The Phenoxaphosphinic Acid and Phenothiaphosphinic Acid Ring Systems[1]

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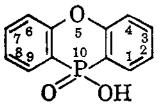
The phenoxaphosphinic acid ring system (I) was found to be remarkably stable. 2,8-Dimethylphenoxaphosphinic acid was oxidized to the corresponding dicarboxy compound, and dinitro derivatives of both the dimethyl and the dicarboxy compounds were prepared. 2,8-Dimethylphenothiaphosphinic acid was prepared by a variant of the Friedel–Crafts reaction in which *p*-tolyl sulfide and phosphorus trichloride were heated together in the presence of aluminum chloride and the reaction mixture was then hydrolyzed. The ultraviolet absorption spectra of the heterocyclic phosphorus compounds are described and discussed.

There are relatively few procedures available for the preparation of phosphinic acids in which the phosphorus atom is a member of a ring system.[2] The first such compound was prepared by a variant of the Friedel–Crafts reaction in which diphenylamine and phosphorus trichloride were heated together for several hours. When the product was extracted with water and then oxidized, phenazaphosphinic acid[3,4] was obtained. An attempt to extend this method to the preparation of phenoxaphosphinic acid (I) failed, because the phosphorus trichloride attacked a 4-position of phenyl ether rather than a 2-position.[5] Several years ago we reported the preparation of 2,8-dimethylphenoxaphosphinic acid by refluxing a mixture of *p*-tolyl ether and phosphorus trichloride in the presence of aluminum chloride, and then hydrolyzing the reaction mixture.[6] The present paper is concerned with the preparation and properties of several derivatives of phenoxaphosphinic acid and of its sulfur analog, phenothiaphosphinic acid.



I

We have found that the phenoxaphosphinic acid ring system is remarkably stable. Thus, the 2,8-dimethyl derivative can be oxidized with potassium permanganate to the corresponding dicarboxy compound in satisfactory yield. As indicated in Table I, the ultraviolet absorption spectrum of 2,8-dicarboxyphenoxaphosphinic acid is characterized by intense absorption in the 270–285-mμ region. This feature is probably associated with resonance interaction between the ring oxygen atom and the carboxy groups in *para* position to it.[7] Attempts to decarboxylate the compound by the usual methods[8] have led only to recovery of the starting material. Fusion with sodium hydroxide yielded a reaction mixture from which no phosphinic acid could be isolated.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA[a]

Compound	λ_{max}, mμ	ϵ_{max}
2,8-Dimethylphenoxaphosphinic acid[b]	218	39,900
	243	20,500
	281[c]	2,800
	296[c]	5,100
	301	5,430
2,8-Dicarboxyphenoxaphosphinic acid	218	37,800
	271	21,400
	282[c]	21,400
	285	22,100
2,8-Dimethyl-4,6-dinitrophenoxaphosphinic acid	235[c]	17,300
	330	3,980
2,8-Dicarboxy-4,6-dinitrophenoxaphosphinic acid	255	16,200
	271	16,000
	305[c]	4,890
2,8-Dimethylphenothiaphosphinic acid	221	26,800
	267	14,500
	287	5,700
	310[c]	3,450
p-Tolyl sulfide	252	14,100
	275	6,540
2,8-Dimethyl-5,5-dioxophenothiaphosphinic acid	222	43,000
	275	2,570
	284	2,670

[a] The spectra of all compounds were determined in 95% ethanol with a Perkin-Elmer Model 350 spectrophotometer. [b] The spectrum of this compound was previously determined with a Beckman DU spectrophotometer; *cf.* ref. 6. [c] Shoulder.

Nitration of 2,8-dimethylphenoxaphosphinic acid with fuming nitric acid near room temperature gave a dinitro derivative. The structure of this compound was not established unequivocally, but it almost certainly is 2,8-dimethyl-4,6-dinitrophenoxaphosphinic acid for the following reasons. (1) Among the available positions the 4,6-positions are most activated by the ring oxygen atom and least deactivated by the phosphinico (PO_2H) group. (2) The nitration of *p*-tolyl ether leads only to compounds in which the nitro groups are *ortho* to the oxygen atom.[9] (3) The ultraviolet absorption spectrum (*cf.* Table I) of the dinitro compound is *less* intense than that of the starting material, even though nitro groups usually cause increased absorption. This decreased intensity can be explained by assuming steric inhibition of resonance between the ring oxygen atom and the benzene rings and between the nitro groups and the benzene rings. It is of interest that the spectrum of *o*-nitrophenyl phenyl ether[10]

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[2] See, for example, E. R. Lynch, *J. Chem. Soc.*, 3729 (1962).

