[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Reaction of Trialkyl Phosphites and of Triaryl Phosphites with Chloranil. A New Synthesis of Hydroquinone Monoalkyl Ethers[1,2]

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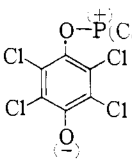
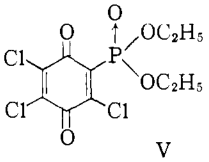
RECEIVED AUGUST 26, 1958

Triethyl phosphite and trimethyl phosphite react with chloranil in benzene solution, at room temperature, giving alkyl ethers of dialkyl-*p*-hydroxyaryl phosphates, VII and VIII, but no dialkyl trichloro-*p*-quinonephosphonates (V) and alkyl chlorides, as had been stated previously. Triphenyl phosphite reacts with chloranil only at 100° and yields an adduct which is hydrolyzed to triphenyl phosphate and tetrachlorohydroquinone. The latter and the trialkyl phosphates are produced, exclusively, when the trialkyl phosphites are added to a benzene solution of chloranil containing aqueous ethanol. A mechanism for this new synthesis of hydroquinone monoalkyl ethers (obtained by hydrolysis of the phosphates) is advanced.

Triphenylphosphine, $(C_6H_5)_3P$, reacts with chloranil (I) at room temperature in benzene solution.[2a] The 1:1 adduct thus formed yields triphenylphosphine oxide, $(C_6H_5)_3PO$, and tetrachlorohydroquinone on treatment with water. Formula II was suggested as a possibility for the structure of the 1:1 adduct.[2a] The reaction of triethyl phosphite (III) with chloranil in dioxane solution was reported[4] to give ethyl chloride and diethyl trichloro-*p*-quinone-phosphonate (V), but no evidence was provided for this structure.

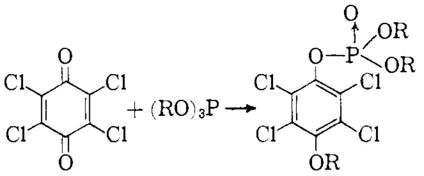

II


V

As part of a more general study of the interaction between tricovalent phosphorus compounds and quinones,[2] we have investigated the reaction of chloranil (I) with triethyl phosphite (III), trimethyl phosphite (IV) and triphenyl phosphite (VI). In dioxane solution, the major product of the reaction with triethyl phosphite was diethyl (4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VII), which was accompanied by a small amount of the bis-phosphate IX; no ethyl chloride or quinone V could be detected.[4] A more thorough study of the reaction was carried out in benzene solution where an excellent yield of ether-phosphate VII (90%) was obtained; in addition, small amounts of the bis-phosphate IX (2%) and of tetrachlorohydroquinone diethyl ether (XI) (*ca.* 1%) were isolated. An interesting feature of the reaction is the development of a deep red color which fades to pale yellow on standing.

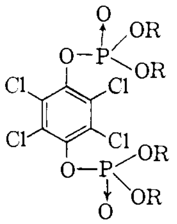
The results with trimethyl phosphite (IV) were similar, except that the colored phase of the reaction was barely detectable when the reagents were mixed in a 1:1 mole ratio. The red color was clearly observable when a large excess of trimethyl phosphite was used. Dimethyl (4-methoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VIII), the main product, was accompanied by some tetrachlorohydroquinone dimethyl ether (XII), but no bis-phosphate X could be isolated. The latter, as well as the other compounds mentioned, VII, VIII and IX were synthesized, independently, from tetrachlorohydroquinone by the procedures described in the Experimental Section.

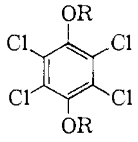
The alkyl ether phosphates VII and VIII were readily hydrolyzed to the corresponding phenolic-ethers, namely, tetrachlorohydroquinone monoethyl ether and tetrachlorohydroquinone monomethyl ether. The reaction of quinones with trialkyl phosphites, therefore, is a promising procedure for the synthesis of quinol monoalkyl ethers.


