[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Trichloromethylphosphonic Acid

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The acidic hydrolysis of dialkyl trichloromethylphosphonates proceeds without cleavage of the carbon–phosphorus bond to yield the expected trichloromethylphosphonic acid, isolated as the dihydrate. The crystalline salts formed from aromatic amines and (1) this acid in particular, (2) other phosphonic acids in general, and (3) phosphoric acid, permit a facile qualitative and quantitative characterization of these acids.

In connection with other work in progress in this Laboratory, it became of interest to investigate the hydrolytic behavior of trichloromethylphosphonic esters. The esters were prepared by the Arbuzov reaction of carbon tetrachloride with the appropriate trialkyl phosphite.[2]

$$CCl_4 + (RO)_3P: \longrightarrow CCl_3P(O)(OR)_2 + RCl$$

The Acidic Hydrolysis of Trichloromethylphosphonic Esters.—The literature reveals the two conflicting reports that the carbon–phosphorus bond of the ester (i) is cleaved to give phosphorous acid, chloroform and carbon monoxide,[2a] and (ii) is not cleaved, but that the hydrolysis yields the expected trichloromethylphosphonic acid, $CCl_3P(O)(OH)_2$, isolated as the monohydrate.[3] The results presented in this paper partially verify the latter observations; the acidic hydrolysis of dimethyl or diethyl trichloromethylphosphonate with 18% hydrochloric acid (1:1 dilution) proceeds without cleavage of the carbon–phosphorus bond to give quantitative yields of trichloromethylphosphonic acid, isolated, however, as the dihydrate (m.p. 81–82°).

$$CCl_3P(O)(OR)_2 + 2\,HCl + 2\,H_2O \longrightarrow CCl_3P(O)(OH)_2{\cdot}2H_2O + 2RCl$$

Yakubovich and Ginsburg (ref. 3b) claim to have isolated trichloromethylphosphonic acid as its monohydrate, m.p. 87°, and that attempts to remove the water of hydration, by heating over P_2O_5, led to the anhydrization of the acid. In their recent paper, published after our work on this problem began, Crofts and Kosolapoff (ref. 3c) also report the isolation of trichloromethylphosphonic acid as the monohydrate, m.p. 85–87°. In addition, they claim to have prepared the anhydrous acid, m.p. 163.5°, by desiccation over P_2O_5 at reduced pressure. No analytical data concerning these compounds is presented in either of the above two papers.

Aromatic Aminium Salts of Trichloromethylphosphonic Acid.—Although phosphonic acids, in general, are crystalline materials, a number of hydroxyl-, amino-, halogen- and other polar-substituted aliphatic phosphonic acids are difficult to characterize because they are either extremely hygroscopic or difficultly crystallizable. In many such previous cases, the acids have been characterized qualitatively by their conversion to crystalline salts of aromatic amines; the salts possess a definite melting or decomposition temperature. It is suggested here that these salts are of even greater value in the quantitative determination of phosphonic acids which are difficult to isolate. Being derived from a strong acid (a phosphonic or phosphoric acid) and a weak base (an aromatic amine), these salts are readily titratable with standard alkaline solutions to yield a neutralization equivalent. In this fashion, the particular acid may be quantitatively characterized, rapidly and accurately, without resorting to tedious carbon–hydrogen or phosphorus analyses of the hitherto-prepared barium salts.[4]

Ethereal solutions of trichloromethylphosphonic acid react instantaneously and quantitatively with aromatic amines to give nicely crystalline salts. All monoamines used, with the exception of *p*-toluidine, yielded the acid salt, *i.e.*, one mole of amine reacts with one mole of the acid as follows (1:1 salt formation, see Table I).

$$CCl_3P(O)(OH)_2 + ArNH_2 \longrightarrow [CCl_3P(O)(OH)O^-][H_3\overset{+}{N}Ar]$$

The observed neutralization equivalent and phosphorus analysis of the salt obtained from the interaction of *p*-toluidine with trichloromethylphosphonic acid corresponds to the calculated value of an equimolar mixture of both the 1:1 salt and the 2:1 salt (involving two moles of *p*-toluidine with one mole of acid).

