of both reactants; (ii) the differences in the transition states for oxygen-attack and for carbon-attack; and (iii) changes in hybridization in both ground and transition state involving the phosphorus compound, PX_3, as the nature of the substituent X is changed.

The P^{31} NMR shifts of a group of stable phosphorus ylides were measured at 40·5 M c/s.

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[35] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.* **62**, 2487 (1940).