arsonic acid in 400 cc. of absolute methyl alcohol a solution of 33.6 g. (0.2 mole) of gluconic acid in 75 cc. of absolute methyl alcohol, was added in small portions with vigorous shaking, and the mixture allowed to stand for several hours. The 3,4-digluconyl-3,4-diamino-phenylarsonic acid, which separated immediately was freed from any unchanged 3,4-diamino-phenylarsonic acid and from free gluconic acid, by shaking it at intervals over a period of several hours with absolute methyl alcohol warmed to 40°. The cream-colored compound is soluble in cold water and dil. alkalies, and is readily hydrolyzed by hot water; yield, 70%.

Analyses. Subs., 0.1989, 0.2002: 16.40, 16.65 cc. of 0.0416 N iodine soln. Calc. for $C_{18}H_{29}O_{16}N_2As$: As, 12.75. Found: 12.86, 12.97.

Summary

1. The reaction of dichloro-*p*-arsinobenzoyl chloride with primary and secondary amines has been studied and the resulting compounds described.

2. Gluconic acid has been condensed with *p*-arsanilic acid and *o*-amino-arsanilic acid to form a new type of arsenical containing a solubilizing carbohydrate grouping.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ADDITION REACTIONS OF THE PHOSPHORUS HALIDES. VII. THE ADDITION OF ALKOXY AND AROXY CHLOROPHOSPHINES TO CARBONYL COMPOUNDS

BY J. B. CONANT, V. H. WALLINGFORD AND S. S. GANDHEKER

Received November 3, 1922

Introduction

The previous papers of this series[1] have dealt with the 1,2 and 1,4 addition of phosphorus trichloride and its aryl derivatives, phosphenylchloride ($C_6H_5PCl_2$) and diphenylchlorophosphine. As a continuation of this work we have investigated the action of substances of the general type $ROPCl_2$ and $(RO)_2PCl$ on simple ketones and aldehydes and on an α,β unsaturated ketone. By carrying out the reaction in the usual manner in the presence of acetic acid or acetic anhydride we have prepared the mono- and di-esters of the phosphonic acids which are formed by the reaction of phosphorus trichloride with the corresponding aldehyde or ketone. This investigation completes the study of the various types of chlorophosphines in regard to their addition reactions with aldehydes, ketones and α,β unsaturated ketones. In general it may be said that phosphorus halides of the type $APCl_2$ and A_2PCl, where A = R or RO, combine with carbonyl compounds in the same manner as phosphorus trichloride. As would be expected, compounds of the type A_3P do not

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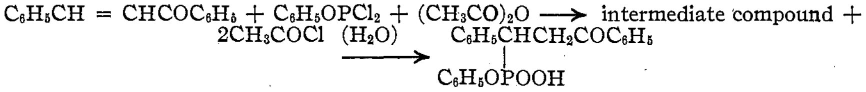
[1] THIS JOURNAL, (a) **39,** 2679 (1917); (b) **42,** 830, (c) 2337 (1920); (d) **43,** 1665, (e) 1677, (f) 1928 (1921); (g) **44,** 165 (1922).

give this reaction. It is interesting to note that while phosphorus tribromide behaves in a similar manner to the trichloride,[2] no addition reaction could be brought about with the tri-iodide. This is undoubtedly connected with the fact that phosphorus tri-iodide, unlike the trichloride and tribromide, does not combine with a further molecule of halogen to form compounds of the type PI_3X_2.

The addition of monophenoxy-, monomethoxy- and mono-ethoxydichlorophosphine to benzaldehyde was effected by bringing the reactants together in glacial acetic acid at room temperature; acetyl chloride was formed and, after pouring the material into water, the mono-esters were isolated as oils insoluble in water but soluble in sodium carbonate solution. Their structure was shown by hydrolysis to the well-known hydroxyphosphonic acid, $C_6H_5CHOHPO_3H_2$, which was isolated and identified as the aniline salt which has a sharp melting point. The general reaction is as follows.

$$C_6H_5CHO + ROPCl_2 + 2CH_3COOH \longrightarrow C_6H_5CHOHPO(OH)OR + 2CH_3COCl$$

The 1,4 addition of monophenoxy-dichlorophosphine to benzalacetophenone yielded the crystalline monophenyl ester previously prepared from the ketophosphonic acid.[3] Somewhat better yields were obtained by using acetic anhydride instead of acetic acid; the mechanism of the reaction with this reagent is undoubtedly the same as that previously established with phosphenyl chloride.[1d]



$$C_6H_5CH = CHCOC_6H_5 + C_6H_5OPCl_2 + (CH_3CO)_2O \longrightarrow \text{intermediate compound} + 2CH_3COCl \quad \xrightarrow{(H_2O)} \underset{C_6H_5OPOOH}{\underset{|}{C_6H_5CHCH_2COC_6H_5}}$$

Abnormal results were obtained on attempting to add ethoxy-dichlorophosphine to benzalacetophenone although normal results were obtained with benzaldehyde. Crystalline compounds containing phosphorus were obtained, but they could not be transformed into the ketophosphonic acid. It is hoped to investigate this reaction at some later time.

