[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

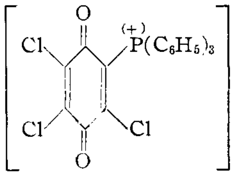
The Structure of Quinone–Donor Adducts. I. The Action of Triphenylphosphine on *p*-Benzoquinone, 2,5-Dichloro-*p*-benzoquinone and Chloranil

BY FAUSTO RAMIREZ AND SAMUEL DERSHOWITZ[1]

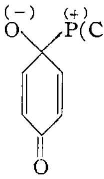
RECEIVED MARCH 26, 1956

The action of triphenylphosphine on chloranil, 2,5-dichloro-*p*-benzoquinone and *p*-benzoquinone in benzene solution has been investigated, and the constitution of the resulting adducts has been elucidated. By means of degradative procedures and of spectral data in the ultraviolet and infrared it was shown that: (1) the various adducts (XIII, XVI, XXIV) have different constitution and contain the donor (phosphine) and the acceptor (quinone) in 1:1, 3:2 and 1:1 molar ratios, respectively; (2) oxygen–phosphorus and/or aryl–phosphorus bonds may be established in the adducts depending on the structure of the quinone, a result interpreted mechanistically in terms of steric effects and oxidation–reduction potential of the quinones; (3) previous formulations[3] of the tertiary phosphine-*p*-quinone adducts are incorrect; (4) substances of composition $R_3P(OAr)OH$ are hydrogen-bonded adducts involving the phosphine oxide and the phenol and not true quasi-phosphonium compounds.[7] It is suggested that the radical $(C_6H_5)_3P\cdot^{(+)}$, that is, the triphenylphosphinium positive ion, may be an intermediate in the reaction of triphenylphosphine with *some* quinones, and perhaps, also, in other reactions of tertiary phosphines.

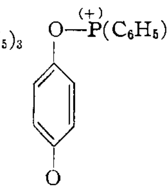
The behavior of quinones toward derivatives of Group VB elements in their trivalent state has been extensively investigated and constitutes a phase of the more general problem of the interaction between electron-acceptors and electron-donors.[2] A number of investigations have dealt more specifically with the structure of the products formed between *p*-quinones, *o*-quinones and their halogen derivatives, on the one hand, and tertiary amines and tertiary phosphines, on the other hand.[3] The over-all picture, at present, is not satisfactory and, in particular in the case of the quinone–phosphine adducts, there appeared to be a need for re-examination of the structures proposed. This paper deals with the action of triphenylphosphine (I) on tetrachloro-*p*-benzoquinone (chloranil) (II), 2,5-dichloro-*p*-benzoquinone (III) and *p*-benzoquinone (IV).



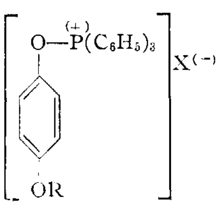
V



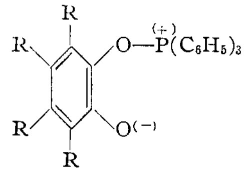
VI



VII (−)



VIII, R = H; X = Cl
IX, R = C_2H_5; X = I



X, R = H
XI, R = Cl

No detailed study of the interaction between triphenylphosphine and chloranil appears to have been made, although structure V was advanced by Schönberg and Ismail[3d] to explain the color observed upon admixture of the reagents in chloroform solution. The adduct formed from triethylphosphine and *p*-benzoquinone was formulated as VI by Davies and Walters.[3f] Later, Schönberg and Michaelis[3e] questioned this type of structure and, working with triphenylphosphine, formulated the adduct as a so-called "phosphonium enolate"[3b] VII. Formulas VIII and IX were assigned to the derivatives obtained when adduct VII was treated with hydrochloric acid and with ethyl iodide, respectively.

In very recent publications Horner and co-workers[3a,b] discussed this problem extensively and accepted the views of Schönberg and Michaelis.[3e] Horner, in turn, advanced "phosphonium enolate" structures X and XI for the adducts formed between triphenylphosphine and *o*-benzoquinone and its tetrachloro derivative, respectively. It should be noted that the reactions of unsubstituted and of substituted *o-quinones* were regarded by Horner as leading to analogous type structures. The main argument advanced[3b,e] in favor of the "phosphonium enolate" structures VII, X and XI for the quinone–phosphine adducts is based on the alkaline degradation of the adducts to triphenylphosphine *oxide* (XII), $(C_6H_5)_3PO$, and the corresponding dihydroxybenzene. It seemed to us, however, that the results of alkaline degradations do not provide rigorous proof for the presence in the adducts of Ar–O–P bonds, as suggested.[3a,b,e] Firstly, it is known[4] that quaternary phosphonium compounds undergo alkaline degradations, which have been interpreted as

$$\overset{(+)(-)}{R_4P\,OX} \longrightarrow [R_4P\cdot OX] \longrightarrow R_3PO + RX$$

Secondly, reasonable pathways can be conceived for the ready alkaline cleavage of *o*-hydroxyphenylphosphonium compounds, as are likely to originate from the interaction of tertiary phosphines with *certain* quinones (*vide infra*).

---

(1) From part of the Ph.D. Thesis of S. Dershowitz.

(2) (a) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954), *cf.* p. 748; (b) E. Weitz, *Angew. Chem.*, **66**, 658 (1954). *cf.* p. 668; (c) R. Kuhn, *ibid.*, **66**, 678 (1954); (d) L. E. Orgel. *Quart. Revs.*, **8**, 422 (1954); (e) T. T. Harding and S. C. Wallwork. *Acta Cryst.*, **6**, 791 (1953); (f) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); (g) W. Brackman, *Rec. trav. chim.*, **68**, 147 (1949); (h) P. Pfeiffer, "Organische Molekulverbindungen," F. Enke, Stuttgart, 1922.

(3) (a) L. Horner and W. Spietschka, *Ann.*, **591**, 1 (1955); (b) L. Horner and K. Klüpfel, *ibid.*, **591**, 69 (1955); (c) A. A. Bothner-By, THIS JOURNAL, **77**, 749 (1955); (d) A. Schönberg and A. F. A. Ismail, *J. Chem. Soc.*, **1374** (1940); (e) A. Schönberg and R. Michaelis, *Ber.*, **69**, 1080 (1936); (f) W. C. Davies and W. P. Walters. *J. Chem. Soc.*, 1786 (1935); (g) G. Ortoleva and G. Di Stefano. *Gazz. chim. ital.*, **31**, II, 256 (1901).

(4) (a) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 85, 104; (b) E. Rothstein, *J. Chem. Soc.*, 3991 (1953); (c) G. Wittig and W. Haag. *Chem. Ber.*, **88**, 1654 (1955). Previous references to important work by Ingold and co-workers are cited here

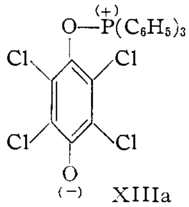
The formulation of the quinone–tertiary phosphine adducts as VII, X and XI and of their derivatives as VIII and IX, raises a number of important questions in organophosphorus chemistry. Structures such as VIII and IX would belong to the class of so-called quasi-phosphonium compounds[5] and can be regarded as variants of the usual phosphonium compounds R_4PX in which one or more R groups are replaced by OR groups. Very few "quasi-phosphonium" compounds have been isolated in pure form and there is considerable doubt concerning the actual structure of some of them. Thus, the sharp-melting substances formed upon fusion of phenols and triarylphosphine oxides[6] have been regarded[5] either as "hydrogen bonded adducts" or as true quasi-phosphonium compounds $(C_6H_5)_3P(OAr)OH$, but experimental data to decide among the alternatives have been lacking. In spite of the instability implied in these descriptions of the quasi-phosphonium compounds, rather drastic alkaline conditions have been employed for the degradation of the quinone–tertiary phosphine adducts.

No study of the action of triphenylphosphine on 2,5-dichloro-*p*-benzoquinone has been reported.

Results

Solutions of triphenylphosphine and of the quinone in *anhydrous* benzene were mixed in a *dry nitrogen atmosphere* (dry-box).

The Action of Triphenylphosphine (I) on Chloranil (II) (Chart I).—When the reagents were mixed in a 1:1 mole ratio an immediate red color developed in the solution accompanied by the slow and quantitative formation of a crystalline, buff-colored precipitate, XIII. One way of formulating the adduct XIII is shown in Chart I. The experimental evidence summarized below *definitely excludes* the previous formulation V but does not allow a distinction from the monomeric structure XIIIa. Formula XIII is favored, since it would place the results in the chloranil case in line with those in the 2,5-dichloro-*p*-benzoquinone case (*vide infra*). The composition of the crystalline aggregate is remarkably constant and appears to be homogeneous throughout the solid phase.



