dark yellow oily precipitate is formed which at once begins to give off nitrogen; the resulting nitrile is taken up by the benzene as soon as it forms. When all has been added the temperature is held at 0–5° for 30 minutes longer and is then allowed to rise to that of the room (20–25°), which usually requires about three hours. After the mixture has been stirred for two hours longer the crock is surrounded by hot water or steam and warmed to 50° without the stirring. The mixture is then allowed to stand until cool, when the aqueous layer is drawn off and the upper, oily layer distilled, first in a current of steam and finally under atmospheric or reduced pressure.

In this manner yields of nitriles amounting to 60–70% of the calculated quantity have been obtained from aniline, o-toluidine, p-toluidine and p-bromo-aniline, while a 55% yield of α-naphthonitrile[7] was obtained from α-naphthylamine. The reaction can be carried out on a considerably larger scale (over 50 g.-mols.) with no diminution of yield.

Summary

The conversion of primary aromatic amines into the corresponding nitriles by diazotization and treatment with cuprocyanide solutions can be carried out in neutral or weakly alkaline solution, so that the liberation of hydrogen cyanide is avoided. The yields fully equal those obtainable by the older method.
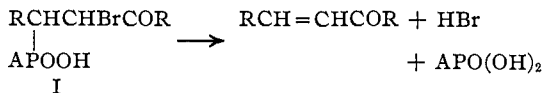
ROCHESTER, NEW YORK

THE MECHANISM OF THE DECOMPOSITION OF BETA-BROMOPHOSPHONIC ACIDS IN ALKALINE SOLUTION

BY JAMES B. CONANT AND ERNEST L. JACKSON

Certain β-bromophosphonic acids are rapidly and quantitatively decomposed by dissolving in aqueous alkaline solutions[1] according to the following equation.

$$\begin{array}{ccc} \text{RCHCHBrCOR} & & \text{RCH=CHCOR + HBr} \\ | & \longrightarrow & \\ \text{APOOH} & & \text{+ APO(OH)}_2 \\ | & & \\ \text{I} & & \end{array}$$

(R = aryl; A = OH, C_6H_5 or C_6H_5O)

In an earlier paper[2] it was suggested that the mechanism of this reaction might be similar to that proposed by Erlenmeyer[3] for the decomposition of β-halogen acids, and might involve the formation of an inner ester
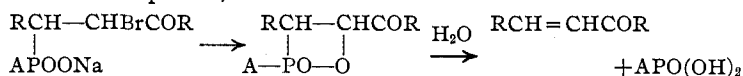
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[7] For the isolation of the nitrile, steam distillation under reduced pressure has been found most satisfactory.

[1] (a) THIS JOURNAL, 42, 830 (1920); (b) ibid., 43, 1665 (1921); (c) ibid., 44, 2530 (1922); see also (d) ibid., 43, 1677 (1921).

[2] Ibid., 43, 1665 (1921).

[3] Erlenmeyer, Ber., 13, 305 (1880).

analogous to a β-lactone (a β-"phostone") and the subsequent decomposition of this compound, thus

$$\underset{\overset{|}{\text{APOONa}}}{\text{RCH}}\text{—}\underset{}{\text{CHBrCOR}} \longrightarrow \underset{\overset{|}{\text{A—PO—O}}}{\text{RCH—CHCOR}} \xrightarrow{\text{H}_2\text{O}} \text{RCH}=\text{CHCOR} \\ +\text{APO(OH)}_2$$

The purpose of the present investigation was to prepare such β-phostones and to discover whether or not they played an intermediate role in the decomposition of the β-bromophosphonic acids. To this end we have synthesized from benzal-p-chloro-acetophenone the monophenyl (A = OC_6H_5, Formula I) and monomethyl esters (A = OCH_3, Formula I) of a β-bromophosphonic acid. The chlorine atom was introduced into one of the phenyl groups in order to obtain a solid monomethyl ester. A study of these esters seemed promising, inasmuch as our previous work had shown that the corresponding monophenyl ester of the bromophosphonic acid prepared from benzalacetophenone formed a stable sodium salt, although the parent acid was immediately decomposed by sodium bicarbonate. The monophenyl ester, which was prepared in this work, also formed a relatively stable salt but we were unable to prepare a β-phostone from it; it is impossible, apparently, to eliminate the bromine atom without at the same time removing the phosphonic acid group and forming the unsaturated ketone. While we were thus unable to carry out our original intention of preparing β-phostones, we have brought to light, nevertheless, certain important facts concerning the decomposition of these β-bromo acids and have been able to exclude by indirect evidence the possibility of this decomposition proceeding through a phostone.

The steps in the synthesis of the bromo esters are given below.

$$C_6H_5CH\text{=}CHCOC_6H_4Cl$$
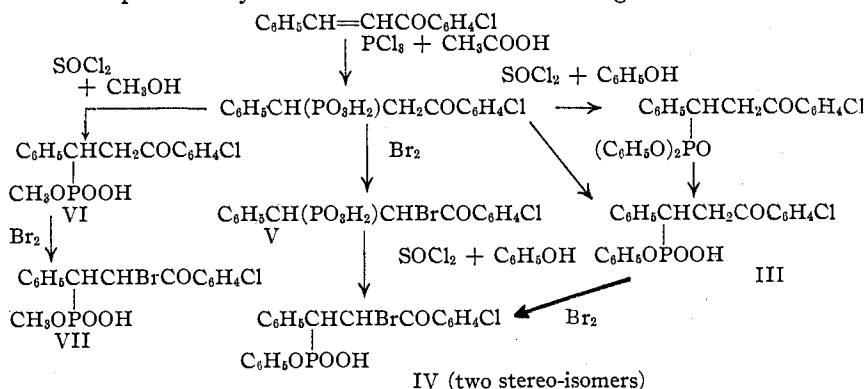
Of the alternative methods of preparing the bromomonophenyl ester (IV), the one involving the direct bromination of the monophenyl ester (III) gave the better yields. Two stereo-isomeric bromo esters were thus obtained which could be separated by fractional crystallization from alcohol. Cold dil. sodium hydroxide decomposed both esters with the

formation of benzal-*p*-chloro-acetophenone; this proves that the two substances are not structural isomers but stereo-isomers. Similar stereo-isomers were previously obtained in the case of β-bromo-β-benzoyl-α-phenyl-ethylphenylphosphonic acid, (A = C_6H_5, R = C_6H_5, Formula I) and their structure determined by a similar reaction.[1b]

