mosphere in 60 ml. of 10% sodium hydroxide in the presence of 4 g. of cuprous oxide for eight hours, no reaction was evident, and on acidification 7.7 g. of the bromo acid was recovered. Repetition of the reaction in a glass liner within a steel autoclave at 140° for six hours also gave negative results. Extension of the reaction period to 48 hours, however, resulted in isolation of phenol as the only product. Intermediate reaction periods gave similar results, and no significant traces of the hydroxy acid were isolated.

From 4-Methoxybenzenephosphonic Acid.—*p*-Methoxybenzenephosphonic acid (10 g.) was refluxed in nitrogen atmosphere with 15 ml. of 57% hydriodic acid, while methyl iodide was being collected in a suitable cooled trap. In no case was it possible to secure over 65% of the theoretical amount of methyl iodide. After 2–3 hours the solution was evaporated to dryness at 50° in nitrogen atmosphere under reduced pressure. The residue contained considerable amounts of phenol, which was removed as much as possible by repeated evaporation, as described above. Its complete removal was impossible owing to continuous generation of this substance. Repetition of the ether cleavage under various conditions with acetic acid diluent gave only phenol and progressively smaller amounts of unchanged methoxy acid. Replacement of the hydriodic acid by 47% hydrobromic acid, and heating the mixture to 125–130° for three hours, followed by evaporation as described above, gave a very water-soluble acidic product, which melted at 171–174° after recrystallization. It gave only a minor melting point depression on being mixed with an authentic specimen of the *p*-hydroxy derivative, indicating that it was substantially pure *p*-hydroxybenzenephosphonic acid. The yield, however, was very poor, amounting to some 1.5 g. Admixture of 25% of *p*-methoxybenzenephosphonic acid to the authentic *p*-hydroxy acid gave a melting point depression of over 30 degrees; only a very minor contamination gave a depression of 1–2 degrees. However, despite the rather considerable difference in solubilities of the individual hydroxy and methoxy acids in water, it was not possible to separate completely the contaminant (*p*-methoxy acid) from the above product. This was in full accord with the concept of association of acids of phosphorus in solutions (Kosolapoff and Powell, ref. 8), according to which the phosphonic acids exist in polymeric chains which can have links of the various acids present in a mixture; in such hydrogen-bonded aggregates the physical properties of the individual acids are no longer in normal evidence.

The relatively low order of hydrolytic stability of the *p*-methoxy acid is also shown by the fact that upon refluxing in concentrated hydrochloric acid for one to two hours, the substance began to evolve gradually increasing amounts of phenol. No *p*-hydroxybenzenephosphonic acid could be isolated from water washings of the residual material, obtained by evaporation of the aqueous filtrate from unchanged *p*-methoxy acid.

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

The Chemistry of Phosphonic Acids with Aromatic Nuclei. II. The Isomeric Tolylphosphonic Acids

BY EUGENE C. ASHBY AND GENNADY M. KOSOLAPOFF

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The apparent dissociation constants of the three isomeric tolylphosphonic acids were determined; these, in ascending order, are in series of: ortho, meta, para. The apparent molecular weights of the isomeric acids were determined in various solvents. The para isomer shows a consistently higher degree of association, followed in order by the meta and the ortho isomers. The differences of solubilities of the three isomers are interpreted in terms of these data.

It has been known for a long time that considerable differences in physical constants are found in the group of isomeric tolylphosphonic acids. These differences are expressed particularly strikingly in the solubilities of these acids. Whereas the *p*-tolylphosphonic acid is moderately soluble in water, the other two isomers are extremely soluble. The para isomer is essentially insoluble in various hydrocarbon solvents, while the other two isomers are appreciably soluble in benzene and other hydrocarbons. The melting points of the three isomers are unusual, in that the meta isomer has the lowest one.

In order to find some tenable explanation of these facts we examined the dissociation constants and the association tendencies of the three isomers.

The determination of dissociation constants, performed as described previously,[1] yielded results that are given below.

