6. The theory satisfactorily accounts for the different colors of polymorphic forms of inorganic compounds, such as mercuric iodide, thallous iodide, etc. The more symmetrical form is the darker colored, because the electrostatic fields about the atoms are stronger in the more symmetrical forms.

7. According to the theory presented, it is not necessary to assign a different formula to each colored modification of a compound. The entire field of color and constitution should be re-examined on the basis of this theory.

In conclusion, the assistance and valuable criticism of Dr. Arthur A. Noyes and Dr. Roscoe G. Dickinson in connection with the development of the theory are gratefully acknowledged.

PASADENA, CALIF.

ADDITION REACTIONS OF PHOSPHORUS HALIDES. II. THE 1,4-ADDITION OF PHOSPHENYL CHLORIDE.

BY JAMES B. CONANT AND S. M. POLLACK.

I. Introduction.

Phosphorus trichloride readily combines with the carbonyl group of aldehydes[1] and with the conjugated system of a,β unsaturated ketones.[2] This combination involves the formation of a ring containing as one of its members a pentavalent phosphorus atom.

$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O + \geqslant P \rightleftarrows \quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=C -$$
$$\qquad\qquad\qquad\qquad\qquad P - O$$

The reaction is reversible and the product cannot be isolated, but may be transformed by suitable reagents into a stable phosphonic acid or its derivative.

These addition reactions are analogous to the formation of the pentahalides by the addition of chlorine or bromine to phosphorus trichloride. The trivalent phosphorus atom is unsaturated, as shown by its combination with the halogens, the carbonyl group or the ends of a conjugated system in unsaturated ketones. The organic derivatives of phosphorus trichloride (the chloro-phosphines) are also unsaturated since they readily unite with two atoms of chlorine. It is, therefore, to be expected that they will combine with certain unsaturated organic substances in a manner completely parallel to phosphorus trichloride itself. Michaelis, in fact, in his exhaustive study of these compounds showed[3] that benzaldehyde combined

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[1] THIS JOURNAL, **42**, 2337 (1920).

[2] *Ibid.*, **39**, 2679 (1917); **42**, 830 (1920).
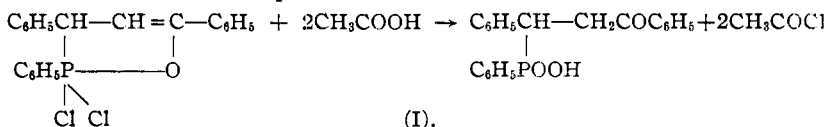
[3] Michaelis, *Ann.*, **293**, 193 (1896).

with dichloro-phenylphosphine (phosphenyl chloride) and he was able to isolate a phosphonic acid by treatment of the addition product with water. This is obviously a case of addition to the carbonyl group.
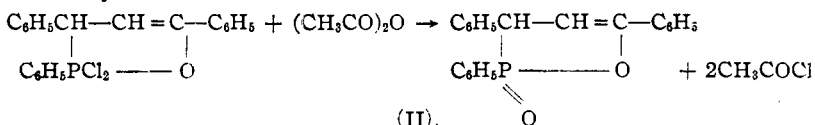
The results here presented show that phosphenyl chloride combines with the ends of the conjugated system of benzal-acetophenone. As in the case of the trichloride an intermediate cyclic compound is first formed.
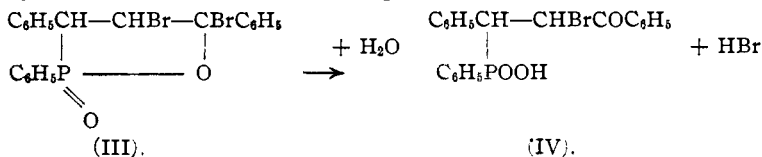
$$C_6H_5CH = CHCOC_6H_5 + C_6H_5PCl_2 \rightleftharpoons C_6H_5CH—CH = C—C_6H_5$$
$$C_6H_5P————O$$
$$Cl\ Cl$$
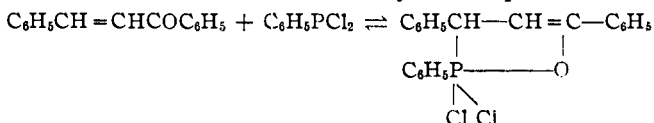
This readily reacts with acetic acid producing acetyl chloride and a keto-phosphonic acid (I). The chlorine atoms of the addition compound, like those of $C_6H_5PCl_4$, are more reactive than those in phosphenyl chloride. As a result phosphenyl chloride and benzal-acetophenone, when mixed with acetic acid, form the keto-phosphonic acid almost quantitatively; the equilibrium of the primary reversible reaction is shifted by the rapid reaction of the addition product with acetic acid.

