## [CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

# Preparation and Determination of Apparent Dissociation Constants of Some Alkylphosphonic and Dialkylphosphinic Acids<sup>1</sup>

## BY PETER C. CROFTS AND GENNADY M. KOSOLAPOFF

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Ten alkylphosphonic and six dialkylphosphinic acids with straight chains and with branched chains were prepared and observations were made relative to the isolation and purification of these substances. It was found that highly branched Grignard reagents react with phosphorus trichloride only to the stage of disubstitution. The apparent dissociation constants of the acids were determined potentiometrically. An approximately linear relationship was found between the number of methyl groups attached to a specific carbon in the alkyl group and the magnitude of pK'.

Only a few determinations of dissociation constants of unsubstituted alkylphosphonic and dialkylphosphinic acids are recorded in the literature.<sup>2-4</sup> The purpose of the present investigation was the study of the effects of variations within the alkyl group of the acids on the apparent dissociation constants of these acids.

Although the reaction of primary alkyl halides with sodium dialkyl phosphites in hydrocarbon solvents is a well-known and useful method for the preparation of alkylphosphonic acids containing a primary alkyl group<sup>5</sup> there is little information on the use of secondary or tertiary halides in this reaction. It was found that isopropyl iodide, sbutyl bromide and t-butyl bromide all reacted with sodium dibutyl phosphite in toluene on heating. The reaction mixtures were worked up in the usual way, but none of the resulting acids were pure. A pure specimen of isopropylphosphonic acid was finally obtained after many recrystallizations. The phosphonic acid from s-butyl bromide was purified by conversion to the phosphonyl dichloride. This was distilled and hydrolyzed, giving an acid which slowly crystallized after months in vacuo over phosphorus pentoxide but failed to solidify completely and appeared to be contaminated with The acid obtained from the reaction isomers. between t-butyl bromide and sodium dibutyl phosphite melted about one hundred degrees lower than the m.p. subsequently found for t-butylphosphonic acid and was obviously a complex mixture containing little if any of the desired product.

Two secondary (isopropyl and s-butyl) and two tertiary (t-butyl and t-amyl) alkylphosphonic acids were prepared by reaction between aluminum trichloride, phosphorus trichloride and alkyl halides to give complexes yielding the alkylphosphonyl dichlorides<sup>6</sup> on hydrolysis, from which the acids were obtained by more drastic hydrolysis. The alkyl halides used were the chlorides except for s-butyl bromide. The use of the bromide seemed to be without effect on the course of the reaction and appeared to give the phosphonyl dichloride substantially free from chlorobromide.

The procedure used by Clay<sup>6</sup> was modified giving greatly improved yields, of the same order as those

(6) J. P. Clay, J. Org. Chem., 16, 892 (1951).

obtained by Kinnear and Perren' who have also investigated this reaction. Equivalent amounts of aluminum trichloride and phosphorus trichloride and either an equivalent amount or up to a 25%excess of alkyl halide were employed; use of excess alkyl halide does not alter the yield (based on phosphorus trichloride). Hydrolysis of the complex was effected very simply by dissolving in chloroform and pouring the solution on a mixture of crushed ice and hydrochloric acid.

Preparation of isopropyl-, s-butyl- and t-butylphosphonic acids by this route was straightforward and gave only a single product. The phosphonyl chloride obtained from t-amyl chloride, on the other hand, boiled over a 30° range. Moreover, the first part of the distillate solidified whereas the higher boiling part remained liquid on cooling. The possibility that this was due to the use of tamyl chloride prepared from practical grade *t*-amyl alcohol was considered; but when the experiment was repeated using t-amyl chloride prepared, via the alcohol, from acetone and ethylmagnesium bromide, the proportion of solid was as high as before and amounted to approximately one-third of the distillate. The solid was separated by fractional distillation, recrystallized several times and converted to the anilide which was recrystallized to constant m.p. On hydrolysis this gave tbutylphosphonic acid showing that the solid was t-butylphosphonyl dichloride. The liquid part of the distillate was t-butylphosphonyl dichloride since it yielded on hydrolysis an acid having the properties expected of *t*-amylphosphonic acid. Although Kinnear and Perren<sup>7</sup> have observed isomerization of alkyl groups, the elimination of a methylene group is unusual in a low temperature reaction.