XIIIa

The ultraviolet absorption spectrum of adduct XIII in 95% ethanol corresponded to the composite spectra of triphenylphosphine oxide (XII) and tetrachlorohydroquinone (XIV). The molar extinction coefficients (ϵ) obtained on the basis of a molecular weight of $(508)_n$ were in good agreement with the values calculated from the expression ($n\epsilon' + n\epsilon''$), where ϵ' and ϵ'' refer to the molar extinction coefficients of pure oxide XII and quinol XIV, respectively. In ethanol solution in the presence of water, therefore, adduct XIII readily breaks down into oxide XII and quinol XIV in a 1:1 molar ratio, and the formation of the adduct from the phosphine I and the quinone II is actually an oxidation–reduction process. A possible path for the hydrolysis (XIII → XVa → XV) is indicated in Chart I and follows the suggested mechanism[4] for the (thermal) decomposition of quaternary phosphonium hydroxides, involving a transient pentacovalent organophosphorus. The difference in electronegativity between carbon and oxygen could account for the difference in stability between structures of type $R_3P(R)OH$ and $R_3P(OAr)OH$.

Hydrolysis of adduct XIII in aqueous methanol afforded tetrachlorohydroquinone (XIV) and a colorless substance, XV, in equimolar ratio. The following observations show that this substance XV, although sharp-melting (180–182°) and readily soluble in benzene, is simply a loose combination of two molecules of triphenylphosphine oxide and one molecule of tetrachlorohydroquinone, which are held together presumably by hydrogen bonding as pictured in Chart I.

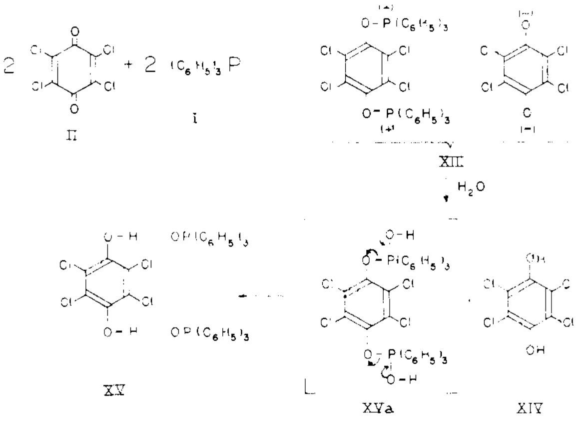


CHART I

(a) The ultraviolet absorption spectrum of XV in 95% ethanol was practically identical with the composite spectra of oxide XII and quinol XIV, with ϵ values corresponding to two moles of XII and one mole of XIV.[7] (b) Treatment of XV with *cold* 5% aqueous sodium hydroxide readily effected a separation into triphenylphosphine oxide and tetrachlorohydroquinone. (c) It was found that fusion of triphenylphosphine oxide (XII) (m.p. 156–157°) and tetrachlorohydroquinone (XIV) (m.p. 234–235°) in a 2:1 molar ratio afforded, on cooling, a solid which remelted sharply at 180–182°. Indeed, the crystalline material obtained on evaporation of, or addition of water to, a methanolic solution containing oxide XII (2 moles) and quinol XIV (1 mole) melted also at 180–182°. Figure 1 discloses that the infrared spectrum of this solid, and the spectrum of complex XV are indistinguishable. On the other hand, these spectra are significantly different (arrows in Fig. 1) from the spectrum of a

---

(5) Reference 4a, Chapter 11.

(6) W. Lommel and H. Munzel, U. S. Patent 1,844,015 (1932); *C. A.*, **26**, 1941 (1932). The statement in ref. 4a, p. 330, which mentions triphenylphosphine rather than the oxide appears to be a misprint

(7) The spectra of XV in anhydrous acetonitrile and in 95% ethanol were nearly identical, which tends to confirm the hydrogen bonded structure suggested. It appears that XV is practically completely dissociated in very dilute solutions of these solvents.

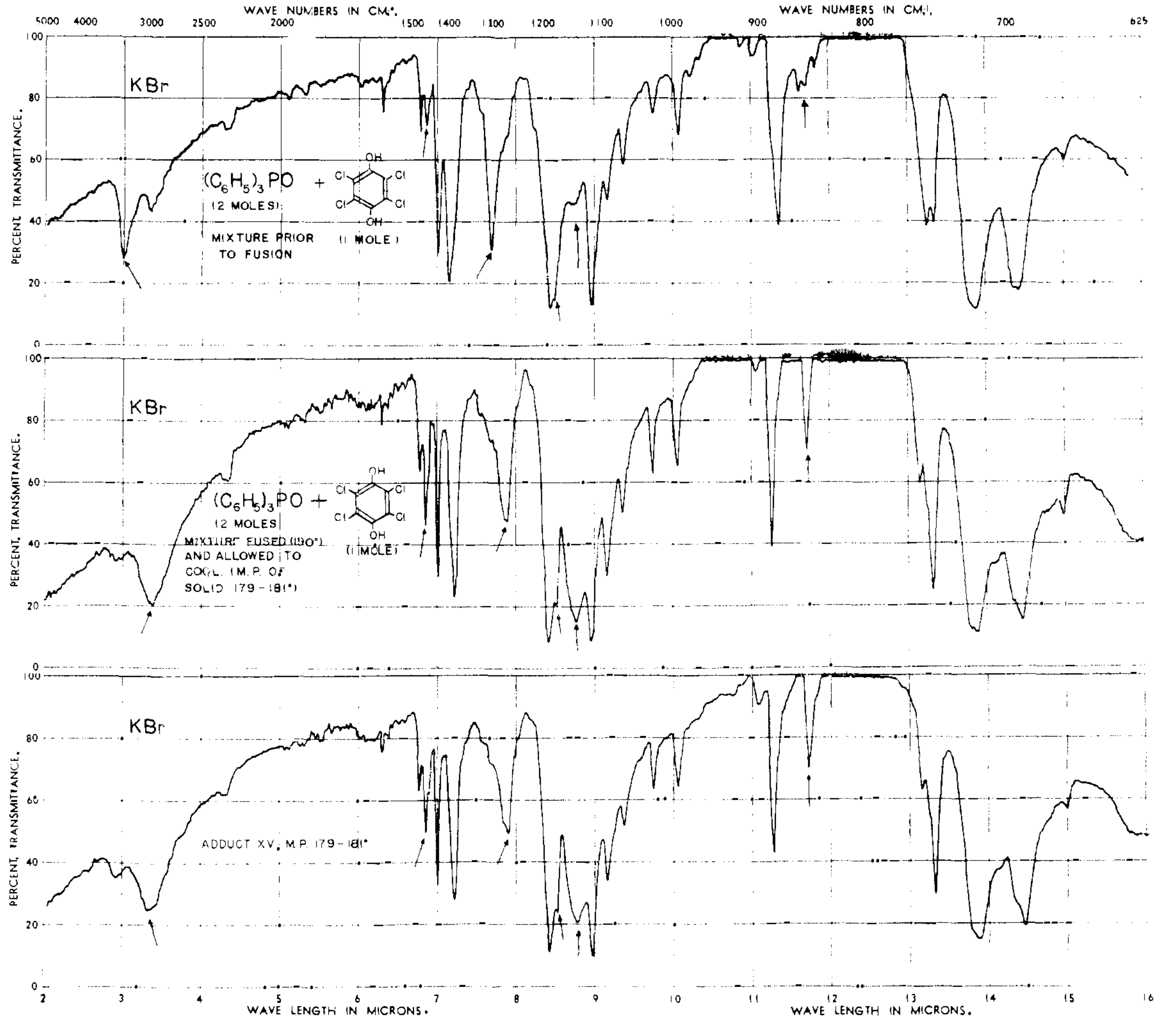


Fig. 1.

finely ground, *but not fused*, mixture of oxide XII and quinol XIV. Of particular interest are the 3–4 μ region, which in complex XV exhibits the appearance characteristic of strongly associated OH, and the 8.5 μ band[8] due to the PO group in oxide XII and still present in XV. (d) The molecular weight (266) of XV determined in camphor was approximately one-third of the formula weight (804) indicating a facile dissociation into three particles.