Acid: $CH_3C_6H_4PO(OH)_2$	pK_1'	pK_2'
Para isomer	1.84	7.33
Meta isomer	1.88	7.44
Ortho isomer	2.10	7.68

It is apparent that the values for the para and the meta isomers are very close to each other, while the ortho isomer shows a very appreciable departure in the direction of weaker acidity. The latter isomer is the only one in this group in which steric hindrance exists between the side chain and the phosphono group, thus prohibiting the free rotation of the PO_3 unit. The results are in accord with the expected consequences of orientation of an electron-repelling group (methyl) in respect to an acidic group.[2]

As stated above, the meta and the ortho isomers, in addition to being very soluble in water, are also soluble in solvents such as benzene. The process of such solution is peculiar, however. These two acids dissolve in hot benzene very slowly to form even a 5% solution, but only part of the dissolved material separates on cooling to nearly the freezing point of the solvent. Details for the best recrystallization procedure are given in the experimental section.

On the basis of studies of association of various phosphorus-bearing organic acids, it has been suggested[3] recently that aliphatic phosphonic acids, $RPO(OH)_2$, are probably linear hydrogen-bonded aggregates, or polymers. The average size of such aggregates, as well as their shapes, can be expected to have a considerable bearing on their solubility.

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

(2) R. L. Herbst and M. E. Jacox, *ibid.*, **74**, 3004 (1952).

(3) G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

For this reason, in continuation of earlier work,[3] we investigated the effect of orientation of the methyl group in tolylphosphonic acids on the apparent molecular weight of the isomeric acid in various solvents by the freezing and the boiling point methods.

Naphthalene, which was used successfully in previous work, gave excellent results with the ortho and the meta isomers. The para isomer was substantially insoluble in this hydrocarbon and direct comparison of the three acids was impossible. Biphenyl, *p*-di-*t*-butylbenzene and *p*-dichlorobenzene dissolved so little of the para isomer as to be worthless for our purpose. Camphor dissolves appreciable amounts of the para isomer, but the high melting point of this solvent and the presence of a polar group in it serve to disrupt the aggregation of phosphonic acids to a very considerable extent. In the admittedly unfavorable group of polar solvents, to which we were forced to turn, neither benzophenone nor benzil were good enough solvents for the para isomer. Boiling point elevation method was used with acetone, which dissolved the para isomer readily. Finally, the freezing points of aqueous solutions of the three isomers were determined. The results of the determinations are given below.

			Solvent					
	$C_{10}H_8$		Me_2CO		H_2O		Camphor	
Isomer	*m.*	Mol. wt.	*m.*	Mol. wt.	*m.*	Mol. wt.	*m.*	Mol. wt.
Ortho	0.0416	660	0.0551	390	0.0904	116	0.434	281
	.0967	769	.1008	428	.1782	129		
	.1384	858	.1530	648	.2854	136		
Meta	.0680	1240			.0747	113		
	.1150	1184			.1836	128		
	.1540	1230			.2800	134		
	.1880	1540						
Para			.0514	439	.0199	98	0.434	338
			.1290	462	.0427	110		
			.2107	594	.0831	120		
					.1602	128		
					.2110	165		

The following points are evident after consideration of the data. In non-polar naphthalene the meta isomer clearly forms much larger units than are formed by association of the ortho isomer. The noticeably greater solubility of the ortho isomer in benzene, thus, can be ascribed at least in part to smaller aggregation of the monomeric units. In camphor, with its disadvantageous properties noted above, the aggregates are very severely disrupted, but it is clear that the para isomer forms larger or more stable aggregates than does the ortho isomer. The degree of association of the monomeric acids in acetone is very much below that found in the non-polar naphthalene, as might be expected. In addition, association of the solvent with the acids evidently takes place; the relatively lower molecular weights of the para isomer in this solvent possibly can be assigned to association of this type. The ortho isomer with its steric hindrance can be expected to be less prone to associate with the solvent than the para isomer. Progressive rise of association with increased concentration is still noted in this solvent. In aqueous solution all the isomers show considerable acidic dissociation. However, a slight increase of the apparent molecular weight with increased concentration is noted in the ortho and the meta isomers. The para isomer, beginning with molality of 0.16, deviates from this order and shows a very rapid increase of the apparent molecular weight with increased concentration. It appears that in this range of concentration the initiation of polymeric chain structure becomes energetically advantageous.

It appears therefore that the para isomer shows a greater tendency for polymeric hydrogen bonding, which can account for its insolubility in many of the common organic solvents. The ortho isomer, with its hindered acid group, can only form helically shaped aggregates, which appear to be less probable than the essentially straight-chain units possible for the para isomer and, to a lesser extent, the meta isomer.