No dialkylphosphinic acids containing secondary or tertiary alkyl groups are described in the literature. Diisopropylphosphinic acid was prepared by the method used by Kosolapoff and Watson<sup>8</sup> for di-*n*-propyl- and di-*n*-butylphosphinic acids, reaction of a dialkyl phosphite with a Grignard reagent and oxidation of the resulting dialkylphosphine oxide. Extraction with benzene in a continuous extraction apparatus was found a very satisfactory method for isolation of the dialkylphosphine oxide after decomposition of the Grignard complex and concentration of the mixture. An attempt to prepare di-*t*-butylphosphinic acid

<sup>(1)</sup> Presented in part before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

<sup>(2)</sup> P. Nylen, "Studien über organische Phosphorverbindungen," Dissertation, Uppsala, 1930, pp. 148-149.

<sup>(3)</sup> P. Rumpf and V. Chavanne, Compl. rend., 224, 919 (1947).

<sup>(4)</sup> J. R. White, THIS JOURNAL, 72, 1859 (1950).

<sup>(5)</sup> G. M. Kosolapoff, *ibid.*, 67, 1180 (1945).

<sup>(7)</sup> A. M. Kinnear and E. A. Perren, J. Chem. Soc., 3437 (1952).
(8) G. M. Kosolapoff and R. M. Watson, THIS JOURNAL, 73, 4101 (1951).

by this means was not successful; addition of dibutyl phosphite to a solution of *t*-butylmagnesium chloride resulted in a vigorous reaction but no identified products were isolated. Attention was therefore directed to the reaction of this Grignard reagent with phosphorus chlorides. It was found that *t*-butylmagnesium chloride reacted readily with phosphorus oxychloride, but reaction became slow when one t-butyl group had been introduced and the only identified product was t-butylphosphonyl dichloride. Di-t-butylphosphinic acid was obtained in poor yield by reaction of t-butylmagnesium chloride with *t*-butylphosphonyl dichloride, the mixture being boiled under reflux after completion of the addition. It was also prepared, again in poor yield, by addition of phosphorus trichloride to t-butylmagnesium chloride and subsequent oxidation with hydrogen peroxide. Although three moles of Grignard reagent were used per mole of phosphorus trichloride, no tri-t-butylphosphine oxide was isolated.

It is of interest to add that the purification of phosphonic and phosphinic acids from mixtures containing sodium and potassium salts of these acids can most readily be accomplished by passage of the aqueous solutions through a column of sulfonate-type ion-exchange resin<sup>9</sup> on the hydrogen cycle. The method is of particular value for the very water-soluble acids such as the alkyl members although the older method in which the salt is evaporated with hydrochloric acid and the residue extracted with benzene or xylene was used in the present investigation.

## Experimental<sup>10</sup>

Methylphosphonic Acid .- A very satisfactory method of preparation of methylphosphonic acid, from the point of view of purity of the product, consists of the isomerization of trimethyl phosphite to dimethyl methylphosphonate and hydrolysis of this ester. However, the preparation of trimethyl phosphite by reaction of phosphorus trichloride with methanol in presence of a tertiary base requires a large volume of solvent while the yield is considerably lower than in the preparation of higher trialkyl phosphites. For these reasons trimethyl phosphite was prepared from sodium methoxide and phosphorus trichloride and isomerized without isolation. The dimethyl methylphosphonate could not be distilled from the reaction mixture, however, and a rather lengthy isolation procedure was necessary.

