2. The conditions investigated were: the rate of addition of ethyl iodide, stirring, refluxing, excess magnesium, quantity of ether, protection from air, kind of magnesium, catalysts and temperature.
3. The quantitative methods used for determining yields were two of those discussed in the preceding paper, titration with acid and gas analysis.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ADDITION REACTIONS OF PHOSPHORUS HALIDES. VI. THE 1,2 AND 1,4 ADDITION OF DIPHENYL-CHLOROPHOSPHINE

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Introduction

This work was undertaken for several reasons. In the first place no disubstituted derivative of phosphorus trichloride had hitherto been added to saturated or unsaturated aldehydes or ketones; the theoretical interpretation of the addition reactions of trivalent phosphorus halides was, therefore, obviously incomplete.[1] Furthermore, it was hoped that certain β-bromo compounds might be prepared by brominating the product of the reaction between diphenyl-chlorophosphine and an unsaturated ketone. A study of the action of alkali on such bromo compounds promised to be of interest in connection with the peculiar decomposition of many β-bromo acids.[2] Finally, it was thought probable that the products would be high-melting stable substances and that this reagent might be used, therefore, for investigating the addition reactions of benzoquinone and related substances.

As the results presented in this paper show, diphenyl-chlorophosphine behaves exactly as we had hoped, and experiments with quinone indicate that tractable substances can be obtained; the work with quinone has not yet, however, passed beyond the preliminary stage and will, therefore, be considered in a later paper.

The reaction between diphenyl-chlorophosphine and either benzaldehyde or benzalacetophenone is entirely parallel to the corresponding reaction with the trichloride or phosphenyl chloride.[3] As in the previous work in this Laboratory, either acetic acid or acetic anhydride was used in order to cause the reaction to go to completion. The products of the reaction are acetyl chloride and the keto-phosphine oxide which often separates

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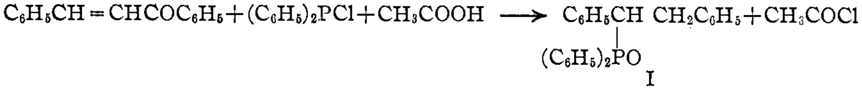
[1] THIS JOURNAL, **43**, 1705 (1921).

[2] *Ibid.*, **42**, 833 (1920); **43**, 1667 (1921); **44**, 2530 (1922).

[3] Compare other papers of this series.

from the reaction mixture in the course of a few minutes. The reactions may be represented thus.

$$C_6H_5CHO + (C_6H_5)_2PCl + CH_3COOH \longrightarrow C_6H_5CHOHPO(C_6H_5)_2 + CH_3COCl$$



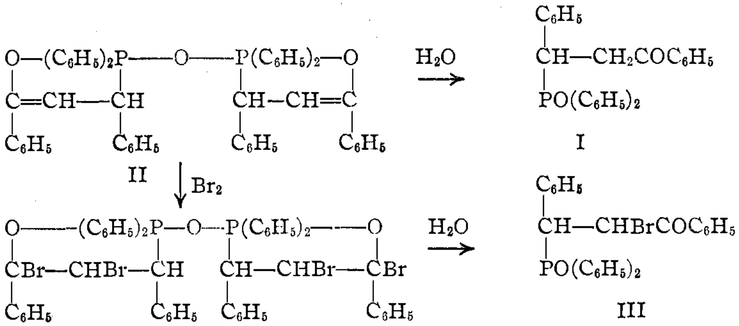
$$C_6H_5CH{=}CHCOC_6H_5 + (C_6H_5)_2PCl + CH_3COOH \longrightarrow \underset{(C_6H_5)_2PO}{C_6H_5CH}\,CH_2C_6H_5 + CH_3COCl$$

