employed at 25° without oxalic acid being formed. Hence it is seen that considering the difficulty of handling the white compound of mercury there is a satisfactory concordance in the results of these different experiments.[11]

Summary.

1. Vinyl mercury oxychloride is obtained when alkaline solutions of acetaldehyde are treated with mercuric chloride.

2. The yield of vinyl mercury oxychloride is proportional to the concentration of the alkali present, showing that the production of vinyl alcohol is likewise proportional to the concentration of the alkali.

3. Since the formation of vinyl alcohol is necessary to account for the presence of oxalic acid in the oxidation of ethyl alcohol and acetaldehyde, it follows from (2) that the yield of oxalic acid is also proportional to the concentration of the alkali used.

4. A concentration of about 1.40 g. of potassium hydroxide is necessary for the formation of vinyl at alcohol 25°. This result is in accord with those obtained on the oxidation of acetaldehyde.

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ADDITION REACTIONS OF PHOSPHORUS HALIDES. IV. THE ACTION OF THE TRICHLORIDE ON SATURATED ALDEHYDES AND KETONES.

BY J. B. CONANT, A. D. MACDONALD AND A. McB. KINNEY.
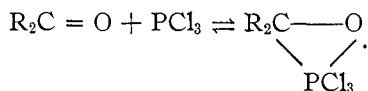
Introduction.

The first paper of this series dealt with the action of phosphorus trichloride on benzaldehyde. The primary addition product formed by these two substances could be decomposed by the action of water or glacial acetic acid with the formation of an α-hydroxyphosphonic acid. By the use of glacial acetic acid as a medium very good yields of this substance were obtained.[1] The results presented in this paper show that the reaction can be similarly employed for the preparation of hydroxyphosphonic acids from other aldehydes and ketones. The reaction as applied to ketones, however, is of somewhat limited scope. With certain ketones the yields are rather low (about 50%). Aromatic ketones such as benzophenone and benzil, either react only under very much modified conditions, or not at all. Camphor, also, has been found to be very unreactive.

[11] Compare THIS JOURNAL, 41, 1282 (1919); Am. Chem. J., 37, 28 (1907).
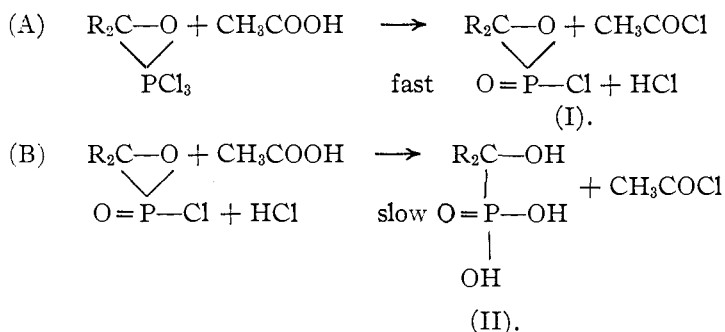
[1] THIS JOURNAL, 42, 2337 (1920).

The Limits of the Reaction.

The initial reaction between the carbonyl group and the trichloride is reversible. In the case of benzaldehyde,[1] the equilibrium point is such that only about 30% of the material is in combination.

$$R_2C = O + PCl_3 \rightleftharpoons R_2C\!\!\overbrace{}\!\!O$$
$$PCl_3$$

The addition product is more reactive than phosphorus trichloride towards acetic acid or acetic anhydride. Therefore, with these reagents it is possible to cause the reaction to run to completion and, in the case of benzaldehyde, to obtain excellent yields with equimolecular amounts of materials. When the temperature is kept below 30° to 35° the acetic acid reacts so rapidly with the addition product that there is no appreciable reaction with the trichloride.

(A) $R_2C\!-\!O + CH_3COOH \longrightarrow R_2C\!-\!O + CH_3COCl$

          PCl_3 fast $O = P\!-\!Cl + HCl$

                                          (I).

(B) $R_2C\!-\!O + CH_3COOH \longrightarrow R_2C\!-\!OH$

          $O = P\!-\!Cl + HCl$ slow $O = P\!-\!OH$ $+ CH_3COCl$

                                          OH

                                          (II).

These equations show the probable course of this reaction; a mixture of both the phostonic (I) and phosphonic (II) acids (or perhaps their acid chlorides) is actually produced. To obtain the hydroxyphosphonic acid (II), the reaction mixture is always poured into water and heated; this completes the conversion of the phostonic acid into the hydroxyphosphonic acid, (Reaction B).