To a solution of sodium methoxide, prepared by dissolving sodium (69 g.) in methanol (750 ml.), phosphorus trichloride (137.5 g.) was added with rapid stirring at  $0-5^{\circ}$ during seven hours. After a further five hours, methyl iodide (147 g.) was added and the mixture boiled under gentle reflux with stirring for 24 hours. At the end of this period the temperature was 65° and the odor of trimethyl phosphite could no longer be detected. The mixture was filtered without difficulty and the methanol distilled from the filtrate. The residue of dimethyl methylphosphonate retained some sodium chloride in solution which caused decomposition when distillation was attempted at water-pump pressure using a water-bath for heating. It was diluted with carbon tetrachloride (300 ml.), phosphorus penta-chloride (450 g.) added, the mixture heated under reflux overnight, cooled, filtered and sulfur dioxide passed in to remove excess phospherus pentachloride. The mixture was distilled giving (after removal of carbon tetrachloride, with iodine from the methyl iodide. This was added drop-wise with stirring and ice cooling to dry butanol (160 g.) at

20 mm. pressure during five hours. After stirring under reduced pressure for a further two hours and refluxing with stirring under reduced pressure for 15 minutes the mixture was distilled giving, after a forerun of butanol, 130 g. of di*n*-butyl methylphosphonate, b.p.  $86-91^{\circ}$  (1.5 mm.),  $n^{20}$ D 1.4246,  $d^{20}$ , 0.9770, *MR*, 54.45 (calculated *MR* using Kabachnik's<sup>11</sup> value for phosphorus in phosphonates, 54.63).

The ester (120 g.) was hydrolyzed by refluxing with hy-drochloric acid, the solution evaporated and the residue evaporated with benzene, in which it was insoluble. The acid was dissolved in water, treated with charcoal, filtered and the filtrate evaporated giving, after thorough drying in vacuo over phosphorus pentoxide, 55.0 g. (63%) of methyl-

phosphonic acid, m.p. 104–106°. Ethylphosphonic Acid.—Diethyl ethylphosphonate, pre-pared by isomerization of triethyl phosphite and carefully redistilled, was hydrolyzed by refluxing with hydrochloric acid. Since no solvent suitable for recrystallization could be found, the acid was treated with phosphorus pentachloride. The redistilled ethylphosphonyl dichloride (b.p. 177–179°) was dissolved in chloroform and hydrolyzed by stirring with The solution was evaporated giving ethylphosphonic water. acid, m.p. 57-60°

Reaction of Alkyl Halides with Sodium Dibutyl Phosphite in Toluene.—n-Propyl, n-butyl and isobutyl bromides all reacted smoothly with sodium dibutyl phosphite in tolu-After completion of the reaction, the sodium bromide ene. was filtered off, the toluene distilled from the filtrate, the esters distilled and hydrolyzed by refluxing with hydro-chloric acid. The acids were recrystallized from benzene giving 60-70% yields of *n*-propylphosphonic acid, m.p. 73°, *n*-butylphosphonic acid, m.p.  $105-106^{\circ}$  and isobutylphosphonic acid, m.p.  $118.5-119^{\circ}$ . The latter was the anhydrous acid (Calcd. for C<sub>4</sub>H<sub>11</sub>O<sub>3</sub>P: neut. equiv., 138.2; found: neut. equiv., 138.3, 138.0) and not the hemi-hydrate (m.p.  $124^{\circ}$ ) reported by Arbusov and Ivanov.<sup>12</sup>

Isopropyl iodide (50.3 g.) was added to a solution of so-dium dibutyl phosphite prepared from sodium (5.8 g.) and dibutyl phosphite (48.5 g.) in toluene (300 ml.). The mixture was slowly heated until precipitation of sodium iodide began, maintained at this temperature for 17 hours and the

began, maintained at this temperature for 17 hours and the acid isolated as described above. The yield of distilled ester, b.p.  $58-62^{\circ}$  (0.05 mm.), was 70%. After hydrolysis and many recrystallizations from benzene isopropylphos-phonic acid, m.p.  $74-75^{\circ}$ , was obtained in poor yield. *s*-Butyl bromide (27.4 g.) was heated below boiling point for two days with the solution prepared from sodium (4.6 g.) and dibutyl phosphite (38.8 g.) in toluene (300 ml.). On working up the mixture 25.0 g. of the ester, b.p. 70-80° (0.05 mm.), was obtained giving, on hydrolysis, 13.9 g. of acid as an uncrystallizable oil. This was treated with phosphorus pentachloride (42 g.) giving, after two distillations, 11.6 g. pentachloride (42 g.) giving, after two distillations, 11.6 g. of the phosphoryl dichloride, b.p.  $97-98^{\circ}$  (17 mm.). This phosphonyl dichloride was hydrolyzed by stirring with water and the solution evaporated. The residue, after six months in vacuo over phosphorus pentoxide, partially crystallized.

