

benzol was not obtained. The reaction of aluminum chloride with cymene offers the opportunity for the formation of many compounds that might readily be overlooked when the reaction is carried out on a small scale.

Summary.

1. By the action of aluminum chloride on cymene there is formed diisopropyl, benzene, toluene, *m*-xylene, and 1-methyl-3,5-diisopropylbenzene. The latter compound so far as known has never been previously described.

2. Small amounts of the catalyzer favor the formation of toluene, while the formation of benzene increases with the amount of catalyzer employed.

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THE ACTION OF PHOSPHORUS TRICHLORIDE ON UNSATURATED KETONES.

[PRELIMINARY PAPER.]

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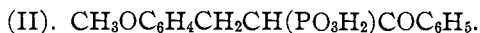
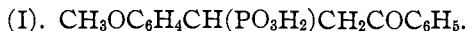
During the course of some experiments on the action of acid chlorides on α,β -unsaturated ketones it was discovered that benzalacetophenone in glacial acetic acid solution reacted with phosphorus trichloride. On diluting with water, a substance was precipitated which was found to be a ketonic phosphonic acid. Satisfactory results could only be obtained by the use of glacial acetic acid as the solvent. An attempt to find a similar case in the literature, revealed the fact that Fossick¹ had studied a somewhat analogous reaction between aldehydes and phosphorus trichloride, but had employed no solvent. The oily addition compounds which he obtained yielded, on treatment with water, oxyphosphonic acids of the type $RCHOHPO_3H_2$. Aside from this work and one or two isolated observations,² no investigation has been made of the action of phosphorus trichloride on substances having a carbonyl group, other than acids. A further study was hence undertaken, not only of the action of the reagent on unsaturated ketones, but also of the reaction with various types of aldehydes and ketones when dissolved in glacial acetic acid. The branch of the work dealing with unsaturated ketones has unfortunately been interrupted, so that the following is only an account of the preliminary experiments. It is hoped that this research may be soon continued with a view to determining the mechanism of the reaction and the limits of its applicability.

Three unsaturated ketones were employed in this work: anisalacetophe-

¹ *Monatsh.*, **5**, 527 (1885); **7**, 31 (1887).

² *Ann.*, **281**, 363; *Ber.*, **18**, 899 (1885); **34**, 1291 (1901).

none, benzalacetophenone and dibenzalacetone. Of these, anisalacetophenone may be considered as typical for the purposes of the following discussion: When 20% excess of phosphorus trichloride was added to a glacial acetic acid solution of the unsaturated ketone, a deep red color was at once produced. On standing the color changed to yellow, the solution became warm and evolved acetyl chloride and hydrochloric acid. After the reaction was completed, the mixture was diluted with water which precipitated the product as an oil that soon solidified. The analysis of the substance corresponded to a compound formed from the original unsaturated ketone by the addition of H_3PO_3 . Titration with standard alkali showed that it was a dibasic acid. Prolonged boiling with concentrated sodium hydroxide or hydrochloric acid failed to produce any change. This stability towards hydrolytic agents is a characteristic of the alkyl phosphonic acids and serves to distinguish them from the esters of phosphoric or phosphorous acids. The compound was not oxidized by potassium permanganate in alkaline solution, nor did it combine with bromine in cold chloroform solution; this inertness indicates the absence of an ethylene linkage. The presence of a carbonyl group in the molecule was readily recognized by the formation of a crystalline oxime. These facts definitely prove that the substance is a ketonic phosphonic acid and must be represented by either Formula I or II.



There is at present no direct experimental evidence to distinguish between the two alternative formulas. However, a consideration of the reaction involved in the formation of the compound leads to the conclusion that Formula I is correct. The behavior of phosphorus trichloride with unsaturated ketones is very closely related to the action of the same reagent on aldehydes. Both reactions proceed smoothly in glacial acetic acid at room temperature.¹ In both cases the final product is a phosphonic acid containing the acidic group attached to a previously unsaturated carbon atom, the valence of the phosphorus having increased from three to five. This parallelism in the action of unsaturated ketones and aldehydes with a particular reagent is not confined, of course, to this reaction with phosphorus trichloride. It appears to be a rather general phenomenon and has been studied with such reagents as sodium bisulfite, ammonia, hydroxylamine, and the organomagnesium compounds. In all such cases the final product of the action of the reagent on the unsaturated ketone, if the ethylene linkage is involved, has a structure comparable to that represented by Formula I and not by Formula II. That is, the

¹ As will be shown in a later paper, this procedure may be advantageously employed with aldehydes, the substances formed being identical with those isolated by Fossick.

radical which in the one case is found joined to the carbon atom of the carbonyl group, becomes attached, in the other case, to the β atom of the ethylene linkage. Thus it appears from analogy, that Formula I is correct, if phosphorus trichloride is to be classified with those reagents which react similarly with both aldehydes and unsaturated ketones.

