and control of reaction temperature are facilitated. Higher product yields are obtained.

Two types of reactors are currently in use in these laboratories, each having advantages depending upon the particular situation. Procedures using these reactors are:

Procedure I: This method employs a reactor which is simple to construct and provides a quick method of obtaining small quantities of fluorocarbon iodides in the laboratory. It is also adapted to reactions of this type in which the absence of any atmosphere other than the reaction gases is desired. The reactor is a vertical Pyrex tube, closed at the bottom and stoppered at the top. An exit line attached near the top connects it through two cold traps to a vacuum source. A manometer is attached to the exit line. A KOH tube for removal of CO_2 is placed between the traps and the vacuum source. Reaction temperature is followed by means of a thermocouple or thermometer extending into the tube through the top.

Experimental.—The entire apparatus is vacuum dried. Iodine followed by phosphorus pentoxide (P) is poured into the tube. (S) may be either suspended over the iodine and (P) in a steel wire cage or poured directly into the tube with a layer of glass wool separating (S) from (P). The apparatus is flushed with dry air. The reactor tube is heated in an oil-bath. The pressure is reduced in order to provide adequate volatilization of iodine at the optimum reaction temperature (130–160°). Completion of reaction is noted by cessation of evolution of gases. The bath is heated to 185° to assure complete conversion of (S). The iodide is collected in the cold traps. All products were fractionated. Iodine was determined by peroxide decomposition and thiosulfate titration. Reaction conditions and yields are in Table I.

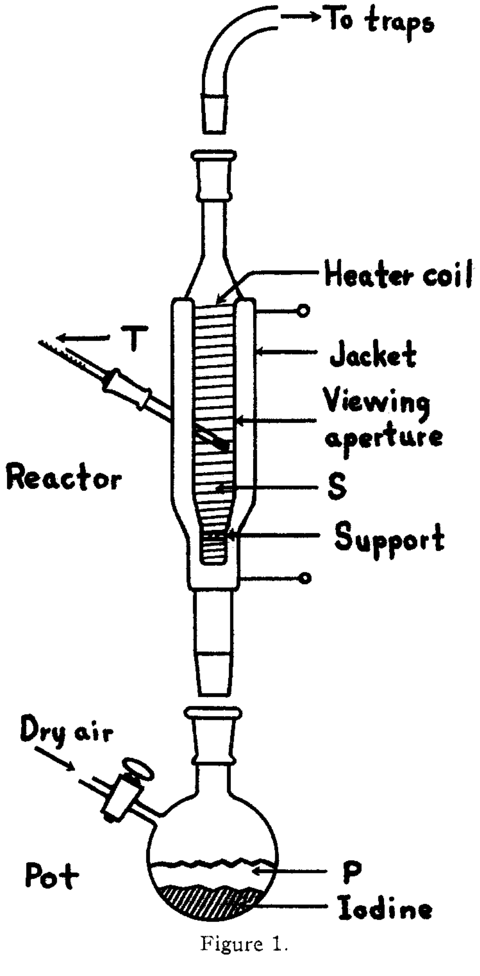

Figure 1.

TABLE I

PROCEDURE I

Starting material, g.	Heating time, min.	Operating temp., °C.	Operating pressure, mm.	Basket support	Yield, g.	Yield, %
CF_3COOAg, 75.1	60	140–145	400–450	Not used	47.6	71
C_3F_7COOAg, 15.5	80	140–145	450–500	Not used	13.1	93
CF_3COOAg, 75.4	140	150–160	400–500	Used	52.5	78
C_3F_7COOAg, 21.2	115	150–160	400–500	Used	16.5	87

Procedure II: This method is superior in cases in which relatively large amounts of various fluorocarbon iodides must be synthesized in the laboratory. The apparatus is shown in the accompanying figure. Operation is at atmospheric pressure. A stream of dry air carries the iodine vapor from the pot to the reaction zone. (S) is supported in the reactor by means of a glass "X" member and a thin layer of glass wool. The reactor and the iodine container are separate units whose temperatures are controlled independently.

Experimental.—The apparatus is assembled. (S) is poured into the reactor from the top. Final drying is effected by passing a current of dry air through the reactor while heating it to 70–80°. Excess iodine followed by (P) is placed in the pot. The iodine is heated to sublimation temperature and an extremely gentle air current started. The heat of reaction tends to increase the reactor temperature. The jacket heating is adjusted so as to maintain an optimum reaction temperature of 130–160°. The reaction requires 20–40 minutes, depending on the type and amount of (S). The iodide is collected in cold traps. Purification and identification were carried out as in procedure I. Reaction conditions and yields are in Table II.