In the case of benzophenone, anthraquinone, benzil and camphor no phosphonic acid can be obtained by such a procedure. Obviously, it is not expedient to attempt to accelerate the reaction by raising the temperature; acetic acid and phosphorus trichloride react so rapidly above 30° that no satisfactory results can be obtained even with benzaldehyde. Acetic anhydride is less active and, in certain cases which will be considered in a later paper, it has been possible to obtain results by using this reagent at a temperature of 30° to 35°. It was of no service, however, with the ketones just mentioned.

The failure of the reaction with benzophenone can be attributed to one of three possible causes. (1) The equilibrium of the initial reaction is very

far to the left; (2) the addition product is relatively unreactive with the reagents employed; (3) the rate at which the equilibrium of the initial reaction is attained is very slow. The fact that the materials were recovered quantitatively argues against the second possibility—apparently the initial addition reaction had proceeded to only a very slight extent. An increase in temperature would be expected to accelerate the reaction greatly. By thus making the equilibrium more mobile, it should be possible to approach the conditions which are realized at 25° with simple aldehydes and ketones. The effect of temperature on the equilibrium point cannot be predicted, but the position of the equilibrium is of not much importance *provided the rate of the reaction is relatively great.* In order to parallel the usual procedure at a higher temperature, it is necessary to find some substance to replace the acetic acid. This substance must react only slowly with the trichloride at the given temperature, but rapidly with the addition product. The similarity between the addition product and the pentachloride enabled us to investigate this point by studying the behavior of several reagents towards the pentachloride. A number of experiments with various compounds led us to believe that benzoic acid would be suitable. A trial with this reagent and benzaldehyde at a temperature of 145° to 150° was successful. Benzoyl chloride and the phosphonic acid were formed. The method was then applied to benzophenone with satisfactory results. At a temperature of 155° the reaction seemed to run with benzoic acid much as it did with simple ketones and acetic acid at room temperature; a 50% yield of the desired hydroxyphosphonic acid was obtained. With camphor there was also apparently a reaction, although the product was not isolated in a pure state. Anthraquinone and benzil could not be made to react even by this procedure, and it has not been possible, as yet, to cause them to combine with phosphorus trichloride.

Isolation of the Product.

The isolation of the hydroxyphosphonic acid is a difficult problem in many cases. Many of the substances crystallize with difficulty and are very soluble in water. Evaporation of the aqueous solution in some instances yields a gum which slowly solidifies. After drying on a porous plate it can be recrystallized. In some cases no crystalline acid could be obtained and the product was isolated as the lead salt.

The reaction with acetophenone and acetone is complicated by the fact that an unsaturated phosphonic acid is also formed to some extent. This was first noticed because the aqueous solution of the product rapidly decolorizes bromine water. In this work the weight of the crude mixture of saturated and unsaturated acids was determined and the yield calculated from this. A subsequent paper will discuss the mechanism of the

formation of these acids which have the formula $RC(PO_3H_2) = CH_2$.   The unsaturated acid was obtained pure in the case of acetophenone.   Its structure follows from its oxidation to formaldehyde by chromic acid.

The results of this research indicate the limits of the reaction of the trichloride with unsubstituted aldehydes and ketones.   The results are summarized in the following table.   An excess of trichloride was used in every case.   As this varied with the experiment and the conditions of isolating the material are obviously inaccurate, the variations in the yields are of no great significance.

Carbonyl compound.	Medium.	Yield of phosphonic acid. %	How isolated.
$C_6H_5COCH_3$	CH_3COOH	96	crude mixture, partially unsaturated.
CH_3COCH_3	CH_3COOH	91	crude mixture, partially unsaturated.
$CH_3COCH_2CH_3$	CH_3COOH	76	as lead salt.
$C_2H_5COC_3H_7$	CH_3COOH	67	as lead salt.
$(CH_3)_3CCOCH_3$	$(CH_3CO)_2O$	56	as lead salt.
$CH_3(CH_2)_5CHO$	CH_3COOH	76	as lead salt.
$(C_6H_5CH_2)_2CO$	CH_3COOH	44	crude crystals.
$C_6H_5CH_2CH_2COC_6H_5$	CH_3COOH	48	recrystallized acid.
$(C_6H_5CH_2CH_2)_2CO$	$(CH_3CO)_2O$	56	recrystallized acid.
$C_6H_5COC_6H_5$	C_6H_5COOH ($150°$)	50	recrystallized acid.
Camphor	C_6H_5COOH ($150°$)		not isolated.
$C_6H_5COCOC_6H_5$			no reaction under **any conditions.**
Anthraquinone			no reaction under any conditions.

Experimental.

General Procedure with Acetic Acid.