$$C_6H_5CH—CH = C—C_6H_5 + 2CH_3COOH \rightarrow C_6H_5CH—CH_2COC_6H_5 + 2CH_3COCl$$
$$C_6H_5P————O \qquad\qquad C_6H_5POOH$$
$$Cl\ Cl \qquad\qquad (I).$$

The proof of the structure of the intermediate cyclic compound rests on the structure of a cyclic anhydride (II) obtained by the action of acetic anhydride. Here again the addition product is more reactive than phosphenyl chloride and the reaction goes to completion in the presence of acetic anhydride.

$$C_6H_5CH—CH = C—C_6H_5 + (CH_3CO)_2O \rightarrow C_6H_5CH—CH = C—C_6H_5$$
$$C_6H_5PCl_2 ——— O \qquad\qquad C_6H_5P ——— O \quad + 2CH_3COCl$$
$$(II). \qquad O$$

The cyclic anhydride (II) could be isolated only as an impure gum, but its structure is clearly established by its reactions. On treatment with water it yields the phosphonic acid (I). It combines with two atoms of bromine, thus showing that it is unsaturated. The resulting dibromide (III) on treatment with water forms hydrobromic acid and two isomeric β-bromoketo-phosphonic acids (IV) which are identical with the substances made by the bromination of the keto-phosphonic acid (I).

$$C_6H_5CH—CHBr—CBrC_6H_5 \qquad\qquad C_6H_5CH—CHBrCOC_6H_5$$
$$C_6H_5P ——— O \quad + H_2O \quad\rightarrow\quad C_6H_5POOH \qquad + HBr$$
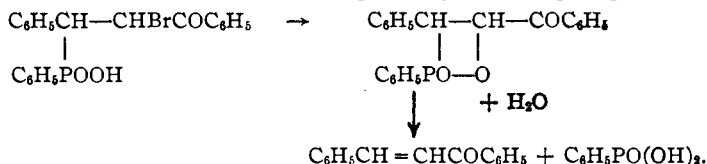$$O$$
$$(III). \qquad\qquad\qquad\qquad (IV).$$

The bromo acid contains two asymmetric carbon atoms, and thus two

racemic stereo-isomers are possible; both were formed by the bromination of the keto-phosphonic acid, and also by the action of water on the cyclic dibromide.   This evidence seems to establish clearly the structure of the anhydride and in turn that of the addition product.   Thus, the phosphorus atom in phosphenyl chloride like that in the trichloride,[2] adds to the 1,4 position of the conjugated system.

The two isomeric bromine compounds are stereo-isomers and not structural isomers since they are both decomposed by alkaline reagents with the formation of benzal-acetophenone.   This reaction is parallel to the behavior of the β-bromo acid previously studied[2] and establishes the fact that the bromine atom is in the β position.   The low-melting isomer may be transformed into the high-melting one by the prolonged action of sunlight on its chloroform solution.

It is interesting to note that the two isomers decompose in aqueous sodium carbonate at appreciably different rates, and both seem to be somewhat more stable in this regard then the β-bromo acid obtained in the work with phosphorus trichloride.   It seems possible that this reaction may involve the intermediate formation of a β-phostone (analogous to a β-lactone) which then easily decomposes in the presence of water to form the unsaturated ketone, and the corresponding acid of phosphorus.

$$C_6H_5CH\text{---}CHBrCOC_6H_5 \quad \rightarrow \quad C_6H_5CH\text{---}CH\text{---}COC_6H_5$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad |\quad |$$
$$C_6H_5POOH \qquad\qquad\qquad\qquad C_6H_5PO\text{---}O$$
$$\downarrow \quad + H_2O$$

$$C_6H_5CH = CHCOC_6H_5 + C_6H_5PO(OH)_2.$$

Many β-lactones easily lose carbon dioxide with the production of unsaturated compounds, which is a reaction analogous to that shown above.