t-Butyl bromide (27.4 g.) was heated below boiling point for 4.5 days with the solution prepared from sodium (4.6 g.) and dibutyl phosphite (38.8 g.) in toluene (300 ml.), and the mixture filtered and distilled giving 16.5 g. of ester, b.p. 98 (1.4 mm.)-117° (2.5 mm.). Hydrolysis gave a complex mixture of acids, m.p., after crystallization from benzene,

80–90° only slightly changed on recrystallization. **Preparation of Phosphonyl Dichlorides.**—Phosphorus tri-chloride (1.0 mole) was added to aluminum trichloride (1.0 mole) and the alkyl halide (isopropyl chloride, *s*-butyl bromide, *t*-butyl chloride or *t*-amyl chloride) (1.0-1.25 moles) added with stirring at 5–15°, the reaction flask being cooled in ice. Toward the end of the addition the mixture usually became very viscous and stirring had to be discontinued.

After standing overnight, chloroform (500 ml.) was added, the mixture stirred well to disintegrate the solid and poured on a mixture of crushed ice (1500 g.) and hydrochloric acid (300 ml.). The chloroform layer was separated and the aqueous layer extracted once with chloroform (100 ml.). The combined chloroform solutions were dried with calcium chloride, filtered, the chloroform distilled from the filtrate and the residue distilled. Yields of once-distilled phos-

(12) A. E. Arbusov and A. Ivanov, J. Russ. Phys. Chem. Soc., 45, 690 (1913)

<sup>(9)</sup> We are grateful to the Dow Chemical Company for supplying a variety of such ion-exchange resins

<sup>(10)</sup> Melting points are uncorrected.

<sup>(11)</sup> M. I. Kabachnik, Izvestiva Akad, Nauk S.S.S.R., otdel, khim. nauk., 219 (1948).

phonyl dichlorides were: isopropyl 67.1%, s-butyl 77.5, tbutyl 83.3 and t-amyl 61.5 and 59.9.

Isopropylphosphonic Acid.—The isopropylphosphonyl dichloride was redistilled and then had b.p.  $77-79^{\circ}$  (14 mm.) (Clay<sup>6</sup> gives b.p. 76° (23 mm.)). The chloride was added dropwise with stirring to water during 20 minutes, the solution evaporated and re-evaporated with xylene to remove hydrogen chloride. The crude acid was dissolved in water, treated with charcoal, filtered and the filtrate evaporated. The residue was recrystallized twice from benzene giving isopropylphosphonic acid, m.p. 74–75°, undepressed in a mixed m.p. determination with acid prepared from isopropyl iodide and sodium dibutyl phosphite as described above.

s-Butylphosphonic Acid.—The s-butylphosphonyl dichloride was carefully redistilled and the middle fraction hydrolyzed by stirring with aqueous alcohol, the resulting solution evaporated, re-evaporated with xylene, the residue dissolved in water, treated with charcoal, filtered and evaporated. The acid resisted several attempts to cause crystallization but eventually crystallized when the sirupy acid was left in contact with a little water overnight. It was recrystallized from benzene-light petroleum (crystallizing readily when seeded) giving s-butylphosphonic acid, small very deliquescent plates, m.p.  $54-56^\circ$ . It should be noted that this acid contains an asymmetric carbon atom.

Anal. Calcd. for C<sub>4</sub>H<sub>11</sub>O<sub>3</sub>P: P, 22.43. Found: P, 22.57. t-Butylphosphonic Acid.—t-Butylphosphonyl dichloride (109 g.) was recrystallized once from ligroin (60 ml.) giving 83 g., m.p. 121–122.5° (raised to 122.5–123.5° by further recrystallization, Clay<sup>6</sup> gives 123°, Kinnear and Perren<sup>7</sup> 110°). This was dissolved in ethanol (100 ml.), hydrochloric acid (300 ml.) added and the mixture refluxed for seven hours. The solution was evaporated and the residue re-evaporated with benzene to remove hydrogen chloride. The crude acid was recrystallized from a mixture of ligroin (200 ml.) and acetic acid (55 ml.) giving 50 g. of t-butylphosphonic acid, m.p. 191.5–192°, unchanged on further recrystallization from xylene. It forms fine white needles crumbling to a non-deliquescent powder on drying.