Both isomeric bromomonophenyl esters (IV) dissolved in aqueous sodium bicarbonate without decomposition and the resulting solutions were stable at room temperature for long periods of time. It was hoped that the sodium salt of these monobasic bromo acids would decompose on standing or on heating with the elimination of sodium bromide and the formation of an insoluble β-phostone. No such transformation could be realized, however; at 25° no sodium bromide was formed even after many hours. On gently warming the solution both the bromine atom and the phosphonic acid were eliminated from the molecule with the formation of the unsaturated ketone. Repeated experiments failed to indicate any conditions under which the solution would give a test for bromide ions without at the same time giving an equally strong test for phosphate ions and phenol.

The Influence of the Hydroxyl Ion

This failure to obtain a β-phostone might be taken as an indication that such a compound was very unstable and rapidly decomposed with the formation of the unsaturated ketone; in short, that it was an intermediate in the reaction we were studying. This hypothesis is made very unlikely, however, by a most surprising fact which soon came to our attention, namely that the rate of decomposition of the bromo esters was a function of the hydroxyl-ion concentration of the solution. This can be beautifully demonstrated by dissolving the bromo ester in "buffer solutions" of various alkalinities and observing the rate of formation of the very fine precipitate of unsaturated ketone. Table I records the
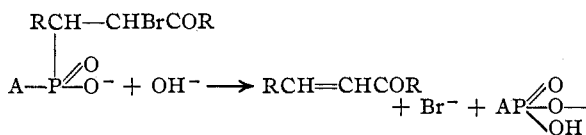
TABLE I

RATE OF DECOMPOSITION OF BROMO COMPOUNDS IN BUFFER SOLUTIONS AT 20° ± 3°

Hydroxyl-ion conc. of solution assuming $[OH^-][H^+]=1.0 \times 10^{-14}$ $[OH^-]$	Time in minutes for appreciable turbidity (About 10% decomposition) (t)	Constant = $[OH] \times t \times 10$
1. LOW-MELTING ISOMER OF BROMOMONOPHENYL ESTER		
10^{-1}	2	2
2×10^{-3}	90	1.8
4×10^{-5}	3,600	1.4
3.3×10^{-6}	70,000	2.3
2. HIGH-MELTING ISOMER OF α-PHENYL-β-BROMO-β-BENZOYL ETHYLPHENYLPHOSPHONIC ACID		
10^{-1}	2	2
2×10^{-3}	40	0.8
4×10^{-5}	540	.2
3.3×10^{-6}	3,600	.12

results of such experiments; although the measurements, which were made by roughly comparing the amount of turbidity with a standard are only approximate, they clearly show the direct proportionality between the hydroxyl-ion concentration and the rate of decomposition.

It is conceivable that this influence of the hydroxyl-ion concentration on the decomposition of the bromo esters might be due to the acceleration of the hydrolysis of the ester to the dibasic acid which is rapidly decomposed even in essentially "neutral" solutions. This explanation must be discarded, however, for two reasons. In the first place, a comparison of the speed of decomposition of the bromo ester in 0.03 N sodium hydroxide solution and the rate of hydrolysis of the corresponding unbrominated mono-ester (VIII) showed that the former process proceeds some 300 times faster than the latter. Consequently, unless one assumes that the presence of a bromine atom has some very great accelerating influence on the speed of hydrolysis of the ester group, the relatively rapid decomposition of the bromo ester cannot be accounted for by assuming a primary hydrolysis to the unstable dibasic acid. In the second place, experiments with one of the stereo-isomeric bromophenylphosphonic acids (A = C_6H_5, Formula I) previously prepared,[1b] showed that the rate of its decomposition was also a function of the hydroxyl-ion concentration as shown in Section 2 of Table I, although with this compound there is no possibility of hydrolysis to a dibasic acid.

Since no primary hydrolysis is possible in this case the hydroxyl ion must be directly concerned with the decomposition. The ionic equation representing this reaction and that of both the monophenyl bromo esters must be written, therefore, as

$$\text{RCH-CHBrCOR}$$
$$\text{A-P}\overset{O}{\underset{O^-}{\diagdown}} + \text{OH}^- \longrightarrow \text{RCH=CHCOR} + \text{Br}^- + \text{AP}\overset{O}{\underset{OH}{\diagdown}}\text{-O-}$$

(where A = C_6H_5 or C_6H_5O; in certain alkalinities the compound APO-(OH)OH$^-$ will be neutralized, forming the disodium salt; if A = C_6H_5O, phenol and phosphoric acid are produced by subsequent hydrolysis).

Since the mechanism of the reaction under investigation in some way involves the hydroxyl ion, the formation of a β-phostone seems to be definitely excluded as an intermediate phase in this decomposition, as there is no reason to suppose that the formation or decomposition of such a compound would depend on the alkalinity of the solution. It should be pointed out, perhaps, that inasmuch as the acids in question are practically insoluble in water there can be no appreciable hydrolysis of the sodium salts in any aqueous solution in which the compounds are wholly dissolved; such results as those recorded in Table I must be interpreted,

therefore, in terms of a reaction involving the unhydrolyzed sodium salt irrespective of the alkalinity of the solution.