In view of these observations, there can be little doubt concerning the hydrogen-bonded formulation for XV; the quasi-phosphonium compound XVa is presumably an intermediate in its formation. Previously reported[5,6] systems of this type are probably hydrogen-bonded complexes also. The "hydrate" of m.p. 122° reported by Horner[3b] in the tetrachloro-*o*-benzoquinone series is probably of the same nature.

The Action of Triphenylphosphine (I) **on 2,5-Dichloro-*p*-benzoquinone** (III) (**Chart** II).—In this case, a pure adduct formed quantitatively only when the reagents were mixed in a 3:2 (phosphine: quinone) mole ratio. The adduct is formulated as XVI; *one of the four chlorine atoms present* in the *adduct*, $C_{66}H_{49}O_4P_3Cl_4$, *was ionic*. The ultraviolet absorption spectrum of adduct XVI in 95% ethanol suggested the occurrence upon solution of a hydrolytic cleavage into triphenylphosphine oxide (2 moles), 2,5-dichlorohydroquinone (XVII) (1 mole) and a *third component* having maximum absorption above that of the quinol XVII.

Hydrolysis of adduct XVI in aqueous methanol afforded two substances in equimolar ratio: one, m.p. 297–298°, was shown to be (4-chloro-2,5-dihydroxyphenyl)-triphenylphosphonium chloride (XVIII) and the other, m.p. 163–165°, proved to be the hydrogen-bonded complex XIX. XIX is analogous, *mutatis mutandis*, to the complex XV (Chart I) obtained from the hydrolysis of the chloranil–adduct XIII. The same type of experimental evidence already discussed in connection with complex XV was secured for complex XIX. It is evident that in the formation of adduct XVI a displacement of a ring-chlorine took place, in addition to the oxidation–reduction already observed in the chloranil case.

The phosphonium chloride XVIII had *one* ionic chlorine. Its ultraviolet absorption spectrum (Fig. 2) was affected by addition of alkali in the ex-

---

[8] (a) L. W. Daasch and D. C. Smith, *J. Chem. Phys.*, **19**, 22 (1951); (b) L. J. Bellamy, "The Infrared Spectra of Complex Molecules." John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 18.

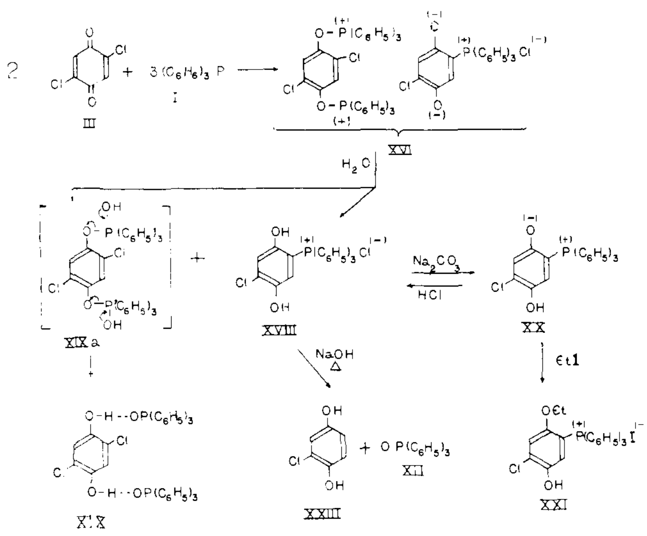
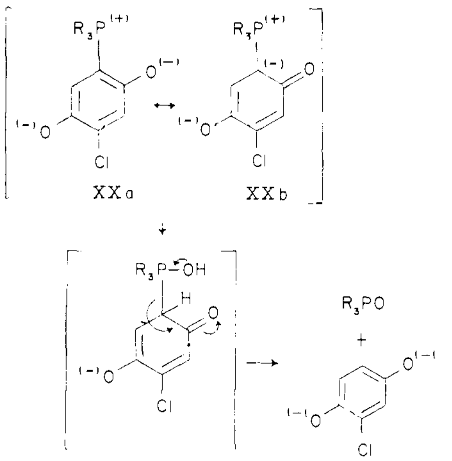


CHART II

pected manner and the original spectrum could be restored upon addition of hydrochloric acid. The chloride XVIII was soluble in cold aqueous sodium hydroxide, and from this solution it could be recovered unchanged by the addition of hydrochloric acid. However, on prolonged heating in alkali the chloride XVIII was cleaved into triphenylphosphine oxide (XII) and *chlorohydroquinone* (XXIII). These observations provide unequivocal evidence for the establishment of an aryl—phosphorus bond (rather than an Ar–O–P bond) in the formation of chloride XVIII. The course of the alkaline cleavage (XVIII→XXIII + XII) can be pictured as



The preparation of a phenolic tetraarylphosphonium halide of type XVIII is of considerable interest since it permits the exploration of a new kind of phosphinemethylene[9] XX. Accordingly, the chloride XVIII was treated with aqueous sodium carbonate and transformed into the light yellow phosphinemethylene XX (or betaine). Alkylation of XX with ethyl iodide yielded (4-chloro-2-ethoxy-5-hydroxyphenyl)-triphenylphosphonium iodide (XXI). Other properties of these phosphinemethylenes will be reported soon.

The Action of Triphenylphosphine (I) on *p*-Benzoquinone (IV) (Chart III).—A red color developed and a yellow solid slowly precipitated out in quantitative yield. The experimental evidence summarized below is *consistent only with formulation XXIV for the adduct and definitely excludes previous formulations VI and VII.* A clue to the structural problem follows immediately from a comparison of curve 1A of Fig. 3 and curve 1A of Fig. 2. It can be seen that the *p*-benzoquinone adduct XXIV is structurally analogous to the phosphinemethylene XX (Chart II) which was in turn derived from (2,5-dihydroxy-4-chlorophenyl)-triphenylphosphonium chloride (XVIII). This inference was independently proven as follows:

Treatment of adduct XXIV with hydrochloric acid yielded (2,5-dihydroxyphenyl)-triphenylphosphonium chloride (XXV), whose ultraviolet spectrum in neutral and in alkaline solution (Fig. 3) corresponded to that of the chlorine-analog XVIII of Chart II (Fig. 2).[10] Sodium carbonate regenerated the adduct XXIV from the chloride XXV.

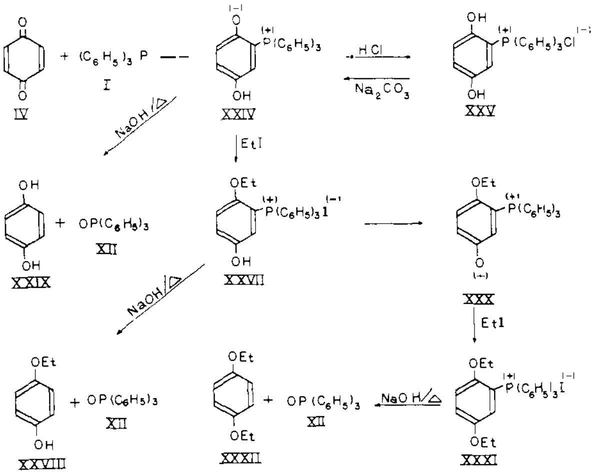


CHART III

With ethyl iodide, the adduct XXIV afforded (2-ethoxy-5-hydroxyphenyl)-triphenylphosphonium iodide (XXVII) and here, again, a spectral correspondence with the chlorine-analog XXI (Chart II) could be noted in neutral and alkaline solution. Further reaction of the ethiodide XXVII with ethyl iodide could be effected, this time in the presence of sodium methoxide. As expected, the ultraviolet spectrum of the resulting (2,5-diethoxyphenyl)-triphenylphosphonium iodide (XXXI) was not significantly affected by addition of alkali.

It is of interest that both (2-ethoxy-5-hydroxyphenyl)-triphenylphosphonium iodide (XXVII) and (2,5-diethoxyphenyl)-triphenylphosphonium

---

(9) Phosphinemethylenes are substances of structure $R_3P{=}CXY$ which have received considerable attention recently (*cf.* ref. 4c; F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 488 (1956)).

(10) There are marked differences in the stability of the chlorides XXV and XVIII (or of the phosphinemethylenes XXIV and XX) in alkali. Curve 2B of Fig. 3 is obtained only if measurements are made within a few seconds after the addition of base. Otherwise, the curve is replaced by one which suggests oxidation to a quinone.