I

III, R = C_2H_5
IV, R = CH_3

VII, R = C_2H_5
VIII, R = CH_3


IX, R = C_2H_5
X, R = CH_3


XI, R = C_2H_5
XII, R = CH_3

Triphenyl phosphite (VI) did not react to any appreciable extent with chloranil at room temperature in benzene solution. However, when a suspension of chloranil in excess of triphenyl phosphite was heated to 100°, a transient red color was observed and a viscous solution resulted. Hydrolysis afforded tetrachlorohydroquinone (XIV) and triphenyl phosphate, $(C_6H_5O)_3PO$.

It is evident that trialkyl phosphites do not effect a replacement of the chlorine atoms of chloranil, but instead they lead to products in which phosphorus–oxygen bonds are formed. An intermediate of type XIII would explain the results. This intermediate is entirely analogous to structure II, previously suggested[2] for the triphenylphosphine-chloranil adduct. A group-translocation is now possible in the aryloxy-trialkoxyphosphonium structure XIII, giving rise to the observed dialkyl-(*p*-alkoxyaryl) phosphates VII and VIII. The

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(1) The Structure of Quinone-Donor Adducts. IV.

(2) (a) Part I, F. Ramirez and S. Dershowitz, *Chemistry & Industry*, 665 (1956); THIS JOURNAL, **78**, 5614 (1956); (b) part II, *J. Org. Chem.*, **22**, 856 (1957); (c) part III, *ibid.*, **23**, 778 (1958).

(3) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Ill.

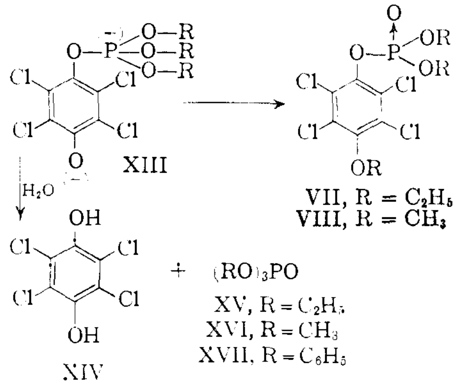
(4) E. C. Ladd and M. R. Harvey, U. S. Patent 2,609,376, Sept. 2, 1952; *C. A.*, **47**, P7540 (1953).

group translocation is analogous to the Arbuzov–Michaelis transformation[5] in which dialkyl alkanephosphonates are formed from trialkyl phosphites and alkyl halides, presumably *via* an alkyltrialkoxyphosphonium intermediate

$$(RO)_3P + R'X \longrightarrow [(RO)_3PR']^{(+)}X^{(-)} \longrightarrow (RO)_2P(O)R' + RX$$

No group translocation is possible in the adduct derived from triphenyl phosphite, *i.e.*, XIII with R = C_6H_5. Hence, on hydrolysis, tetrachlorohydroquinone (XIV) and triphenyl phosphate (XVII) are produced. The hydrolysis probably involves a pentacovalent phosphorus intermediate

$$(RO)_3P(OH)(OAr) \longrightarrow (RO)_3P(O) + HOAr$$



XIII

VII, R = C_2H_5
VIII, R = CH_3

XIV

XV, R = C_2H_5
XVI, R = CH_3
XVII, R = C_6H_5

If adduct XIII is, indeed, an intermediate in the reaction of the trialkyl phosphites, it might be possible to intercept it under suitable conditions. In fact, it was found that if the trialkyl phosphites were added slowly to a solution of chloranil in benzene containing aqueous ethanol, the only products isolated were tetrachlorohydroquinone (XIV) and the trialkyl phosphates XV or XVI. In our opinion, these observations have a further mechanistic significance in that they essentially represent the coupling of the two half equations

$$X_3P + H_2O \longrightarrow X_3PO + 2H^{(+)} + 2e \qquad (1)$$

$$Q + 2H^{(+)} + 2e \longrightarrow QH_2 \qquad (2)$$

where Q = quinone and QH_2 = hydroquinone. Here, X_3P is a tricovalent phosphorus compound with phosphorus in the +3 oxidation state. The intermediate XIII serves to ascribe a definite role to the oxidizing agent (quinone) and the reducing agent (X_3P) in the process of splitting the water molecule into hydrogen and oxygen as in the overall equation