Diphenoxy-chlorophosphine

Diphenoxy-chlorophosphine was added to a number of aldehydes and ketones and gave crystalline diphenyl esters. The constitution of the ester formed from benzaldehyde was shown by hydrolysis, the known phosphonic acid being formed; the ester prepared from benzalacetophenone was identified by a mixed melting point with the ester previously prepared from the known ketophosphonic acid.[3] Crystalline esters were formed by the reaction with benzaldehyde, acetone, methylethyl ketone, acetophenone and chloro-acetone. In the case of this last substance it was found impossible to obtain any reaction in acetic acid or acetic an-

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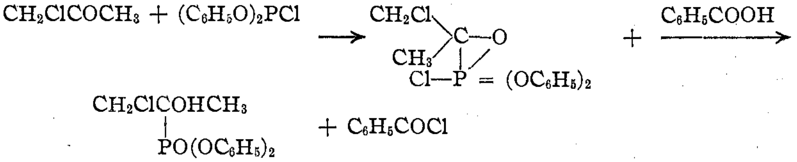
[2] This Journal, **43,** 1713 (1921); PBr_3 also reacts in the usual way with C_6H_5CHO.

[3] Ref. 1b, p. 839.

hydride; however, by using benzoic acid and allowing the mixture to stand for several days at room temperature a low yield of the desired diphenyl ester was obtained. In the light of our previous work with benzophenone and phosphorus trichloride, a probable explanation of these results can be formulated. The speed of the primary addition reaction is very slow,[4] and the diphenoxy-chlorophosphine is decomposed by the acetic acid or anhydride before it has reacted appreciably with the ketone. Benzoic acid, on the other hand, does not react with the phosphorus halide at room temperature and thus the addition reaction can proceed slowly when benzoic acid is present; as fast as the primary addition product is formed it reacts with the acid, producing the desired diphenyl ester and benzoyl chloride.[5]



Preparation of Diphenoxy-chlorophosphine

It was found convenient to prepare diphenoxy-chlorophosphine by a somewhat novel reaction. Triphenoxy-phosphine was prepared in the usual way from phenol and phosphorus trichloride; this substance was then heated in a sealed tube with phosphorus trichloride and the following reactions took place: $2(C_6H_5O)_3P + PCl_3 \rightleftharpoons 3(C_6H_5O)_2PCl$; $(C_6H_5O)_2PCl + PCl_3 \rightleftharpoons 2C_6H_5OPCl_2$. The products can be separated by distillation. The following figures (the average of several experiments) indicate the effect of increasing the concentration of phosphorus trichloride.

TABLE I

REACTION BETWEEN TRIPHENOXY-PHOSPHINE AND PHOSPHORUS TRICHLORIDE AT 150° FOR 8 HOURS

Moles of PCl_3 per mole of	Approximate percentages of products			
$(C_6H_5O)_3P$	PCl_3	$C_6H_5OPCl_2$	$(C_6H_5O)_2PCl$	$(C_6H_5O)_3P$
0.5	negligible	12	55	32
1.0	0.5	25	50	23
2.0	13	47	27	9

It is obvious that the results are such as would be expected if the two reversible reactions written above were involved; increasing the amounts of trichloride increases the conversion of the triphenoxy-phosphine into chlorophosphines. However, as the ratio of trichloride to phosphine is increased the yield of monophenoxy compound increases at the expense of

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[4] Unpublished work on the action of other phosphorus halides on α-chloro ketones indicates that the addition reaction proceeds with difficulty.

[5] Compare Ref. 1f, p. 1929.

the diphenoxy-chlorophosphine. The diphenoxy compound is best prepared by using only 0.5 mole of phosphorus trichloride per mole of triphenoxy-chlorophosphine and using over again the recovered triphenoxy compound. The yields so obtained (90%, based on the material used up) were far superior to those we were able to obtain by the direct action of 3 moles of phenol and 1 of trichloride.[6] Equilibrium is apparently reached at 150° in 8 hours as longer heating produced no appreciable change in the composition of the mixture. Essentially the same results were obtained at 110° (16 hours) and at 225° (8 hours). Similar reversible reactions have been found to occur when aryl arsines are heated with arsenic trichloride.[7] It is interesting that this reaction should also take place with phosphorus compounds in which an interchange of phenoxy groups is involved and perhaps surprising that side reactions involving the formation of chlorobenzene do not take place to any appreciable extent.