TABLE II

PROCEDURE II

Starting material, g.	Heating time, min.	Temp., °C.	Yield, g.	Yield, %
CF_3COOAg, 33.8	21	150–160	22.3	74
CF_3COOAg, 202.1	48	150–160	161.0	90
C_3F_7COOAg, 42.0	25	130–160	36.5	94
C_3F_7COOAg, 200.4	45	150–160	175.5	95

Procedure II was used in the preparation of C_3F_7Br. No air current was employed. Reflux action of bromine was provided by an ice–water-cooled condenser on the upper end of the reactor. Reaction temperature was 130–150°. Products were fractionated and analyzed for bromine. A 67% yield was obtained.

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The Preparation and the Determination of Apparent Dissociation Constants of Some Substituted Aliphatic Phosphonic Acids

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In the previous paper[1] we described the acidic properties of several aliphatic phosphonic and phos-

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[1] P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, 75, 3379 (1953).

phinic acids. At this time we wish to report some results along these lines as secured with some substituted methylphosphonic acids. Specifically, we examined the effect on the dissociation constant of methylphosphonic acid that is produced by the substitution of one, two or three chlorine atoms, one chlorine, one bromine or one iodine atom, or a hydroxyl group in the aliphatic radical of this, the simplest phosphonic acid.

In the course of this work we established new melting points for several compounds that had been reported previously by other workers. These results, as well as the synthetic procedures, are given in the Experimental part of this paper.

The acids, with which we have been concerned at this time, produce on titration the expected curves with two inflection points, that are typical of phosphonic acids in general. It must be noted, however, that owing to the very considerable acid strength of the second hydrogen of trichloromethyl acid, the first inflection point, or break, is very shallow and cannot be satisfactorily determined by chemical indicators.

The results of the determination of the apparent dissociation constants, performed precisely as described earlier,[1] are given in Table I.

TABLE I

Compound	pK'_{a_1}	pK'_{a_2}
$ClCH_2PO_3H_2$	1.40	6.30
$Cl_2CHPO_3H_2$	1.14	5.61
$Cl_3CPO_3H_2$	1.63	4.81
$BrCH_2PO_3H_2$	1.14	6.52
$ICH_2PO_3H_2$	1.30	6.72
$HOCH_2PO_3H_2$	1.91	7.15
$CH_3PO_3H_2$[1]	2.38	7.74

It is clear that the substitution of halogens or of a hydroxyl increases the acid strength of methylphosphonic acid. This is, of course, to be expected from the general considerations. The second dissociation constant shows the steadily increasing acid properties as the number of chlorines in the molecule rises from one to three. A gradual decrease of acidic properties is also observed in the series: chlorine, bromine, iodine. The moderate increase of the dissociation constant upon the substitution of the hydroxyl on the carbon adjacent to the phosphorus is also noted; in this case the hydroxyl acts as an acid-strengthening agency.[2]

The first dissociation constants shown above indicate that the present group of acids represents very strong acids. The trend discussed above for the second dissociation constants is approximately true in this instance as well. The deviation of the trichloromethyl acid from this trend is probably not real and is caused by the relative proximity of the two dissociation constants of this acid, a situation that does not arise in the other examples. We expect to return to the consideration of this apparent anomaly at a later date, when we expect to have the necessary data on the activity coefficients of the various acids of phosphorus. Such data are not found in the literature at this time.

Experimental Part

Preparation of the Compounds. Chloromethylphosphonic Acid.—An unsuccessful attempt to prepare this acid by treatment of hydroxymethylphosphonic acid with phosphorus trichloride, followed by admission of the theoretical amount of chlorine to form phosphorus pentachloride *in situ*, was made. The preparation had to be abandoned owing to the formation of untractable semi-solid materials which could not be purified.

The compound was prepared readily from its dichloride.[3] This was obtained in 67% yield by heating 10 g. of paraformaldehyde with 71 g. of phosphorus trichloride in a sealed tube for 11.5 hours at 240–250°; the product boiled at 93° at 16.5 mm. The dichloride was added slowly to an excess of water with stirring and the resulting solution was evaporated to dryness *in vacuo*. The resulting product was redissolved in water, treated with charcoal and the clear filtrate was again taken to dryness, yielding the pure acid, which softened at 85° and melted at 88°. Kinnear and Perren[4] give m.p. 89–90°.

Dichloromethylphosphonic Acid.—Several preliminary experiments were performed in attempts to find a satisfactory preparation of this acid. Chlorination of chloromethylphosphonyl dichloride, $ClCH_2POCl_2$ (the intermediate in the previous preparation) failed to take place at 45° under ultraviolet irradiation. Some chlorination did take place in four hours at 165–169°, but the product was not homogeneous and not purifiable by fractional vacuum distillation. The reaction proceeded more readily in the presence of a small amount of iron filings, but again the product was not purifiable.

