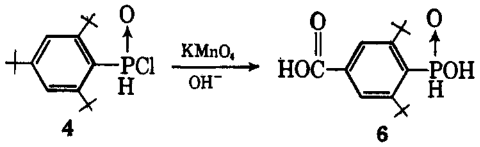
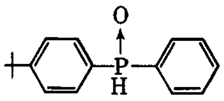


4 6

in a potassium bromide pellet, showed no bands in the 3500–3600-cm.$^{-1}$ region. It did exhibit several bands in the 2500–3000-cm.$^{-1}$ region and a band at 1705 cm.$^{-1}$. The infrared spectrum of **6** in dioxane solvent (in which carboxylic acids are usually monomeric[10]) showed a strong doublet appearing at 3550 and 3625 cm.$^{-1}$ along with a band at 1735 cm.$^{-1}$. This indicates that there is intermolecular rather than intramolecular hydrogen bonding present. Therefore the carboxylic acid group probably is *para* to the phosphinic acid group, assuming no rearrangement has taken place. There have been very few reports of a *t*-butyl group on an aromatic ring being oxidized to an aromatic carboxylic acid.[11]

The treatment of 1,3,5-tri-*t*-butylbenzene with phenylphosphonous dichloride and aluminum chloride resulted in the formation of *p*-*t*-butylphenylphenylphosphine oxide (**7**) in about a 4% yield as the only product isolated. The excess of phenylphosphonous dichloride in conjunction with the aluminum chloride caused the dealkylation of the 1,3,5-tri-*t*-butylbenzene.[12] The position of the *t*-butyl group was assigned as *para* on the basis of the infrared spectrum of **7** which exhibited strong maxima at 820 (due to *para* disubstitution), 755, and 725 cm.$^{-1}$, the latter two bands being due to a monosubstituted benzene ring.



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Experimental

2,4,6-Tri-*t*-butylphenylphosphinic Chloride.—A stirred mixture of 42.23 g. (0.17 mole) of 1,3,5-tri-*t*-butylbenzene,[9] 60 ml. (0.68 mole) of phosphorus trichloride, and 33.3 g. (0.25 mole) of aluminum chloride was refluxed for 4 hr. After the reaction mixture was cooled to room temperature, 250 ml. of methylene chloride was added (when chlorine gas was added at this point no oxidation was found to take place) and the reaction mixture was poured into a water–ice mixture. The methylene chloride phase was separated, and the aqueous phase was extracted several times with fresh methylene chloride. The combined methylene chloride extracts were dried and filtered and the solvent was removed to yield a crystalline solid product. After one recrystallization from petroleum ether (b.p. 30–60°) a total of 38.0 g. (0.12 mole) of product was obtained representing a yield of 71%. It crystallized from petroleum ether as colorless needles, m.p. 133–134°, $\lambda_{\max}^{\text{KBr}}$ 2340 cm.$^{-1}$ (P–H).

Anal. Calcd. for $C_{18}H_{30}ClOP$: C, 65.74; H, 9.20; P, 9.42. Found: C, 65.62; H, 9.24; P, 9.76.

The product could not be oxidized with alkaline hydrogen peroxide.

Attempted Oxidation of 2,4,6-Tri-*t*-butylphenylphosphinic Chloride with Alkaline Potassium Ferricyanide.—A stirred mixture of 45.8 g. (0.14 mole) of 2,4,6-tri-*t*-butylphenylphosphinic chloride, 54.0 g. (0.16 mole) of potassium ferricyanide, 32.8 g. of sodium hydroxide, and 2 l. of water was heated at 80–100° for 22 hr. The solution was acidified with hydrochloric acid and extracted twice with benzene. The combined benzene extracts were dried and filtered and the solvent was removed. Some petroleum ether (b.p. 20–40°) was added to the residual oil to remove starting material and all but some colorless solid dissolved. Upon filtration, a total of 6.2 g. (0.01 mole) of 2,4,6-tri-*t*-butylphenylphosphinic anhydride was obtained representing a yield of 15%. It crystallized from ethyl acetate as colorless needles, m.p. 259.5–260.5°, $\lambda_{\max}^{\text{KBr}}$ 2340 cm.$^{-1}$ (P–H).

Anal. Calcd. for $C_{36}H_{60}O_3P_2$: C, 71.72; H, 10.03; P, 10.28. Found: C, 71.74; H, 10.40; P, 10.21.