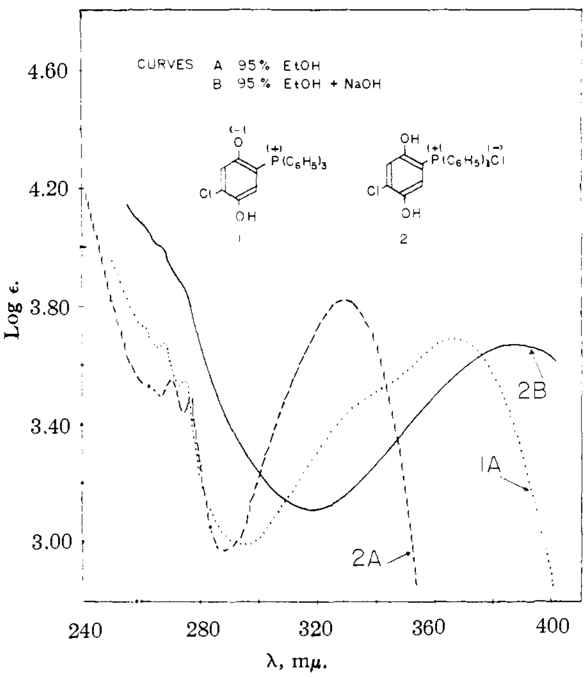
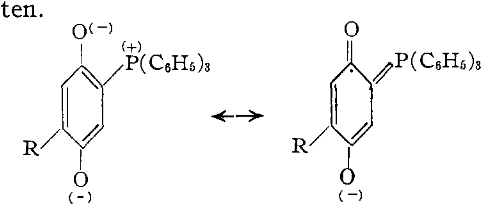


Fig. 2.

iodide (XXXI) could be cleaved by prolonged heating with 5% aqueous sodium hydroxide, yielding triphenylphosphine oxide and hydroquinone monoethyl ether (XXVIII) or hydroquinone diethyl ether (XXXII), respectively, which were identified.

Ultraviolet Absorption Spectra (Figs. 2 and 3).—The maxima at *ca.* 330 mμ presumably correspond to the diprotonated species, *i.e.*, to substituted hydroquinones (XVIII), Chart II; XXV, Chart III). The replacement of phenolic hydrogens by alkyl groups in the ethiodides (XXI, Chart II; XXVII, Chart III) does not affect the spectrum significantly. The maxima at *ca.* 390 mμ in alkaline solutions reflect the presence of the triply charged species, for which resonance forms can be written.



The presence of two species in the solutions of the phosphinemethylenes (XX, Chart II; XXIV, Chart III) in 95% ethanol is suggested by the shape of the spectra (Fig. 2, curve 1A; Fig. 3, curve 1A) with maxima at *ca.* 335 and 370 mμ. In other words, in these solutions the phosphinemethylenes appear to be partially protonated.

The presence of maxima at the relatively short wave length of 355 mμ in the spectra of the ethiodides XXI and XXVII *in alkaline medium* is consistent with the structures shown. If the ethiodides had the alternate structures (5-ethoxy), their spectra in *alkaline medium* should exhibit maxima at 370 mμ or longer, corresponding to those of XX and XXIV in *neutral* ethanol.

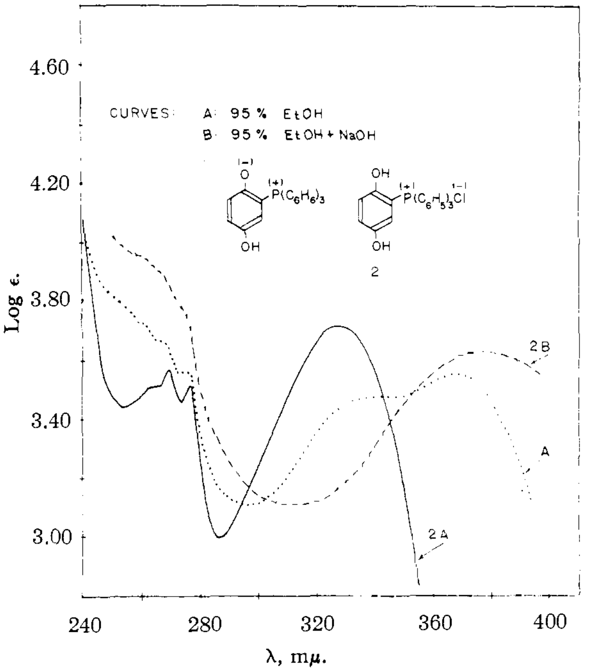
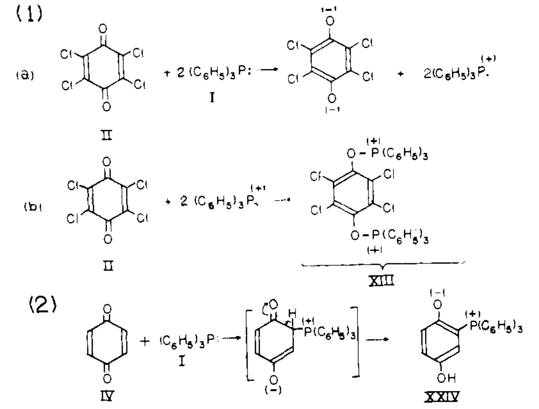


Fig. 3.

Discussion

The present study shows that the mode of action of tertiary phosphines on *p*-quinones depends markedly on the nature of the quinones. Two types of interactions were observed and these are rationalized in the sequence of reactions 1a,b and 2.



(1) A sterically hindered quinone of high oxidation–reduction potential[11] such as chloranil yielded an adduct in which the electron-acceptor and the electron-donor are present in a 1:1 mole ratio and in which oxygen–phosphorus bonds are established.

(2) A simple quinone such as *p*-benzoquinone yielded a 1:1 adduct, in which an aryl–phosphorus bond is formed, resulting from the typical 1,4-addition of anionoid reagents to the ring carbon. The difference in behavior between chloranil and *p*-benzoquinone is attributed to the known reluc-

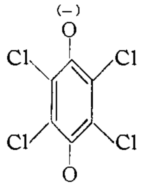
---

[11] Although it is known (F. J. Lopez Aparicio and W. A. Waters, *J. Chem. Soc.*, 4666 (1952)) that in *ethanol solution* chloranil exhibits a lower oxidation–reduction potential (703 mv.) than *p*-benzoquinone (711 mv.), the opposite is the case in *benzene solution* (*cf.* M. G. Evans and J. De Heer, *Quart. Revs.*, **5**, 106 (1950)).

tance of chloranil toward nuclear additions and to its higher oxidation–reduction potential (in benzene).

Step 1a represents an oxidation of the tertiary phosphine I by the chloranil II, involving presumably two one-electron transfer steps[12] and giving rise to the triphenylphosphinium positive ion $(C_6H_5)_3P^{(+)}$.

Supportive evidence for the formation of this radical was sought in paramagnetic resonance absorption measurements. Paramagnetic resonance absorption was observed in the benzene solution shortly after the reagents (chloranil and triphenylphosphine) were mixed. The spectrum showed two peaks of about equal intensity; the relative intensity of these peaks did not change when the reagents were initially mixed in different molar ratios. The center of the spectrum (*g*-value) was 2.0055. The spectrum *is not* due to the semiquinone radical ion derived from chloranil and it is probably due to a single radical species present in significantly high concentration.[13,14]

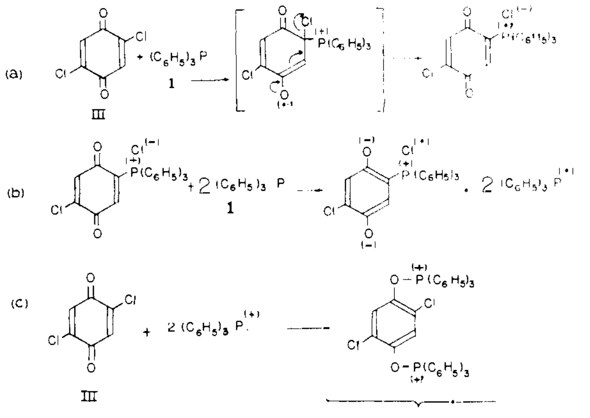


The existence of radical ions derived from trivalent nitrogen has aroused considerable interest[15]; examples of these are the Würster salts $R_2NC_6H_4\underset{\bullet}{\overset{(+)}{N}}R_2$ and the tri-*p*-tolylaminium ion[16] $(p\text{-}CH_3C_6H_4)_3\underset{\bullet}{\overset{(+)}{N}}$. The concept of a tertiary phosphinium radical ion as a reaction intermediate may prove useful in organophosphorus chemistry and its implications are being explored.

