The infrared absorption shown in this report was observed in nujol or in KBr disks with a Koken Infrared Recording Spectrophotometer, Model DS 301.

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[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis of Diarylphosphine Oxides by the Friedel-Crafts Method

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The reaction of mesitylene, durene, or pentamethylbenzene with phosphorus trichloride and aluminum chloride catalyst under conditions normally employed for the synthesis of primary phosphonous dichlorides gave instead good yields of secondary phosphine oxides (after hydrolysis). Small amounts of secondary phosphinic acids were obtained as by-products. The three new phosphine oxides were found to be exceptionally stable to oxidation. With a simpler aromatic hydrocarbon, ethylbenzene, the only secondary product obtained was the phosphinic acid.

Very few secondary phosphine oxides[1] (I) have been reported in the literature. Early attempts to prepare them by careful hydrolysis of phosphinous chlorides,[2] esters,[3] or amides[4] showed that they disproportionated readily, even under the mildest conditions, into equal parts of phosphine (II) and phosphinic acid (III).[5] When atmospheric oxygen was not excluded, the phosphine was oxidized and the only product found was the phosphinic acid.

$$\underset{\text{I}}{2R_2P(O)H} \longrightarrow \underset{\text{II}}{R_2PH} + \underset{\text{III}}{R_2P(O)OH}$$

In only two instances were secondary phosphine oxides obtained which were apparently stable to air. They were obtained by hydrolysis of the corresponding phosphinous chlorides (V). The reaction of phosphorus trichloride with dimethylaniline[6] at reflux temperature gave, among other products, a small amount of bis(*p*-dimethylaminophenyl)-phosphine oxide (I, $R = Me_2NC_6H_4$-): and 9,10-dihydro-10-phenophosphazine oxide[7] was isolated from the products of the reaction of phosphorus trichloride and diphenylamine[8] in a sealed tube at 200°.

A synthesis of aliphatic secondary phosphine oxides by treatment of dibutyl phosphite with the appropriate Grignard reagent was described by Williams and Hamilton,[9] but their attempts to extend this reaction to the aromatic series were unsuccessful. The synthesis of aromatic secondary phosphine oxides was recently accomplished by treatment of diethyl phosphite with a Grignard reagent[10] or an aryllithium compound.[11] The three phosphine oxides obtained by these methods (I, $R = C_6H_5$-, *o*-$MeOC_6H_4$- and *p*-$MeOC_6H_4$-) were readily oxidizable by hydrogen peroxide.

In the present work a series of diarylphosphine oxides of high oxidative stability were prepared by a method based on the Friedel-Crafts synthesis of aromatic phosphonous dichlorides (IV).[12]

$$RH + PCl_3 \longrightarrow \underset{\text{IV}}{RPCl_2} + \underset{\text{V}}{R_2PCl}$$

When this synthesis was applied without modification to durene, none of the expected product (IV, $R = 2,3,5,6\text{-}Me_4C_6H$-) was found. From the gum which was coprecipitated with the $AlCl_3 \cdot$-$POCl_3$ complex there were isolated two crystalline compounds, one acidic and the other neutral, identified as bis(2,3,5,6-tetramethylphenyl)phosphinic acid (III, $R = 2,3,5,6\text{-}Me_4C_6H$-) and bis(2,3,5,6-tetramethylphenyl)phosphine oxide (I, $R = 2,3,5,6\text{-}Me_4C_6H$-), respectively. The acidic com-

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[1] In the report of the ACS Nomenclature Committee on organophosphorus compounds, *Chem. Eng. News*, **30**, 4515 (1952), these compounds were named phosphine oxides when written $R_2P(O)H$ and phosphinous acids when written R_2POH. In this article they have been named as P^{IV} compounds rather than P^{III}, in keeping with their chemical character.

[2] A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

[3] A. Michaelis and W. LaCoste, *Ber.*, **18**, 2109 (1885).

[4] A. Michaelis, *Ann.*, **315**, 43 (1901).

[5] The hydrolysis of di-*n*-octylphosphinous bromide and diphenylphosphinous chloride to the corresponding phosphine oxide without disproportionation was recently accomplished by R. C. Miller, private communication.

[6] R. K. Robins and B. E. Christensen, *J. Org. Chem.*, **16**, 324 (1951); see also M. Bourneuf, *Bull. soc. chim. France*, **33**, 1808 (1923); H. Raudnitz, *Ber.*, **60**, 743 (1927); G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

[7] This compound has also been called 10-hydroxy-5(or 9),10-dihydrophenophosphazine.