I

Mechanism of the Reaction

The fact that this reagent adds in the 1,4 position to a typical α,β unsaturated ketone (benzalacetophenenone) was established in exactly the same manner as with the trichloride and phosphenyl chloride. The reaction was carried out with acetic anhydride which was free from acetic acid. The resulting product could not be isolated in a crystalline condition, but its reactions prove its essential structure. On treatment with water, this intermediate product gives the keto-phosphine oxide (I) in excellent yields. In solution in chloroform or acetic anhydride it readily combines with two equivalents of bromine without the evolution of hydrogen bromide, thus showing that it is unsaturated. The resulting dibromide was not obtained crystalline but, ont reatment with water, a mixture of 2 stereo-isomeric monobromo-ketophosphine oxides (III) was formed. This shows that a substance containing the linkage $RCH(PR_2)CH{=}CRO$— must be formed in the initial reaction with acetic anhydride; in other words, that 1,4 addition has taken place. This intermediate unsaturated substance, which must contain the linkage just mentioned, is best represented by Formula II in the following equations. It is extraordinarily sensitive to acetic acid or moisture, being converted by these into the keto-phosphine oxide; this is in keeping with the anhydride-like formula.

$$C_6H_5CH{=}CHCOC_6H_5 + (C_6H_5)_2PCl + (CH_3CO)_2O \longrightarrow$$

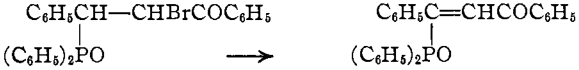


A comparison of these facts with the earlier work done in this Laboratory shows that the behaviors of the three halides,—phosphorus trichloride, phosphenyl chloride and diphenyl-chlorophosphine,—are completely parallel. It may, therefore, be considered that combination with carbonyl compounds (under suitable conditions) is a general reaction of the halides of trivalent phosphorus.

Reactions of the Bromo Compounds

Two stereo-isomeric bromides corresponding to Formula III were obtained in the manner just described. One of them was also obtained by the direct bromination of the keto-phosphine oxide (I). The above series of reactions was carried out with both benzalacetophenone and benzal-*p*-chloro-acetophenone; in each case both a high-melting and a low-melting bromide could be obtained by the action of bromine on the intermediate unsaturated compound. Furthermore, in each case direct bromination of the keto-phosphine oxide yielded one of the two isomers; in the benzalacetophenone series the high-melting isomer was formed,[4] in the other series the low-melting isomer.

The high-melting isomer in both series loses hydrogen bromide when treated with alcoholic sodium hydroxide at room temperature and forms an unsaturated keto-phosphine oxide (IV), which is reduced by zinc and acetic acid to the saturated keto-phosphine oxide (I).



$$\underset{(C_6H_5)_2PO}{C_6H_5CH}{-}CHBrCOC_6H_5 \longrightarrow \underset{(C_6H_5)_2PO}{C_6H_5C}{=}CHCOC_6H_5$$

III IV

Each of the low-melting isomers, on the other hand, under the same conditions is reduced to the keto-phosphine oxide (I). Both the elimination and reduction reactions are almost quantitative. This distinctive behavior of each isomer with alcoholic sodium hydroxide does not hold with other reagents. Thus, the high-melting isomer from the benzalacetophenone is quantitatively reduced by boiling it with potassium acetate in alcohol, and the low-melting isomer of each series can be partially converted into the unsaturated keto-phosphine oxide under suitable conditions as shown in the following table.

REACTIONS OF THE ISOMERIC BROMIDES

Reagents	Benzalacetophenone Series		Benzal-*p*-chloro-acetophenone Series	
	High-melting isomer	Low-melting isomer	High-melting isomer	Low-melting isomer
Alcoholic NaOH; 25°	Elimination of HBr	Reduction	Elimination of HBr	Reduction
Pot. acetate, CH_3OH boiled for 5 hrs.	Reduction	No crystalline product	Elimination of HBr	Small amount of elimination; most of material unchanged
Pyridine in boiling solution 5 hrs.	No reaction (insoluble)	Small amount of elimination of HBr	No reaction	Trace of elimination

The fact that both the high- and low-melting isomers can form *either* the unsaturated compound or the saturated compound, depending upon

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[4] In one experiment a trace of the other isomer was obtained.

the reagent employed, indicates that we are dealing with stereo-isomers. Further evidence for this point of view is found, of course, in the analogy with the stereo-isomeric bromides obtained in the work with phosphenyl chloride. From their similar behavior with alcoholic sodium hydroxide, it seems probable that both high-melting isomers have the configuration most favorable for elimination of hydrogen bromide. It would be very hard to interpret all the facts given above on the assumption that we are dealing with structural isomers.