Step 1b constitutes a free radical attack on the oxygen atoms of an unexcited quinone. The studies of Waters and co-workers[17] have disclosed examples of carbon-free-radical attack on the oxygen atoms of chloranil and other quinones.

The schemes presented above (1a-b and 2) for the reactions of chloranil and *p*-benzoquinone, gain in plausibility by their application to the reaction of 2,5-dichloro-*p*-benzoquinone. In the latter, both addition of the phosphine to the quinone ring and oxidation of the phosphine by a quinone of high oxidation–reduction potential take place. Step 3a is a nuclear addition which now results in displacement of chloride ion. The phosphonium–quinone postulated as an intermediate would have a relatively high oxidation–reduction potential associated with the presence of the strong electron-attracting phosphonium group, and could in turn oxidize the triphenylphosphine as in step 3b. Free radical attack on the original quinone III, as in step 3c, would yield an adduct XVI, which although differing in stoichiometry from the chloranil adduct XIII has many features similar to it. The direction of the initial attack on the quinone III (step 3a) could be rationalized in terms of the lower electron density at the chlorine-substituted ring position.

(3)



XVI

Experimental[18]

Formation of Adduct XIII from Triphenylphosphine (I) and Chloranil (II).—A solution of freshly recrystallized chloranil (II) (0.330 g., 1.35 mmoles) in the minimum amount of anhydrous benzene was added to a solution of triphenylphosphine (I) (0.352 g., 1.35 mmoles) in benzene. The solutions were rapidly mixed in a dry nitrogen atmosphere. A deep red color appeared instantaneously, together with a crystalline precipitate. After a total of 12 hours the color had completely faded. The precipitate was then quickly filtered, washed with dry benzene and dried *in vacuo*. The yield of the chloranil adduct XIII, m.p. *ca*. 163° dec., was 0.639 g.; a sample of this material was analyzed. The benzene filtrate was evaporated to dryness yielding practically no residue; infrared absorption spectrum of adduct XIII in KBr, bands at: 7.00(s), 8.5(m), 8.82(m), 8.95(s), 10.52(m) and 11.3(s) μ.

Anal. Calcd. for $(C_{24}H_{15}O_2PCl_4)_n$: C, 56.7; H, 3.0; P, 6.1; Cl, 27.8. Found[19]: C, 56.5; H, 3.6; P, 6.1; Cl, 27.1.

Hydrolysis of Chloranil Adduct XIII. (a) With Aqueous Methanol.—A solution of adduct XIII (0.410 g.) in 35 ml. of methanol containing 1% of water was refluxed for 3 hours. The methanol was removed under reduced pressure and the residue was treated with benzene (10 ml.). The benzene-

---

[12] An analogous picture involving an electron transfer between one molecule each of chloranil and triphenylphosphine, followed by coupling of the semiquinone radical ion and the phosphinium radical cation, would lead to the alternate formulation of the adduct XIIIa.

[13] We are grateful to Drs. B. Venkataraman and G. K. Fraenkel of this Department for the paramagnetic resonance absorption measurements. For a discussion of semiquinone radical ions, with references to the work of L. Michaelis and of Weissberger, see B. Venkataraman and G. K. Fraenkel, THIS JOURNAL, **77**, 2707 (1955).

[14] It is significant that the addition of a benzene solution of chloranil to a benzene solution containing triphenylphosphine and triphenylmethyl radicals results in no immediate color change and *yields no precipitate*. Even after several days no precipitate appeared, although the solution became red. In the absence of triphenylphosphine, chloranil and triphenylmethyl radicals react in benzene with formation of a colorless precipitate (m.p. 170–173°) which, on the basis of previous work (*cf*. J. B. Conant and H. W. Scherp, THIS JOURNAL, **53**, 1941 (1931); W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 2nd Ed., 1948, p. 49) is probably the di-triphenylmethyl ether of tetrachlorohydroquinone.

[15] For recent contributions to this field see (a) L. Horner and W. Kirmse, *Ann.*, **597**, 66 (1955); (b) p. 48; (c) V. Boekelheide and D. L. Harrington, *Chemistry & Industry*, **44**, 1423 (1955).

[16] For an extensive discussion see ref. 2b, pp. 661, 669.

[17] (a) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); (b) F. Bickel and W. A. Waters, *ibid.*, 1764 (1950); (c) *cf*. Footnote 14; (d) Reference 2b, p. 673.

[18] Analyses by Micro-Tech Laboratories, Skokie, Ill., and Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

[19] Calcd. for 2(I) + 1(II): C, 65.5; H, 3.9; P, 8.4; Cl, 18.4. Calcd. for 3(I) + 2(II): C, 62.0; H, 3.5; P, 7.3; Cl, 22.2.

ULTRAVIOLET ABSORPTION SPECTRUM OF ADDUCT XIII IN 95% ETHANOL

λ_{max}, mμ	Found[a] ϵ_{max}	Calcd.[b] ϵ_{max}
223	80,000	76,400
261	5,000	5,000
267	5,700	5,600
273	5,400	4,900
310	10,400	10,600

[a] Based on mol. wt. 1016 ($n = 2$ in formula). [b] Calculated from ($2\epsilon' + 2\epsilon''$), where ϵ' and ϵ'' refer to triphenylphosphine oxide (XII) and tetrachlorohydroquinone (XIV), respectively, in the same solvent.

insoluble material (0.088 g.) had m.p. 233–236° and was shown to be tetrachlorohydroquinone (XIV) by mixed melting point and infrared spectrum. The benzene solution was concentrated and then diluted with petroleum ether. On cooling, 0.305 g. of colorless crystals (XV), m.p. 178–181°, was obtained. The analytical sample of XV, obtained after three recrystallizations from benzene–petroleum ether had m.p. 179.4–181.6°; infrared absorption spectrum of XV in KBr, bands at: 3.1–3.5(s), 6.78(w), 6.88(w), 7.00(s), 7.20(s), 7.90(m), 8.40(s), 8.50(s), 8.75(s), 8.95(s), 9.75(w), 10.08(w), 11.28(m) and 11.7(w)μ.

ULTRAVIOLET ABSORPTION SPECTRUM OF XV IN 95% ETHANOL

λ_{max}, mμ	Found[a] ϵ_{max}	Calcd.[b] ϵ_{max}
224	64,300	63,700
261	3,900	4,200
267	4,700	4,900
273	4,100	4,300
311	5,300	5,300

[a] Based on mol. wt. 804. [b] Calculated from ($2\epsilon' + 1\epsilon''$), where ϵ' and ϵ'' refer to triphenylphosphine oxide (XII) and tetrachlorohydroquinone (XIV), respectively.

Anal. Calcd. for $C_{42}H_{32}O_4P_2Cl_4$: C, 62.7; H, 4.0; P, 7.7; Cl, 17.6. Found: C, 63.2; H, 4.3; P, 7.6; Cl, 17.5.

Alternatively, the solution of the adduct XIII (2.016 g.) in methanol containing 1% of water (40 ml.) was allowed to stand at room temperature for a few minutes and then diluted with water (30 ml.). The complex XV (1.495 g., m.p. 178–181°; theory 1.589 g.) precipitated and was removed by filtration. Evaporation of the methanol and most of the water from the filtrate afforded 0.398 g. of tetrachlorohydroquinone (XIV), m.p. 233–235° (theory 0.490 g.).

(b) **With Aqueous Alkali.**—When the adduct XIII (1.2 g.) was shaken for *1–2 minutes* with 5% aqueous sodium hydroxide solution (*ca.* 40 ml.) and the mixture filtered quickly, an alkali-insoluble material (0.763 g.) was obtained. This material consisted of a mixture of complex XV and triphenylphosphine oxide (XII), as shown by isolation of the components *via* recrystallization from benzene–petroleum ether. The alkaline solution obtained above was acidified with concentrated hydrochloric acid, yielding 0.440 g. of tetrachlorohydroquinone (XIV). The partial isolation of XV in this manner is attributable to the somewhat hydrophobic nature of the solid.