[8] P. G. Sergeev and D. G. Kudryashov, *J. Gen. Chem. (U.S.S.R.)*, **8**, 266 (1938); see also A. Michaelis and A. Schenk, *Ber.*, **21**, 1497 (1888); *Ann.*, **260**, 1 (1890).

[9] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952); **77**, 3411 (1955).

[10] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

[11] J. L. Willans, *Chem. & Ind. (London)*, **1957**, 235.

[12] B. Buchner and L. B. Lockhart, Jr., *Org. Syntheses*, **31**, 88 (1951); *J. Am. Chem. Soc.*, **73**, 755 (1951).

pound, obtained in much smaller amount, was considered to be a by-product of the hydrolysis of the intermediate phosphinous chloride to the phosphine oxide. Similar results were obtained when the phosphonous dichloride synthesis was applied to mesitylene or pentamethylbenzene.

Michaelis recognized many years ago that secondary organophosphorus compounds were sometimes produced in the Friedel-Crafts reaction of aromatic hydrocarbons with phosphorus trichloride. Diarylphosphinic acids were isolated from the petroleum ether–insoluble fractions of the reactions with ethylbenzene,[13] cumene,[14] and pseudocumene.[14] The yield from pseudocumene amounted to 20%. Since the experimental procedures have been considerably improved since Michaelis' time, particularly with respect to the removal of the aluminum chloride, it was of interest to see whether a secondary phosphine oxide could be isolated from one of these hydrocarbons, *e.g.*, ethylbenzene, with the aid of the newer techniques.[15]

When the phosphonous dichloride synthesis[12] was applied to ethylbenzene under the same conditions as for durene, the diaryl fraction isolated from the $AlCl_3 \cdot POCl_3$ complex was found to be completely alkali-soluble, and therefore contained no phosphine oxide.

The stability of the diarylphosphine oxides toward oxidizing agents increased markedly with increasing methyl substitution on the ring. The mesityl compound (I, $R = Me_3C_6H_2$-) was completely oxidized by alkaline ferricyanide in 30 min. at 80–90° and the duryl compound (I, $R = Me_4C_6H$-) in 2 hr., but the pentamethylphenyl compound (I, $R = Me_5C_6$) was only 14% oxidized in 17 hr.

The secondary phosphine oxides reported in the literature have sometimes been called phosphinous acids, and written with the phosphorus atom in the trivalent form. The chemical evidence accumulated in this article, including the very method of their isolation, supports the tetracovalent form for the phosphine oxides. Also, their infrared spectra (Table I) clearly show the presence of bands assigned[16] to P—H and to P→O and the absence of the P—OH band.

The phosphinic acid, bis(2,3,5,6-tetramethylphenyl)phosphinic acid, exhibited the same *P*→O doublet as the corresponding phosphine oxide, but the P—H band was replaced by the P—OH band.

TABLE I

INFRARED SPECTRA OF SECONDARY PHOSPHORUS COMPOUNDS

No.	R	P—H[a]	P → O[b]	P—OH[c]
I	$Me_3C_6H_2$-	2335	1175, 1189	—
I	Me_4C_6H-	2380	1160, 1190	—
I	Me_5C_6-	2340	1170	—
III	Me_4C_6H-	—	1160, 1175[d]	2500–2780

[a] Assigned[16] frequency, 2280–2440 cm.$^{-1}$ [b] 1200–1300 cm.$^{-1}$ [c] 2650–2700 cm.$^{-1}$ [d] This doublet was clearly resolved in a pressed potassium bromide disk spectrum.

EXPERIMENTAL

All of the reagents were the best commercially available and were used without further purification. The experiments were conducted in a well ventilated hood because of the possible toxicity of the phosphorus compounds, and where moisture-sensitive compounds were involved the operations were carried out as rapidly as possible. Melting points were not corrected. The infrared spectra were determined in Nujol mulls.

Phosphonous dichlorides, $RPCl_2$. The procedure described in *Organic Syntheses*[12] for the synthesis of phenylphosphonous dichloride from benzene was applied without modification to ethylbenzene, mesitylene, durene, and pentamethylbenzene. The aromatic hydrocarbon (0.3 mole) was mixed with 105 ml. (1.2 mole) of phosphorus trichloride and 53.3 g. (0.4 mole) of anhydrous aluminum chloride, and heated under reflux for 4 hr. with stirring and exclusion of moisture. The heat source was then removed and 37 ml. (0.4 mole) of phosphorus oxychloride was run in from a dropping funnel at a rate sufficiently rapid to maintain reflux. This caused the separation of a partly granular, partly gummy $AlCl_3 \cdot POCl_3$ complex. The mixture was heated another 30 min. to complete the reaction, allowed to cool, and diluted with 300 ml. of low boiling (30–60°) petroleum ether. The liquid was decanted through a sintered glass filter into a large round bottom flask under suction. The gummy $AlCl_3 \cdot POCl_3$ complex was washed twice with 100-ml. portions of petroleum ether and the washings added to the filtrate. These extractions were performed as rapidly as possible. The solids were saved for the isolation of the diaryl compounds, described below.