It is interesting to note that Johansson[4] has recently shown that β-lactones are not intermediate compounds in the decomposition of such β-bromo acids as β-bromobutyric acid. He has found that the neutral solutions of the sodium salts of a great variety of β-bromo acids undergo two simultaneous reactions, one being the formation of a β-lactone, the other the cleavage into an unsaturated compound, sodium bromide and sodium carbonate. The β-lactones thus prepared show no tendency to lose carbon dioxide at ordinary temperatures and are, therefore, not intermediates in the formation of the unsaturated compound; they are, however, easily hydrolyzed and the formation of β-hydroxy acids from β-bromo acids probably proceeds in this way. There seems to be no information at present available in regard to the effect of the hydroxyl ion on the elimination of carbon dioxide and bromine from β-bromo acids; it seems likely that it will be found that the hydroxyl ion has the same effect on this reaction as on the decomposition of β-bromophosphonic acids as there is every reason to believe that the fundamental mechanism of both reactions is the same.

The Abnormal Reaction of the Monomethyl Ester

The bromomonomethyl ester (VII) like the monophenyl esters dissolved in sodium bicarbonate without change. It was rapidly decomposed by dil. sodium hydroxide as shown by the formation of sodium bromide; strangely enough, no unsaturated ketone or other insoluble material was formed and after the reaction was complete (as shown by the bromide-ion analysis) only a very little phosphate ion was present in the solution. The product was obtained in an impure state by acidifying the solution; it was not found possible to establish its structure definitely, as it was not easily purified. However, its properties indicated that it was either the monomethyl ester of an unsaturated acid (VIII) or a monomethyl ester of an hydroxy acid (IX); it was obviously not a phostone, as it was soluble in alkaline solution.

$$C_6H_5C\!\!=\!\!CHCOC_6H_4Cl \qquad C_6H_5CH\!\!-\!\!CHOHCOC_6H_4Cl$$

$$CH_3OP\!\!\overset{O}{\diagup}\!\!OH \qquad\qquad CH_3OP\!\!\overset{O}{\diagup}\!\!OH$$

$$\text{VIII} \qquad\qquad\qquad \text{IX}$$
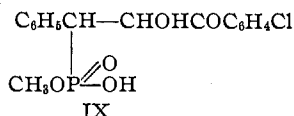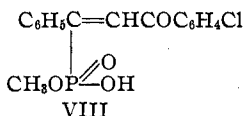
Because of its acidic properties and the fact that it contained phosphorus as well as chlorine it was evidently a phosphonic acid. An alkaline solution of it rapidly decolorized potassium permanganate in the cold, requiring an amount of permanganate corresponding to 80% of one oxygen equivalent. The yield of this phosphonic acid was only about 20%;

[4] Johansson and Hagman, Ber., 55, 647 (1922).

TABLE II

THE DECOMPOSITION IN ALKALINE SOLUTION OF CERTAIN BETA-HALOGEN-PHOSPHONIC ACIDS AND THEIR DERIVATIVES

	Compound	Conditions of decomposition	Organic product
1	C_6H_5CH—$CHBrCOC_6H_5$ | $PO(OH)_2$	$NaHCO_3$ or more alkaline aqueous solution at 20°	C_6H_5CH=$CHCOC_6H_5$
2	C_6H_5CH—$CHBrCOC_6H_5$ | C_6H_5POOH	See Table I	C_6H_5CH=$CHCOC_6H_5$
3	C_6H_5CH—$CHBrCOC_6H_4Cl$ | C_6H_5OPOOH	See Table I	C_6H_5CH=$CHCOC_6H_4Cl$
4	$C_6H_5CHCHBrCOC_6H_4Cl$ | CH_3OPOOH	Dil. NaOH at 20°	Unsaturated or hydroxy-phosphonic acid
5	C_6H_5CH—$CHBrCOC_6H_5$ | $(C_6H_5)_2PO$	(a) NaOH + C_2H_5OH at 20° (b) CH_3COONa + CH_3OH at 60°	C_6H_5C=$CHCOC_6H_5$ | $(C_6H_5)_2PO$ C_6H_5CH—$CH_2COC_6H_5$ | $(C_6H_5)_2PO$
6	C_6H_5CH—CH_2Br | $PO(OH)_2$	Aqueous Na_2CO_3 at 20°	C_6H_5CH=CH_2 (Some hydroxy acid may be formed)
7	C_6H_5C=$CHBr$ | $PO(OH)_2$	Aqueous Na_2CO_3 at 20°	C_6H_5C≡CH (Some hydroxy acid may be formed)
8	$C_6H_5CBrCH_2Br$ | $PO(OH)_2$	Aqueous Na_2CO_3 at 20°	C_6H_5CBr=CH_2 and $C_6H_5COHCH_2OH$ | $PO(OH)_2$
9	$C_6H_5COHCH_2Cl^a$ | $PO(OH)_2$	Aqueous Na_2CO_3 more rapid in NaOH at 20°	$C_6H_5COHCH_2OH$, trace of $C_6H_5COCH_3$ | $PO(OH)_2$
10	$CH_3COHCH_2Cl^a$ | $PO(OH)_2$	Aqueous Na_2CO_3 at 20°	CH_3COHCH_2OH, trace of CH_3COCH_3 | $PO(OH)_2$
11	$C_6H_5COHCH_2Cl^a$ | C_6H_5POOH	NaOH at 20° (stable in Na_2CO_3)	$C_6H_5COHCH_2OH$, trace of $C_6H_5COCH_3$ | C_6H_5POOH
12	$CH_3COHCH_2Cl^a$ | C_6H_5POOH	NaOH on warming (stable at 20° in NaOH)	CH_3COHCH_2OH, trace of CH_3COCH_3 | C_6H_5POOH

^{a} Unpublished work performed by V. H. Wallingford in this Laboratory; the formation of ketones with these compounds corresponds to the formation of the unsaturated compound R—C=CH_2.
         \|
         OH

considerable further decomposition evidently had taken place in the alkaline solution during the course of the experiment (12–16 hours). These further decomposition products were not identified, although the presence of chlorobenzoic acid was strongly indicated. This rather complete disintegration of the bromomonomethyl ester in sodium hydroxide without the formation of benzal-p-chloro-acetophenone might proceed through either the unsaturated acid (VIII) or the hydroxyketo acid (IX). There is no evidence to distinguish between the alternatives, and very possibly both substances may be formed. This much is certain, however: no unsaturated ketone is formed, no phostone is formed and only a very small fraction of the compound decomposes in such a way that the phosphonic acid group is eliminated from the molecule.