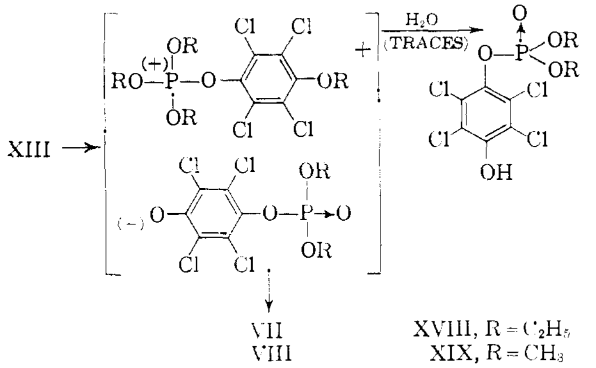
$$X_3P + Q + H_2O \longrightarrow X_3PO + QH_2$$

In the cases where X = phenyl, phenoxy or alkoxy in X_3P, no structural ambiguity arises from the uncertainty in the location of mobile hydrogens, as in the case of phosphorous acid (X = OH) and hypophosphorous acid.[6] Chloranil and phosphorous acid also react on heating and produce, after hydrolysis, tetrachlorohydroquinone. Standard potentials are known for the half-equations

$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H^{(+)} + 2e; \quad E^0 = 0.276 \text{ v.}$$

$$H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2H^{(+)} + 2e; \quad E^0 = 0.50 \text{ v.}$$

The group translocation observed in the reaction of trialkyl phosphites with quinones is probably intermolecular and stepwise. It may be significant that, if *small* amounts of water are present, some dialkyl (*p*-hydroxyaryl)-phosphates XVIII or XIX are isolated, in addition to the expected products: dialkyl (*p*-alkoxyaryl)-phosphates VII or VIII, tetrachlorohydroquinone (XIV) and the trialkyl phosphates XV or XVI. This can be explained as



VII
VIII

XVIII, R = C_2H_5
XIX, R = CH_3

One way of explaining the small amounts of dialkyl ethers XI or XII isolated in the reaction is to assume alkylation by intermediate XIII, of small amounts of tetrachlorohydroquinone produced from XIII by unavoidable traces of water. The origin of the bis-phosphate IX is not easy to explain; IX could originate from adduct XIII *via* an attack on the phosphorus by the phenoxide oxygen (as an alternative to the preponderant attack on the alkyl carbon by the phenoxide oxygen observed in the group translocation). However, other paths can be devised.[2b]

The problem posed by the appearance of deep red colors in the early stages of the reaction of chloranil with triphenylphosphine and with trialkyl phosphites is an interesting one. We have reported[2b] that the benzene solutions exhibit strong paramagnetic resonance absorption. These phenomena are probably related to the formation of charge-transfer complexes[7] $[(A,D) \leftrightarrow (A^{-}\text{-}^{+}D)]$ between the electron-acceptor quinone (A) and the donor(D). More information is being sought in a detailed spectrophotometric study now in progress.

Acknowledgment.—We are grateful to the Eli Lilly Research Grants Committee and to the National Cancer Institute of the National Institute of Health (Grant CY-3250) for financial support.

Experimental[8]

Triethyl phosphite and trimethyl phosphite were treated with sodium, decanted from it and distilled with protection against moisture. Operations were carried out in a dry-box under nitrogen. The chloranil was freshly recrystallized and dried.

Reaction of Chloranil (I) with Triethyl Phosphite (III) in Dioxane Solution.—To a solution of chloranil (10.7 g., 43.5 mmoles) in purified dioxane (150 ml.) was added an excess of triethyl phosphite (25 g., 150 mmoles) dropwise and

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[5] G. M. Kosolapoff in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. VI, p. 273.

[6] *Cf.* H. H. Sisler in M. C. Sneed and R. C. Brasted, "Comprehensive Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1956, Vol. V, pp. 118, 126.