[3] P. G. Sergeev and D. G. Kudryashov, *Zh. Obshch. Khim.*, **8**, 266 (1938); see also M. Häring, *Helv. Chim. Acta*, **43**, 1826 (1960).

[4] The nomenclature used in the present paper is based, in general, on the usage of F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon," Interscience Publishers, Inc., New York, N. Y., 1950. At the suggestion of Dr. Leonard T. Capell, slight changes have been made in order to conform to current nomenclature practices.

[5] W. C. Davies and C. J. O. R. Morris, *J. Chem. Soc.*, 2880 (1932).

[6] L. D. Freedman, G. O. Doak, and J. R. Edmisten, *J. Org. Chem.*, **26**, 284 (1961).

[7] *Cf.* L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

[8] J. March, *J. Chem. Educ.*, **40**, 212 (1963).

[9] J. Reilly, P. J. Drumm, and H. S. B. Barrett, *J. Chem. Soc.*, 67 (1927).

[10] H. E. Ungnade and I. Ortega, *J. Org. Chem.*, **17**, 1475 (1952).

is characterized by a shoulder at 260 mμ (log ε 3.62) and a maximum at 315 mμ (log ε 3.33) and is thus somewhat similar to the spectrum of the dinitro derivative of 2,8-dimethylphenoxaphosphinic acid.

Nitration of 2,8-dicarboxyphenoxaphosphinic acid with fuming nitric acid gave a satisfactory yield of a dinitro compound. The structure of this material was not proven, but it undoubtedly is 2,8-dicarboxy-4,6-dinitrophenoxaphosphinic acid since both the carboxy and phosphinico groups are *meta* directing and the phenoxy group is *ortho*, *para* directing. The spectrum of this compound given in Table I is consistent with this formulation if we assume (as we did in the above paragraph) that the nitro groups are in the sterically hindered 4,6-positions.

We have extended the Friedel–Crafts reaction to the preparation of 2,8-dimethylphenothiaphosphinic acid by heating *p*-tolyl sulfide with phosphorus trichloride in the presence of aluminum chloride[11] and then hydrolyzing the reaction mixture. The success of this synthesis was somewhat surprising since it had been reported[12] that the reaction of phenyl sulfide, arsenic trichloride, and aluminum chloride at 175° yields hydrogen chloride and diphenylene disulfide but no organoarsenic compounds; when phenyl sulfide and aluminum chloride were heated together in the absence of arsenic trichloride, benzene and diphenylene disulfide were obtained.[13] The aluminum chloride catalyzed reaction between phosphorus trichloride and *p*-tolyl sulfide does seem to be considerably more complex than the corresponding reaction with *p*-tolyl ether. Thus, in spite of numerous attempts, we were unable to obtain more than a 25% yield of 2,8-dimethylphenothiaphosphinic acid (compared to a 73% yield of 2,8-dimethylphenoxaphosphinic acid). Traces of *p*-tolylphosphonic acid[14] and *p*-tolyl disulfide[15] were also isolated from the reaction mixture; it is clear, therefore, that the aryl sulfide system must be cleaved to some extent under the conditions of the reaction. No information was obtained concerning the mechanism of this cleavage.

It has been pointed out[16a] that the ultraviolet absorption spectra of aryl sulfides exhibit larger bathochromic shifts than do the spectra of the corresponding aryl ethers. This effect is apparently seen in the spectrum of 2,8-dimethylphenothiaphosphinic acid. The maximum at 267 mμ is probably the "first primary band" in the sense used by Doub and Vandenbelt[7] and corresponds to the 252-mμ band in *p*-tolyl sulfide and the 243-mμ band in 2,8-dimethylphenoxaphosphinic acid.