The Different Modes of Decomposition

In attempting to account for the behavior of the monomethyl ester and for the influence of the hydroxyl ion on the decomposition of the bromophosphonic acids it is necessary to take into account the similar reactions of a variety of β-halogen-phosphonic acids which have been previously studied in this Laboratory; Table II summarizes these facts. An inspection of this table shows that four different types of reactions have been observed with the β-halogen-phosphonic acid derivatives investigated; they are: (1) replacement of halogen by the hydroxyl group; (2) elimination of halogen and the phosphonic acid residue; (3) elimination of halogen acid; (4) replacement of halogen by hydrogen. The last two reactions have been definitely noted only in the case of the phosphine oxides which are but distantly related to the phosphonic acids; for this reason a consideration of these reactions is unnecessary, perhaps, in a general account of the behavior of the β-halogen-phosphonic acids.

The two reactions involving either the formation of an hydroxy phosphonic acid or an unsaturated compound are apparently closely connected. With certain compounds both reactions take place simultaneously (8–12, Table II) while in the case of other compounds with only a slightly different structure the one or the other reaction predominates to such an extent that almost all the substance decomposes in but one way (compare 3 and 4 and also 6, 8 and 9, Table II). The speed of both reactions seems to be proportional to the hydroxyl-ion concentration; most of the evidence for this generalization is of a qualitative nature; nevertheless, in a number of cases (2, 3, 4, 9, 11) it is very definite. In this connection it is very interesting to observe that the speed of elimination of bromine from both isomeric bromomonophenyl esters and the bromomonomethyl ester in 0.03 N sodium hydroxide solution is essentially the same although the last compound is decomposed in an entirely different manner from the first two. In each case the reaction velocities corresponded to a mono-

molecular reaction if a large excess of sodium hydroxide was employed to compensate for the hydrobromic and phosphonic acids formed; if only a small excess of sodium hydroxide was used this was, after a time, neutralized by the products of the reaction, and at this point the speed decreased since the hydroxyl-ion concentration was then essentially that of a solution of sodium phosphate. The actual monomolecular velocity constants at 26° in a large excess of 0.031 N sodium hydroxide were: high-melting bromomonophenyl ester, 0.0312; low-melting bromomonophenyl ester, 0.0329; bromomonomethyl ester, 0.0301.

Discussion of a Possible Mechanism

An adequate mechanism of the decomposition of these β-halogen-phosphonic acids must account for the following: (1) the influence of the hydroxyl-ion concentration on the formation of an unsaturated compound free from phosphorus; (2) the fact that these two reactions often occur together, while in other cases slight changes in structure cause the one or the other to be the main reaction; (3) the fact that the speed of the reaction with sodium hydroxide of the bromomonomethyl ester and bromomonophenyl ester are comparable. A consideration of these facts seems to indicate that the first step in both reactions is identical and involves the interaction of the bromo acid and the hydroxyl ion. If as a result of this interaction the halogen is eliminated as halide ion the hydroxyl ion need not necessarily occupy the position thus left vacant. Such phenomena as Walden's inversion clearly point to the fact that in "simple" metathesis there may be a more or less drastic intramolecular regrouping before the entering radical finally becomes attached to the compound.[5] In the case in question this change may involve the union of the hydroxyl ion to the phosphorous atom and a severing of the phosphorus-carbon linkage, an unsaturated compound being thus formed. Expressed in other language one can conceive of the first product as being an "ionized" hydroxyl derivative of the organic molecule, such as $R^+ OH^-$, whose existence may be only momentary but which can rearrange in at least two ways with the formation of an hydroxy acid or an unsaturated compound, thus

$$
\begin{array}{ccc}
\text{RCHCHXR} + \text{OH}^- \longrightarrow & \left[\text{RCHCHR}\right]^+\text{OH}^- + \text{X}^- \\
\quad\mid & \quad\mid \\
\text{APOO}^- & \text{APOO}^- \\
& \swarrow \qquad \qquad (A) \qquad \searrow \\
\text{RCHCHOHR} & \qquad \qquad \text{RCH=CHR} \\
\quad\mid & \\
\text{APOO}^- & \qquad \qquad + \text{AP} \begin{array}{l} \nearrow \text{OH} \\ = \text{O} \\ \searrow \text{O}^- \end{array}
\end{array}
$$

The ionized hydroxyl compound (A) might also lose water, forming an unsaturated phosphorus compound, and this may be the explanation of

[5] Compare Fischer's explanation of Walden's inversion, *Ann.*, **381**, 123 (1911).

the formation of such compounds in the case of the phosphine oxides (Table II). The rearrangement of this intermediate compound in one or the other of these two (or possibly three) ways would be affected by slight changes in structure, involving the groups attached to the phosphorus atom and the α carbon atom. The rate of the initial reaction, on the other hand, would depend on the reactivity of the bromine atom; with such an hypothesis it is easy to account for the similarity in the speeds of decomposition of the bromomonomethyl and monophenyl esters.

The extension of such a mechanism to the decomposition of β-bromo acids such as β-bromobutyric acid or β-bromohydrocinnamic acid is obvious; in the case of these compounds the third method of rearrangement involving the loss of water would account for the behavior of such acids as β-bromohydrocinnamic acid towards alkalies, which to some extent yields an unsaturated acid as well as the unsaturated hydrocarbon. As the more recent exponents of the electron theory of valence have stated, the conception of the formation of polar organic compounds during a reaction does not, of course, in the least imply that the initial or final product is ionized; the ionic complex may be momentarily formed only under the influence of the reacting ion. Some such picture of many metathetical reactions would seem to be necessary to account for the well recognized fact that in the replacement of one atom by another a simple interchange of places does not necessarily take place; the formation of unsaturated compounds from β-halogen acids seems to be merely a special and rather striking illustration of this general phenomenon.