[7] R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

[8] Analyses by Micro-Tech Laboratories, Skokie, Ill.

with stirring. The solution turned dark and heat was evolved. No ethyl chloride was formed. The solvent and the excess of triethyl phosphite were removed *in vacuo*. The crystals which separated out when the resulting oil was allowed to stand, were filtered and washed with petr. ether. This crystalline material (1.3 g., 6%) was shown to be diethyl [4-(diethoxyphosphinyloxy)-2,3,5,6-tetrachlorophenyl]-phosphate (IX). The analytical sample had m.p. 170–171° (from cyclohexane); bands at 7.8 μ (strong, non-bonded P → O) and 9.5 μ (broad, probably P–OEt) in KBr.

Anal. Calcd. for $C_{14}H_{20}Cl_4O_8P_2$: C, 32.3; H, 3.9; P, 11.9; Cl, 27.3. Found: C, 32.6; H, 3.9; P, 12.1; Cl, 28.2.

The oil from which the bis-phosphate IX had separated was submitted to a short-path distillation at a bath temperature of 190–210° (0.1 mm.). The distillate (9.2 g., 52%) crystallized on cooling (m.p. 37–41°). The analytical sample of this material, which is diethyl (4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VII) had m.p. 38–40° after several recrystallizations from hexane (−70°); bands at 7.8 and 9.7 μ in KBr.

Anal. Calcd. for $C_{12}H_{15}O_5Cl_4P$: C, 35.0; H, 3.7; P, 7.5; Cl, 34.4. Found: C, 34.7; H, 3.8; P, 7.6; Cl, 33.7.

Reaction of Chloranil (I) **with Triethyl Phosphite** (III) **in Benzene Solution.**—(a) To a solution of chloranil (13.67 g., 55.5 mmoles) in dry benzene (1 l.) was added 9.30 g. (56 mmoles) of triethyl phosphite, in a dry-box under a dry nitrogen atmosphere. The red color which developed persisted for *ca.* one minute and faded to light yellow. After 15 hours, the solvent was removed and the residue was treated with hexane and cooled. The hexane-insoluble bis-phosphate IX (0.32 g., 1.1%) was removed by filtration and the filtrate was evaporated under reduced pressure. From the residual oil, 0.035 g. (0.2%) of tetrachlorohydroquinone diethyl ether[9] (XI) was obtained by sublimation at a bath-temperature of 100–120° (0.2 mm.). The remaining oil was submitted to a short-path distillation and gave 0.30 g. of triethyl phosphate (collected at a bath temperature of 150°, 0.2 mm.) and 18.65 g. (82%) of diethyl(4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (IX) (collected at a bath temperature of 190–220°, 0.2 mm.).

(b) With one or two mole-equivalents of triethyl phosphite per mole of chloranil comparable results were obtained; the initial red color persisted for variable periods of time (15–30 minutes). Without attempting to isolate the traces of by-products, the yields of crystalline diethyl (4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (IX) were 90–92%.

Reaction of Chloranil with Triethyl Phosphite in the Presence of Water.—(a) Chloranil (5.0 g.) was dissolved in 600 ml. of benzene containing 100 ml. of 95% aqueous ethanol. To this solution was added, dropwise, a solution of triethyl phosphite (3.4 g.) in 100 ml. of benzene. The residue obtained upon evaporation of solvents was separated into a hexane-insoluble and a hexane-soluble fraction. The hexane-insoluble fraction (2.65 g.) was shown to be tetrachlorohydroquinone. The hexane-soluble fraction was evaporated to dryness and the residue was treated with a small amount of 95% ethanol and chloroform; from this solution, an additional 1.35 g. of tetrachlorohydroquinone deposited on standing. Removal of the ethanol–chloroform left 4.3 g. of triethyl phosphate (XV).

(b) A solution of chloranil (10.0 g.), and triethyl phosphite (6.8 g.) in 40 ml. of benzene (not dried) was stirred for 20 hr. in an open flask. A deep-red color appeared and persisted for 5 hr. The solvent was removed and the residue was treated with hexane. On cooling, 1.55 g. of diethyl (4-hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XVIII) (*vide infra*) was obtained. Distillation of the hexane filtrate gave 0.42 g. of triethyl phosphate (<150° at 0.35 mm.). The residue from the distillation was taken up in benzene and the solution was extracted with 5% aq. sodium hydroxide. Acidification gave 0.59 g. of tetrachlorohydroquinone (XIV). From the benzene layer, 12.7 g. of diethyl (4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VII) was obtained.