Experimental Part

Preparation of the Compounds. *p*-Tolylphosphonic Acid.—This isomer was prepared by the diazonium fluoborate method, which consists of the treatment of a diazonium fluoborate with phosphorus trichloride, followed by hydrolysis. The procedure was a slight modification of that given by Doak and Freedman[4] in that dioxane was used as the solvent and cuprous chloride as the catalyst. These changes gave us a 60% yield, instead of the reported 45% yield and eliminated the formation of any phosphinic acid.

***m*-Tolylphosphonic Acid.**—This isomer was also prepared by the fluoborate procedure. The diazonium fluoborate in this instance is rather unstable and must be used as rapidly as possible, consistent with air-drying. The reaction with phosphorus trichloride is best run at 55°. In the isolation of this acid it was found that the mono-sodium salt does not precipitate immediately upon the adjustment of the *p*H, but requires a period of several minutes. The best solvent for crystallization of this acid was concentrated hydrochloric acid or a mixture of benzene and ligroin. The product, obtained in 69.8% yield, melted at 121°.

***o*-Tolylphosphonic Acid.**—Attempts to prepare this isomer by the fluoborate method were fruitless. Although the general behavior of the reaction mixture of the diazonium fluoborate and phosphorus trichloride was normal, no more than traces of the phosphonic acid could be found in the concentrate after the removal of copper. The solubility of the mono-sodium salt of this acid prevented the use of it for isolation of the product from the reaction mixture. It may be mentioned that our experience with *o*-tolyldiazonium fluoborate in this synthesis did not agree with published information.[5] It was prepared readily in 70% yield and showed no signs of instability. It melted at 106°. In order that a satisfactory product be formed, it is only necessary to use freshly distilled *o*-toluidine. The product has been exposed to the ordinary laboratory atmosphere for 12 days without showing any signs of decomposition. This is in direct contrast to the behavior of the meta isomer.

o-Tolylphosphonic acid was prepared by the Grignard method of Burger and Dawson[6] through the diethyl ester (b.p. 148–150° at 14 mm.), obtained in 59% yield. The ester was hydrolyzed with concentrated hydrochloric acid, the resulting solution evaporated with an infrared lamp and the crude product recrystallized by the following procedure. The acid was dissolved in twenty parts of boiling benzene with addition of a few drops of *n*-propanol until a clear solution was obtained; the warm solution was then treated with ligroin (b.p. 90–120°) until it became cloudy, and the solution was allowed to come to room temperature slowly. Substantially theoretical recovery of the acid, m.p. 141°, was attained.

Isomeric Ethylphenylphosphonic Acids.—The failure of the fluoborate method in the instance of *o*-tolyl isomer (see above) led to a brief examination of the homologous ethylphenyl compounds. The *o*-ethylphenyldiazonium fluoborate was obtained in 70% yield, but no phosphonic acid could

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[4] G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951).

[5] A. Roe, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 200.

[6] A. Burger and N. D. Dawson, *J. Org. Chem.*, **16**, 1250 (1951).

be obtained from this substance by the Doak–Freedman method. *m*-Ethylphenyldiazonium fluoborate was prepared conventionally, but this proved to be even less stable than its tolyl analog. Usually within 15 minutes of isolation by filtration from the reaction mixture, the colorless solid showed signs of vigorous decomposition, being transformed to a red liquid. An attempt to employ this fluoborate for the preparation of the phosphonic acid, after rapid drying by washing with ether, failed to yield any of the desired product.

Determination of Apparent Dissociation Constants.—The technique of the determinations as well as the apparatus and the mode of calculations were precisely as described in an earlier paper from this Laboratory.[1]

Determination of Apparent Molecular Weights.—The determinations by lowering of freezing points were run as described earlier.[3] Di-*p*-*t*-butylbenzene was used as the standard for calibration. The boiling point determinations were made in the conventional Cottrell apparatus.

The molal constants were determined experimentally. These were: 7.20 for naphthalene, 39.7 for camphor, 1.55 for acetone and 1.86 for water.

AUBURN, ALA.

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Preparation of Arsenic and Phosphorus Compounds from Stable Diazonium Salts

BY LEON D. FREEDMAN AND G. O. DOAK

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Diazonium fluosilicates or chlorozincates can be used for the preparation of organoarsenic and organophosphorus compounds. The yields of these compounds are compared with the yields obtained from the corresponding diazonium fluoborates.