Oxidation of 2,4,6-Tri-*t*-butylphenylphosphinic Chloride with Alkaline Potassium Permanganate.—A stirred mixture of 18.6 g. (0.06 mole) of 2,4,6-tri-*t*-butylphenylphosphinic chloride, 39.5 g. (0.25 mole) of potassium permanganate, and 250 ml. of 2 *N* aqueous sodium hydroxide was refluxed for 16 hr. All of the potassium permanganate had reacted by this time and the manganese dioxide precipitate was removed by filtration. The basic aqueous solution was washed with benzene, acidified with hydrochloric acid (at which time a gas was evolved from the solution), and extracted with benzene and 3-hexanone. The solvents were removed from the combined solutions and a thick oil remained. Addition of petroleum ether (b.p. 30–60°) to the oil caused a white insoluble precipitate to separate. A total of 1.2 g. (0.004 mole) of the white crystalline product, **2,6-di-*t*-butyl-4-carboxylphenylphosphinic acid**, was isolated by filtration representing a yield of 7%. It was dissolved in aqueous sodium hydroxide, washed with benzene, and reprecipitated with hydrochloric acid. It crystallized from *n*-heptane as colorless plates, m.p. 226–227°.

Anal. Calcd. for $C_{15}H_{23}O_4P$: C, 60.39; H, 7.77; P, 10.38; neut. equiv., 149. Found: C, 59.97; H, 7.59; P, 10.77; neut. equiv., 144.

The infrared spectrum (KBr pellet) exhibited a band at 1705 cm.$^{-1}$, and the spectrum using dioxane solvent showed bands at 3625, 3550, and 1735 cm.$^{-1}$. Likewise bands were found (KBr pellet) at 2360 (P–H) and 2650 cm.$^{-1}$ (P–OH).

Reaction of 1,3,5-Tri-*t*-butylbenzene with Phenylphosphonous Dichloride.—A stirred mixture of 45.4 g. (0.18 mole) of 1,3,5-tri-*t*-butylbenzene, 128.9 g. (0.72 mole) of phenylphosphonous dichloride, and 40 g. (0.3 mole) of anhydrous aluminum chloride was refluxed for 4 hr. Then, after adding 28 ml. (0.3 mole) of phosphorus oxychloride, refluxing for 0.5 hr., and washing with petroleum ether (b.p. 30–60°), the residue was added to a water–ice mixture. The aqueous solution was extracted with benzene, the combined benzene extracts were washed with aqueous sodium hydroxide and water, dried, and filtered, and the solvent was removed. Acetone was added to the residual oil and a colorless solid remained insoluble. A total of 2.02 g. (0.008 mole) of *p*-*t*-butylphenylphenylphosphine oxide was obtained which represents a yield of 4%. It separated from *n*-heptane as colorless needles: m.p. 130–131°; $\lambda_{\max}^{\text{KBr}}$ 2370 (P–H), 820, 755, and 725 cm.$^{-1}$. It can also be purified by sublimation.

Anal. Calcd. for $C_{16}H_{19}OP$: C, 74.40; H, 7.41; P, 11.99; mol. wt., 258. Found: C, 74.31; H, 7.39; P, 12.19; mol. wt. (ebulliscopic determination in benzene), 248.

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[10] M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).

[11] I. V. Butina and V. G. Plyusnin, *Tr. Vses. Soveshch. po Khim. Pererabotke Neft. Uglevodorodov v Poluprod. dlya Sinteza Volokon i Plast. Masls, Baku*, 131 (1957).

[12] V. N. Ipatieff and B. B. Corson, *J. Am. Chem. Soc.*, **59**, 1417 (1937).

Problems of Orientation in Arylphosphonic Acids. I. 3-Chloro-4-tolylphosphonic Acid[1]

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Received August 4, 1964

3-Chloro-4-tolylphosphonic acid was first reported by Melchiker[2] and is listed in Kosolapoff's monograph[3]; it is also mentioned in the patent literature.[4] The synthetic procedure used by Melchiker involved a Friedel-

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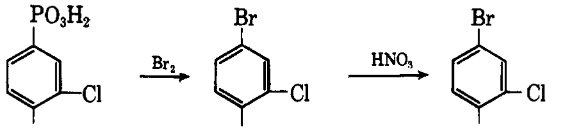
[1] The work was supported in part by Research Grant GM-09479 from the National Institutes of Health, Public Health Service.

[2] P. Melchiker, *Ber.*, **31**, 2915 (1898).

[3] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 166.