Reaction of Chloranil (I) **with Trimethyl Phosphite** (IV) **in Benzene Solution.**—(a) To a solution of chloranil (11.6 g.) in 1 l. of dry benzene was added 5.8 g. of freshly distilled trimethyl phosphite. No red color was detectable under these conditions. After 24 hours, the solvent was removed and the residue was treated with 50 ml. of benzene. On cooling, 2.5 g. of dimethyl (4-methoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VIII) of m.p. 87–92° (*vide infra*) crystallized out and was filtered. The solvent was removed from the filtrate and the residue was treated with hexane. The hexane-insoluble material weighed 11.5 g. and had m.p. 87–92°. The total yield of ether phosphate VIII was 14.0 g. The analytical sample had m.p. 94–95° (from cyclohexane) and band at 7.78 μ (non-bonded P→O).

Anal. Calcd. for $C_9H_9O_5Cl_4P$: C, 29.2; H, 2.5. Found: C, 29.4; H, 2.7.

The hexane solution obtained above was evaporated and the residue was treated with 95% ethanol, yielding 0.28 g. of tetrachlorohydroquinone dimethyl ether (XII), m.p. 162–163°, alone and mixed with an authentic sample; reported[9] m.p. 160–162°. No evidence for bis-phosphate X (*vide infra*) was obtained.

(b) To a solution of chloranil (14.1 g.) in 1200 ml. of dry benzene was added 14.0 g. (2 mol equiv.) of trimethyl phosphite. The yellow color of the chloranil solution deepened. A large excess (*ca.* 10 mol equiv.) of trimethyl phosphite then was added at once, whereupon a red color developed in the solution. The color faded to pale yellow in *ca.* 3 minutes. The solvent and the excess of trimethyl phosphite were removed after 2 hours. The residue was treated with cold hexane and the insoluble portion (20.2 g.) was recrystallized from cyclohexane yielding 17.2 g. of ether phosphate VIII of m.p. 87–92°.

The hexane solution obtained above furnished 0.90 g. of tetrachlorohydroquinone dimethyl ether (X).

Reaction of Chloranil with Trimethyl Phosphite in the Presence of Water.—(a) To a solution of chloranil (5.0 g.) in benzene (600 ml.) containing 100 ml. of 95% ethanol was added slowly (45 minutes) a solution of trimethyl phosphite (2.5 g.) in benzene (200 ml.). The residue obtained after removal of solvents was treated with 5% aq. sodium hydroxide. Acidification of the alkaline layer gave 4.45 g. (90% yield) of tetrachlorohydroquinone.

(b) When a solution of chloranil (7.1 g.) and trimethyl phosphite (3.55 g.) in 4.50 ml. of benzene (not dried) was stirred for 20 hr. in an open flask, a deep red color developed and persisted for 3–4 hr. From the solution, 0.89 g. of dimethyl (4-hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XIX) was obtained (*vide infra*).

Alkaline Hydrolysis of Ether Phosphates VII and VIII.—(a) A solution of diethyl (4-ethoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VII) (2.0 g.) in 35 ml. of 95% ethanol containing 1.3 g. of potassium hydroxide was refluxed for 20 hr. The solution was poured into concd. hydrochloric acid, diluted with water and filtered. The yield of tetrachlorohydroquinone monomethyl ether of m.p. 84–85° was 1.31 g. (89%). From 0.22 g. of this phenolic ether, 2 g. of sodium carbonate, excess diethyl sulfate and 25 ml. of water, 0.21 g. of tetrachlorohydroquinone diethyl ether (XI), m.p. 110–112°, was obtained after 2 hr. at reflux temperature; reported[9] m.p. 112°.