The Behavior of Stereo-isomeric Bromo-esters

The facts in regard to the behavior of stereo-isomeric bromophosphonic acids are contradictory. The two stereo-isomers in the case of the bromomonophenyl esters behave exactly alike in regard to their decomposition in alkaline solution; as pointed out above, even the rates of reaction in 0.031 N sodium hydroxide solution are identical within the experimental error. On the other hand, the two isomeric bromophenylphosphonic acids, $C_6H_5CH(C_6H_5POOH)CHBrCOC_6H_5$, to which reference has already been made, show a marked difference. A solution of the sodium salt of the high-melting isomer is stable for some time; its decomposition is affected by changes in hydroxyl-ion concentration as shown in Table I, in a manner not very different from the monophenyl ester and the rate of its decomposition in 0.03 N sodium hydroxide is comparable. The low-melting isomer, on the other hand, behaves more like the dibasic bromophosphonic acid, $C_6H_5CH(PO_3H_2)CHBrCOC_6H_5$, being rapidly decomposed in any buffer solution in which it is soluble (such as sodium bicarbonate). The product formed by the decomposition of both isomers is benzalacetophenone, but for some reason one isomer undergoes this decomposition

much more rapidly than the other. Until other similar cases have been examined it is impossible to decide whether this difference between stereo-isomeric bromine compounds is a general phenomenon and whether or not it is due to some spatial influence on the reactivity of the bromine atom.

We wish to express our indebtedness to E. I. Du Pont de Nemours and Company for a scholarship which one of us (E. L. J.) held during the course of this investigation.

Experimental Part

α-Phenyl-β-p-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH(PO_3H_2)CH_2CO-C_6H_4Cl$.—Forty g. of benzal-$p$-chloro-acetophenone, 26 g. of phosphorus trichloride and 44 g. of glacial acetic acid were allowed to interact in the usual manner;[1a] the mixture was poured into water and the precipitated phosphonic acid purified by dissolving it in sodium hydroxide, extracting the solution with ether and reprecipitating the substance with acid. The acid crystallizes with one molecule of water in colorless crystals which melt at 112–114° with loss of water of crystallization; yield, 103 g., or 91%.

Analysis of crystalline compound. Calc. for $C_{15}H_{14}O_4ClP.H_2O$: H_2O, 5.2. Found: 5.1.

Analysis after loss of water. Calc. for $C_{15}H_{14}O_4ClP$: Cl, 10.9. Found: 11.1.

α-Phenyl-β-bromo-p-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH(PO_3H_2)CHBr-COC_6H_4Cl$.—The phosphonic acid was dried at 130°, dissolved in dry chloroform and treated with the calculated quantity of bromine in small portions; the reaction mixture was warmed on the steam-bath to start the reaction, hydrogen bromide being evolved as the reaction proceeded. The bromo acid separated from the solution in a somewhat impure condition and was filtered off; yield, 75%. The material thus prepared melted at 195–200°; by extraction of the more soluble impurities with ether the melting point was raised to 204°. It was not possible to recrystallize this acid without decomposition and therefore a satisfactory analytical sample could not be obtained. The compound dissolves in sodium bicarbonate solution immediately, forming benzal-p-chloro-aceto-phenone, sodium bromide and sodium phosphate. Its structure is evident from this reaction, its method of formation and by analogy with the chlorine-free acid which was obtained analytically pure.[1a]

Diphenyl Ester of α-Phenyl-β-p-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH-[PO(OC_6H_5)_2]CH_2COC_6H_4Cl$.—The dehydrated phosphonic acid was dissolved in dry chloroform and treated with a 10% excess of thionyl chloride in small portions during 30 minutes; the chloroform was then removed by distillation and the residual oil heated on the steam-bath for one hour. A 10% excess of 2 molecular equivalents of phenol was dissolved in chloroform, added to the oil, the mixture warmed until homogeneous and the solvent removed by evaporation; the residue was then heated for 2.5 hours at 150°. A mixture of monophenyl and diphenyl esters was thus obtained which was separated partially by crystallization from ether and finally by treatment with sodium carbonate solution. The diphenyl ester which was insoluble in the carbonate solution was re-crystallized from alcohol. From 33 g. of phosphonic acid, 15.6 g. of pure diphenyl ester and 15.0 g. of monophenyl ester were obtained. The diphenyl ester melted at 109°.

Analysis. Calc. for $C_{27}H_{22}O_4ClP$: Cl, 7.4. Found: 7.4.

Monophenyl Ester of α-Phenyl-β-p-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH[POOH(OC_6H_5)]CH_2COC_6H_4Cl$.—This compound was prepared, together with the diphenyl ester, as described above, or by the partial hydrolysis of the diphenyl ester as follows. A solution of 22 g. of diphenyl ester in 85 cc. of an alcoholic solution of sodium ethylate containing 1.05 g. of sodium was allowed to stand overnight at room tempera-

ture and then poured into dil. hydrochloric acid. The precipitated solid was filtered off and purified by dissolving it in sodium carbonate, extracting the solution with ether and reprecipitating the substance with acid. After recrystallizing from alcohol 7 g. melting at 175–176° and 4 g. of less pure material were obtained. The monophenyl ester after recrystallization from alcohol melts at 178–179°; by recrystallization of the substance from chloroform the melting point can be raised to 180°. It is insoluble in water and difficultly soluble in organic solvents.

Analyses. Calc. for $C_{21}H_{18}O_4ClP$: Cl, 8.8. Found: 8.6, 8.7.

Diphenyl Ester of α-Phenyl-β-bromo-*p*-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH[PO(OC_6H_5)_2]CHBrCOC_6H_4Cl$.—The bromination of the diphenyl ester was carried out in the usual manner, chloroform being employed as a solvent. The product was recrystallized from alcohol; a yield of 85% of pure material was obtained; m. p., 127–129°.