The low boiling liquids in the filtrate, mostly petroleum ether, phosphorus trichloride, and phosphorus oxychloride, were removed by distillation at atmospheric pressure. The phosphonous dichloride was then distilled through a 20 cm. Vigreux column under vacuum.

Ethylphenylphosphonous dichloride. Colorless liquid, 32.3 g. (52% yield), distilling at 70–82°/0.8 mm.

No phosphonous dichlorides were obtained under these conditions[17] from mesitylene, durene, or pentamethylbenzene. The recovery of unchanged hydrocarbon from mesitylene and pentamethylbenzene was 11.4 g. (32%) and 15.6 g. (35%), respectively, but from durene there was recovered only 5.7 g. of a low boiling liquid, b.p. 53°/5 mm., which did not crystallize when seeded with durene and was probably a mixture of isomerized hydrocarbons.[18]

Phosphinic acids, RPH(O)OH. Hydrolysis of 0.1 mole of the ethylphenylphosphonous dichloride with ethanol-water, carried out as described for phenylphosphonous dichloride,[19]

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[13] A. Michaelis, *Ann.*, **293**, 261 (1896).

[14] A. Michaelis, *Ann.*, **294**, 1 (1897).

[15] A method for the quantitative determination of the ratio of primary to secondary products in the phosphonous dichloride synthesis, developed by G. M. Kosolapoff and W. F. Huber, *J. Am. Chem. Soc.*, **69**, 2020 (1947), does not distinguish phosphine oxides from phosphinic acids.

[16] D. E. C. Corbridge, *J. Appl. Chem.* (*London*), **6**, 456 (1956).

[17] Using much longer reaction times (30–36 hr.) and different proportions of reagents, Michaelis[14] and W. C. Davies, *J. Chem. Soc.*, 462 (1935), have prepared mesitylphosphonous dichloride in 5 to 8% yield.

[18] Durene is known to isomerize under the influence of aluminum chloride; see D. Nightingale and F. Wadsworth, *J. Am. Chem. Soc.*, **63**, 3514 (1941).

[19] G. M. Kosolapoff and J. S. Powell, *J. Am. Chem. Soc.*, **72**, 4291 (1950).

gave an oily mixture of ethylphenylphosphinic acid isomers, from which the crystalline *p*- isomer was isolated by taking advantage of the insolubility of its sodium salt in acetone.[20]

p-Ethylphenylphosphinic acid. White crystals, 5.9 g. (35% yield), melting at 64-65.5°. The melting point was raised to 67–68° by recrystallization from benzene.[21] The acid formed a white crystalline sodium salt which was insoluble in acetone.

o- and m-Ethylphenylphosphinic acid. Colorless oil, 8.9 g. (52% yield). The sodium salt was also an oil and was soluble in acetone.

Phosphine oxides, $R_2P(O)H$. The diaryl compounds produced as by-products of the phosphonous dichloride synthesis described above were found to be coprecipitated with the granular $AlCl_3 \cdot POCl_3$ complex as gums. The smaller the amount of diaryl compounds produced, the more cleanly granular the complex. Whether the diaryl compounds, presumably in the form of phosphinous chlorides, were present in the free state (and simply insoluble in petroleum ether) or as $R_2PCl \cdot AlCl_3$ complexes was not determined. The phosphine oxides were isolated as follows.

The residue containing the $AlCl_3 \cdot POCl_3$ complex was decomposed cautiously by adding it in small portions to 1 l. of water in an open beaker. The reaction was vigorous and exothermic, and fumes of petroleum ether and hydrogen chloride were evolved. At the end of the addition a yellow gummy substance remained undissolved. The liquid was decanted, extracted with three 100-ml. portions of benzene and discarded. The gummy residue was rubbed with small portions of benzene until it dissolved. The benzene solutions and extracts were then combined, washed three times with water to remove most of the hydrogen chloride, extracted with dilute sodium hydroxide solution, again washed with water, filtered, and evaporated to dryness. The sodium hydroxide extracts were saved for the recovery of the diarylphosphinic acids.

Bis(2,4,6-trimethylphenyl)phosphine oxide. An almost colorless viscous oil, 25.5 g. (59% yield), soluble in benzene and ethanol but insoluble in water or sodium hydroxide solution.