Anal. Calcd. for C<sub>4</sub>H<sub>11</sub>O<sub>3</sub>P: P, 22.43. Found: P, 22.54.

Investigation of "t-Amylphosphonyl Dichloride."—The crude phosphonyl dichloride (84.6 g., b.p. 92–123° (19 mm.)) was distilled through a Vigreux column and the following fractions collected: I (2.4 g.), b.p. 82–90° (20.5 mm.), crystals (1.1 g.) and liquid; II (17.5 g.), b.p. 90 (20.5 mm.)– 135° (92 mm.), crystals (16.2 g.) and liquid; III (12.8 g.), b.p. 135–138° (92 mm.), crystals (11.6 g.) and liquid; IV (41.4 g.), b.p. 100.5–109° (18.5 mm.), liquid; V (7.2 g.), b.p. 109–123° (18.5 mm.), liquid.

The liquid portions of fractions I-III were decanted and the combined solids (28.9 g.) recrystallized three times from light petroleum (b.p. 39-41°) giving successively 18.9 g., m.p. 68-93°, 14.9 g., m.p. 85-99° and 9.8 g., m.p. 93-104°.

The dichloride from the third recrystallization was converted to the anilide by boiling under reflux for 16 hours with aniline (20 g.) and pyridine (25 ml.). After cooling, water (250 ml.) and hydrochloric acid (50 ml.) were added, the solid filtered off and dried (12.7 g., m.p. 233–238°). One recrystallization from ethanol-acetone and two from ligroinacetic acid gave 3.3 g., m.p. 255–258°. This was heated under reflux for three days with hydrobromic acid (20 ml.) and acetic acid (5 ml.), evaporated, sodium hydroxide (20 g.) in water (100 ml.) added and the mixture evaporated to remove aniline and pyridine. Hydrochloric acid (25 ml.) was added, the solution evaporated and the solid extracted (Soxhlet) with light petroleum. The acid from evaporation of the extract was recrystallized once from xylene and four times from ligroin-aceid and the neutralization equivalent was close to that required for this acid. (Calcd. for C<sub>4</sub>H<sub>11</sub>-O<sub>3</sub>P: neut. equiv., 138.1. Found: neut. equiv., 138.7.)

Fraction IV (41.4 g.) was hydrolyzed by boiling under reflux with hydrochloric acid and alcohol, evaporated, reevaporated several times with xylene, dissolved in water, treated with charcoal, filtered and the filtrate evaporated. The acid thus obtained was recrystallized five times from ligroin giving 12.0 g., m.p. 139-141°. As the m.p. was unchanged on further recrystallization this was thought to be a pure specimen of *t*-amylphosphonic acid, but both the neutralization equivalent and analysis for phosphorus indicate some contamination by t-butylphosphonic acid. It forms short, white, non-deliquescent needles.

Anal. Calcd. for C<sub>5</sub>H<sub>13</sub>O<sub>3</sub>P: P, 20.36; neut. equiv., 152.1. Found: P, 20.73; neut. equiv., 148.6.

Dimethylphosphinic acid was already available. It had m.p. 87.5–88.5°.

Diethylphosphinic acid was purified by two distillations and had m.p. 16.5–18.5°, b.p. 92° (0.08 mm.). Di-*n*-propylphosphinic acid was purified by two recrystalli-

**Di**-*n*-propylphosphinic acid was purified by two recrystallizations from light petroleum (b.p.  $39-41^{\circ}$ ) cooling to  $-15^{\circ}$ . It had m.p.  $58.5-59^{\circ}$ .