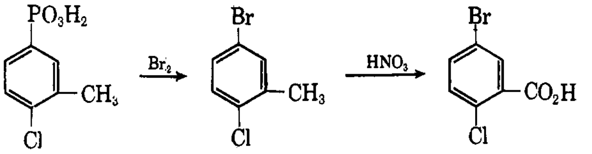
[4] K. C. Whitehouse and H. Z. Lecher, U. S. Patent 2,894,024 (July 7, 1959).

Crafts reaction between *o*-chlorotoluene and phosphorus trichloride to yield a phosphonous dichloride which was subsequently oxidized to a phosphonic dichloride; hydrolysis of the latter compound yielded a phosphonic acid which was reported to melt at 190°. In an attempt to establish the structure of this acid, Melchiker allowed it to react with bromine to yield a bromochlorotoluene which was then oxidized to a bromochlorobenzoic acid, m.p. 155–156°. He believed that this melting point agreed with the melting point of 2-chloro-4-bromobenzoic acid and that therefore the structure of his phosphonic acid must have been 3-chloro-4-tolylphosphonic acid.



There are several reasons for questioning the correctness of Melchiker's conclusions. In the reaction of electrophilic reagents with *o*-chlorotoluene, the entering group tends to go mainly *para* to the chloro group. This is true both in the Friedel–Crafts reaction[5] and in nitration.[6] Thus one might expect Melchiker's phosphonic acid to be 4-chloro-3-tolylphosphonic acid, although the possibility of the Friedel–Crafts reaction yielding mixtures of organophosphorus compounds should not be overlooked.[7]

A possible flaw in Melchiker's proof of structure concerns the melting point of 2-chloro-4-bromobenzoic acid. According to Heilbron,[8] the melting point of this acid is 166–167° and not 156° as stated by Melchiker. The melting point of 2-chloro-5-bromobenzoic acid, on the other hand, *is* 155–156°.[8] This evidence also suggested that Melchiker's phosphonic acid was 4-chloro-3-tolylphosphonic acid.



In connection with another problem,[9] we had the occasion to prepare 3-chloro-4-tolylphosphonic acid from the corresponding diazonium fluoroborate. The melting point of this acid was 160-162°. Nitration yielded a mononitro derivative which melted with decomposition at 223–227°. Melchiker had reported that nitration of his phosphonic acid yielded a compound, m.p. 200°. At this point in our study it seemed certain to us that he had not prepared 3-chloro-4-tolylphosphonic acid, and we assumed at first that his material must have been 4-chloro-3-tolylphosphonic acid. When we prepared the latter compound by an unequivocal route, however, we found that it melted at 158–161°; and thus the nature of Melchiker's phosphonic acid had still not been elucidated.

In order to obtain further information concerning this material, the Friedel–Crafts reaction between *o*-chlorotoluene and phosphorus trichloride was reinvestigated. We employed two different Friedel–Crafts procedures, *viz.*, the one used by Melchiker and the more convenient technique recently described by Gefter.[10] The results obtained by both procedures were very similar, except that the yield of phosphonous dichloride was 57% by Gefter's method and only 6% by Melchiker's. Hydrolysis of either phosphonous dichloride yielded the same phosphinic acid, m.p. 77.5–80°,[11] which was oxidized to a phosphonic acid. The melting point of this phosphonic acid could not be raised above 149–151° even after several recrystallizations from 6 *N* hydrochloric acid and was not depressed by admixture with either 3-chloro-4-tolylphosphonic acid or 4-chloro-3-tolylphosphonic acid. The infrared spectra of the latter two acids were, of course, quite similar, but each spectrum contained a number of distinct maxima which were absent in the spectrum of the other compound. The spectrum of the phosphonic acid obtained from either Friedel–Crafts reaction exhibited every peak present in the spectra of the two known acids. When a mixture of equal weights of the two known acids was recrystallized from 6 *N* hydrochloric acid, a material was obtained which melted at 147–150° and whose infrared spectrum was virtually identical with that of the phosphonic acid obtained from the Friedel–Crafts reaction. This evidence strongly suggests that Melchiker's recorded melting point of 190° is in error and that the Friedel–Crafts reaction between *o*-chlorotoluene and phosphorus trichloride yields a mixture of the 3-chloro-4-tolyl and the 4-chloro-3-tolyl isomers.