Analysis. Calc. for $C_{27}H_{21}O_4BrClP$: Br, 14.4. Found: 14.7.

Monophenyl Ester of α-Phenyl-β-bromo-β-*p*-chlorobenzoylethyl-phosphonic Acid, $C_6H_5CH[POOH(OC_6H_5)]CHBrCOC_6H_4Cl$.—The bromination of the monophenyl ester suspended in hot chloroform yielded a mixture of the two isomeric bromo compounds which could be separated by fractional crystallization from alcohol or a mixture of alcohol and acetone; the total yield of the mixture of bromo esters was 74%, each isomer being formed to about the same extent. By the action of thionyl chloride and phenol on α-phenyl-β-bromo-β-*p*-chlorobenzoylethyl-phosphonic acid in the usual way, a small yield of a mixture of the isomeric monophenyl esters was obtained. Also by the partial hydrolysis of the diphenyl ester of α-phenyl-β-bromo-β-*p*-chlorobenzoylethyl-phosphonic acid a little of the high-melting isomer was obtained. Neither of these methods was as satisfactory as the direct bromination of the monophenyl ester.

HIGH-MELTING ISOMER.—This compound, which melts at 195–196°, is insoluble in water and difficultly soluble in ether, alcohol and benzene but fairly soluble in chloroform. It is difficultly soluble in 5% sodium bicarbonate and sodium carbonate solutions, more than 200 cc. of the solution being required to dissolve 1 g. of substance.

Analysis. Calc. for $C_{21}H_{17}O_4BrClP$: Br, 16.7. Found: 16.7.

LOW-MELTING ISOMER.—This isomer is the more difficult to obtain completely pure; it melts at 150–151°, is insoluble in water, difficultly soluble in ether, alcohol and benzene, fairly soluble in chloroform and easily soluble in acetone. It dissolves readily in 5% sodium bicarbonate and carbonate solutions.

Analysis. Calc. for $C_{21}H_{17}O_4BrClP$: Br, 16.7. Found: 16.7.

Behavior of Isomeric Bromo Esters towards Alkaline Reagents.—HIGH-MELTING ISOMER.—A solution of this compound in 0.03 N sodium hydroxide began to precipitate benzal-*p*-chloro-acetophenone in less than five minutes, the solution giving strong tests for bromide ion, phosphate ion and phenol. A sodium carbonate solution (5%) of the compound gave no test for bromide or phosphate ions after five minutes, and only a very slight test after 90 minutes; after the substance had stood for 24 hours at 25°, tests for both bromide and phosphate ions were obtained, a 5 to 10% decomposition being estimated by comparing the precipitates of silver bromide and phosphomolybdate with those obtained by the decomposition of a known amount of the dibasic bromo-phosphonic acid. When the sodium carbonate solution was warmed to 100° for two minutes, about 50% decomposition took place, as judged by the bromide and phosphate tests and the formation of a precipitate of organic material. Similarly, although a sodium bicarbonate solution of the high-melting isomer showed no tests for decomposition after standing for 24 hours at 25°, when it was warmed to 100° for five minutes 15–20% decomposition took place. An essentially neutral solution of the sodium salt was prepared by sus-

pending the high-melting isomer in water and very gradually adding dil. sodium hydroxide solution, care being taken to avoid an excess. This solution gave negative tests for bromide and phosphate ions after 24 hours at 25°; attempts to eliminate bromide ion without phosphate ion by heating this solution failed; after 15 minutes at 100° comparable positive tests for both ions were obtained.

Low-MELTING ISOMER.—The reaction with sodium hydroxide was identical with that of the high-melting isomer, benzal-p-chloro-acetophenone being rapidly formed. In sodium carbonate solution and sodium bicarbonate solution the compound behaved essentially in the same manner as the other isomer; after 48 hours at 25° in sodium carbonate solution, tests indicated 25–30% decomposition while in bicarbonate solution no decomposition after 90 hours was noted. The stabilities of various buffer solutions of this compound are recorded in Table I in the theoretical portion of this paper.

Dimethyl Ester of α-Phenyl-β-p-chlorobenzoylethyl-phosphonic Acid, C_6H_5CH-[PO(OCH$_3$)$_2$]CH$_2$COC$_6$H$_4$Cl.—Thirty g. of crystalline phosphonic acid was dehydrated by heating in an oil-bath at 125–130°, the solid cake thus produced dissolved in dry chloroform and 30 g. of thionyl chloride added during 30 minutes. The solvent was then removed by heating on the steam-bath and the residue kept at this temperature for one hour. The melt was dissolved in a small quantity of hot chloroform and the solution placed in a Carius tube. Anhydrous methyl alcohol (10 g.) was cautiously added while the tube was cooled in ice, considerable heat being evolved. The tube was then sealed, heated for one hour at 100–120° and for one hour at 150–160°. After cooling, the contents of the tube were diluted with ether and the ethereal solution was extracted with sodium carbonate. From the ethereal solution 1.1 g. of oil was obtained which partially solidified and after crystallizing from alcohol weighed 0.5 g. The compound melted at 123–124° and was insoluble in water but soluble in organic solvents.

Analysis. Calc. for $C_{17}H_{18}O_4ClP$: Cl, 10.1. Found: 10.2.

Monomethyl Ester of α-Phenyl-β-p-chlorobenzoylethyl-phosphonic Acid, C_6H_5CH-(POOHOCH$_3$)CH$_2$COC$_6$H$_4$Cl.—The main product of the reaction between the phosphonic acid, thionyl chloride and methyl alcohol, carried out as just described, is the monomethyl ester. This was obtained by acidifying the sodium carbonate extract of the ethereal solution of the reaction mixture. It was somewhat contaminated by unchanged phosphonic acid but after several crystallizations a pure product melting at 152–153° was obtained. The yields of monomethyl ester prepared in this way varied from 65 to 74%. Attempts to prepare the ester without heating in a sealed tube resulted in many cases in oils which did not crystallize. By heating the reaction mixture to 150° in an open flask after the addition of methyl alcohol an 18% yield of monomethyl ester resulted; when the temperature was kept at 100° or lower only non-crystalline oils were obtained and but little dimethyl ester. The monomethyl ester was also formed in 75% yield by the partial hydrolysis of the dimethyl ester by the action of sodium hydroxide in methyl alcohol at room temperature for 50 hours.