Experimental Part

Addition of Monophenoxy-dichlorophosphine to Benzaldehyde.—Nine g. of benzaldehyde, 16.5 g. of monophenoxy-dichlorophosphine (b. p. 213–217°) and 15 g. of acetic acid were mixed and allowed to stand for 5 hours in a flask fitted with a calcium chloride tube. The fumes of acetyl chloride were noticed when the flask was opened from time to time. The mixture was poured into water and extracted with ether; the ether layer was in turn extracted with an aqueous solution of sodium carbonate and, on acidification of the aqueous solution, the monophenyl ester of the hydroxyphosphonic acid was obtained as an oil. The yield of dry oil was 20 g. or 90%; it slowly hardened on standing, but could not be obtained crystalline. Seven g. of the oil was hydrolyzed by boiling it for 5 hours with 15% hydrochloric acid under a return condenser. The solution was then extracted with ether to remove the phenol and any unchanged ester. On evaporation of the hydrochloric acid solution, 4 g. of somewhat impure hydroxybenzylphosphonic acid was obtained. This was dissolved in a little alcohol; the solution was diluted with ether and treated with a slight excess of aniline. The aniline salt of the hydroxyphosphonic acid separated as a white precipitate which, after recrystallization from alcohol, melted at 199° and was identified by a mixed melting point with a pure sample of the aniline salt of the hydroxyphosphonic acid.

Addition of Monomethoxy-dichlorophosphine to Benzaldehyde.—This reaction was carried out exactly as described above for the phenoxy compound. Ten g. of benzaldehyde and 12.5 g. of the monomethoxy-dichlorophosphine (b. p., 95–96°) yielded 7.5 g. of the monomethyl ester as an oil, insoluble in water but soluble in sodium carbonate solution. It could not be obtained crystalline. It was hydrolyzed by boiling with hydrochloric acid; 3.5 g. of the ester yielded 1.6 g. of crude hydroxyphosphonic acid and 1.9 g. of the aniline salt which was identified by a mixed melting point. The formation of methyl alcohol as the other product of hydrolysis was proved by the usual qualitative tests.

Addition of Ethoxy-dichlorophosphine to Benzaldehyde.—Five g. of benzaldehyde, 7 g. of ethoxy-dichlorophosphine (b. p., 117–118°) and 8 g. of acetic acid yielded, after the usual treatment, 9.3 g. of the mono-ethyl ester as an oil which could not be crystallized. It was converted into the hydroxyphosphonic acid by hydrolysis with hydro-

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[6] Noack, *Ann.*, **218**, 85 (1883).

[7] Michaelis and Reese, *Ber.*, **15**, 2876 (1882).

chloric acid, ethyl alcohol being identified as the other product. The acid was identified as the aniline salt; 4.5 g. of pure aniline salt was obtained from 3.8 g. of the oily ester.

Addition of Monophenoxy-dichlorophosphine to Benzalacetophenone.—The addition to benzalacetophenone can be carried out in the presence of either acetic acid or acetic anhydride. The best results are obtained by working with the latter reagent. Five g. of benzalacetophenone, 4.7 g. of the chlorophosphine and 7.3 g. of acetic anhydride were mixed and allowed to stand for 2 hours; the temperature was then raised to 35° in the course of 5 hours and finally to 40° during 1 hour and then the mixture allowed to stand overnight at room temperature. It was then poured into water and the insoluble oil formed was dissolved in ether. The ethereal solution was extracted with sodium bicarbonate solution and this solution was then acidified. The monophenylester was thus precipitated as an oil which was dissolved in ether; after drying, the ethereal solution was evaporated and the product was obtained as a crystalline mass weighing 5.5 g. After 2 recrystallizations from alcohol, 1.3 g. of pure monophenyl ester was obtained which melted at 145–146°. It was identified as the monophenyl ester of α-phenyl-β-benzoylethyl-phosphonic acid by a mixed-melting-point determination. About 2 g. of unchanged benzalacetophenone was recovered from the first ethereal solution showing that the initial reaction had been far from complete.