II. Experimental.

α-Phenyl-β-benzoyl-ethyl-phenylphosphonic Acid, $C_6H_5CH(C_6H_5POOH)CH_2CO\text{-}$ C_6H_5.—Ten g. of benzal-acetophenone was dissolved in a mixture of 9 g. of phosphenyl chloride and 15 g. of glacial acetic acid.   The ketone went quickly into solution, which in the course of a few minutes began to become warm and deposit a white crystalline material; the presence of acetyl chloride could be recognized by its odor. The mixture was cooled with running water and after considerable solid had separated 70 cc. of glacial acetic acid was added with stirring.   At the end of 30 minutes the mixture was poured into water and the solid filtered off, washed with ethyl alcohol and dried.   19 g. was thus obtained; this is slightly more than the calculated amount.   The crude product thus obtained can be best purified by dissolving in sodium carbonate, extracting with ether and reprecipitating with acid.   It is very insoluble in all solvents but may be recrystallized from its very dilute solutions in hot glacial acetic acid or ethyl alcohol.   It melts with decomposition at 220° to 225°.

Analysis.   Calc. for $C_{21}H_{19}O_3P$: P, 8.9.   Found: 8.7.

Titration with standard sodium hydroxide solution using phenolphthalein as an indicator, showed the compound to be a monobasic acid.

α-Phenyl-β-bromo-β-benzoyl-ethyl-phenylphosphonic Acid, $C_6H_5CH(C_6H_5POOH)\text{-}$

CHBrCOC₆H₅.—The phosphonic acid was so insoluble that it could be brominated only in glacial acetic acid.   Five g. of the crude acid was brominated with 2.7 g. of bromine by the following procedure.   The acid was suspended in 20 cc. of glacial acetic acid and the mixture heated to the boiling point.   A small portion of the bromine was added and the heating continued until the color disappeared (about 5 minutes).   The bromine was then added slowly and the temperature kept a little below the boiling point of the acetic acid.   The reaction proceeded rapidly after it had once started and hydrogen bromide was given off freely.   The solid went into solution as the reaction continued, and at the end a clear colorless solution resulted.   This was poured into 500 cc. of water, and the solid filtered off and dried.   It weighed 6.5 g. and had a melting point of 160° to 180°. This mixture of stereo-isomeric bromine compounds could be separated only with difficulty, as much decomposition took place on heating them in any solvent, particularly methyl and ethyl alcohols.   The separation was best effected by treating with 50 cc. of hot chloroform, filtering off the insoluble compound and evaporating the chloroform solution to a volume of 20 cc.   On the addition of petroleum ether the low-melting isomer slowly crystallized.   2 g. of substance melting at 150° was thus obtained.   The insoluble material was recrystallized from ethyl alcohol; 1 g. of substance melting at 195° was obtained.   Recrystallization from the same solvent did not change the melting point.

High-melting isomer.—This substance melted with decomposition at 195°.   It is very insoluble in all solvents.

Analysis.   Calc. for $C_{21}H_{18}O_3PBr$: Br, 18.7.   Found: 18.6.

Low-melting isomer.—This substance melted at 150°; it is fairly soluble in methyl and ethyl alcohols and very soluble in chloroform.   It is only sparingly soluble in petroleum ether.

Analysis.   Calc. for $C_{21}H_{18}O_3PBr$: Br, 18.7.   Found: 19.1.

Both isomers dissolve in aqueous sodium carbonate-although the high-melting isomer only slowly (probably because of its extreme insolubility).   When treated with sodium hydroxide solution both substances dissolve and are almost immediately decomposed with the formation of benzal-acetophenone which separates as a precipitate.   This same decomposition takes place more slowly in sodium carbonate solution.   A dilute sodium carbonate solution of the low-melting isomer became milky after standing for 5 minutes at room temperature.   In a parallel experiment with the high-melting substance the solution reached the same degree of opalescence after standing for about 40 minutes.   An increase in temperature greatly facilitates this decomposition.