Aromatic compounds of arsenic, phosphorus and antimony can be prepared readily through the use of diazonium fluoborates.[1] It was of interest to determine whether other stable diazonium salts could be used in place of fluoborates. In particular, the diazonium fluosilicates seemed worth considering since they are, at least in some cases, more stable[2] and easier to isolate[3] than the corresponding fluoborates.

Table I compares the yields of phosphonic and phosphinic acids obtained from diazonium fluosilicates with the yields obtained from the corresponding diazonium fluoborates. Although the end results are similar, the reactions of the diazonium fluosilicates were less vigorous, and the organophosphorus compounds obtained were purified with less difficulty.

TABLE I

YIELDS OF ARYLPHOSPHONIC AND DIARYLPHOSPHINIC ACIDS PREPARED FROM DIAZONIUM SALTS[a]

$RC_6H_4N_2X$ R =	Yield from diazonium fluosilicate, % Phosphonic acid	Phosphinic acid	Yield from diazonium fluoborate,[b] % Phosphonic acid	Phosphinic acid
H	19	10	17	4
m-Cl	35	9	43	7
m-O_2N	48	3	37	6
p-O_2N	50	3	47	6

[a] The following quantities of reactants were used: 0.1 equivalent of diazonium salt, 0.1 mole of phosphorus trichloride, 125 ml. of ethyl acetate, 2 g. of cuprous bromide. The yield data in this and succeeding tables were, in most cases, obtained from single experiments. However, enough of the reactions were run in duplicate to indicate that the yields given can probably be reproduced to about 3 absolute %. [b] These results are taken from ref. 1b.

Organoarsenic compounds also can be prepared by the use of diazonium fluosilicates. For example, *p*-nitrobenzenearsonic and bis-(*p*-nitrophenyl)-arsinic acids were obtained in 1 and 14% yields, respectively, when arsenic trichloride reacted with *p*-nitrobenzenediazonium fluosilicate in 80% alcohol in the presence of cuprous bromide. The fluoborate under the same conditions gave 19% arsonic acid and 21% arsinic acid.[1a]

The diazonium fluosilicates also were used for the preparation of phosphinic acids from phenyldichlorophosphine; the yields obtained are given in Table II. Also given in Table II are the results we obtained using fluoborates and considerably less catalyst than previously employed. Evidence was presented previously[1d] which indicates that the unsymmetrical phosphorus compounds disproportionate to some extent under the conditions of the reaction. It seems reasonable to suggest that the lower temperatures prevailing in the diazonium fluosilicate reactions lead to less disproportionation and hence to higher yields of unsymmetrical phosphinic acids. This view is consistent with the fact that the use of 0.8 g. of cuprous bromide per 0.1 mole of diazonium fluoborate moderates the violence of the reaction with phenyldichlorophosphine and, in three out of four cases, increases the yields of the unsymmetrical acids (*cf.* Table II).[4]

Because of their stability and ease of isolation, diazonium chlorozincates (zinc chloride double salts of diazonium chlorides) have been used for many purposes.[5] We have found that these salts also can be used for the preparation of arsenic and phosphorus compounds but they offer no advantage over the fluoborates or fluosilicates. Table III

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(1) (a) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5656 (1951); (b) *ibid.*, **73**, 5658 (1951); (c) G. O. Doak, L. D. Freedman and S. M. Efland, *ibid.*, **74**, 830 (1952); (d) L. D. Freedman and G. O. Doak, *ibid.*, **74**, 2884 (1952); (e) G. O. Doak and L. D. Freedman, *ibid.*, **75**, 683 (1953); (f) L. D. Freedman, H. Tauber, G. O. Doak and H. J. Magnuson, *ibid.*, **75**, 1379 (1953).

(2) R. D. Beaty and W. K. R. Musgrave, *J. Chem. Soc.*, 875 (1952).

(3) G. F. Hawkins and A. Roe, *J. Org. Chem.*, **14**, 328 (1949).

(4) Unpublished work from this Laboratory indicates that the yields of phosphonic acids obtained from diazonium fluoborates and phosphorus trihalides are unaffected by using 0.8 g. of cuprous bromide instead of the usual 2.0 g. per 0.1 mole of diazonium fluoborate. However, such a decrease makes these reactions less vigorous. Thus, using the smaller ratio of catalyst to fluoborate, we have found that two moles of *p*-nitrobenzenediazonium fluoborate can react safely with phosphorus trichloride in a 12-l. flask equipped with an 18-mm. gas outlet tube.

(5) K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," 2nd edition, Edward Arnold and Co., London, 1949, p. 78.