Treatment of Complex XV with Alkali.—(a) When XV was shaken with 5% aqueous sodium hydroxide solution for some time, a quantitative separation of alkali-insoluble triphenylphosphine oxide (XII) and alkali-soluble tetrachlorohydroquinone (XIV) (obtained by acidification of the alkaline solution) was effected. The weights of oxide XII and quinol XIV corresponded to a 2:1 molar ratio in XV.

(b) To reproduce the results under previously employed procedures,[3e] XV (1.181 g.) was refluxed with 40 ml. of 40% aqueous sodium hydroxide solution for 45 minutes. From the cooled mixture, 0.768 g. of triphenylphosphine oxide (XII) was obtained. Acidification of the alkaline solution afforded 0.37 g. of tetrachlorohydroquinone (XIV). XV was recovered unchanged after having been shaken with 10% aqueous hydrochloric acid.

Preparation of Complex XV from Triphenylphosphine Oxide (XII) and Tetrachlorohydroquinone (XIV).—A mixture of oxide XII (0.250 g.) and quinol XIV (0.126 g.) was finely ground and was heated for a few minutes at 190°, under nitrogen. On cooling, the melt solidified; the melting point of this material was 179–181°. Recrystallization from benzene–petroleum ether afforded a solid (m.p. 179–181°, 0.26 g.) identical in all respects (mixed m.p. and infrared spectrum in KBr) with XV obtained above.

Alternatively, a solution containing the oxide XII (0.430 g.) and the quinol XIV (0.190 g.) in methanol (20 ml.) was diluted with water (35 ml.). XV (0.475 g., m.p. 180–181°) precipitated in pure form.

Neutralization Equivalent of XIII and XV.—When a solution of tetrachlorohydroquinone (XIV) in 95% ethanol was neutralized with two equivalents of 0.0304 *N* aqueous sodium hydroxide, the reading of a Beckman *p*H meter, taken immediately after neutralization, was 11.1. Solutions of XIII and XV in 95% ethanol were then titrated with the same base to an 11.1 reading. The neutral equivalents so obtained were: for adduct XIII, 291 (calcd. 254); for XV, 445 (calcd. 402).

Formation of Adduct XVI from Triphenylphosphine (I) and 2,5-Dichloro-*p*-benzoquinone (III).—Triphenylphosphine (1.574 g., 6 mmoles) and freshly recrystallized 2,5-dichloro-*p*-benzoquinone (III) (0.708 g., 4 mmoles) were dissolved in anhydrous benzene and the solutions mixed in a dry-box under a dry nitrogen atmosphere. A deep red color developed on mixing, and shortly thereafter a buff-colored precipitate began to form. After 15 hours at room temperature (in the dry-box) precipitation was complete and the color had faded. The precipitate was filtered quickly, the last traces of benzene were removed *in vacuo* and the solid adduct XVI was analyzed as such. Evaporation of the mother liquid from which XVI had precipitated gave less than 40 mg. of residue.

Anal. Calcd. for $C_{66}H_{49}O_4P_3Cl_4$: C, 69.5; H, 4.3; P, 8.2; Cl, 12.4. Found[20]: C, 69.1; H, 4.3; P, 7.4; Cl, 11.8.

Analysis for Ionic Chlorine.—A solution of adduct XVI (0.2066 g.) in methanol afforded 0.0287 g. of silver chloride on treatment with methanolic silver nitrate; calculated for one ionic chlorine in XVI, 0.0256 g. of silver chloride; infrared absorption spectrum of adduct XVI in KBr, bands at: 7.00(s), 8.16(s), 8.5(m), 8.7(m), 8.9(s) and 10.2(m)μ.

ULTRAVIOLET ABSORPTION SPECTRUM OF ADDUCT XVI IN 95% ETHANOL

λ_{max}, mμ	Found[a] ϵ_{max}	Calcd.[b] ϵ_{max}
223	104,500	110,500
261	8,700	7,100
266	9,500	8,100
273	8,500	6,900
304	6,000	7,200
327[c]	6,400	6,500

[a] Based on mol. wt. 1140. [b] Calculated from ($2\epsilon' + 1\epsilon''' + 1\epsilon''''$), where ϵ', ϵ''' and ϵ'''' refer to triphenylphosphine oxide (XII), 2,5-dichlorohydroquinone (XVII) and (4-chloro-2,5-dihydroxyphenyl)-triphenylphosphonium chloride (XVIII) (*vide infra*), respectively, in ethanol. [c] λ_{max} of XVIII.

Hydrolysis of 2,5-Dichloro-*p*-benzoquinone Adduct XVI. (a) With Aqueous Methanol.—A solution of adduct XVI (0.930 g.) in 25 ml. of methanol containing 1% of water was allowed to stand at room temperature for *ca.* 30 minutes. The solution was diluted with ethyl acetate (100 ml.) and on cooling it yielded a first crop (0.220 g.) of colorless (4-chloro-2,5-dihydroxyphenyl)-triphenylphosphonium chloride (XVIII). A second crop of XVIII was obtained by concentration of the filtrate and further dilution with ethyl acetate; yield of chloride XVIII, 0.335 g., m.p. 292–298° (theory 0.350 g.). The analytical sample (four recrystallizations from methanol–ethyl acetate) had m.p. 297–298°.

Anal. Calcd. for $C_{24}H_{19}O_2PCl_2$: C, 65.3; H, 4.3; P, 7.0; Cl, 16.1. Found: C, 65.3; H, 4.5; P, 7.8; Cl, 16.1.

Analysis for Ionic Chlorine.—A solution of chloride XVIII (0.1649 g.) in methanol afforded 0.0472 g. of silver chloride on treatment with methanolic silver nitrate; calculated for

---

(20) Calcd. for 1(1) + 1(III): C, 65.6; H, 3.9; P, 7.1; Cl, 16.1. Calcd. for 2(I) + 1(III): C, 71.9; H, 4.7; P, 8.8; Cl, 10.1.

one ionic chlorine in XVIII, 0.0536 g. of silver chloride; infrared absorption spectrum of chloride XVIII in KBr, bands at: 6.3(w), 6.65(w), 6.78(w), 7.00(m-s), 7.15(s), 8.15(m), 8.4(m), 9.11(s) and 10.2(m); ultraviolet absorption spectrum of chloride XVIII in 95% ethanol, $\lambda_{\max}$ (ϵ) at: 224 mμ (48,000), 263 mμ (3,400), 270 mμ (3,600), 277 mμ (3,100) and 329 mμ (6,500).

The methanol–ethyl acetate solution described above, from which the chloride XVIII separated, was evaporated to dryness. The residue so obtained was dissolved in hot benzene, and the solution was diluted with petroleum ether. On cooling, XIX (0.515 g.), m.p. 163–165° (theory 0.580 g.) separated. The analytical sample of XIX, obtained after four recrystallizations from benzene–petroleum ether, had m.p. 163.0–164.6°; infrared absorption spectrum of XIX in KBr, bands at: 3.2–3.5(s), 7.00(s), 7.10(m-s), 8.2(m), 8.35(m-s), 8.5(s) and 8.95(s) μ.

Anal. Calcd. for $C_{42}H_{34}O_4P_2Cl_2$: C, 68.6; H, 4.7; P, 8.4; Cl, 9.4. Found: C, 68.5; H, 4.9; P, 8.5; Cl, 9.4.

ULTRAVIOLET ABSORPTION SPECTRUM OF XIX IN 95% ETHANOL

$\lambda_{\max}$, mμ	Found[a] $\epsilon_{\max}$	Calcd.[b] $\epsilon_{\max}$
224	60,000	62,500
261	3,300	3,600
267	4,400	4,600
273	4,000	4,200
304	5,000	5,000

[a] Based on mol. wt. 735. [b] Calculated from ($2\epsilon' + 1\epsilon'''$), where ϵ' and ϵ''' refer to triphenylphosphine oxide (XII) and 2,5-dichlorohydroquinone (XVII), respectively.

(b) A second experiment in which 2.300 g. of adduct XVI was warmed with 50 ml. of methanol containing 1% of water, afforded 0.830 g. of chloride XVIII (theory 0.865 g.) and 1.255 g. of complex XIX (theory 1.435 g.).

(c) When the adduct XVI (0.460 g.) was shaken for *ca. one minute* with 5% aqueous sodium hydroxide and the mixture filtered quickly, a separation was effected. The alkali-insoluble material (0.20 g.) was recrystallized from benzene–petroleum ether affording mostly complex XIX and some triphenylphosphine oxide (XII) (resulting from the splitting of XIX by base). Acidification of the alkaline filtrate gave 0.230 g., consisting mostly of chloride XVIII and some 2,5-dichlorohydroquinone (XVII) (resulting from the partial cleavage of XIX by base).