The general procedure which was employed when acetic acid was used as a medium is essentially as follows.   The phosphorus trichloride was added to the carbonyl compound, while the temperature was kept below $35°$; this requires considerable cooling in some cases.   An excess of the trichloride was employed; this was usually only about 10%, but in certain cases was much more.   The mixture was protected from moisture and allowed to stand for from 2 to 3 hours.   A slight excess (three times the molecular amount) of glacial acetic acid was then added, while the temperature was kept between $20°$ and $30°$.   After the reaction mixture had stood 12 hours longer, it was poured into 300 cc. of ice-water and shaken vigorously.   The aqueous solution was now evaporated to dryness on the steam-bath.   The gum which formed was allowed to crystallize.   In some cases this was a very slow process and took from one day to two weeks. The crystalline mass could then be dried on a clay plate and finally in a vacuum desiccator over sodium hydroxide.

In those cases in which no crystallization took place, the lead salt was prepared.   The gum was dissolved in about 200 cc. of water, made strongly alkaline with ammonia and then treated with magnesium nitrate.   After

it had stood overnight, the precipitated magnesium ammonium phosphate was filtered off. The solution was then diluted to 500 cc., made just acid with acetic acid, and heated to boiling. A solution of lead acetate or nitrate was added in excess, the mixture was boiled for 5 or 10 minutes to coagulate the lead salt and the solution was filtered. The lead salt was washed with boiling water and then dried. Prepared in this way, the lead salt was free from phosphate and practically free from chloride. Experiments had shown that the phosphorous acid, first formed by the excess of the trichloride and the water, would be completely oxidized to phosphoric acid during the evaporation. Thus, there was no necessity of removing this acid from the mixture. Most of the hydrochloric acid also is removed during the evaporation; the amount that is left does not interfere, since lead chloride is soluble in boiling solution whereas the lead salts of the phosphonic acids are practically insoluble.

Acetophenone.—Ten g. of acetophenone and 15 g. of trichloride (25% excess) yielded 16 g. of crude acid after it had been dried for 15 hours. The crude material contained about 63% of the unsaturated acid. The theoretical yield of the hydroxy acid would be 16.7 g. Percentage yield, about 96%. The pure unsaturated acid may be obtained by crystallization from a mixture of benzene and carbon tetrachloride.

α-Phenyl-vinyl-phosphonic Acid, $C_6H_5C(PO_3H_2)=CH_2$.—The acid, thus prepared, is very soluble in water, fairly soluble in alcohol and only slightly soluble in benzene. It melts at 112°.

Analyses. Calc. for $C_8H_9O_3P$: P, 16.9; C, 52.2; H, 4.9. Found: P, 16.6; C, 52.2; H, 5.2.

The acid was shown to be dibasic by titration with standard alkali. The aniline salt was made by the action of aniline on an alcohol-ether solution of the acid. It was recrystallized from alcohol and melted at 180° to 181°. It was soluble in water and insoluble in ether.

Analysis. Calc. for $C_{14}H_{16}O_3NP$: N, 5.15. Found: 5.09.

The phenyl-vinyl-phosphonic acid decolorizes bromine water immediately and bleaches permanganate solution. Its structure follows from these reactions, its analysis and the formation of formaldehyde on oxidation with chromic acid. 0.1 g. of substance was oxidized with 0.2 g. of chromic acid and the evolved gases passed into water. The water gave the characteristic resorcin test for formaldehyde.

Acetone.—Ten g. of acetone and 30 g. of trichloride (12% excess) yielded a crystalline mass which, when dry, weighed 17 g. A sample titrated with bromine water showed that it contained about 30% of an unsaturated acid. By recrystallization from hot glacial acetic acid, the α-hydroxy-*iso*propyl-phosphonic acid was obtained, m. p. 167° to 169°. The same acid has been prepared by Marie[2] by adding phosphorous acid to acetone and oxidizing the product. The percentage yield, based on the weight of the crude material was 91%.

Methylethyl Ketone.—Ten g. of methylethyl ketone and 25 g. of trichloride (30% excess) yielded 38 g. of the lead salt, or 76% calculated amount. No crystalline acid could be obtained.

Lead Salt of α-hydroxy-α-methyl-propyl-phosphonic Acid, $C_2H_5C(PO_3Pb)OHCH_3$.—The salt is insoluble in hot and cold water, but soluble in fairly strong nitric acid. It

² Marie, *Compt. rend.,* **133,** 221 (1901).

was free from phosphates and chlorides. A sample of it, when tested with bromine water, showed that it contained only a trace of unsaturated acid.

Analysis. Calc. for $C_4H_9O_4PPb$: Pb, 55.7. Found: 55.5.