2,8-Dimethylphenothiaphosphinic acid was readily oxidized with hydrogen peroxide to the corresponding sulfone. The ultraviolet absorption of the sulfone in the 270–285-mμ region is less intense than that of the parent sulfide and undoubtedly reflects the lower conjugative ability of the sulfonyl group.[17] It is of interest that the "first primary band" of the heterocyclic sulfone occurs at 222 mμ which is a lower wave length than the corresponding band of *p*-tolyl sulfone.[18] This result is difficult to explain unless we assume, as Price and Oae[16b] have suggested, that the conjugation of two benzene rings through a sulfone group does not operate when the two rings are held in coplanar position. A scale model[19] indicates that 2,8-dimethyl-5,5-dioxophenothiaphosphinic acid has a nearly planar structure.

Experimental[20]

2,8-Dicarboxyphenoxaphosphinic Acid.—2,8-Dimethylphenoxaphosphinic acid (2.6 g.), dissolved in a mixture of 15 ml. of pyridine and 15 ml. of water, was oxidized with 25 g. of potassium permanganate by the method of Morgan and Herr.[21] After the excess pyridine was removed by steam distillation, the reaction mixture was filtered, decolorized with charcoal, and then added slowly with good stirring to 100 ml. of 10% hydrochloric acid. The analytically pure dicarboxy compound precipitated; the yield was 1.8 g. (56%), m.p. >300°.

Anal. Calcd. for $C_{14}H_9O_7P$: P, 9.67; neut. equiv., 106.7. Found: P, 9.45; neut. equiv., 106.9.

2,8-Dimethyl-4,6-dinitrophenoxaphosphinic Acid.–2,8-Dimethylphenoxaphosphinic acid (2.6 g.) was nitrated at 30–35° with 25 ml. of fuming nitric acid (*d* 1.5). The reaction mixture was poured onto 30 g. of ice, whereupon 1.4 g. (40%) of crude dinitrocompound crystallized from solution. Recrystallization from aqueous acetone yielded 0.52 g. of yellow needles, m.p. >300°. The analysis and spectrum of this material was not affected by further recrystallization.

Anal. Calcd. for $C_{14}H_{11}N_2O_7P$: N, 8.00; P, 8.84. Found: N, 7.87; P, 8.96.

2,8-Dicarboxy-4,6-dinitrophenoxaphosphinic Acid.—A solution of 3.2 g. of 2,8-dicarboxyphenoxaphosphinic acid in 25 ml. of freshly prepared 100% nitric acid[22] was gently heated for about 3 hr. until approximately two-thirds of the nitric acid was distilled. On cooling the reaction mixture to −25°, crystals were obtained which were removed by filtration and washed with a few milliliters of cold water. The yield was 3.0 g. (78%), m.p. >300°. The sample used for analysis and for the determination of the ultraviolet absorption spectrum was recrystallized from a mixture of acetone and ether and then dried *in vacuo* at 100°.

Anal. Calcd. for $C_{14}H_7N_2O_{11}P$: C, 40.99; H, 1.72; N, 6.83; P, 7.55; neut. equiv., 136.7. Found: C, 40.72; H, 1.85; N, 6.85; P, 7.33; neut. equiv , 138.6.

2,8-Dimethylphenothiaphosphinic Acid.—*p*-Tolyl sulfide[23] (21.4 g.), 35 ml. of phosphorus trichloride, and 17 g. of anhydrous aluminum chloride were placed in a 500-ml. two-necked flask equipped with a sealed stirrer and a reflux condenser protected with a drying tube. The mixture was stirred and refluxed gently for about 7 hr. and then allowed to stand overnight at room temperature. On pouring the reaction mixture over 800 g. of cracked ice, a heavy oil was obtained. The aqueous supernatant solution was poured off, and the oil was dissolved in 400 ml. of boiling 5% sodium hydroxide solution. The resulting solution was treated with decolorizing charcoal and then made very acid (pH <0) by the addition of concentrated hydrochloric acid. A white solid separated which was removed by filtration

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[11] In the absence of aluminum chloride there was no reaction upon refluxing a mixture of *p*-tolyl sulfide and phosphorus trichloride for 24 hr.

[12] E. E. Turner and A. B. Sheppard, *J. Chem. Soc.*, **127**, 544 (1925).

[13] However, W. Dilthey, L. Neuhau, E. Reis, and W. Schommer [*J. prakt. Chem.*, **124**, 81 (1930)] found that phenyl sulfide is not cleaved under Friedel–Crafts conditions and can be acylated normally by acetyl chloride and aluminum chloride.