It will be noted that these compounds have the bromine atom in the position β to the phosphorus atom. However, no elimination of the phosphorus takes place when they are treated with alkaline reagents. This is in marked contrast to the behavior of the various β-bromophosphonic acids which easily and quantitatively lose both bromine and phosphorus; for example,

$$\begin{array}{l} C_6H_5CH—CHBrCOC_6H_5 \\ \;|\\ C_6H_5PO_2H \end{array} \longrightarrow \begin{array}{l} C_6H_5CH{=}CHCOC_6H_5 + \\ C_6H_5PO_3H_2 + HBr \end{array}$$

We have at present no final explanation to account for this marked difference between the phosphine oxides and phosphonic acids. Experiments are in progress which should throw more light on this subject and it is hoped in a later paper to deal with this and related problems concerning β-bromophosphonic acids and phosphine oxides.

We wish to acknowledge our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant which enabled us to prepare considerable amounts of diphenyl-chlorophosphine

Experimental

α-Hydroxybenzyl-diphenylphosphine Oxide, $C_6H_5CHOHPO(C_6H_5)_2$.—Five g. of benzaldehyde was dissolved in 3 g. of glacial acetic acid and 10.4 g. of diphenyl-chlorophosphine was added. After standing for 30 minutes the mixture was poured into water. The gummy mass thus precipitated was obtained in crystalline condition by dissolving in ether, washing with sodium hydroxide solution and drying and evaporating the resulting solution. The substance crystallizes from hot toluene in white crystals which melt at 230°.

Analysis. Calc. for $C_{19}H_{17}PO_2$: P, 10.0. Found: 9.8.

This hydroxy-phosphine oxide is stable towards mild oxidizing agents, but on oxidation with chromic anhydride in warm sulfuric acid it yields some benzaldehyde.

α-Phenyl-β-benzoylethyl-diphenylphosphine Oxide, $(C_6H_5)_2POCH(C_6H_5)CH_2CO$-$C_6H_5$.—This compound may be prepared by the action of diphenyl-chlorophosphine on benzalacetophenone in the presence of glacial acetic acid or acetic anhydride followed by treatment with water. In a typical experiment, 5 g. of benzalacetophenone was dissolved in 1.5 g. of glacial acetic acid and 5.3 g. of diphenyl-chlorophosphine was added. The mixture was poured into water after standing for 30 minutes; the product separated as a fine crystalline powder. When dry it weighed 7.6 g. (77% of the theoretical amount). It can be recrystallized from hot alcohol, and melts at 227°.

Analysis. Calc. for $C_{27}H_{23}O_2P$: P, 7.6. Found: 7.7.

α-Phenyl-β-[*p*-chlorobenzoyl] ethyl-diphenylphospine Oxide, $(C_6H_5)_2$ $POCH(C_6H_5)$-$CH_2COC_6H_4Cl$.—This substance was prepared in exactly the same manner as the corresponding halogen-free compound. There was obtained 3.8 g. of the crude material from 2.4 g. of benzal-*p*-chloro-acetophenone, 85% of the theoretical amount. It melted at 225–226°.

Analysis. Calc. for $C_{27}H_{22}O_2PCl$: Cl, 8.0. Found: 7.7.

α-Phenyl-β-bromo-β-benzoylethyl-diphenylphosphine Oxide, $(C_6H_5)_2POCH(C_6H_5)$-$CHBrCOC_6H_5$.—It was found that the phosphine oxide described above could be readily brominated in chloroform solution by heating for a short time (30 minutes) under a reflux condenser. The resulting bromo compound could be purified by recrystallization from alcohol.

HIGH-MELTING ISOMER.—This substance, melting at 187°, was formed in very good yields by the bromination process just described.

Analysis. Calc. for $C_{27}H_{22}O_2PBr$: Br, 16.4. Found: 16.9.