A chloroform solution of the isomer melting at 149° was made faintly red with a trace of iodine and exposed to sunlight.   The high-melting isomer very slowly separated, and after many weeks over half of the material had been transformed.   The product was identified by a mixed-melting-point determination with the pure substance melting at 195°.

Reaction in Acetic Anhydride.

The reaction between benzal-acetophenone, phosphenyl chloride, and acetic anhydride is much slower than the corresponding reaction with acetic acid.   After evaporating the acetyl chloride formed, the reaction product is left as a gum which is soluble in chloroform.   All attempts to obtain a solid substance failed.   The reactions of the material, however, show that an unsaturated cyclic anhydride is present at this point.   The transformations may be carried out with a chloroform solution of the gum, or with the original reaction mixture somewhat diluted with more acetic anhydride.   A typical experiment with each procedure is as follows.

(*a*) Five g. of benzal-acetophenone, 3.8 g. of acetic anhydride and 4.5 g. of phosphenyl chloride were mixed and allowed to stand for one hour at room temperature and then for 3 hours at 40°. The acetyl chloride and excess of acetic anhydride were evaporated under diminished pressure at a temperature of 40° to 50°. The resulting gum was dissolved in 30 cc. of chloroform. Ten cc. of this solution was treated with 1 cc. of water and enough ethyl alcohol to make a homogeneous solution. Crystals of the phosphonic acid soon began to separate. After 4 hours the precipitate was filtered off; weight 1.7 g., or 61%.

The remaining 20 cc. of solution was treated with 2.9 g. of bromine which it decolorized without evolution of hydrogen bromide. The solution was then treated with 2 cc. of water and 30 cc. of alcohol. After 48 hours the solid was filtered off; 2.7 g. of mixed bromides, m. p. 160° to 170°, was obtained.

(*b*) Five g. of benzal-acetophenone, 4.5 g. of phosphenyl chloride and 3.5 g. of acetic anhydride were allowed to react as in (*a*), except that the mixture stood overnight. The solution was diluted to 25 cc. with acetic anhydride. Five cc. of this solution was poured into water; a white precipitate resulted. It was separated, dissolved in sodium hydroxide solution and reprecipitated with acid; 1.6 g. of phosphonic acid, m. p. 220° to 225°, was thus obtained. This was a yield of 94%.

The remaining 20 cc. of solution was treated with 3.9 g. of bromine which was readily taken up, producing only a faint red color at the very end of the addition. The solution was poured into 500 cc. of water; a crystalline precipitate formed which was filtered off; 7 g. of mixed bromides was thus obtained, a yield of 85%. This mixture was separated in the same way as described in the account of the preparation of the bromo acids from the phosphonic acid; 3.3 g. of the low-melting isomer was obtained which melted at 149°. A mixed-melting-point determination showed that it was identical with the low-melting isomer prepared by the bromination of the keto-phosphonic acid. Only about 0.5 g. of high-melting isomer was obtained in the pure condition after recrystallization. Its identity was also established by a mixed-melting-point determination.

Summary.

1. Benzal-acetophenone reacts with phosphenyl chloride in glacial acetic acid producing a keto-phosphonic acid and acetyl chloride.

2. In acetic anhydride solution the product is an unsaturated cyclic anhydride which readily reacts with water forming the keto-phosphonic acid.

3. The structure of this anhydride follows from the fact that it combines with one equivalent of bromine and the product with water gives two stereo-isomeric β-bromoketo-phosphonic acids. These β-bromo acids were also prepared by bromination of the keto-phosphonic acid.

4. Both β-bromo acids decompose in the presence of aqueous alkali to give benzal-acetophenone, hydrogen bromide and phenylphosphonic acid. This proves they are stereo-isomeric and are β-bromo compounds.

5. The structure of the compound formed in acetic anhydride shows that the first step in the process is the 1,4 addition to the conjugated system of the phosphorus atom of the phosphenyl chloride.

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