Diisopropylphosphinic Acid.—Dibutyl phosphite (63 g.) in dry ether (190 ml.) was added with stirring to the Grignard reagent from magnesium (32 g.) and isopropyl chloride (120 g.) in dry ether (400 ml.) during three hours. The mixture became very gelatinous; it was heated under gentle reflux for two hours, allowed to stand overnight and decomposed with a mixture of crushed ice (1000 g.) and hydrochloric acid (120 ml.). The mixture was evaporated to ca. 400 ml. and extracted with benzene in a continuous extraction apparatus for 60 hours. The benzene was distilled from the combined extracts, a little water being added to remove the last traces. Hydrogen peroxide (50 ml. 30%) was added cautiously in small portions resulting in a vigorous oxidation; the excess was decomposed by adding a solution of sodium hydroxide and boiling. Excess hydrochloric acid and xylene (100 ml.) were added and the water removed by azeotroping (Dean and Stark apparatus). The sodium chloride was filtered off, washed with dry benzene and the solvents evaporated from the combined filtrate and washings. The residue was dissolved in water, treated with charcoal, filtered and the filtrate evaporated leaving a yellow oil (32 g.) which crystallized on cooling. This was purified by two distillations giving 21.2 g. (43.5%) of di-isopropylphosphinic acid, b.p. 84-86° (0.02 mm.), m.p. 47.5-49.5°. It forms white crystals which, like di-*n*-pro-subcectain acid and in marked contrasts to the low pylphosphinic acid and in marked contrasts to the lowmelting alkylphosphonic acids, are not deliquescent.

Anal. Calcd. for C<sub>5</sub>H<sub>15</sub>O<sub>2</sub>P: P, 20.63. Found: P, 20.62.

Di-n-butylphosphinic Acid.—This was prepared from dibutyl phosphite and n-butylmagnesium bromide in ether and isolated as described by Kosolapoff and Watson.<sup>8</sup> It had m.p. 68.5-69°.

**Di-t-butylphosphinic Acid.**—A solution of *t*-butylmagnesium chloride in dry ether was prepared as described by Whitmore and Badertscher.<sup>13</sup> Aliquots were taken and the Grignard reagent determined by titration with acid.<sup>14</sup>

the Grignard reagent determined by titration with acid.<sup>14</sup> To *t*-butylphosphonyl dichloride (15.0 g.) in dry ether (100 ml.), *t*-butylmagnesium bromide (0.087 mole) in dry ether (120 ml.) was added dropwise with stirring during 8.5 hours after which the mixture was heated under reflux for 16 hours. The ether was distilled off and hydrobromic acid (40 ml.) added slowly and cautiously. The mixture was heated under reflux for 17 hours, evaporated to dryness and sodium hydroxide (20 g.) in water (400 ml.) added, the mixture heated to boiling and filtered hot from the precipitated magnesium oxide. The filtrate was acidified with hydrochloric acid (50 ml.), xylene (100 ml.) added and the water removed by azeotroping, using a Dean and Stark apparatus. The xylene solution was filtered from the sodium chloride, the filtrate evaporated, the residue dissolved in water (600 ml.), charcoal and celite added, heated to boiling and filtered hot. The filtrate was evaporated to about 120 ml. when crystals began to separate from the hot solution which was cooled and filtered giving 2.5 g. (16%) di-*b*utylphosphinic acid, m.p. 207-209°, raised to 208-210° by recrystallization from water.

Phosphorus trichloride (26 g.) in dry ether (125 ml.) was added dropwise with stirring to *t*-butylmagnesium chloride (0.62 mole) in dry ether (volume of Grignard solution, 220 ml.) during three hours. The reaction was vigorous. The mixture was heated under reflux for 30 minutes, the heater removed and a solution of ammonium chloride (80 g.) in water (400 ml.) added (cautiously since considerable heat was evolved). The ether layer was separated, filtered and evaporated, water (50 ml.) was added and distilled off to remove the last of the ether. Hydrogen peroxide (25 ml.,

(13) F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 1559 (1983).

(14) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *ibid.*, **45**, 150 (1923).

30%) was added and the mixture warmed; no reaction was apparent, but the unpleasant odor disappeared. The solution was diluted to 300 ml., left overnight, filtered from a small amount of sticky material and evaporated to about 50 ml. Sodium hydroxide (20 g.) in water (100 ml.) was added cautiously and the solution boiled until the hydrogen peroxide was decomposed. On cooling, crystals were deposited which were filtered off and dissolved in water (100 ml.). The solution was acidified with hydrochloric acid, precipitating 2.0 g. (6%) of di-t-butylphosphinic acid, m.p.  $208-210^\circ$ , unchanged on recrystallization from water from which it crystallizes in small colorless plates. There was no depression in a mixed melting point with the acid obtained from t-butylphosphonyl dichloride.