Treatment of (4-Chloro-2,5-dihydroxyphenyl)-triphenylphosphonium Chloride (XVIII) with Picric Acid. Formation of Picrate XXII.—A solution of chloride XVIII in methanol was treated with a methanolic solution of picric acid. Addition of water precipitated the picrate XXII, which had m.p. 220–226°. After three recrystallizations from aqueous methanol XXII had m.p. 225.0–226.5; ultraviolet absorption spectrum of picrate XXII in 95% ethanol, $\lambda_{\max}$ (ϵ) at: 225 mμ (100,000), 268 mμ (7,200), 276 mμ (5,400), 341 mμ (16,700) and 357 mμ (16,500).

Anal. Calcd. for $C_{30}H_{21}N_3O_9PCl$: C, 56.7; H, 3.3. Found: C, 57.3; H, 3.4.

Alkaline Degradation of (4-Chloro-2,5-dihydroxyphenyl)-triphenylphosphonium Chloride (XVIII).—(a) The chloride XVIII was reprecipitated unchanged from its solution in *cold* 5% aqueous sodium hydroxide by addition of hydrochloric acid.

(b) A solution of chloride XVIII (0.325 g.) in 5% aqueous sodium hydroxide (20 ml.) was refluxed for 12 hours under nitrogen. The mixture was filtered directly into an excess of benzoyl chloride. The alkali-insoluble material in the filter (0.185 g., m.p. 154–156°) proved to be triphenylphosphine oxide (XII). The material obtained by benzoylation of the alkali-soluble filtrate (yield 0.205 g., theory 0.225 g.) was shown to be *chlorohydroquinone dibenzoate* (dibenzoate of XXIII). Identification was made by mixed melting point and comparison of the infrared spectrum with that of an authentic sample.

(c) A solution of chloride XVIII (0.200 g.) in 30 ml. of 20% methanolic potassium hydroxide was allowed to stand *at room temperature* for 15 hours. Addition of water (20 ml.) followed by ether extraction effected a separation. From the ether extract, 0.038 g. of triphenylphosphine oxide (XII) was obtained. Acidification of the alkaline layer with hydrochloric acid gave 0.110 g. of unreacted chloride XVIII.

Preparation of Phosphonium Betaine XX from (4-Chloro-2,5-dihydroxyphenyl)-triphenylphosphonium Chloride (XVIII).—A suspension of chloride XVIII (0.080 g.) in 15 ml. of 15% aqueous sodium carbonate was shaken for 15 hours. The initially white solid turned yellow. The solid was filtered and washed with water; yield of betaine XX, 0.060 g. (m.p. 236–238°); analytical sample, yellow crystals, m.p. 249–251° (from methanol–ethyl acetate); infrared spectrum of betaine XX in KBr, bands at: 3.0(m), 6.75(m), 6.82(m), 7.00(s), 7.5(s), 8.42(s) and 9.05(s); ultraviolet absorption spectrum of betaine XX in 95% ethanol, $\lambda_{\max}$ (ϵ) at: 225 mμ (45,600), 262 mμ (5,300), 268 mμ (4,700), 275 mμ (3,500) and 367 mμ (4,900).

Anal. Calcd. for $C_{24}H_{18}O_2PCl$: C, 71.2; H, 4.5; P, 7.7. Found: C, 70.9; H, 4.5; P, 8.2.

The yellow betaine XX was converted into the colorless chloride XVIII by shaking with 5% aqueous hydrochloric acid.

(4-Chloro-2-ethoxy-5-hydroxyphenyl)-triphenylphosphonium Iodide (XXI).—A solution of phosphonium betaine XX (0.700 g.) in methanol (*ca.* 40 ml.) was refluxed for 12 hours with excess ethyl iodide; evaporation to dryness left a residue (0.750 g.) which was dissolved in methanol. Addition of ethyl acetate to the hot solution to the point of cloudiness, followed by cooling, afforded 45 mg. of a solid (m.p. 248–254°) which was discarded. Repetition of this procedure afforded 0.675 g. of (4-chloro-2-ethoxy-5-hydroxyphenyl)-triphenylphosphonium iodide (XXI), m.p. 217–218°. The analytical sample had m.p. 217–219° (from methanol–ethyl acetate); infrared spectrum of ethiodide XXI in KBr, bands at: 6.2(w), 6.78(m), 7.00(m), 7.22(s), 8.28(m) and 9.02(s); ultraviolet spectrum of ethiodide XXI in 95% ethanol, $\lambda_{\max}$(ϵ) at: 224 mμ (59,800), 262 mμ (3,700) (shoulder), 269 mμ (3,600), 277 mμ (3,000) and 328 mμ (6,800).

Anal. Calcd. for $C_{26}H_{23}O_2PClI$: C, 55.7; H, 4.1; P, 5.5. Found: C, 55.5; H, 4.5; P, 5.7.

Treatment of Complex XIX with Alkali.—XIX (0.630 g.) was shaken with 25 ml. of 5% aqueous sodium hydroxide solution for 15 minutes. Filtration yielded 0.455 g. of alkali insoluble material, m.p. 154–156°, shown to be triphenylphosphine oxide (XII) (theoretical for a 2:1 ratio, 0.478 g.). The alkaline solution was acidified with concentrated hydrochloric acid; the material that precipitated (0.124 g., m.p 170–172°) was shown to be 2,5-dichlorohydroquinone (XVII) (theoretical 0.152 g.).

Preparation of Complex XIX from Triphenylphosphine Oxide (XII) and 2,5-Dichlorohydroquinone (XVII).—(a) A mixture of oxide XII (0.784 g.) and quinol XVII (0.253 g.) was heated at 185° for a few minutes, under nitrogen. The cooled mixture was triturated with petroleum ether, giving 0.9 g. of material, m.p. 163–165°. The infrared spectrum was indistinguishable from that of XIX previously obtained.

(b) Alternatively, a solution of the oxide XII (0.557 g.) and the quinol XVII (0.179 g.) in methanol (35 ml.) was diluted with water (35 ml.). The colorless material that precipitated (0.642 g.) had m.p. 163–165° and exhibited, in KBr, an infrared spectrum indistinguishable from that of XIX.

Formation of Adduct (Betaine **XXIV**) **from Triphenylphosphine (I) and** *p*-Benzoquinone (**IV**).—Solutions of freshly recrystallized *p*-benzoquinone (IV) (1.250 g., 11.6 mmoles) and triphenylphosphine (I) (3.040 g., 11.6 mmoles) in anhydrous benzene were mixed in a dry nitrogen atmosphere (dry-box). There was no immediate change; gradually, after several minutes, a deep red color developed in the solution and a precipitate began to appear. After 20 hours at room temperature (dry-box) the precipitate of adduct XX1V was collected (3.475 g.); it consisted of fine, yellow-greenish crystals, m.p. 262–266°. The benzene filtrate was returned to the dry-box and after several days it had deposited 0.800 g. of additional adduct XXIV (total yield 4.275 g.). A sample of this material *was dried at* 150° *in vacuo* and analyzed without further purification; infrared spectrum of adduct XXIV (betaine) in KBr, bands at: 6.82(m), 7.00(s), 7.4(m-s), 8.00(s), 8.10(m-s) and 9.15(m-s) μ; ultraviolet spectrum of adduct XXIV (betaine) in 95% ethanol, $\lambda_{\max}$ (ϵ) at: 255 mμ (5,100), 261 mμ (4,300), 267 mμ (3,800), 340 mμ (2,400) and 367 mμ (2,900).

Anal. Calcd. for $C_{24}H_{19}O_2P$: C, 77.8; H, 5.2; P, 8.4. Found: C, 78.2; H, 5.5; P, 9.0.

The adduct XXIV retained benzene tenaciously; a sample of the original precipitate dried at 60° (0.1 mm.) was analyzed.

Anal. Calcd. for $C_{24}H_{19}O_2P{\cdot}C_6H_6$: C, 80.3; H, 5.6. Found: C, 79.8; H, 6.0.

The ultraviolet spectrum of this material in 95% ethanol had λ_{max} (ϵ) at: 255 mμ (6,100), 261 mμ (5,400), 267 mμ (4,600), 340 mμ (2,800) and 367 mμ (3,500).