Since *o*-chlorotoluene can be isomerized by heating with aluminum chloride and hydrogen chloride,[12] there was a possibility that the methyl and chloro groups in the phosphonic acid obtained by the Friedel–Crafts reaction might no longer be *ortho* to one another. This possibility was effectively eliminated when we found that heating this phosphonic acid to 300° caused it to decompose to give pure *o*-chlorotoluene (identified by its infrared spectrum) and a residue of inorganic phosphate. The usefulness of thermal dephosphonation as an aid in elucidating the structures of arylphosphonic acids has been previously described.[13]

Experimental[14]

3-Chloro-4-tolylphosphonic Acid and Bis(3-chloro-4-tolyl)-phosphinic Acid.—3-Chloro-4-methylaniline (Eastman P6877)

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[5] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 223–225.

[6] J. B. Wibaut, *Rec. trav. chim.*, **32**, 243 (1913).

[7] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **74**, 4119 (1952); R. A. Baldwin, K. A. Smitheman, and R. M. Washburn, *J. Org. Chem.*, **26**, 3547 (1961); R. Schmutzler, *J. Inorg. Nucl. Chem.*, **25**, 335 (1963).

[8] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1953, p. 477.

[9] *Cf.* L. D. Freedman, G. O. Doak, and J. W. Clark, Jr., *Clin. Med.*, **71**, 351 (1964).

[10] E. L. Gefter, *Zh. Obshch. Khim.*, **28**, 1338 (1958); *Chem. Abstr.*, **52**, 19999 (1958).

[11] Melchiker[2] reported m.p. 70° for his phosphinic acid. The melting point of authentic 3-chloro-4-tolylphosphinic acid is 97.5–98.5°: L. D. Quin and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **83**, 4124 (1961).

[12] J. F. Norris and H. S. Turner, *ibid.*, **61**, 2128 (1939).

[13] L. D. Freedman, G. O. Doak, and E. L. Petit, *J. Org. Chem.*, **25**, 140 (1960); C. E. Griffin and J. T. Brown, *ibid.*, **26**, 853 (1961).

[14] Melting points were determined as previously described: *cf.* ref. 15. The carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

was purified by vacuum distillation and then converted to the corresponding diazonium fluoroborate by Roe's procedure IIA.[16] The dried diazonium salt was suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide in the usual manner.[15] When the reaction mixture was steam distilled, an oil, consisting largely of phosphinic acid, separated in the distilling flask. The hot aqueous layer was decanted through a filter, and the oil remaining in the beaker was washed several times with boiling water. The crude phosphinic acid was then purified by reprecipitation from alkaline solution and subsequent recrystallization from 95% ethanol. The yield of pure bis(3-chloro-4-tolyl)phosphinic acid was 3%, m.p. 189–192°.

Anal. Calcd. for $C_{14}H_{13}Cl_2O_2P$: Cl, 22.50; P, 9.83; neut. equiv., 315.1. Found: Cl, 22.26; P, 9.86; neut. equiv., 310.5.

The phosphonic acid was isolated as its hemi-sodium salt[15] from the aqueous layer mentioned above, and the salt was converted to the free acid by recrystallization from a mixture of 1 vol. of 95% ethanol to 5 vol. of 6 *N* hydrochloric acid. The yield was 50%, m.p. 160–162°.

Anal. Calcd. for $C_7H_8ClO_3P$: Cl, 17.16; P, 15.00; neut. equiv., 103.3. Found: Cl, 16.97; P, 14.50; neut. equiv., 104.4.

2-Nitro-5-chloro-4-tolylphosphonic Acid.[17]—3-Chloro-4-tolyl phosphonic acid (40.6 g.) was added in small portions to 185 ml. of stirred fuming nitric acid (*d* 1.5) maintained at 15–20°. Stirring was continued for 1 hr. after the addition was complete, and the reaction mixture was then poured onto 400 g. of cracked ice. The mixture was allowed to stand in the ice box overnight after which the solid was removed by filtration. The yield of crude mononitrated material was 36.5 g. (73%), m.p. 169–184°. After several recrystallizations from 3 *N* hydrochloric acid, the material melted with decomposition at 223–227°.

Anal. Calcd. for $C_7H_7ClNO_5P$: Cl, 14.09; N, 5.57; P, 12.31; neut. equiv., 125.8. Found: Cl, 14.12; N, 5.54; P, 12.06; neut. equiv., 126.0.