The structure of the monomethyl ester was established by hydrolysis to the phosphonic acid which was brought about by boiling with 10% sodium hydroxide for 4 to 5 hours. This hydrolysis is a slow process, as a sample of monomethyl ester dissolved in 0.2 N sodium hydroxide was recovered unchanged after it had been heated for two hours at 100°.

The pure compound melts at 152–153°, is insoluble in water but soluble in organic solvents and sodium carbonate solution.

Analysis. Calc. for $C_{17}H_{18}O_4ClP$: Cl, 10.1. Found: 10.2.

Titration with standard sodium hydroxide of an alcoholic solution using phenolphthalein as the indicator showed the acid to be monobasic.

Monomethyl Ester of α-Phenyl-β-bromo-β-p-chlorobenzoylethyl-phosphonic Acid,

$C_6H_5CH[POOH(OCH_3)]CHBrCOC_6H_4Cl$.—When the monomethyl ester was brominated under the conditions employed with the monophenyl ester, difficulty was experienced in purifying the product. The impurity present was the bromophosphonic acid; apparently the hydrogen bromide formed during the bromination caused a rather surprisingly rapid hydrolysis of either the brominated or unbrominated monomethyl ester. Slow bromination at room temperature in sunlight instead of at the boiling point of chloroform seemed to diminish somewhat this unfortunate side reaction, but the procedure was not satisfactory because of the time required and the presence of unbrominated material in the product. The most satisfactory scheme was found to be that of carrying out the bromination in boiling chloroform in the usual way, followed by treatment with sodium bicarbonate solution. The bromomonomethyl ester dissolves in this reagent without appreciable decomposition, whereas the bromophosphonic acid is instantly decomposed with the formation of benzal-p-chloro-acetophenone which was extracted with ether and thus removed. When the aqueous solution was acidified, the bromomonomethyl ester was obtained somewhat impure. Crystallization from alcohol gave a product melting at 161–163° and small amounts of less pure substance. The yield was about 25%. The pure ester melts at 163–164°, is insoluble in water and difficultly soluble in alcohol; it dissolves in sodium bicarbonate solution without decomposition.

Analysis. Calc. for $C_{16}H_{15}O_4BrClP$: Br, 19.1. Found: 19.4.

Action of Sodium Hydroxide on Bromomonomethyl Ester.—A solution of the bromomonomethyl ester in sodium hydroxide remains perfectly clear after 48 hours at 25°, or when boiled. The bromine atom is, however, removed as shown by the appearance of bromide ion in the solution. The rate of this decomposition is given in the section dealing with kinetic measurements; the reaction is complete at the end of several hours.

The organic product of this reaction was obtained as an oil on acidifying the alkaline solution. In one experiment with 2 g. of ester in 500 cc. of 0.1 N sodium hydroxide after 17 hours there was obtained on acidification 2.0 g. of oil of which all but 0.1 g. was soluble in sodium carbonate solution. This material was recovered from the sodium carbonate solution by adding acid; when it was treated with a mixture of methyl alcohol and water, 0.3 g. of solid melting at 145–148° was obtained; the residue was non-crystalline. An analysis of the acidified aqueous solution in this same experiment showed that the phosphate content corresponded only to a 5.2% decomposition of the 2 g. of ester in such a way as to form phosphate ions. In another experiment the phosphate analysis of the solution showed only 4.9% of the total phosphorus originally present in the molecule.

The solid material which melted at 144–148° with decomposition was obviously impure; in some experiments the melting point was even less definite, being 125–140°. It was not found possible to obtain a pure crystalline compound from this mixture by crystallization. The substance or substances present were obviously acids (the material was completely soluble in sodium carbonate) and contained phosphorus and chlorine as the following analyses show, but not enough phosphorus to correspond to an hydroxy phosphonic acid.

Analyses. Calc. for $C_{16}H_{16}O_5Cl$: P, 8.7; Cl, 10.0. Found: P, 5.1; Cl, 10.2.

The material when dissolved in sodium carbonate solution decolorized potassium permanganate solution rapidly, 0.01 g. requiring 0.0074 g. of permanganate, 80% of one oxygen equivalent per molecule if the substance were an hydroxy or unsaturated acid. In addition to the solid melting at 140–148°, a small amount of solid melting at about 220° was also obtained by fractional crystallization of the acidic oils; this material contained only 1.8% of phosphorus, was an acid and contained chlorine. It is probable that it was impure p-chlorobenzoic acid (m. p., 243°) formed by further decomposition of the

hydroxy or unsaturated acid; the presence of a certain amount of this compound in the material melting at 144–148° might account for the somewhat high chlorine and very low phosphorus analysis. The total solid obtained corresponded to only 15–25% of the original bromomonomethyl ester; the other products were apparently in the oils which could not be obtained crystalline.

Kinetic Measurements

Speed of Hydrolysis of the Monophenyl Ester of α-Phenyl-β-benzoylethyl-phosphonic Acid.—A weighed amount of the monophenyl ester was dissolved in sodium hydroxide solution and made up to a definite volume, the concentration of sodium hydroxide being 0.10 N. The solution was left in a thermostat at 25° and aliquot portions were removed from time to time, acidified, the precipitates filtered off and the filtrates analyzed for phenol. The analytical procedure was standardized by using known amounts of pure phenol; it consisted of adding an excess of a standard solution of bromine in potassium bromide to the acidified solution and at the end of 30 minutes (the flask having been closed) an excess of potassium iodide and 3 cc. of chloroform were added. The iodine liberated was titrated with thiosulfate solution; the amount of bromine used up in the formation of tribromophenol was thus determined by difference. The results are given in Table III.