(b) From 3.0 g. of dimethyl (4-methoxy-2,3,5,6-tetrachlorophenyl)-phosphate (VIII), there was obtained by alkaline hydrolysis, 1.95 g. (92%) of tetrachlorohydroquinone monomethyl ether[10] of m.p. 114–115°, reported[9,10] m.p. 114–116°. The phenolic ether (0.50 g.) was converted into tetrachlorohydroquinonedimethyl ether (XII) (0.42 g.) of m.p. 162–164°, by means of dimethyl sulfate; reported[9] m.p. 160°.

Preparation of Bis-phosphates IX and X; of Phenolic Phosphates XVIII and XIX and of Ether Phosphates VII and VIII from Tetrachlorohydroquinone (XIV).—(a) A solution of tetrachlorohydroquinone in ethanol was converted into its sodium salt with two mole equivalents of sodium ethoxide. A suspension of the salt in dry benzene was treated with two mole equivalents of diethyl phosphorochloridate or dimethyl phosphorochloridate, $(RO)_2P(O)Cl$ (3 hr. reflux). The bis-phosphates IX and X were produced in *ca.* 90% yield. The properties of the methyl compound X which was not isolated from the reaction of chloranil with trimethyl phosphite are: dimethyl [(4-(dimethoxyphosphinyl-

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[9] (a) C. Graebe, *Ann.*, **146**, 19 (1868); (b) A. Binz and C. Rath, *Ber.*, **58**, 309 (1925); (c) E. Bures and J. Hutter, *Casopis Ceskoslov. Lekarnictva*, **11**, 29, 57 (1931); *C. A.*, **25**, 5153 (1931).

[10] The naturally occurring antibiotic Drosophilin A has been identified as tetrachlorohydroquinone monomethyl ether (*cf.* M. Anchel, THIS JOURNAL, **74**, 2943 (1952).

oxy)-2,3,5,6-tetrachlorophenyl)]-phosphate (X), m.p. 162–164° (benzene), band at 7.82 μ (strong).

Anal. Calcd. for $C_{10}H_{12}O_8Cl_4P$: C, 25.9; H, 2.6. Found: C, 26.5; H, 2.3.

(b) Tetrachlorohydroquinone was treated with one mole equivalent of sodium ethoxide in ethanol solution. A suspension of the dry salt in benzene was treated with one mole equivalent of diethyl phosphorochloridate or dimethyl phosphorochloridate. The phenolic phosphates XVIII and XIX were isolated in *ca.* 10%, together with *ca.* 20% of bis-phosphates IX and X and *ca.* 25% of recovered tetrachlorohydroquinone.

Diethyl (4-hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XVIII), m.p. 179–180° (cyclohexane), bands (KBr) at 2.9–3.4 and 7.95 μ bonded P→O.

Anal. Calcd. for $C_{10}H_{11}O_5Cl_4P$: C, 31.3; H, 2.9. Found: C, 31.5; H, 3.1.

Dimethyl (4-(hydroxy-2,3,5,6-tetrachlorophenyl)-phosphate (XIX), m.p. 236–238° (methanol), bands (KBr) at 3.0–3.4 μ and 7.97 μ.

Anal. Calcd. for $C_8H_7Cl_4O_5P$: C, 27.0; H, 2.0. Found: C, 27.2; H, 2.2.

(c) From the phenolic phosphates XVIII and XIX, the corresponding ether phosphates VII and VIII were prepared in *ca.* 90% yield utilizing diethyl sulfate or dimethyl sulfate, sodium carbonate and water (3 hr. reflux).

Reaction of Chloranil (I) with Triphenyl Phosphite (V).—(a) A suspension of 10.0 g. of chloranil in 24.3 g. of freshly distilled triphenyl phosphite was heated to 100° for 16 hr. After some time, the chloranil went into solution and a red color was formed. The color faded and the mixture became viscous. Some benzene (25 ml.) was added to effect dilution of the mixture. An additional 13.0 g. portion of chloranil was added and heating was continued. After 24 hr., the mixture was dissolved in 100 ml. of benzene and the solution was extracted with cold 3% aqueous sodium hydroxide. Acidification afforded 21.6 g. of tetrachlorohydroquinone. The benzene layer was washed with water, dried and evaporated. The residue crystallized and was washed with cold hexane; it was shown to be triphenyl phosphate (17.8 g.). The products were identified by melting points and by comparison of the infrared spectra with authentic samples.