As all of the aromatic monoamines, with the exception of *p*-toluidine, reacted with only one acid function of the dibasic acid, it was of interest to investigate the salt formation between trichloromethylphosphonic acid and aromatic diamines. It was observed that whereas two moles of *o*-phenylenediamine react with one mole of acid (only one amino group per *o*-phenylenediamine molecule is employed in salt formation), *p*-phenylenediamine reacts with an equimolar quantity of the acid. Both of the amino groups of the *para*-substituted diamine are employed in salt formation.[5] This observed difference in the molar ratios of base/acid in the

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(2) (a) G. Kamaĭ and L. P. Egorova, *Zhur. Obshcheĭ Khim.* (*J. Gen. Chem. U.S.S.R.*), **16**, 1521 (1946); (b) G. Kamaĭ, *Doklady Akad. Nauk. S.S.S.R.*, **55**, 223 (1947); (c) G. M. Kosolapoff, THIS JOURNAL, **69**, 1002 (1947).

(3) (a) A. Ya. Yakubovich, V. A. Ginsburg and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950); (b) A. Ya. Yakubovich and V. A. Ginsburg, *ibid.*, **82**, 273 (1952); (c) P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, **75**, 5738 (1953).

(4) After this work began, a prior paper by A. Ya. Yakubovich and V. A. Ginsburg, *Zhur. Obshcheĭ Khim.* (*J. Gen. Chem. U.S.S.R.*), **22**, 1534 (1952), was noticed, wherein it is reported that both chloromethyl- and bromomethylphosphonic acid are analyzed by the alkaline titration of their respective anilinium salts.

(5) The above-observed molar ratios of phenylenediamine/trichloromethylphosphonic acid have also been observed for salts prepared from dicarboxylic acids and phenylene diamines; F. Feigl and L. Popp-Halpern, *Monatsh. Chem.*, **59**, 136 (1932).

TABLE I

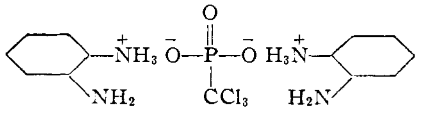
AROMATIC AMINIUM SALTS OF TRICHLOROMETHYLPHOSPHONIC ACID

Aromatic amine	M.p. (dec.), °C.	Molar ratio base/acid	Formula	Neutralization equiv. Calcd.	Neutralization equiv. Found	Phosphorus, % Calcd.	Phosphorus, % Found
$C_6H_5NH_2$	262–263	1:1	$C_7H_9O_3NCl_3P$	146.25	147.0	10.59	10.8
o-$CH_3C_6H_4NH_2$	243–245	1:1	$C_8H_{11}O_3NCl_3P$	153.26	153.2	10.11	10.3
m-$CH_3C_6H_4NH_2$	254	1:1	$C_8H_{11}O_3NCl_3P$	153.26	153.4	10.11	10.3
p-$CH_3C_6H_4NH_2$	254–255	1:1[a] 2:1	. . . .	180.05	180.9	8.6	8.7
$C_6H_5NHCH_3$	224–225	1:1	$C_8H_{11}O_3NCl_3P$	153.26	152.8	10.11	10.3
$C_6H_5N(CH_3)_2$	153–154	1:1	$C_9H_{13}O_3NCl_3P$	160.27	160.6	9.66	9.8
p-$ClC_6H_4NH_2$	253–254	1:1	$C_7H_8O_3NCl_4P$	163.47	164.5	9.47	9.0
p-$BrC_6H_4NH_2$	253–254	1:1	$C_7H_8O_3NCl_3BrP$	185.70	186.0	8.15	7.8
o-$H_2NC_6H_4NH_2$	220–221	2:1	$C_{13}H_{18}O_3N_4Cl_3P$	207.83	207.2	7.45	7.3
p-$H_2NC_6H_4NH_2$	>360	1:1	$C_7H_{10}O_3N_2Cl_3P$	153.76	154.4	10.0	9.6

[a] Equimolar mixture.

two phenylenediamine salts is a consequence of the greater second basic dissociation constant of *p*-phenylenediamine; it is 88 times that of the *o*-phenylenediamine.[6]

The large proportion of organic residue in the *o*-phenylenediamine salt is reflected by the fact that this salt (I) exhibits the lowest melting point observed for any salt except that derived from dimethylaniline. Conversely, the high lattice energy to be expected of a "polymeric" salt of the *p*-phenylenediamine type (II) is shown by the fact that it exhibits no definite melting point; it slowly darkens up to, but is not molten at, 360°.