Ethylpropyl Ketone.—Ten g. of ethylpropyl ketone and 15 g. of trichloride (7% excess) yielded 25.8 g. of lead salt, (67%). No crystalline acid could be obtained; a thick oil only partially soluble in water but soluble in alkalies could be isolated but not purified.

Lead Salt of α-Hydroxy-α-ethyl-butyl-phosphonic Acid, $C_3H_7C(PO_3Pb)OHC_2H_5$.— The salt was free from chlorides and contained only a trace of unsaturated acid.

Analysis. Calc. for $C_6H_{13}PO_4Pb$: Pb, 53.5. Found: 54.4.

Pinacoline.—Acetic anhydride was substituted for the acetic acid in the experiments with this compound. The resulting phosphonic acid is very unstable and there seemed to be less decomposition with acetic anhydride as a medium than with acetic acid. During the mixing of the ketone and the trichloride the temperature must be kept below 25°. After the addition of the anhydride the temperature was kept at 30° to 35° for several hours, then the mixture was poured into water. A dark oil separated from the aqueous solution. The acid was unstable, particularly when warmed, and could not be obtained crystalline. A lead salt was prepared by the usual procedure. 10 g. of pinacoline and 15 g. of trichloride (17% excess) gave 22.6 g. of lead salt, a 56% yield.

Lead Salt of α-hydroxy-α-methyl-β-dimethyl-propyl-phosphonic Acid, $(CH_3)_3$- C—C($PO_3Pb)(OH)(CH_3)$. The salt was very hygroscopic. After drying it for a month in a vacuum desiccator over sulfuric acid it gave the following analysis.

Calc. for $C_6H_{13}O_4PPb$: Pb, 52.6. Found: 51.4, 51.4.

The low values may be due to water still in combination with the compound. The salt was free from phosphate, chloride and unsaturated compounds.

Heptyl Aldehyde.—Ten g. of *n*-heptyl aldehyde and 16 g. (25% excess) of trichloride gave 12 g. of a lead salt or a yield of 76%. The gum obtained by evaporation of the aqueous solution of the reaction mixture slowly solidified; it was converted into the lead salt in order to determine the yield. When the lead salt was decomposed with hydrogen sulfide and the aqueous solution evaporated, the crystalline acid could be obtained.

In another experiment in which a somewhat purer sample of aldehyde was used in slight excess, 11 g. of solid phosphonic acid was obtained (76%) yield. Recrystallization from water yielded the pure hydroxyphosphonic acid melting at 165° to 173°. The compound is identical in its properties with the hydroxyphosphonic acid made by Fossick from an excess of trichloride and heptylaldehyde.[3]

Dibenzyl Ketone.—Five g. of the ketone and 6 g. of the trichloride (90% excess) yielded a crystalline mass which weighed 3 g. when dry. A test showed that no unsaturated acid was present.

α-Benzyl-α-hydroxy-β-phenyl-ethyl-phosphonic Acid, $C_6H_5CH_2(PO_3H_2)OHCH_2$- C_6H_5.—The acid can be recrystallized from benzene. It melts at 181° to 182°.

Analysis. Calc. for $C_{15}H_{17}O_4P$: C, 61.4; H, 5.8; P, 10.6. Found: C, 61.3; H, 5.9; P, 10.6.

Benzyl-acetophenone.—Three g. of the ketone and 3 g. of trichloride (20% excess) yielded 5 g. of sticky crystals. These were dissolved in glacial acetic acid, and water was added very slowly to the solution kept at —10°. The crystals which formed could be recrystallized from benzene. Two g. of purified acid was obtained, a 48% yield.

α-Phenyl-α-hydroxy-γ-phenol-propyl-phosphonic Acid, $C_6H_5C(PO_3H_2)OHCH_2CH_2$-

³ Fossick, *Monatsh.*, **7**, 27 (1886).

C_6H_5.—The acid melts at 165° to 168°; it is practically insoluble in water, but is soluble in alcohol, ether and acetic acid.   It did not decolorize bromine water.

Analysis.   Calc. for $C_{15}H_{15}PO_4$: P, 10.6.   Found: 10.8.

Dibenzyl-acetone.—Two g. of the ketone and 2 g. of the trichloride (80% excess) yielded 5 g. of very impure crystals which, however, contained no unsaturated acid. Recrystallization from benzene yielded 1.5 g. of pure solid (56%).   Acetic anhydride was used as the medium in this experiment.

α-hydroxy-α-(β-phenyl ethyl)-γ-phenyl-propyl-phosphonic Acid, $(C_6H_5CH_2CH_2)_2$-$C(OH)(PO_3H_2)$.—This substance melts at 173° to 174°.   It is insoluble in water but completely soluble in a solution of sodium hydrogen carbonate.