LOW-MELTING ISOMER.—This compound was formed, together with the high-melting isomer, by the action of bromine on the intermediate product formed when acetic anhydride was employed; 5.3 g. of diphenyl-chlorophosphine was added to 5 g. of benzalacetophenone (dried over phosphorus pentoxide) and then 1.25 g. of acetic anhydride was added and the mixture allowed to stand for 1 hour. An acetic anhydride solution of bromine (freshly prepared) was added. The color of the bromine disappeared rapidly as the solution was added. After standing for 10 minutes, the mixture was poured into water and allowed to stand overnight. The solid material was filtered off, dissolved in chloroform, the chloroform solution dried and the solvent evaporated. By crystallizing this mixture several times there was obtained 1.2 g. of bromine-free, α-phenyl-β-benzoylethyl-diphenylphosphine oxide, 0.7 g. of the high-melting bromide described above and 1.6 g. of a bromo compound melting at 158°. In a similar experiment the acetyl chloride and acetic anhydride were removed after the initial reaction by distillation in a vacuum. The resulting gum was dissolved in chloroform and treated with bromine. The bromine was taken up rapidly without the evolution of hydrogen bromide; on treatment with water a mixture of the 2 bromides was obtained. A portion of the chloroform solution was taken before the addition of bromine and treated directly with water; an 82% yield of α-phenyl-β-benzoylethyl-diphenylphosphine oxide was obtained. This clearly shows we are dealing with an intermediate product, but all attempts to isolate it or the bromine addition product were without avail.

The low-melting isomeric bromide, thus obtained, was more soluble in alcohol than the high-melting isomer. A mixture of the 2 substances could therefore be separated by repeated crystallization. In one experiment a trace of this low-melting isomer was found in the product of the direct bromination of α-phenyl-β-benzoylethyl-diphenylphosphine oxide.

The compound is colorless and melts at 158°.

Analysis. Calc. for $C_{27}H_{22}O_2PBr$: Br, 16.4. Found: 16.5.

α-Phenyl-β-bromo-[*p*-chlorobenzoyl]ethyl-diphenylphospine Oxide, $(C_6H_5)_2$ POCH-$(C_6H_5)CHBrCOC_6H_4Cl$. HIGH-MELTING ISOMER.—This compound together with the low-melting isomer was formed by the action of bromine on the intermediate product formed in acetic anhydride solution. The experiments were carried out exactly as described above for the chlorine-free substances. In all this work, of course, extreme precautions had to be employed to guard against moisture or acetic acid. The presence of either of these substances in any appreciable amount caused the decomposition of the intermediate product forming the keto-phosphine oxide. The acetic anhydride was freshly prepared from acetyl chloride and fused sodium acetate, carefully fractionated in a suitable apparatus and used at once. From 3.2 g. of benzal-*p*-chloro-acetophenone there was obtained 6 g. of crude product (the procedure involving a chloroform solution was used in this case). By repeated crystallization there was obtained 3.9 g. of a bromide melting at 187° and 1.2 g. of a bromide melting at 196°.

The high-melting isomer thus prepared melted at 196°.

Analysis. Calc. for $C_{27}H_{21}O_2PClBr$: total halogen 22.0. Found: 21.9.

LOW-MELTING ISOMER.—The keto-phosphine oxide was dissolved in chloroform and treated with the calculated quantity of bromine. The reaction took place slowly at the boiling point of the solvent and was complete after 3 hours. The substance melted at 187° and was identical with one of the two compounds formed in the experiments with acetic anhydride as just described.

Analysis. Calc. for $C_{27}H_{21}O_2PClBr$: total halogen, 22.0. Found: 22.0.

Reactions of the Bromides

α-Phenyl-β-benzoylvinyl-diphenylphosphine Oxide, $(C_6H_5)_2POC(C_6H_5)=CHCOC_6H_5$.—This compound was obtained in 80% yields by the elimination of hydrogen bromide from the corresponding high-melting bromide; 3 g. of the bromide (m. p. 187°) was dissolved in hot alcohol and, after cooling the solution to room temperature, the solution was treated with a concentrated aqueous solution of sodium hydroxide. After the mixture had stood for 1 hour it was poured into water, acidified and allowed to stand overnight. Two g. of pale yellow crystals was obtained which, after recrystallizing, melted at 143°. The substance reduced potassium permanganate in acetone solution but did not combine with bromine or hydrobromic acid in acetic acid. It was reduced to the corresponding saturated keto-phosphine oxide by warming it for a few minutes with glacial acetic acid and zinc dust. Dry ozone combines with the substance in chloroform solution.