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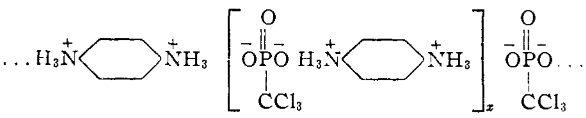

II

Another point of interest is the observed decrease in melting point of the salt as the hydrogen atoms of the amino group of aniline are substituted by methyl groups. Thus, the melting point of the salts of aniline, methylaniline and dimethylaniline are 263°, 225° and 154°, respectively.

The Alkaline Hydrolysis of Trichloromethylphosphonic Esters.—Yakubovich and Ginsburg[3b] indicate that the treatment of dialkyl trichloromethylphosphonates with aqueous barium hydroxide cleaves the carbon–phosphorus bond, according to the following indefinite scheme; no experimental conditions or data are described.

$$CCl_3P(O)(OR)_2 \xrightarrow[Ba(OH)_2]{H_2O} CCl_3H + H_3PO_4 + 2ROH$$

Preliminary experiments verify the above cleavage reaction; the products and stoichiometry of the reaction, however, are in error. A detailed study of the alkaline hydrolysis of these esters will be reported shortly.

Experimental

General.—Samples of trimethyl and triethyl phosphite were provided by Monsanto Chemical Co. and Virginia–Carolina Chemical Corp., respectively. All melting points are corrected.

Dialkyl Trichloromethylphosphonates.—Carbon tetrachloride (111.5 g., 0.72 mole, b.p. 76°) and trimethyl phosphite (21 g., 0.15 mole, b.p. 111°, $n^{20}D$ 1.4089) were refluxed on a steam-bath for 19 hours. Excess CCl_4 was removed at reduced pressure, and the residue was distilled to give dimethyl trichloromethylphosphonate, a low-melting solid which solidified in the distillation condenser (23.5 g., 69% yield, b.p. 122° (18 mm.), $n^{25}D$ 1.4659).

Anal. Calcd. for $C_3H_6O_3Cl_3P$: P, 13.6. Found: P, 13.8.

Carbon tetrachloride (193 g., 1.25 moles, b.p. 76°) and triethyl phosphite (25 g., 0.15 mole, b.p. 55° (18 mm.), $n^{25}D$ 1.4112) were refluxed on a steam-bath for 14 hours. Excess CCl_4 was removed at reduced pressure, and the residue was distilled to give diethyl trichloromethylphosphonate (33.1 g., 86% yield, b.p. 67–68° (0.5 mm.), $n^{25}D$ 1.4610).

Anal. Calcd. for $C_5H_{10}O_3Cl_3P$: P, 12.1; mol. wt., 255. Found: P, 12.1; mol. wt., 258 (cryoscopic, benzene).

Trichloromethylphosphonic Acid.—The acid may be prepared by the acidic hydrolysis of either the diethyl or dimethyl ester; the procedure for the hydrolysis of the latter material is described here. A mixture of dimethyl trichloromethylphosphonate (3 g.), 25 ml. of water and 25 ml. of concd. hydrochloric acid was refluxed for seven hours. The hot solution was treated with charcoal, filtered, and the filtrate was concentrated to dryness. The crude acid (2.9 g., 94.5% yield) was recrystallized as long, white needles from benzene containing a small amount of absolute ethanol. The acid softened in the temperature range 68–81° and melted at 81–82°. The analytical results suggest that the material is the dihydrate of trichloromethylphosphonic acid.