TABLE III

SPEED OF HYDROLYSIS

Concn. of monophenyl ester = 0.025 M; concn. of NaOH = 0.10 N

Time, hours	0.17	1.5	5.0	24.0	47.0	70.0	173.0
Hydrolysis, %	1.7	2.3	4.4	15.0	25.0	33.0	56.5

A comparison of these figures with the rates of decomposition of the bromo esters in sodium hydroxide shows that the latter reaction is approximately 300 times as fast as the hydrolysis of this monophenyl ester.

Speed of Reaction between Bromo Esters and Sodium Hydroxide.— A weighed amount of the bromo compound was suspended in 500 cc. of water, and 0.095 N sodium hydroxide was added from a buret in small increments, care being taken so that at no time was there a large excess of sodium hydroxide as shown by the phenolphthalein reaction. When the compound was almost completely dissolved the solution was filtered through a weighed Gooch crucible which was then dried at 80–90° until constant in weight. The actual amount of bromo compound in the solution was thus known. Sodium hydroxide (0.95 N) was now added to the filtrate in sufficient amount to make a 0.031 N solution if the whole was diluted to 1 liter which was then done. The flask containing this solution was kept in a water-bath at constant temperature and aliquot samples removed from time to time. These samples were acidified with nitric acid, filtered and the filtrates and wash waters analyzed for bromide ion by the Volhard method. The results obtained are given below; the

velocity constant was calculated from the equation $k = \dfrac{1}{0.434t} \log \dfrac{a}{a - x}$, where a is the concentration of bromo compound in moles per liter and t is the time in minutes.

TABLE IV

REACTION OF BROMO ESTERS IN 0.031 N SODIUM HYDROXIDE SOLUTION AT 23–25°

1. HIGH-MELTING ISOMER OF BROMO-MONOPHENYL ESTER; $a = 0.0019$			2. LOW-MELTING ISOMER OF BROMO-MONOPHENYL ESTER; $a = 0.00182$		
Time in minutes (t)	Fraction reacted	k	Time in minutes (t)	Fraction reacted	k
8	0.205	0.0287	9	0.225	0.0283
20	.4890	.0335	20	.554	.0402
40	.7460	.0342	40	.768	.0364
105	.9500	.0285	110	.948	.0268
		Av. .0312			Av. .0329

3. BROMOMONOMETHYL ESTER; $a = 0.00175$			4. HIGH-MELTING ISOMER OF α-PHENYL β-BROMO-β-BENZOYLETHYLPHENYL-PHOSPHONIC ACID		
10	.321	.0394	7	.261	.0431
30	.532	.0254	20	.536	.0383
145	.975	.0254	45	.863	.0442
		Av. .0301	131	.968	.0264
					Av. .0380

In all of the above experiments, except the third, titration of a sample after the mixture had stood long enough for the reaction to be complete (more than 1000 minutes) showed 98.4 to 97.6% completion; the discrepancy between this value and 100% represents the experimental error of the procedure. In the third experiment a titration at 180 minutes showed the reaction complete within the experimental error (101%). It will be noted that in these determinations the ratio of moles of compound to moles of sodium hydroxide is about 1 : 16; in some other experiments in which the concentration of organic substance was higher this ratio was only 1 : 5. In this case, as the following shows, although the initial speed was nearly the same as that in the more dilute solutions, towards the end so much sodium hydroxide was neutralized by the products of the reaction that the alkalinity was greatly lowered, and the speed correspondingly diminished; the reaction was only 90.8% complete after 1215 minutes.

TABLE V

HIGH-MELTING ISOMER OF BROMOMONOPHENYL ESTER

Conc. of NaOH = 0.033 $N;$ $a = 0.00585$

Time, min.	7	26	105	133	.1215
Fract. reacted	0.236	0.501	0.853	0.853	0.908
k	.0384	.0267	.0182	.0144	.0019

Summary

1. The monophenyl and monomethyl esters of α-phenyl-β-bromo-β-p-chlorobenzoylethyl-phosphonic acid have been prepared and their behaviors in alkaline solution studied.

2. The two stereo-isomeric bromomonophenyl esters form stable sodium salts but are decomposed in alkaline solution with the formation of an unsaturated ketone and the elimination of the bromine atom and the phosphonic acid group from the molecule. The speed of the decomposition is proportional to the hydroxyl-ion concentration. The reaction does not proceed through an initial hydrolysis of the ester group since the hydrolysis of the unbrominated ester is relatively a very slow reaction. The rate of decomposition of one of the stereo-isomers of α-phenyl-β-bromo-β-benzoylethylphenyl-phosphonic acid is also proportional to the hydroxyl-ion concentration.

3. The bromomonomethyl ester is stable in neutral solutions but easily loses the bromine atom in alkaline solution, although the phosphonic acid group is not removed in this reaction. The product is probably an unsaturated or hydroxy phosphonic acid.

4. These facts cannot be explained in terms of a mechanism involving the intermediate formation of a β-phostone. It is suggested that the first step is the interaction of the organic molecule and the hydroxyl ion with the formation of an unstable ionized hydroxyl compound. The decomposition of this intermediate compound could take place in several ways corresponding to the several products obtained by the action of alkalies on different types of bromophosphonic acids.

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THE ADDITION REACTIONS OF CERTAIN PENTADIENONES

BY E. P. KOHLER AND R. W. HELMKAMP

The addition reactions of pentadienones of the type represented by phorone and dibenzal-acetone have been the subject of many investigations. As a result it is known that under the influence of basic condensing agents these ketones combine with a great variety of substances that have reactive hydrogen. The mode of addition is in all cases the same but the ease of addition depends upon the character of the groups in the β-position, and when these groups are aromatic it is affected to a quite remarkable degree by substitution in the nucleus. Thus Vorländer,[1] using an equivalent of sodium alcoholate, was able to add malonic ester to phorone but failed to get definite products with dibenzal-acetone, and

[1] Vorländer, Ann., 304, 1 (1899).