Since triethyl phosphite failed to react after many hours of refluxing with chloroform, in an attempt to prepare diethyl dichloromethylphosphonate, these two substances were heated in a glass liner of an autoclave at 160° for seven hours. None of the desired product was obtained, much triethyl phosphite (67%) being recovered along with a 12% yield of its isomerization product, diethyl ethylphosphonate. It must be concluded that the Arbuzov reaction does not occur with chloroform, in contrast to the facile reaction of carbon tetrachloride.

Dichloromethylphosphonyl dichloride was readily prepared by the method outlined by Kinnear and Perren[4] and the product was hydrolyzed with water as described above. Careful evaporation of the aqueous solution and thorough vacuum drying of the product gave the desired acid, melting at 116–119°. It must be mentioned that this acid, as well as the other halogenated derivatives cited in this paper, showed extreme hygroscopicity. This acid was previously reported with m.p. 54°.[5] In view of this discrepancy our product was analyzed.

Anal. Calcd. for $CH_3O_3Cl_2P$: Cl, 43.0. Found: Cl, 42.53.

The identity of the acid was further confirmed by perfect agreement of the breaks in its titration curve with the calculated values.

Trichloromethylphosphonic Acid.—A small amount of this acid was prepared by hydrolysis of the corresponding phosphonyl dichloride, which was secured from carbon tetrachloride, phosphorus trichloride and aluminum chloride.[4] We found, however, that for preparation of this acid in moderate quantities the above method is not too satisfactory, owing to some undesirable characteristics of the dichloride.

Therefore, the acid was prepared by hydrolysis of its diethyl ester which is readily obtainable from triethyl phosphite and carbon tetrachloride.[6]

The ester (20 g.) was refluxed for 6 hours with 100 ml. of concentrated hydrochloric acid and 50 ml. of water, and the resulting solution was carefully evaporated, after treatment with charcoal. The crude acid, m.p. 80–82°, was recrystallizable from a minimum amount of water at −15° and the product melted at 85–87°. This material was then dried over phosphorus pentoxide at approximately 0.05 mm. after which the pure product melted at 163.5°, softening at

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[2] W. D. Kumler and J. J. Eiler, THIS JOURNAL, **65**, 2355 (1943).

[3] M. I. Kabachnik and E. S. Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 185 (1951).

[4] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

[5] A. Ya. Yakubovich and V. A. Ginzburg, *Doklady Akad. Nauk S.S.S.R.*, **82**, 273 (1952).

[6] G. M. Kosolapoff, THIS JOURNAL, **69**, 1002 (1947).

161°. The above-mentioned melting point of the hydrate agrees with that cited earlier,[6] but the present melting point of the anhydrous acid is given for the first time. The acid liberates a considerable amount of heat when placed in contact with water.

Bromomethylphosphonic Acid.—In an attempt to form bromomethylphosphonyl dibromide, formaldehyde and phosphorus tribromide were heated in a sealed vessel precisely as described above for the chloro analog. Very considerable decomposition took place and the only identified products were unchanged phosphorus tribromide and a small amount of methylene bromide. Bromine failed to react after many hours with methylphosphonyl dichloride under ultraviolet irradiation at 120–125°. A similar failure was recorded in a reaction of hydroxymethylphosphonic acid with phosphorus pentabromide, obtained *in situ* by addition of bromine to phosphorus tribromide.

Ford-Moore and Williams,[7] in describing the Arbuzov reaction of triethyl phosphite with methylene bromide, state that: "the reaction is very slow with a poor yield of the diphosphonate, the monophosphonate being almost absent." We carried out this reaction under somewhat drastic conditions and obtained rather satisfactory results. Triethyl phosphite (126 g.) and methylene bromide (162 g.) were heated in an autoclave at 172° for four hours. The resulting mixture was distilled under reduced pressure and yielded 23 g. of diethyl bromomethylphosphonate, b.p. 50° at 0.05 mm., n^{20}_{D} 1.4592, d^{20}_{4} 1.4363, *MR* 43.99 (calcd. *MR* 43.92). The product also boils at 66° at 0.25 mm. The compound was reported previously with b.p. 99° at 1 mm., d^{20}_{20} 1.4474, n^{20}_{D} 1.4587.[8]

The ester was hydrolyzed by refluxing for nine hours with 48% hydrobromic acid, the solution was concentrated under reduced pressure and the residue was taken up in water. Re-evaporation under reduced pressure after treatment with charcoal, yielded an uncrystallizable sirup. A small portion of this was seeded with a tiny crystal of chloromethylphosphonic acid; this resulted in rapid crystallization of the product. A small portion of this was then used to seed the main batch. After drying *in vacuo* over phosphorus pentoxide the resulting acid melted at 62°, softening at 54°.