Anal. Calcd. for $CH_6O_5Cl_3P$: P, 13.16; neut. equiv., 117.7. Found: P, 13.15, 13.25; neut. equiv., 117.6, 116.7.

Arylaminium Salts.—All of the salts, Table I, were prepared and utilized in an identical manner. The preparation and titration procedure concerning the N-methylanilinium salt is offered as a typical case. N-Methylaniline was added slowly to an ethereal solution of trichloromethylphosphonic acid until no further precipitation was evident. The subsequent addition of petroleum ether (b.p. 35°) caused the precipitate to become more flocculent and coarser, and thus easier to collect on a filter. The collected crude salt was recrystallized from absolute ethanol (charcoal) to give small white platelets of N-methylanilinium trichloromethylphosphonate. The pure salt was collected on a filter, washed with diethyl ether, and dried in air (m.p. 224–225° dec.). Its neutralization equivalent was determined by dissolving 0.0473 g. in a mixture of 20 ml. of water and 5 ml. of ethanol and titrating the resulting solution with 2.57 ml. of 0.1205 N sodium hydroxide (phenolphthalein).

Anal. Calcd. for $C_8H_{11}O_3NCl_3P$: P, 10.11; neut. equiv., 153.26. Found: P, 10.3; neut. equiv., 152.8.

Treatment of phosphoric acid, overlayered with ether, with an excess of aniline gave an immediate white precipitate.

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(6) R. Kuhn and F. Zumstein, *Ber.*, **59**, 488 (1926), have observed the following:

	$K_{b_1} \times 10^{10}$	$K_{b_2} \times 10^{13}$
o-Phenylenediamine	3.2	1.6
p-Phenylenediamine	123	141

Subsequent purification procedures as outlined above yielded white platelets of dianilinium phosphate (m.p. 182–183° dec.).

Anal. Calcd. for $C_{12}H_{17}O_4N_2P$: P, 10.9; neut. equiv., 142.12. Found: P, 10.8; neut. equiv., 141.1.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF WESTVACO CHLOR-ALKALI DIVISION OF FOOD MACHINERY AND CHEMICAL CORPORATION]

The Synthesis of Monovinyl Esters of Phosphorus(V) Acids

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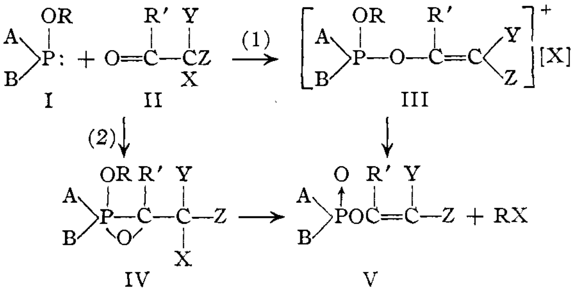
The reaction of completely esterified acids of trivalent phosphorus containing at least one alkyl ester group with α-halogenated aldehydes, ketones, and some carboxylic acid esters and amides produces a monovinyl ester of the corresponding pentavalent phosphorus acid.

Several investigators have attempted to use α-halo ketones[1] and esters[2] instead of alkyl halides in the Michaelis–Arbuzov reaction involving esters of phosphorus(III) acids, but in all cases the products have been assumed to be phosphonates of the type expected from a normal Michaelis–Arbuzov reaction. When this work was begun no one had reported the reaction of a polyhalogen compound of the type under consideration with a completely esterified acid of trivalent phosphorus, but recently ethyl trichloroacetate[2f] and chloral[3] have been reported to yield phosphonates, ,and even more recently chloral,[4a] bromal[4a] and methyl 2-chloroacetoacetate[4b] have been reported to yield vinyl phosphates. It has been shown in this Laboratory also that α-halogenated aldehydes, ketones, and the esters and amides of certain carboxylic acids react with completely esterified acids of trivalent phosphorus to form vinyl esters of the corresponding pentavalent phosphorus acid. The proof of structure of these compounds will be given in detail in another paper, but the structure assignment rests upon the following experimental facts: (a) In the independent synthesis of diethyl vinyl phosphate by the dehydrobromination of diethyl 2-bromoethyl phosphate the product obtained was identical with that obtained by the reaction of triethyl phosphite and chloroacetaldehyde. (b) The products show strong infrared absorption at 6.1 μ which is characteristic of the ethylenic double bond. (c) Diethyl vinyl phosphate, obtained from triethyl phosphite and chloroacetaldehyde, was hydrogenated over a nickel catalyst to triethyl phosphate. (d) The products add chlorine and bromine to form dihalides. (e) Hydrolysis of the product obtained from chloral and triethyl phosphite gave dichloroacetaldehyde.