Analysis. Calc. for $C_{27}H_{21}O_2P$: P, 7.6. Found: 7.6.

The low-melting isomeric bromide (m. p. 158°), under conditions exactly parallel to the above, yielded 1.6 g. of the keto-phosphine oxide melting at 227°. A replacement of bromine by hydrogen, but no elimination, had taken place.

The experiments with other reagents were briefly as follows.

Potassium Acetate.—The high-melting bromide (0.4 g.), boiled for 5 hours in methyl alcohol with potassium acetate, yielded 0.25 g. of the keto-phosphine oxide; no trace of the unsaturated compound was found. The low-melting isomer, under similar conditions, yielded a gum which did not crystallize.

Pyridine.—The high-melting isomer failed to react when boiled with this reagent in alcohol. The low-melting isomer yielded a gum in methyl alcohol. In ether, after 6 hours' boiling, most of the material was unchanged, but a little unsaturated compound was obtained and identified.

α-Phenyl-β-(*p*-chlorobenzoyl)vinyl-diphenylphosphine Oxide, $(C_6H_5)_2POC(C_6H_5)=CHCOC_6H_4Cl$.—This compound was formed from the corresponding high-melting bromide (196°) by the action of sodium hydroxide in alcohol. The yield was almost quantitative. The compound crystallizes in yellow needles which melt at 151°.

Analysis. Calc. for $C_{27}H_{20}O_2PCl$: Cl, 8.0. Found: Cl, 7.7.

Under the same conditions the low-melting isomer (m. p. 187°) gives a 95% yield of the keto-phosphine oxide; no trace of the unsaturated compound could be found.

Potassium acetate.—A 78% yield of the same unsaturated compound was obtained by boiling the high-melting bromide (196°) with potassium acetate in alcohol for 3 hours. The low-melting bromide (187°) under the same conditions gave a poor yield of unsaturated compound, but no trace of the reduction product could be found.

Pyridine.—No reaction took place with this reagent and the high-melting bromide in ether or alcohol even after long boiling. The low-melting bromide with the same reagent gave a trace of unsaturated compound after boiling for 5 hours in alcohol; the rest of the material was unchanged.

Summary

1. Diphenylchlorophosphine reacts with benzaldehyde and benzalacetophenone in the presence of glacial acetic acid. The products are an hydroxy and a keto-phosphine oxide, respectively.
2. The mechanism of the reaction with the unsaturated ketone has been established, as in the previous work with the trichloride, by using acetic anhydride. With this reagent an unsaturated intermediate compound is formed; it combines with bromine and after treatment with water yields 2 stereo-isomeric α-bromo-keto-phosphine oxides.
3. The stereo-isomeric bromides on treatment with alkaline reagents either lose hydrogen bromide or are reduced to the halogen-free keto-phosphine oxide. A study of the behavior of 2 pairs of closely related isomeric bromides has shown that each isomer may either be reduced or lose hydrogen bromide, according to the reagent employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE OXIDATION OF PROPYLENE GLYCOL WITH POTASSIUM PERMANGANATE[1]

BY WILLIAM LLOYD EVANS

Received July 31, 1922

The experiments described here are a continuation of a series of oxidation studies being made in this Laboratory, the principal purpose of which is to establish from exact quantitative data the molecular stages through which organic compounds of the more simple structure pass when they undergo this type of chemical change. Obviously many factors, such as temperature, the nature of oxidizing agents, concentration of reacting materials and time, exercise a marked influence on the nature of the results obtained both from the qualitative and quantitative standpoints. The oxidation of propylene glycol with potassium permanganate in both neutral and alkaline solutions has been previously studied by Witzemann and the author.[2] The results of those experiments showed that carbon dioxide, acetic and oxalic acids were the final oxidation products in alkaline solutions, while carbon dioxide and acetic acid were the only products obtained in neutral solutions. In this paper an account is given of the results that were obtained by the oxidation of propylene glycol at conditions of con-

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[1] This paper was read at the Chicago Meeting of the American Chemical Society, 1920.

[2] Evans and Witzemann, THIS JOURNAL, 34, 1086 (1912).