The crude betaine XXIV as initially obtained was soluble in hot methanol. The solution, apparently saturated, did not deposit crystals on cooling, but on evaporation to a small volume it afforded well defined yellow crystals, m.p. 270–271° (dried at 60°, 0.1 mm.).

Anal. Calcd. for $C_{24}H_{19}O_2P{\cdot}CH_3OH$: C, 74.6; H, 5.8; P, 7.7. Found: C, 75.0; H, 5.6.

In the 4–12 μ region the infrared spectra of the original adduct XXIV and of this solvate were identical; ultraviolet spectrum of solvate in 95% ethanol, λ_{max} (ϵ) at: 255 mμ (6,000), 261 mμ (5,400), 267 mμ (4,100), 340 mμ (3,000) and 367 mμ (3,600).

Treatment of Betaine XXIV with Hydrochloric Acid. Formation of (2,5-Dihydroxyphenyl)-triphenylphosphonium Chloride (XXV).—When the adduct XXIV (0.50 g.) was shaken for 24 hours with 50 ml. of 5% hydrochloric acid, the original yellow-greenish solid turned colorless. The chloride XXV (0.39 g.) collected by filtration had m.p. 285–290°. The analytical sample was obtained by solution in methanol and precipitation with ether and had m.p. 296.5–298.5° (the chloride XXV also can be recrystallized from methanol–ethyl acetate); infrared spectrum of chloride XXV in KBr, bands at: 6.70(m), 7.00(s), 7.5(m), 8.05(m), 8.3(m) and 9.1(s); ultraviolet spectrum of chloride XXV in 95% ethanol, λ_{max} (ϵ) at: 225 mμ (43,500), 263 mμ (3,300), 269 mμ (3,700), 277 mμ (3,300) and 328 mμ (5,300).

Anal. Calcd. for $C_{24}H_{20}O_2PCl$: C, 70.8; H, 4.9; P, 7.6; Cl, 8.7. Found: C, 70.6; H, 4.9; P, 7.7; Cl, 8.2.

Betaine XXIV from Chloride XXV.—A suspension of chloride XXV (0.70 g.) in 20 ml. of 10% aqueous potassium carbonate was shaken for 2 hours. The resulting yellow solid (0.65 g.) had m.p. 262–264° and was identical in all respects with betaine XXIV.

(2,5-Dihydroxyphenyl)-triphenylphosphonium Nitrate.—(a) A suspension of adduct XXIV (0.45 g.) in 5% nitric acid was shaken for several minutes. The resulting colorless nitrate (m.p. 272–276°, 0.40 g.) was recrystallized from methanol–ethyl acetate; analytical sample, m.p. 276.5–278.5°; ultraviolet spectrum of nitrate in 9% ethanol, λ_{max} (ϵ) at: 225 mμ (46,000), 263 mμ (3,600), 269 mμ (3,800), 277 mμ (3,500) and 328 mμ (5,300).

Anal. Calcd. for $C_{24}H_{20}NO_5P$: C, 66.5; H, 4.6; P, 7.2. Found: C, 65.9; H, 4.9; P, 7.7.

(b) A solution of chloride XXV (0.605 g.) in methanol was treated with methanolic silver nitrate. Removal of the silver chloride left a solution from which, on evaporation, 0.46 g. of nitrate, m.p. 274–276°, was obtained. This material was shown to be identical with nitrate previously obtained.

(2,5-Dihydroxyphenyl)-triphenylphosphonium picrate (XXVI) was prepared from the betaine XXIV in methanol solution by addition of picric acid, followed by water; m.p. 187.5–189° (methanol–water); ultraviolet spectrum of picrate XXVI in 95% ethanol, λ_{max} (ϵ) at: 267 mμ (6,900), 275 mμ (5,200) and 358 mμ (16,800).

Anal. Calcd. for $C_{30}H_{22}N_3O_9P$: C, 60.1; H, 3.7. Found: C, 60.3; H, 3.8.

(2-Ethoxy-5-hydroxyphenyl)-triphenylphosphonium Iodide (XXVII).—A solution of betaine XXIV (5.0 g.) in methanol was refluxed with excess ethyl iodide for 10 hours. Removal of the solvent left a residue which was dissolved in chloroform and re-precipitated with ether; yield 4.8 g., m.p. 224–231°. The analytical sample of ethiodide XXVII had m.p. 237.0–238.5° (from methanol–ethyl acetate); infrared spectrum of ethiodide XXVII in KBr, bands at: 6.38(w), 6.75(s), 7.00(m-s), 7.6(m), 7.82(s), 8.28(s) and 9.05(s) μ; ultraviolet spectrum of ethiodide XXVII in 95% ethanol, λ_{max} (ϵ) at: 220 mμ (59,500), 263 mμ (3,300), 270 mμ (3,700), 277 mμ (3,300) and 327 mμ (5,300).

Anal. Calcd. for $C_{26}H_{24}O_2PI$: C, 59.3; H, 4.6; P, 5.9; I, 24.1. Found: C, 59.1; H, 4.8; P, 6.0; I, 24.7.

(2,5-Diethoxyphenyl)-triphenylphosphonium Iodide (XXXI).—(2-Ethoxy-5-hydroxyphenyl)-triphenylphosphonium iodide (XXVII) (3.5 g.) was added to a solution of sodium (0.15 g.) in methanol (35 ml.). Excess ethyl iodide was added and the solution was refluxed for 12 hours. The residue (4.72 g.) remaining after evaporation was taken up in chloroform (0.93 g. of insoluble material was removed by filtration) and the chloroform solution was washed with 5% aqueous sodium hydroxide and with water. Evaporation of the dried chloroform solution left 2.2 g. of material, which afforded 1.37 g. of (2,5-diethoxyphenyl)-triphenylphosphonium iodide (XXXI), m.p. 212–215°, upon recrystallization from methanol–ethyl acetate; infrared spectrum of ethyl ether–ethiodide XXXI in KBr, bands at: 6.35(m), 6.72(s), 6.80(s), 7.00(s), 7.10(m), 7.22(m), 7.65(m), 7.9(s), 8.22(s), 8.7(m) and 9.02(s); ultraviolet spectrum of ethyl ether–ethiodide XXXI, λ_{max} (ϵ) at: 262 mμ (3,400), 269 mμ (4,000), 276 mμ (3,500) and 323 mμ (3,300).

Anal. Calcd. for $C_{28}H_{28}O_2PI$: C, 60.7; H, 5.1; P, 5.6. Found: C, 60.2; H, 5.1; P, 6.1.

Alkaline Cleavage of Betaine XXIV.—A solution of betaine (*i.e.*, adduct) XXIV (0.850 g.) in 35 ml. of 5% aqueous sodium hydroxide was refluxed for 8 hours *under nitrogen*. The mixture was directly filtered into an excess of benzoyl chloride. The base-insoluble material in the filter (0.516 g., theory 0.544 g.) was shown to be triphenylphosphine oxide (XII). From the benzoylation of the alkaline filtrate there was obtained 0.565 g. (theory 0.603 g.) of hydroquinone dibenzoate (dibenzoate of XXIX), whose identity was established by comparisons with an authentic sample.

Alkaline Cleavage of (2-Ethoxy-5-hydroxyphenyl)-triphenylphosphonium Iodide (XXVII).—A solution of ethiodide XXVII (0.880 g.) in 35 ml. of 5% aqueous sodium hydroxide was refluxed for 15 hours *under nitrogen*. The mixture was filtered into excess benzoyl chloride. In this manner, 0.390 g. (theory 0.466 g.) of triphenylphosphine oxide (XII) and 0.210 g. of hydroquinone monoethyl ether benzoate (benzoate of XXVIII) was obtained. The benzoate was identified by its melting point, 100–103° (reported m.p. 104°) and infrared spectrum.

Alkaline Cleavage of (2,5-Diethoxyphenyl)-triphenylphosphonium Iodide (XXXI).—A mixture of ethyl ether–ethiodide XXXI (1.36 g.) and 60 ml. of 5% aqueous sodium hydroxide was refluxed for two days, utilizing a "cold finger" to collect material volatile with steam. The alkali-insoluble material (0.655 g.) obtained by filtration was shown to be triphenylphosphine oxide (theory 0.684). The crystalline material collected in the "cold finger" (0.360 g.) was shown to be hydroquinone diethyl ether (XXXII) (theory 0.408) by its m.p. (70–72°, reported 72°) and infrared spectrum.

NEW YORK 27, N. Y.