Anal. Calcd. for $C_{18}H_{23}OP$: C, 75.50; H, 8.10; P, 10.82. Found: C, 74.83, 74.86; H, 7.87, 8.05; P, 10.53, 10.66.

Bis(2,3,5,6-tetramethylphenyl)phosphine oxide. A white crystalline solid, 20.1 g. (43% yield), soluble in benzene, ethanol, and chloroform, and insoluble in ethyl acetate, water, and sodium hydroxide solution. After two recrystallizations from benzene, the compound melted with decomposition at about 150°.

Anal. Calcd. for $C_{20}H_{27}OP$: C, 76.40; H, 8.66; P, 9.85. Found: C, 76.48, 76.19; H, 8.79, 8.34; P, 9.66, 9.60.

Bis(pentamethylphenyl)phosphine oxide. A white crystalline solid, 13.8 g. (27% yield). After two recrystallizations from benzene the compound melted with decomposition at 240°.

Anal. Calcd. for $C_{22}H_{31}OP$: C, 77.16; H, 9.12; P, 9.05. Found: C, 77.57, 77.32; H, 9.08, 9.27; P, 9.57, 9.34.

No phosphine oxide was obtained from ethylbenzene, as the diaryl fraction was completely soluble in alkali.

Phosphinic acids, $R_2P(O)OH$. The diarylphosphinic acids were isolated from the sodium hydroxide extracts (see above) by acidification with dilute hydrochloric acid and extraction with benzene.

Bis(ethylphenyl)phosphinic acid. A yellow gum, 15.0 g. (36% yield), probably a mixture of isomers. The acid formed a pale blue crystalline copper salt, as described by Michaelis.[13]

Bis(2,4,6-trimethylphenyl)phosphinic acid. A white crystalline solid, 2.4 g. (5% yield). After two recrystallizations from benzene the acid melted at 167–168°.

Anal. Calcd. for $C_{18}H_{23}O_2P$: C, 71.50; H, 7.67; P, 10.25. Found: C, 73.77; H, 8.00; P, 9.82.

Bis(2,3,5,6-tetramethylphenyl)phosphinic acid. A white crystalline solid, 2.0 g. (4% yield). After two recrystallizations from benzene the acid melted at 234–235°. It was soluble in hot benzene and hot ethanol, and insoluble in water.

Anal. Calcd. for $C_{20}H_{27}O_2P$: C, 72.70; H, 8.24; P, 9.38. Found: C, 72.71, 72.88; H, 8.41, 8.54; P, 9.38, 9.36.

In an earlier experiment the acid was prepared from the phosphine oxide by fractional crystallization from benzene, the acid being much the less soluble.

Bis(pentamethylphenyl)phosphinic acid. An amorphous substance, 2.3 g. (4% yield), which frothed when dried under reduced pressure.

Oxidation of the phosphine oxides. The oxidation of the phosphine oxides described above was desired to establish their relationship with the phosphinic acids. The initial experiments were performed on the duryl compound, bis(2,3,5,6-tetramethylphenyl)phosphine oxide.

An attempted oxidation with alkaline hydrogen peroxide according to a method used with other phosphine oxides[10,11] failed, the phosphine oxide being recovered unchanged in almost quantitative yield. Another attempt with alkaline permanganate also failed because the oxidant was too vigorous. Oxidation was finally found to proceed smoothly with alkaline ferricyanide. At room temperature, a 70% yield of bis(2,3,5,6-tetramethylphenyl)phosphinic acid was obtained after 27 hr. and 26% of the phosphine oxide was recovered. At 80–90° the oxidation was complete in 2 hr. Details of the experimental procedure follow.

The diarylphosphine oxide (1 mmole) was slurried with a solution of 0.40 g. of sodium hydroxide and 0.66 g. (2 mmoles) of potassium ferricyanide in 50 ml. of water. The mixture was heated with stirring to 80–90° and held at that temperature until the phosphine oxide was all dissolved. The solution was then cooled, filtered to remove a small amount of rust-colored solid, acidified with hydrochloric acid, and extracted three times with benzene. The benzene extracts were combined, extracted twice with water, filtered, and evaporated to dryness.

The mesityl compound required 30 min. for complete oxidation, the duryl compound 2 hr., but the pentamethylphenyl compound was only 14% oxidized in 14 hr. The products in each case were identical to the acids isolated as by-products of the Friedel-Crafts reactions.

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(20) An approximate measure of the ratio of isomers in the ethylbenzene reaction was also reported by G. M. Kosolapoff, *J. Am. Chem. Soc.*, **74**, 4119 (1952), using another method.

(21) Michaelis[13] gives m.p. 63–64°.