Diphenyl Ester of Hydroxybenzyl-phosphonic Acid, $C_6H_5CHOHPO(OC_6H_5)_2$.—To a mixture of 9.2 g. of diphenoxy-chlorophosphine (prepared as described below) and 3.9 g. of benzaldehyde was added 8 g. of acetic acid. The mixture became slightly warm and within an hour crystals began to separate. After standing overnight the crystals were filtered off, washed with ether and dried; they weighed 4.8 g. After recrystallization from methyl alcohol, the compound melted at 146°. It was insoluble in benzene, in water and in sodium carbonate solution. It was hydrolyzed to the hydroxyphosphonic acid by boiling it with hydrochloric acid and the acid was identified in the usual manner.

Analysis. Calc. for $C_{19}H_{17}O_4P$: P, 9.1. Found: 9.2.

Diphenyl Ester of α-Hydroxy*iso*propyl-phosphonic Acid, $(CH_3)_2COHPO(OC_6H_5)_2$.—Ten g. of diphenoxy-chlorophosphine was treated with 2.5 g. of acetone (a slight excess); heat was evolved during the mixing. Glacial acetic acid (6 cc.) was then added and a fairly rapid reaction took place, judged by the evolution of heat and formation of acetyl chloride. After standing for 12 hours, the mixture was poured into water, and the ester dissolved in ether. Evaporation of the ethereal solution yielded 13 g. of a pasty mass which was spread on a porous plate. After recrystallization of the resulting crystals from petroleum ether, 4.5 g. of the compound was obtained which melted at 113–114°.

Analysis. Calc. for $C_{15}H_{17}O_4P$: P, 10.6. Found: 10.8.

Acetyl Derivative of the Diphenyl Ester of α-Hydroxy*iso*propyl-phosphonic Acid, $(CH_3)_2C(OCOCH_3)PO(OC_6H_5)_2$.—The mother liquor from the crystallization of the diphenyl ester just described yielded on evaporation a small amount of a crystalline compound which melted at 71–73.5°. This was the acetyl derivative of the diphenyl ester formed by the action of the acetyl chloride during the reaction as the following experiment shows. One g. of diphenyl ester was allowed to stand overnight with acetyl chloride; there was thus obtained a substance which after recrystallization from petroleum ether melted at 72–72.5° and was identical with the compound just described.

Analysis. Calc. for $C_{17}H_{19}O_5P$: P, 9.3. Found: 9.3.

Diphenyl Ester of α-Hydroxy-α-methylpropyl-phosphonic Acid, $C_2H_5C(CH_3)(OH)PO(OC_6H_5)_2$.—Three g. of methylethyl ketone was mixed with 10 g. of diphenoxy-chlorophosphine and then 3 cc. of glacial acetic was added during 1 hour. The whole was allowed to stand for 2 days at room temperature when the mixture had become a crystalline mass. The crystals were washed several times with water by decantation, filtered and washed with ether. Five g. of diphenyl ester was thus obtained which after crystallization from alcohol melted at 128.5°.

Analysis. Calc. for $C_{16}H_{19}O_4P$: P, 10.2. Found: 10.2.

Diphenyl Ester of α-Hydroxy-α-methylbenzyl-phosphonic Acid, $C_6H_5C(CH_3)(OH)PO(OC_6H_5)_2$.—A mixture of 5 g. of diphenoxy-chlorophosphine, 2.5 g. of acetophenone and 1.1 g. of glacial acetic acid was allowed to stand for 4 days at room temperature. At the end of this time the crystalline product was filtered from the reaction mixture, washed with ether and recrystallized from alcohol. The yield of crude ester was 4.5 g.; the compound melted at 143.5°.

Analysis. Calc. for $C_{20}H_{19}O_4P$: P, 8.8. Found: 8.9.

Diphenyl Ester of α-Hydroxy-α-methyl-β-chloro-ethyl-phosphonic Acid, $CH_2ClC(CH_3)(OH)PO(OC_6H_5)_2$.—Attempts to add diphenoxy-chlorophosphine to chloroacetone in the presence of acetic acid were without success. By using benzoic acid, however, the desired ester was obtained in a small yield. Five g. of chloro-acetone, 14 g. of diphenoxy-chlorophosphine and 6.5 g. of benzoic acid were mixed and allowed to stand for 2 days; at the end of this time white cubic crystals were visible in the mixture. These crystals were collected and washed with ether; they weighed 1 g. and melted sharply at 119°.

Analyses. Calc. for $C_{15}H_{16}O_4PCl$: Cl, 10.9. Found: 10.4, 10.9.