[14] Identified by analysis, melting point, and mixture melting point with an authentic sample.

[15] Identified by analysis, melting point, and ultraviolet absorption, which was virtually identical with that reported by L. Bauer and J. Cymerman [*J. Chem. Soc.*, 109 (1950)].

[16] C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962: (a) p. 30; (b) p. 100.

[17] E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 231 (1949).

[18] The "first primary band" of *p*-tolyl sulfone occurs at 245 mμ (log ε 4.32); *cf.* H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 485.

[19] Constructed with an atom model set manufactured by Waltham Enterprises, Ltd., England.

[20] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 421 spectrophotometer.

[21] P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 5264 (1952).

[22] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, p. 468.

[23] J. Reilly, P. J. Drumm, and B. Daly, *Proc. Roy. Irish Acad.*, **39B**, 515 (1930).

and dried *in vacuo*. It was then extracted for 24 hr. with 500 ml. of anhydrous ether in a Soxhlet apparatus.[24] The ether-insoluble material in the thimble was then extracted for 48 hr. with 500 ml. of 95% ethanol. Pure 2,8-dimethylphenothiaphosphinic acid crystallized from the alcoholic solution, and a second crop could be obtained by evaporating the mother liquor to incipient crystallization. The yield was 6.90 g. (25%), m.p. >300°.

Anal. Calcd. for $C_{14}H_{13}O_2PS$: P, 11.21; S, 11.60; neut. equiv., 276.3. Found: P, 11.13; S, 11.80; neut. equiv. 279.1.

2,8-Dimethyl-5,5-dioxophenothiaphosphinic Acid.—When a suspension of 1.05 g. of 2,8-dimethylphenothiaphosphinic acid in 20 ml. of boiling glacial acetic acid was treated with 3.0 ml. of 30% hydrogen peroxide, virtually all the solid went into solution and soon a voluminous precipitate separated. The reaction mixture was then allowed to sit on a steam bath for 2 hr. and finally cooled. The precipitate was removed by filtration and washed with copious quantities of water. The yield was 1.02 g. (87%), m.p. >300°. The infrared absorption spectrum in potassium bromide exhibited strong maxima at 1158 and 1315 cm.$^{-1}$, which were assigned to the symmetric and asymmetric stretching modes of the SO_2 group.[25] These bands were absent in the parent sulfide.

Anal. Calcd. for $C_{14}H_{13}O_4PS$: C, 54.54; H, 4.25. Found: C, 54.39; H, 4.29.

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[24] This step served to remove an oily material which was not identified.

[25] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 360-363.

Kinetics of the Reaction of Aromatic Aldehydes with Ammonia

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The kinetics of the reaction of aromatic aldehydes with ammonia to form hydrobenzamides have been studied spectrophotometrically in methanol at 30°. The reaction is first order with respect to aldehyde and first order with ammonia. The effect of water, potassium hydroxide, and temperature on the rate has been studied. The application of Hammett's law to the rates gives a positive ρ-value for the reaction of aldehydes with electron-releasing substituents and a negative ρ-value with electron-withdrawing substituents. Induction periods were observed in the formation of hydrobenzamides with electron-withdrawing substituents. These results suggest a probable mechanism involving α-aminobenzyl alcohol and benzylidenimine, etc.

The reaction of benzaldehydes with ammonia gives hydrobenzamides, ArCH=NCH(Ar)N=CHAr. Dobler has observed the rate of the reaction by means of acidimetry to be second order.[1] He observed no systematic substituent effect. The analogous condensation of aromatic aldehydes with *n*-butylamine,[2] semicarbazide,[3,4] or anilines[5] has been studied, Hammett's rule not being applicable for the benzylidenimine or semicarbazone formation. Some investigators have reported that the reaction of benzaldehyde with ammonia also produces benzylidenimine,[6,7] NH=CHPh; α,α'-dioxydibenzylamine,[8] NH(CH(OH)Ph)$_2$; and 2,4,6-triphenyl-1,3,5-hexahydrotriazine,[9] (—NH—CH-Ph—)$_3$. The present paper summarizes our data on the kinetic investigation of the reaction involving the effect of basicity of the solution, the effect of substituents, and a probable mechanism derived from the results. Since acidimetry gave no accurate rates of reaction, we employed spectrophotometry.