This evidence as to the structure of the phosphonic acid is quite apart from any consideration of the mechanism of the reaction. Fossick¹ has suggested as the first step in the reaction with aldehydes an addition of the phosphorus trichloride to the carbonyl group by means of the two "free bonds" of the phosphorus atom. A corresponding stage in the reaction with unsaturated ketones would be a 1,4 addition to the conjugated system. The subsequent transformation of this addition compound into the phosphonic acid would be brought about presumably by the glacial acetic acid and the water used as the diluent in the final step. No mechanism can at present be even suggested for the later stages of the reaction. The acetic acid besides functioning as a solvent, is apparently involved in the reaction since acetyl chloride is one of the products. Moreover, attempts to use other solvents yielded no phosphonic acid even after treatment with water. By using no solvent (Fossick's procedure), only a poor yield of the acid could be obtained.

Such a case of 1,4 addition, as that suggested above as a tentative mechanism, has not been hitherto observed. If further investigation confirms this hypothesis, the matter should be of considerable interest, since a 1,4 addition of one atom of a molecule by reason of its increase in valence would appear to be the simplest possible case of 1,4 addition.

Experimental.

Reaction of Phosphorus Trichloride and Anisalacetophenone.—When phosphorus trichloride is added to a solution of anisalacetophenone in glacial acetic acid the original yellow color is at once changed to red, an absorption of heat taking place at the same time. If the solution is at once diluted with water until all the organic material is precipitated, it is found that the unsaturated ketone can be recovered unchanged, since no phosphonic acid is produced. However, if the mixture is allowed to stand until the red color disappears, precipitation with water yields a substance which is completely soluble in sodium carbonate (if an excess of phosphorus trichloride has been employed). The speed at which this reaction proceeds varies greatly with the concentration of the reacting substances. If the reagent is added to a solution of the ketone less concentrated than about 50% the color disappears very slowly. Under these conditions the reaction is completed after standing overnight. With more concentrated solutions, the color begins to lighten in the course of a few minutes and the reaction may proceed so rapidly that the solu-

¹ *Loc. cit.*

tion becomes hot. In this case, acetyl chloride can be seen condensing on the sides of the flask while copious fumes of hydrochloric acid are evolved. It has not yet been determined whether the hydrochloric acid is a product of the reaction or whether it is formed by a decomposition of the acetyl chloride by the moisture of the air. About a 25% excess of phosphorus trichloride is necessary in order to cause the reaction to run to completion; with less amounts some unchanged ketone contaminates the reaction product.

It is conceivable that the reaction might be due to the phosphorous acid formed in small amounts at room temperature from the acetic acid and the trichloride. It can be easily proved that this is not the case. A mixture of phosphorus trichloride and acetic acid, treated with enough water to decompose the chloride, is without action on the unsaturated ketone. Further evidence against this possibility is found in the fact that the phosphonic acid may be obtained (though in very poor yield) by the action of the reagent on the ketone without any solvent, if the mixture is subsequently treated with water.

The following is typical of the procedure found most suitable for carrying out the reaction: 19 g. of anisalacetophenone were partially dissolved in 40 cc. of glacial acetic acid and 14 g. of phosphorus trichloride were added to the solution. The ketone soon dissolved completely, the solution becoming red and perceptibly cold. After standing overnight, the reaction was completed. The mixture was poured into 500 cc. of water. A heavy oil was at once precipitated which was stirred with the aqueous layer until it began to solidify. It was purified by dissolving in sodium carbonate and extracting the solution several times with ether. A very small amount of yellow material was thus removed. On now acidifying the solution, the acid was precipitated as a white crystalline solid. The crude acid could be further purified by recrystallization from dilute alcohol. Twenty-three grams of pure acid were thus obtained, a yield of 89%. On evaporating the mother liquor, a further amount of material (about 3 g.) was obtained as an oil. This was probably also the phosphonic acid together with some other substance which prevented crystallization.

α -(4-Methoxyphenyl)- β -benzoylethylphosphonic Acid, $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}(\text{PO}_3\text{H}_2)\text{CH}_2\text{COC}_6\text{H}_5$.—Thus prepared, the acid crystallizes in small, colorless needles which melt at 189°. It is almost insoluble in cold water and ether and only sparingly soluble in boiling water; it dissolves readily in alcohol. A solution of the substance in sodium bicarbonate solution does not decolorize potassium permanganate solution. Dissolved in cold chloroform, the substance does not react with bromine even on standing for several hours. Attempts to hydrolyze the compound by boiling it with 50% sodium hydroxide failed; the entire amount of the substance

was recovered unchanged on acidification. Likewise, when a concentrated hydrochloric acid solution of the compound was heated for some time no reaction occurred. The salts of the acid were not studied in detail, but a crystalline sodium salt could be easily obtained by concentrating a sodium hydroxide solution of the substance. The barium and calcium salts were apparently soluble while the salts of the heavy metals such as silver and lead, were precipitated on adding a solution of the sodium salt to the corresponding chlorides. Titration with standard tenth-normal sodium hydroxide, using phenolphthalein as an indicator, showed that the acid was dibasic.