The reaction may involve a nucleophilic attack by the phosphorus atom on the oxygen of the carbonyl compound (mechanism 1) and the simultaneous expulsion of a chloride ion from the latter. In most cases a stable intermediate is not obtained, but intermediates have been obtained when the phosphorus compound has phosphorus in a ring system (*e.g.*, I, A + B = OCH_2CH_2O). This mechanism is unusual in that it represents the normally nucleophilic oxygen atom of the carbonyl group as being electrophilic. Furthermore, this mechanism would be expected to involve an intermediate having the structure III, but the infrared spectrogram prepared from a mineral oil mull of the intermediate resulting from chloral and ethyl ethylene phosphite did not show the absorption at 6.1 μ which is characteristic of the vinyl or substituted vinyl phosphates, and chloride ion was not precipitated by methanolic silver nitrate. A second possible mechanism (2) involves a nucleophilic attack by the phosphorus atom on the carbonyl carbon and a similar attack by the carbonyl oxygen on the phosphorus to form a 3-membered ring (IV) of the type suggested by Conant and MacDonald.[5]



Of the various classes of phosphorus compounds which would be expected to enter into this reaction, only phosphites, amidophosphites, phosphonites and phosphinites have been investigated. The limitations of the reaction with respect to the phosphorus compound appears to be about the same as observed with the Michaelis–Arbuzov reaction. Aromatic esters do not react, at least under normal conditions, but mixed aliphatic and aromatic esters react readily. For example, triphenyl phos-

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[1] (a) A. E. Arbuzov and A. I. Razumov, *J. Gen. Chem. (U.S.S.R.)*, **4**, 834 (1934); (b) A. I. Razumov and N. Petrov, *Trudy Kazan. Khim.-Tekhnol. Inst.*, **10**, 35 (1946); (c) B. A. Arbuzov, B. P. Lugovkin and N. P. Bogonostseva, *J. Gen. Chem. (U.S.S.R.)*, **20**, (8) 1468 (1950); (d) Norman D. Dawson and Alfred Burger, THIS JOURNAL, **74**, 5312 (1952).

[2] (a) A. E. Arbuzov and A. A. Dunin, *J. Russ. Phys.-Chem. Soc.*, **46**, 295 (1914); (b) G. M. Kosolapoff, THIS JOURNAL, **68**, 1103 (1946); (c) A. E. Arbuzov and G. Kamai, *J. Gen. Chem. (U.S.S.R.)*, **17**, 2149 (1947); (d) Richard H. Wiley, U. S. Patent 2,478,441 (1949); (e) G. Kamai and E. Sh. Bastanov, *Zhur. Obshchei Khim. (J. Gen. Chem.)*, **21**, 2188 (1951); (f) Denham Harmon and Roy E. Thorpe, U. S. Patent 2,614,990 (1952).

[3] (a) A. E. Arbuzov and P. I. Alimov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 530 (1951); (b) Elbert C. Ladd and Merlin P. Harvey, U. S. Patent 2,597,938 (1952); (c) Elbert C. Ladd and Merlin P. Harvey, U. S. Patent 2,631,162 (1953).

[4] (a) Werner Perkow, *Chem. Ber.*, **87**, 755 (1954); (b) Alan R. Stiles, U. S. Patent 2,685,552 (1954).

[5] J. B. Conant and A. D. MacDonald, THIS JOURNAL, **42**, 2337 (1920).