Experimental

Materials.—Commercial benzaldehyde, b.p. 78.8° (26 mm.), and *p*-anisaldehyde, b.p. 159.0° (44 mm.), were purified by vacuum distillation under nitrogen. *p*-Chlorobenzaldehyde, m.p. 46.5–47.5°, and *p*-cyanobenzaldehyde, m.p. 101–102°, were prepared by the chromic acid oxidation of *p*-chlorotoluene and *p*-tolunitrile,[10] respectively. Commercial methanol was purified by distillations and used as the solvent. Aqueous ammonia was of guaranteed reagent grade. Methanolic ammonia free of water was prepared by passing ammonia gas, dried with sodium hydroxide, into methanol dried by boiling with magnesium.

Products.—Hydrobenzamides were prepared by the reaction of concentrated aqueous ammonia and aldehydes in methanol, the resulting precipitates being recrystallized from methanolic ammonia: hydrobenzamide, m.p. 100–101° (lit.[11] m.p. 102°); hydroanisamide, m.p. 128.5–130.5 (lit.[12] m.p. 130°); 4,4',4''-trichlorohydrobenzamide, m.p. 87–90°; 4,4',4''-tricyanohydrobenzamide, m.p. 130–132°. Infrared spectra[13] of these products showed the C=N band at 1632–1636 cm.$^{-1}$, but no absorption corresponding to the C=O, =NH, or —OH band was observed. 4,4',4''-Trichlorohydrobenzamide and 4,4',4''-tricyanohydrobenzamide are new compounds.

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2$: C, 62.78; H, 3.76; N, 6.97. Found: C, 62.73; H, 3.87; N, 6.87.

Anal. Calcd. for $C_{24}H_{15}N_5$: C, 77.20; H, 4.05; N, 18.76. Found: C, 77.62; H, 4.10; N, 18.18.

Rate Measurements.—For the determination of the concentrations of benzaldehyde [B] and hydrobenzamide [H], two wave lengths of benzaldehyde at 245 (absorption max.) and 270 mμ (absorption min.) were selected. Their concentrations were determined by ultraviolet spectrophotometry for binary mixtures.[14] The values of the molar extinction coefficient were determined experimentally: for benzaldehyde, ϵ_{max} 1.319 × 10^4 (lit.[15] $\epsilon_{240\ m\mu}$ 1.32 × 10^4), ϵ_{min} 1.098 × 10^3; for hydrobenzamide, ϵ_{max} 2.800 × 10^4, ϵ_{min} 1.016 × 10^4. The absorption of the product, hydrobenzamide, could be determined by converting the remaining benzaldehyde into acetal with a drop of sulfuric acid in methanol. The spectrum of hydrobenzamide (λ_{max} 251 mμ) showed a bathochromic shift (λ_{max} 281 mμ) by addition of sulfuric acid. A methanolic solution of hydrobenzamide was stable at room temperature. Since the decomposition of hydrobenzamide

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[1] F. Dobler, *Z. physik. Chem.* (Leipzig), **101**, 1 (1922).

[2] G. M. Santerre, C. J. Hansrote, and T. I. Crowell, *J. Am. Chem. Soc.*, **80**, 1254 (1958).

[3] J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 3036 (1959).

[4] B. M. Anderson and W. P. Jencks, *J. Am. Chem. Soc.*, **82**, 1773 (1960).

[5] E. F. Pratt and M. J. Kamlet, *J. Org. Chem.*, **26**, 4029 (1961).

[6] R. K. McLeod and T. I. Crowell, *ibid.*, **26**, 1094 (1961).

[7] H. H. Strain, *J. Am. Chem. Soc.*, **49**, 1561 (1927).

[8] F. Francis, *Ber.*, **42**, 2216 (1909).

[9] S. V. Svetozarskii, E. N. Zil'berman, and A. I. Finkel'shtein, *Zh. Obshch. Khim.*, **31**, 1717 (1961).

[10] S. V. Lieberman and R. Connor, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 441.

[11] A. Fürth, *Monatsh.*, **27**, 839 (1906).

[12] O. Fischer, *J. prakt. Chem.*, [2]**77**, 129 (1908).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[14] C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth and Co. (Publishers) Lmt., London, 1961, p. 73.

[15] J. VanAllan and J. F. Tinker, *J. Org. Chem.*, **19**, 1243 (1954).