Calc. for $C_{16}H_{17}O_5P$: C, 60.0; H, 5.3. Found: C, 59.8; H, 5.5.

α -(4-Methoxyphenyl)- β -benzoylethylphosphonic Acid Oxime, $CH_3OC_6H_4CH(PO_3H_2)CH_2C(=NOH)C_6H_5$.—Three grams of the phosphonic acid, 1.5 g. of sodium bicarbonate, and 1.5 g. of potassium acetate were dissolved in 10 cc. of water, and to this solution 1 g. of hydroxylamine hydrochloride was added. The mixture was heated on the water bath for three hours and then allowed to stand overnight. On cautious acidification an oil was precipitated which was dissolved in ether and the ethereal solution washed several times with very dilute acid, in order to remove as much of the excess reagent as possible. On standing, the ethereal solution deposited a crystalline solid which was filtered off and washed with ether. This substance was the desired oxime contaminated by some hydroxylamine which was apparently present as the salt of the oximephosphonic acid. The analysis was consequently too high in nitrogen and too low in carbon and hydrogen. Neither recrystallization nor washing with dilute acid were successful in purifying the oxime. The substance was finally obtained analytically pure by suspending it in water and then adding a little sodium nitrite solution and a small amount of dilute acid. This mixture on stirring evolved some gas and the solid became soft and then after a short time resolidified. The resulting product was found to be pure enough to analyze, the dilute nitrous acid having decomposed the hydroxylamine and not the oxime. The oxime is a white crystalline solid melting at 156° with slight decomposition; it is soluble in both sodium bicarbonate and hydrochloric acid and can be precipitated from both solutions by neutralization. The acid solution of the oxime readily undergoes hydrolysis on boiling, the original ketonic phosphonic acid being formed. Titration with tenth-normal sodium hydroxide, using phenolphthalein as an indicator, showed that the compound was a dibasic acid.

Calc. for $C_{18}H_{18}O_5PN$: N, 4.2. Found: N, 4.1.

α -Phenyl- β -benzoylethylphosphonic Acid, $C_6H_5CH(PO_3H_2)CH_2COC_6H_5$.—This acid was prepared from benzalacetophenone by exactly the same procedure that was used with anisalacetophenone. The color change

which was characteristic of the reaction which has been described, did not take place with benzalacetophenone, a fact probably connected with the absence of the auxochrome group CH_3O on the aromatic nucleus. When first precipitated from the reaction mixture as an oil, the acid is soluble in ether, but the ethereal solution slowly deposits the crystalline substance which is insoluble in both ether and cold water. The crystals contain water of crystallization when they separate from an ethereal solution or from dilute alcohol. The substance melts at 116° with loss of its water of crystallization. In its general reactions it was similar to the phosphonic acid just discussed, being unreactive with potassium permanganate, cold bromine and hydrolytic agents. Titration showed it to be a dibasic acid. The water of crystallization was determined by heating to constant weight at 130° ; a clear colorless melt resulted which was subsequently used for the combustion.

Calc. for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{P}\cdot 0.75\text{H}_2\text{O}$: H_2O , 4.5. Found: H_2O , 4.6.

Calc. for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{P}$: C, 62.1; H, 5.2. Found: C, 62.2; H, 5.3.

α -Phenyl- β -cinnamoylethylphosphonic Acid, $\text{C}_6\text{H}_5\text{CH}(\text{PO}_3\text{H}_2)\text{CH}_2\text{CO}-\text{CH}=\text{CHC}_6\text{H}_5$.—Twelve grams of dibenzalacetone were dissolved in 50 cc. of glacial acetic acid and 7 g. of phosphorus trichloride (one molecule) were added to the solution. After standing for some hours the mixture was poured into water and the resulting oil taken up in ether. The phosphonic acid was extracted from the ethereal solution with sodium carbonate and then precipitated by acidification. The substance could be easily purified by recrystallization from dilute alcohol; yield, 12 g. A small amount of material was obtained on evaporating the ethereal solution; it was probably unchanged ketone. The compound crystallizes with water of crystallization, which it loses at 108° when heated in a melting-point tube. As would be expected from the fact that the acid still contains an ethylene linkage, it readily reduces permanganate solution and combines with bromine in cold chloroform. Titration in the usual manner showed the acid to be dibasic.

Calc. for $\text{C}_{17}\text{H}_{17}\text{O}_4\text{P}\cdot 1.25\text{H}_2\text{O}$: H_2O , 6.6. Found: H_2O , 6.8, 6.6, 6.7.

Calc. for $\text{C}_{17}\text{H}_{17}\text{O}_4\text{P}$: C, 64.5; H, 5.4. Found: C, 64.7; H, 5.5.

Summary.

1. It has been found that phosphorus trichloride reacts with α,β -unsaturated ketones in glacial acetic acid solution. When the solution is diluted with water, a substance is obtained which has been shown to be a ketonic phosphonic acid.

2. It seems probable that the first stage in the reaction is similar to the 1,4-addition of certain reagents to unsaturated ketones. If this analogy is correct, the final product is a β -ketonic phosphonic acid.