Analysis.   Calc. for $C_{17}H_{21}O_4P$: P, 9.7.   Found: 10.6.

Procedure with Benzoic Acid at a High Temperature.

As stated in the introduction, benzil, camphor, benzophenone and anthraquinone were recovered completely unchanged by all procedures involving acetic acid or anhydride.   Not a trace of a phosphonic acid could be detected.   The high temperature procedure in which benzoic acid is used was first tried with benzaldehyde as described in the following experiment.

Ten g. of benzaldehyde and 40 g. of benzoic acid were mixed in a flask equipped with a reflux condenser, and heated on the steam-bath.   Sixteen g. of phosphorus trichloride (1.3 mols) was added and the reaction mixture heated to 150°.   After 45 minutes the molten mass was poured into 300 cc. of water and the mixture was heated on the steam-bath until all the material had dissolved.   The solution was then cooled in ice and the benzoic acid filtered off.   The filtrate was evaporated to dryness, the residue dissolved in 10 cc. of water and a small amount of benzoic acid filtered off.   The filtrate was evaporated to dryness and the phosphonic acid converted into the aniline salt by treatment with aniline in an alcohol-ether solution.   Several crystallizations of the aniline salt from alcohol yielded 7.4 g. of material melting at 201°.   It was identical with the aniline salt previously described.[1]   The yield of purified material was 26% of that calculated.

Benzophenone.—Ten g. of benzophenone and 20 g. of benzoic acid were mixed and heated on the steam-bath until molten.   Ten g. of phosphorus trichloride (55% of excess) was added in small portions during a period of 5 to 10 minutes.   The temperature was gradually raised in the course of 10 minutes to 155°, and then allowed to fall to 130° and kept constant at this point for 2 to 3 hours.   The melt was cooled to 90° and poured into 500 cc. of water.   The mixture was made strongly alkaline with sodium hydroxide and heated on the steam-bath for from 4 to 5 hours.   During this treatment, the oil which separated when the melt was first poured into water, decreased appreciably.   The solution was diluted to 750 cc., cooled and the unchanged benzophenone removed by extracting it with ether.   To separate the benzoic acid, the solution was acidified strongly with hydrochloric acid, then cooled and filtered.   The filtrate was evaporated to a volume of 250 cc. and extracted thrice with ether.   The ethereal solution on evaporating yielded an oil which finally solidified.   Fractional crystallization from slightly acidulated water gave 7 g. of a phosphonic acid melting at 171° to 172°, and 2.5 g. of another acid containing phosphorus whose constitution was not established. Perhaps it was formed by the replacement of a hydrogen atom of the nucleus by the radical —PCl_2.

α-Hydroxy-diphenyl-methyl-phosphonic Acid, $(C_6H_5)_2C(OH)(PO_3H_2)$.—The acid melts at 171° to 172°. It is readily soluble in alcohol, in ether and in hot water and somewhat soluble in cold water.

Analysis. Calc. for $C_{13}H_{13}O_4P$: P, 11.7. Found: 11.7.

The constitution of the acid is established by the fact that it is oxidized by permanganate with the formation of benzophenone and phosphonic acid. Two g. of the acid dissolved in 10 cc. of sodium carbonate solution was treated with potassium permanganate until a permanent pink color resulted. The dioxide and a yellow solid separated and were filtered off. The filtrate gave a strong test for the phosphate ion. The yellow solid on recrystallization gave 0.5 g. of benzophenone which was identified by the method of mixed melting points.

Camphor.—The procedure just outlined for benzophenone was applied to camphor. A few grams of an oil was obtained, evidently an acid material, slightly soluble in water and containing phosphorus. No large amount of crystalline material could be secured, so the compound was not investigated further.

Anthraquinone and benzil showed no evidence of reaction when treated by the high temperature-benzoic acid procedure. The materials were recovered unchanged and no trace of a phosphonic acid could be detected.

Summary.

1. The limits of the action of phosphorus trichloride on saturated aldehydes and ketones has been studied. By the use of glacial acetic acid or acetic anhydride as a medium, hydroxyphosphonic acid can be obtained from most ketones.

2. The products were isolated either as crystalline acids or as lead salts.

3. With acetophenone and acetone, an unsaturated phosphonic acid is also produced. This has been isolated in one instance and its constitution established.

4. Benzophenone will not combine with phosphorus trichloride by the usual procedure. At 150°, with benzoic acid in place of acetic acid satisfactory results can be obtained.

5. It has not been possible by any procedure to add the trichloride to benzil or anthraquinone.

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