Anal. Calcd. for C<sub>8</sub>H<sub>19</sub>O<sub>2</sub>P: P, 17.38. Found: P, 17.35.

Determination of Apparent Dissociation Constants.—The acids were dissolved in water and their pK' were determined by potentiometric titration with carbonate-free decinormal sodium hydroxide, using a glass electrode and a Fisher Titrimeter, as a pH meter, at 25°. Before each titration the instrument was calibrated against standard acetate buffer which was 0.1 M in both acetic acid and sodium acetate.<sup>15</sup> Hitchcock and Taylor give the pH of this solution as 4.648. This calibration was checked from time to time by measuring the pH of two more buffers recommended by the same authe pri of two more buildry recommended by the same au-thors. These were 0.05 M potassium hydrogen phthalate (pH 4.008) and a solution 0.01 M in hydrochloric acid and 0.09 M in potassium chloride (pH 2.078). The measured values agreed with those given by Hitchcock and Taylor within the accuracy of the setting of the instrument (0.02)units). Samples were weighed out and dissolved in volumes of water such that the mean concentration of phosphonic acids during the titration was 0.005 M and that of the phosphinic acids 0.01 M. For calculations, however, the amount of acid was obtained from the end-point observed and the titration curve (the first end-point for phosphonic acids), because of possible errors in weighing caused by the extreme hygroscopicity of many of these acids. From the experimental results values of pK' were calculated at several points in each titration using the equation

$$pK' = pH + \log [HA]/[A^-]$$
(1)

In the titrations of phosphonic acids the first and the second neutralizations were assumed to occur successively. Since the values of  $pK_1'$  and  $pK_2'$  differ by more than five units in all cases this assumption is quite justified, and the OH<sup>-</sup> contribution was thus neglected in computing the first dissociation constant of the phosphonic acids.<sup>16</sup>

The number of experimental points used for calculation in each titration averaged five for the first dissociation constant of phosphonic acids, seven for the second dissociation constant of phosphonic acids, and ten for the dissociation constant of phosphinic acids. From these a mean pK' was calculated for each titration.

Two titrations were performed for each acid, with the exception of neopentylphosphonic acid of which the quantity available sufficed for only one determination. The results from duplicate determinations agreed well.

The titrations of dimethylphosphinic acid with hydrochloric acid were carried out with a 3.5 N solution of dimethylphosphinic acid and 5 N hydrochloric acid. The titration was followed by the Fischer Titrimeter and the usual glass electrode-calomel electrode combination.

#### **Results and Discussion**

The pK' values determined as described in the experimental section are tabulated below. The average standard deviation of individual results from the recorded mean values was less than 0.03 units, but because of the possible errors in the observed pH values due to uncertainties in the reading and the calibration of the instrument, an accuracy greater than  $\pm 0.05$  unit is not claimed.

In Fig. 1 the second dissociation constants of the phosphonic acids studied are plotted against the

(15) D. I. Hitchcock and A. C. Taylor, THIS JOURNAL, 59, 1817 (1937).
(16) L. Michaelis, "Physical Methods of Organic Chemistry,"
Vol. I-2. Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1746-1747.

TABLE 1	
PHOSPHONIC ACIDS RPO(OH)2	

R	$pK'_1$	$pK_2'$
Methyl	$2.38^a$	$7.74^{b}$
Ethyl	$2.43^{\circ}$	$8.05^{d}$
n-Propyl	$2.49^{e}$	8.18'
Isopropyl	2.66	8.44
n-Butyl	2.59	8.19
Isobutyl	2.70	8.43
s-Butyl	2.74	8.48
t-Butyl	2.79	8.88
Neopenty1 <sup>9</sup>	2.84	8.65
t-Amvl <sup>h</sup>	2.88	8.96