(b) When triphenyl phosphite was added to a solution of chloranil in benzene at room temperature, no reaction took place.

(c) A series of experiments were carried out to detect possible photoacceleration; these were negative. Suspensions of chloranil in excess of triphenyl phosphite were irradiated in a quartz flask with a Hanovia ultraviolet lamp; after 20 hr. at room temperature, all the chloranil was recovered. At 100°, in the dark or with irradiation, after 12 hr., 44% of tetrachlorohydroquinone (after hydrolysis) was obtained.

Reduction of Chloranil by Phosphorous Acid.—When chloranil (1.0 g.) and an excess of phosphorous acid (H_3PO_3, m.p. 74°) was kept 18 hr. on the steam-bath, no change was noticed. After 4 hr. at 125° and 4 hr. at 170°, the mixture was cooled, diluted with water and filtered. The yield of tetrachlorohydroquinones was 0.89 g.

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The Kinetics of the Esterification of the Cyclohexanedicarboxylic Acids with Diphenyldiazomethane

BY HILTON A. SMITH AND PAUL P. HUNT

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The isomeric 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acids together with their monomethyl esters have been prepared, and their rates of reaction with diphenyldiazomethane studied in absolute ethanol solution. Rate constants at 15, 25, 35 and 45° have been calculated and tabulated, together with the heats of activation. The differences between rate constants for reaction of the dicarboxylic acids and the corresponding monomethyl esters are, in general, less than for the processes of acid- or base-catalyzed esterification. The *cis*-1,3- and *trans*-1,4-acids behave quite similarly. This is also true for the *trans*-1,4 and *cis*-1,3 forms. The results are discussed in the light of the conformations of the cyclohexanedicarboxylic acids and esters and of the mechanisms of the reactions involved.

The acid-catalyzed esterification of the cyclohexanedicarboxylic acids and the base-catalyzed hydrolysis of their methyl esters have been previously investigated.[1,2] It was shown that for both processes, the *cis*-1,3 and *trans*-1,4 configurations gave similar rate constants, which differed from those for the *trans*-1,3 and *cis*-1,4 forms, the latter two also resembling each other. The results were explained on the basis of the conformations of the isomers.

For the 1,3- and 1,4-configurations, the ratio of the rate constants for the diacid or diester to the corresponding monomethyl ester was always equal to or greater than the statistical value of 2. This was explained on the basis of steric considerations plus electrical repulsion of the negatively charged half-ester ion and the attacking hydroxyl ion in the case of the base-catalyzed hydrolysis.

Esterification with diphenyldiazomethane would be greatly influenced by steric considerations if the mechanism involved attack on the carbonyl carbon of the acid in a manner similar to that for acid-catalyzed esterification. However, Roberts, Watanabe and McMahon[3] propose a one-step reaction between the diazo compound and the acid which should not be greatly influenced by steric considerations. Also there is no net charge on the half-ester or the attacking diphenyldiazomethane, so that gross electrical effects similar to those found in base-catalyzed ester hydrolysis should not be encountered.

Experimental

The isomeric cyclohexanedicarboxylic acids and their monomethyl esters were prepared in the same manner as that previously described.[1,2] The melting points of the purified acids were: *cis*-1,2, 194°; *trans*-1,2, 227.5–229.4°; *cis*-1,3, 167–168°; *trans*-1,3, 150–151°; *cis*-1,4, 170–172°; *trans*-1,4, 312–313°. The melting points of the purified monomethyl esters were: *cis*-1,2, 67.8–68.6°; *trans*-1.2, 95.2–96.2°; *cis*-1,3, 66.0–66.6°; *trans*-1,3, liquid, $n^{20}D$ 1.4671; *cis*-1,4, 106.8–107.4°; *trans*-1,4, 125.5–126.5°.

Diphenyldiazomethane was prepared from benzophenone hydrazone by treatment with yellow mercuric oxide.[4] After recrystallization from methanol and from petroleum ether,

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[1] H. A. Smith and F. P. Byrne, THIS JOURNAL, **72**, 4406 (1950).

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