The structure of this substance was not established unequivocally, but it is probably 2-nitro-5-chloro-4-tolylphosphonic acid for the following reasons. (1) The compound does not form a water-insoluble magnesium salt either at room temperature or when heated. This behavior is characteristic of arylphosphonic acids containing bulky *ortho* substituents such as the nitro group.[18] (2) The nitration of 3-chloro-4-toluenesulfonic acid yields almost exclusively 2-nitro-5-chloro-4-toluenesulfonic acid.[19] Since the sulfo and the phosphono groups have similar electronic structures, it seems reasonable to assume that the nitration of 3-chloro-4-tolylphosphonic acid gives 2-nitro-5-chloro-4-tolylphosphonic acid.

4-Chloro-3-tolylphosphonic Acid and Bis(4-chloro-3-tolyl)phosphinic Acid.—4-Chloro-3-methylaniline,[20] m.p. 85.5–86.5°, was diazotized in fluoroboric acid in the usual manner.[16] The cold reaction mixture was filtered by suction on a sintered-glass filter, and the solid diazonium fluoroborate was washed with a small amount of cold fluoroboric acid (40 ml./mole of amine) and then several times with copious quantities of ether. After being dried in a desiccator, the salt was converted to the corresponding phosphonic and phosphinic acids, which were separated by the procedure used for the 3-chloro-4-tolyl isomers. After several recrystallizations from aqueous alcohol, the yield of pure bis(4-chloro-3-tolyl)phosphinic acid was 3%, m.p. 178–181°.

Anal. Calcd. for $C_{14}H_{13}Cl_2O_2P$: C, 53.36; H, 4.16. Found: C, 53.48; H, 4.30.

The phosphonic acid was recrystallized from 6 *N* hydrochloric acid; the yield was 15%, m.p. 158–161°.

Anal. Calcd. for $C_7H_8ClO_3P$: C, 40.70; H, 3.90. Found: C, 40.78; H, 4.01.

Acknowledgment.—The authors wish to acknowledge the technical assistance of Mrs. Joyce E. Carevic, Mr. Bobby R. Ezzell, and Mr Dick E. Hoskins.

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(15) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(16) A. Roe, *Org. Reactions*, **5**, 204 (1949).

(17) This compound is mentioned in ref. 4, but no information concerning its structure is presented.

(18) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955).

(19) E. G. Turner and W. P. Wynee, *J. Chem. Soc.*, 707 (1936).

(20) J. P. Lambooy and E. E. Haley, *J. Am. Chem. Soc.*, **74**, 1087 (1952).

Dialkyl Esters of Acylphosphonic Acids[1]

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During the course of studies involving the reaction of compounds containing adjacent carbonyl–phosphoryl groups[3] we have synthesized several new alkyl acylphosphonates by a very convenient method. Early work by Arbuzov[4] and more recent data by Kabachnik[5] demonstrate that acetyl chloride, ethyl chloroformate, phosgene, and benzoyl chloride react with phosphites to give phosphonates in a Michaelis–Arbuzov rearrangement.[6] Acetic anhydride behaves similarly[7] while α-haloacyl halides[8] react in a pattern similar to the Perkow reaction of α-halo ketones with trisubstituted phosphorus esters.

Addition of acyl halide to phosphite required cooling as expected.[3,4] It was found that high yields of dialkyl acylphosphonates could be realized if the reaction mixtures were permitted to stand at room temperature overnight before distillation was attempted. In the case of the cyclohexyl derivatives, an additional 1–2 hr. at reflux was necessary to complete the process after the mixture had stood for a day. In all examples, the vacuum distillation proceeded very smoothly to give colorless oils when this procedure was followed. Physical properties are recorded in Table I for all esters, and the 2,4-dinitrophenylhydrazone derivatives were analyzed for nitrogen and phosphorus. Infrared (Table II) and n.m.r. data (Table III) support the structures. As in the examples with dialkyl aroylphosphonates,[3] the dialkyl acylphosphonates are hygroscopic and presumably undergo carbon–phosphorus bond cleavage. The surprisingly low frequency of absorption for the carbonyl function in these novel esters is similar to the situation reported with the aroylphosphonates. It was suggested that one of the nonbonding orbitals on the oxygen atom of the phosphoryl group could orient properly for overlap with the p-orbital on the carbonyl carbon atom which could result in alteration of the force constant of the carbon–oxygen bond.[3] Such a phenomenon could be operative in the compounds described herein.

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(1) We gratefully acknowledge support of the National Institutes of Health, GM-10367-03.

(2) Postdoctorate, 1963–1965.

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