Addition of Diphenoxy-chlorophosphine to Benzalacetophenone.—Two g. of diphenoxy-chlorophosphine and 2.3 g. of benzalacetophenone were mixed with 1 cc. of glacial acetic acid. The mixture was allowed to stand for 3 days, then poured into water and the solid material crystallized from ether. A solid (1.3 g.) melting at 116–117° was thus obtained; it was identified by a mixed melting point with the known diphenyl ester of α-phenyl-β-benzoylethyl-phosphonic acid.

Attempts to add diphenoxy-chlorophosphine to acetaldehyde, enanthole, cinnamic aldehyde, methyl*iso*propyl ketone and pinacoline resulted only in oily products which could not be obtained crystalline. Apparently in these cases, however, the addition reaction had proceeded at least to some extent.

The Preparation of Diphenoxy-chlorophosphine.—Triphenoxy-phosphine was prepared from phenol and phosphorus trichloride by the method of Noack; the yield of crude product which boiled above 210° at 10 mm. varied from 78 to 81%. This material, in 20g. portions, was heated with various proportions of phosphorus trichloride in sealed tubes in a furnace for a definite time. The tubes were opened and the contents distilled under atmospheric pressure until the thermometer recorded 150° and then at 10 mm. pressure. The fractions boiling at 130–150°, 130–210°, and 210–235° at 10 mm. were considered as $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$ and $(C_6H_5O)_3P$, respectively; the largest portion of each fraction boiled over a much narrower range (about 10°) than that indicated. Essentially the same equilibrium is attained at 110°, 150° and 225° as shown by the following percentages of $C_6H_5OPCl_2$ and $(C_6H_5O)_2PCl$ obtained with a mixture of 1 mole of triphenoxy-phosphine with 2 moles of trichloride: 110° for 16 hours, ratio of $C_6H_5OPCl_2$ to $(C_6H_5O)_2PCl$, 51:31; 150° for 8 hours, ratio 55:24; 225° for 8 hours, ratio 40:32. Other experiments showed that 12 to 14 hours was necessary to obtain equilibrium at 110° and only 6 or 7 hours at 150° or 225°. For preparative purposes, the most convenient temperature is 150° and the best proportions are 0.5 mole of trichloride to 1 of triphenoxy-phosphine; the unchanged triphenoxy-phosphine which is recovered is then used in another run. In a typical run which was made on a larger scale for preparative purposes, 76 g. of triphenoxy-phosphine and 13.7 g. of trichloride yielded 18 g. of crude $C_6H_5OPCl_2$, 38 g. of $(C_6H_5O)_2PCl$ (boiling over a 10° range) and

23.5 g. of $(C_6H_5O)_3P$. The yield of $(C_6H_5O)_2PCl$ based on the $(C_6H_5O)_3P$ used up is 90%.

Table I given in the introduction to this paper summarizes the average of some 10 final experiments and shows the effect of varying the proportions on the yields of the various products.

Summary

1. Monophenoxy-, monomethoxy- and mono-ethoxy-dichlorophosphine were added to benzaldehyde in the presence of acetic acid. Mono-esters of the hydroxyphosphonic acid were formed.

2. Monophenoxy- and monomethoxy-dichlorophosphine were similarly added to benzalacetophenone giving mono-esters of the ketophosphonic acid.

3. Diphenoxy-chlorophosphine was added to benzaldehyde, several ketones and benzalacetophenone, yielding diphenyl esters of the corresponding phosphonic acids.

4. Diphenoxy-chlorophosphine was prepared by heating mixtures of phosphorus trichloride and triphenoxy-phosphine in sealed tubes. An equilibrium is thus established; the composition of the equilibrium mixture varies with the proportion of the 2 reactants employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 23]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. I. PRELIMINARY INVESTIGATIONS

BY CHARLES A. KRAUS AND GEORGE F. WHITE

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Introduction

While the alkali metals and the metals of the alkaline earths are very strong reducing agents at ordinary temperatures, their use in the reduction of organic compounds has been much restricted, owing to the lack of a suitable solvent medium for the reacting constituents. Where reductions have been carried out with these metals as, for example, in the Fittig and the Würtz reactions, the metal has been introduced into a solution of the organic constituent in an inactive solvent. In such heterogeneous systems reaction is confined to the interface between the metal and the solution, as a result of which the rate of reaction is often very low, particularly when the products of reaction are insoluble and precipitate on the surface of the metal.

It has been recognized for some time that the alkali metals and the metals of the alkaline earths in solution in liquid ammonia afford an exceptionally strong and reasonably convenient means for the reduction of