<sup>a</sup> Nylen<sup>2</sup> gives 2.33, Rumpf and Chavanne<sup>8</sup> give 2.35. <sup>b</sup> Nylen<sup>2</sup> gives 7:76, Rumpf and Chavanne<sup>3</sup> give 7.1. <sup>c</sup> Nylen<sup>2</sup> gives 2.39, Rumpf and Chavanne<sup>3</sup> give 2.45. <sup>d</sup> Nylen<sup>2</sup> gives 7.98, Rumpf and Chavanne<sup>3</sup> give 7.85. <sup>e</sup> Nylen<sup>2</sup> gives 2.45. <sup>f</sup> Nylen<sup>2</sup> gives 8.06. <sup>g</sup> We wish to express our thanks to Dr. Carl Noller for a specimen of this acid. <sup>h</sup> Not analytically pure; see experimental section.

#### TABLE II

## PHOSPHINIC ACIDS R<sub>2</sub>POOH

R	pK'
Methyl	3.08
Ethyl	3.29
n-Propyl	3.46
Isopropyl	3.56
n-Butyl	3.41
t-Butyl	4.24

number of carbon atoms in the alkyl group. The series methyl, ethyl, isopropyl and t-butyl are found to lie approximately on a straight line having a slope corresponding to an increment of pK' of 0.38 per methyl group on the first carbon atom. The series of n-propyl, s-butyl and t-amyl, in which again each member has one more methyl group in the same relative location than that which precedes it, also falls about a straight line roughly parallel to that for the first series. Similarly, the series ethyl, n-propyl, isobutyl and neopentyl in which the methyl groups are successively substituted on the second carbon atom, lie about a straight line, the increment in pK' averaging 0.20 unit per methyl group. The single example of substitution of a methyl group on the third carbon (n-propyl and *n*-butyl) produces practically no change in the pK'

Similar trends can be seen also in the first dissociation constants but they are less well marked owing to the smaller range of  $\rho K'$  values and probably lower accuracy of the determinations. Here again, however, branching of the carbon chain always weakens the acid, the effect being most marked when the branching occurs at the first carbon atom. These regularities are quite different from the relationship between dissociation constants and structure exhibited by the unsubstituted aliphatic carboxylic acids.<sup>17</sup>

Among the phosphinic acids (Fig. 2) the series methyl, ethyl, isopropyl, exhibits an approximately linear rise of pK', but the di-t-butylphosphinic acid is weaker by about 0.4 pK' unit than would be expected from its position as the fourth member of this series. The reason for this is not clear, but

(17) J. F. J. Dippy, Chem. Revs., 25, 188 (1939).



Fig. 1.—Second dissociation constants of alkylphosphonic acids.

it may be the result of strain caused by the attachment of two bulky groups to a single phosphorus atom.



Fig. 2.-Dissociation constants of dialkylphosphinic acids.

Cacodylic acid (dimethylarsinic acid) has basic properties, its strength as a base having been measured by several workers, most recently by Kilpatrick.<sup>18</sup>

It was considered of interest to see whether or not any basic properties could be detected in dimethylphosphinic acid by potentiometric titration with a strong acid. The curve obtained in a typical

(18) M. L. Kilpatrick, THIS JOURNAL, 71, 2607 (1949).

instance is shown as Fig. 3. The break occurring at the calculated point of equivalence (about 6 millivolts at 0.1 pH) is quite small and owing to the uncertain behavior of the electrode system in this region no very definite statement can be made about the basicity of this acid.



Fig. 3.—Titration of dimethylphosphinic acid with hydrochloric acid.

This can be added to previous observations by one of us (G.M.K.) in which it was noted that during hydrolysis with hydrochloric acid of esters of various phosphinic acids complete solutions of the products were obtained; on dilution the phosphinic acids were precipitated. It appears that phosphinic acids in general have a certain, although weak, basic character.

In conclusion it may be pointed out that the points of inflection on the titration curves of the phosphonic acids reported here are mostly outside the pH ranges of the commonly used indicators. The first end-point occurred in the range pH 5.3–6.2 and the second in the range pH 9.1–10.3 for all acids. It appears that methyl red should be used instead of methyl orange for titration of the first hydrogen and thymolphthalein instead of phenolphthalein for the second hydrogen of phosphonic acids. Phenolphthalein is the most suitable of the common indicators for titration of phosphinic acids.

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