Anal. Calcd. for CH_4O_3BrP: P, 17.71; Br, 45.68. Found: P, 17.96; Br, 44.71.

Iodomethylphosphonic Acid.—Diethyl iodomethylphosphonate was prepared conventionally from methylene iodide and triethyl phosphite; b.p. 61° at 0.01 mm. The ester (23.6 g.) was dissolved in 100 ml. of concentrated hydrochloric acid and 50 ml. of water and refluxed for one day. After the usual treatment with charcoal, evaporation and drying under reduced pressure a brownish product was obtained which contained free iodine. This evidently originated in partial hydrolysis of the halogen and formation of hydriodic acid. The iodine was removed by prolonged evacuation of finely powdered product, which then melted at 75–82°. It was then recrystallized from ethylene chloride and after drying under reduced pressure melted at 89°, softening at 86°.

Anal. Calcd. for CH_4O_3IP: P, 13.96. Found: P, 13.9.

Attempted Preparation of Fluoromethylphosphonic Acid.—Diethyl iodomethylphosphonate (25 g.) was added to 40.3 g. of thoroughly dried silver fluoride and the mixture was slowly heated in a distillation apparatus to 125° over five hours at about 30 mm. The distillate (2.3 g., b.p. 89–93° at 20 mm.) was redistilled, yielding a product which boiled at 91–92° at 21 mm. The physical constants and a qualitative examination showed this to be diethyl methylphosphonate, formed apparently by a reductive process from the iodo derivative. This was the only recoverable product from the reaction.

Hydroxymethylphosphonic Acid.—This acid is readily prepared by the method outlined by Page.[9] Its purification is a rather tedious process. Crystallization from alcohol-ethyl acetate mixture proposed by Page is rather wasteful of the product. We noted that this acid has a negative coefficient of solubility in ethyl acetate with temperature. It dissolves quite readily in dry ethyl acetate at about −15° and separates from it in the form of fine crystals on warming to room temperature. After thorough drying the product melts at 99–100°. Previously reported highest melting point is 98–99°.[10]

Page[9] stated that in qualitative tests run in the cold this acid inhibits the precipitation of the yellow phosphomolybdate precipitate from solutions containing phosphates. We examined this effect under the normally used conditions of analytical procedure (hot solution in the presence of much ammonium nitrate) and found that such inhibition does not take place under these conditions.

Determination of Apparent Dissociation Constants.—Both the procedure of the determinations and the method of calculation were precisely the same as reported in the previous paper.[1] In all cases the locations of the breaks in the titration curves agreed excellently with the calculated values; no evidence of cleavage of the carbon–phosphorus link in the trichloromethyl acid was observed The approximate locations of the breaks, which may be of interest for titrations with visual indicators were as follows: hydroxymethylphosphonic acid *p*H 5 and 9.5; chloromethylphosphonic acid 4.5 and 8.5; dichloromethylphosphonic acid 4 and 8.5; trichloromethylphosphonic acid 3.5 (very slight) and 7.5; bromo- and iodomethylphosphonic acids 4.5 and 9.

Acknowledgment.—We wish to express our gratitude to the Research Corporation for a Frederick Gardner Cottrell grant that made this study possible.

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The Preparation of Ethyl *o*-Cyanocinnamate and *o*-Carbethoxycinnamonitrile

BY JAMES W. CURRY[1,2]

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Interest in the anomalous conversion of *p*-quinonemonoxime to *p*-azoxyphenol brought about by treatment with benzenesulfonyl chloride in pyridine and subsequent heating[3–5] suggested an examination of the behavior of the isomeric oximes of 1,2-naphthoquinone under the same conditions. It was possible to obtain the benzenesulfonic esters of 1,2-naphthoquinone-1-oxime and 1,2-naphthoquinone-2-oxime when these oximes were treated with benzenesulfonyl chloride and pyridine, followed by isolation through aqueous dilution of the reaction mixture, and recrystallization from a nonhydroxylic solvent. When attempts were made to recrystallize the benzenesulfonic esters from 95% ethanol, smooth conversions were effected to products which did not contain sulfur. Microanalysis indicated that the isomeric products had the composition $C_{12}H_{11}NO_2$, and infrared analysis showed the presence, in both compounds, of conjugated $C{\equiv}N$ and conjugated ester $C{=}O$ groupings. On the basis of the participants in the conversions and analyses of the products, structure III, ethyl *o*-cyanocinnamate, can be assigned to the product, m.p. 76–77°, obtained from the benzenesulfonic ester of 1,2-naphthoquinone-1-oxime (I). Simi-

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[1] U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1952.

[2] Dow Corning Corporation, Midland, Michigan.

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