dispersion in water until the filtrate was no longer turbid when acidified, and dried to obtain 9.0 g. (96.8%), m.p. 87–98°. Acidification of the first filtrate gave 5.7 g. of recovered thiol, m.p. 75–82°.

Two recrystallizations from heptane[9] gave 7.4 g. (80%), m.p. 100–103°. The pure 2-(2-naphthylmercapto)-2-phenylethanol (I) melted at 102–103°, from dilute ethanol.

*Anal.* Calcd. for $C_{18}H_{16}OS$: C, 77.11; H, 5.75. Found: C, 77.29; H, 6.04.

*p-Nitrobenzoate* was prepared as cream colored leaves from dilute ethanol, m.p. 106–108°.

*Anal.* Calcd. for $C_{25}H_{19}NO_4S$: C, 69.90; H, 4.46. Found: C, 70.17; H, 4.60.

*Synthesis of α-(2-naphthylmercapto)phenylacetic acid. From 2-naphthalenethiol and mandelic acid.* A mixture of 2-naphthalenethiol (8.0 g., 0.05 mole) and mandelic acid (6.1 g., 0.04 mole) was heated in a large test tube under nitrogen at an oil bath temperature of 190–195° for one hour.[10] The warm, amber colored reaction mixture, still liquid, was transferred by means of ethanol (100 ml.) to a beaker, and the resulting slurry warmed with 8 g. sodium bicarbonate in 250 ml. water to form the sodium salt. Some insoluble dinaphthyl disulfide was filtered off. Air was then bubbled through the aqueous filtrate at about 40° for 4 hr. to oxidize unreacted thiol to disulfide, finally giving 2.4 g. of the recrystallized disulfide, m.p. 137–139°, reported[11] m.p. 139°. Acidification of the aqueous mixture with concentrated hydrochloric acid produced 7.35 g. solid which, after three recrystallizations from dilute acetic acid (carbon black), gave 5.4 g. (45.9%), m.p. 169–171°. The analytical sample, from dilute ethanol, melted at 171–172°.

*Anal.* Calcd. for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79. Found: C, 73.52; H, 4.97.

*Anilide* was prepared by heating the acid with aniline at 150–170° under nitrogen for 2 hr. and found to melt at 173.5–174.5°, fine white needles from dilute ethanol.

*Anal.* Calcd. for $C_{24}H_{19}NOS$: C, 78.03; H, 5.18. Found: C, 78.09; H, 5.52.

*p-Bromoanilide*, similarly prepared, was a better derivative since its melting point was 188–189°, white needles from dilute ethanol.

*Anal.* Calcd. for $C_{24}H_{18}BrNOS$: C, 64.28; H, 4.05. Found: C, 64.43; H, 4.32.

*From 2-naphthalenethiol and ethyl α-bromophenylacetate.* Ethyl α-bromophenylacetate (6.1 g., 0.025 mole, $n_D^{20}$ 1.5385) was added slowly to a stirred mixture of 2-naphthalenethiol (4.0 g., 0.025 mole) in sodium hydroxide (2.0 g., 0.05 mole) dissolved in water (50 ml.) under nitrogen. A precipitate began to appear after 20 min. at room temperature. At the end of 2 hr. the reaction mixture was transferred to a boiling flask containing 10 g. sodium hydroxide in water. The total volume was finally 200 ml. This was refluxed 2 hr. to produce a clear solution. The warm solution was treated with carbon black, being careful to keep the solution warm enough to prevent the crystallization of the sodium salt. Acidification of the filtrate with concentrated hydrochloric acid and recrystallization of the resulting solid from dilute acetic acid gave 6.6 g. (90.4%) fine, white needles, m.p. 169–172°. A mixed melting point of this acid and that prepared by the alternate method showed no depression.

*Reduction of α-(2-naphthylmercapto)phenylacetic acid to* I. Tetrahydrofuran was preferred to ether as the solvent because the acid was insoluble in ether. The α-(2-naphthylmercapto)phenylacetic acid (4.4 g., 0.015 mole, m.p. 169–117°) in tetrahydrofuran (30 ml.) was added to lithium aluminum hydride (1.0 g., 0.026 mole) in tetrahydrofuran (25 ml.) over a 15-min. period. After an additional 30 min. the mixture was treated with 10 ml. concentrated hydrochloric acid in 40 ml. water. The organic layer was taken up in ether and washed with 4% aqueous sodium hydroxide to remove some acid that was not reduced. After the ether solution was dried over anhydrous potassium carbonate and the solvent removed, the product was recrystallized from heptane[9] (carbon black) to yield 3.1 g. (73.8%), m.p. 100–103°. A mixture melting point with pure 2-(2-naphthylmercapto)-2-phenylethanol (I) from the reaction of styrene oxide with 2-naphthalenethiol was 101–103°.

*Synthesis of 2-(2-naphthylmercapto)-1-phenylethanol.* The preparation of α-(2-naphthylmercapto)acetophenone from phenacyl chloride and 2-naphthalenethiol followed the procedure of Long.[12] A nearly theoretical yield was obtained, m.p. 97–98°, white needles from ethanol.

*Anal.* Calcd. for $C_{18}H_{14}OS$: C, 77.66; H, 5.07. Found: C, 77.41; H, 5.41.

The *2,4-dinitrophenylhydrazone* melted at 209–210°, reddish orange needles from ethyl acetate–benzene.

*Anal.* Calcd. for $C_{24}H_{18}N_4O_4S$: C, 62.87; H, 3.96. Found: C, 63.03; H, 4.21.

Reduction of this ketone with excess lithium aluminum hydride by the conventional procedure provided an oil that soon solidified to a solid, m.p. 57–60° in quantitative yield. Recrystallization from a mixture of heptane[9] and benzene gave fine, white needles, m.p. 59–60°.

*Anal.* Calcd. for $C_{18}H_{16}OS$: C, 77.11; H, 5.75. Found: C, 77.16; H, 6.11.

The *p-nitrobenzoate* of this alcohol melted at 114–115°, yellow, from dilute ethanol.

*Anal.* Calcd. for $C_{25}H_{19}NO_4S$: C, 69.90; H, 4.46. Found: C, 69.80; H, 4.81.

*Acknowledgment.* The authors are grateful to the Research Corp. for a Frederick Gardner Cottrell grant in support of this work.

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[9] Eastman Organic Chemicals, P 2215.

[10] B. I. Arventi and M. Robu-Burnuz, *Ann. sci. univ. Jassy*, 26, 602 (1940).

[11] K. Fries and G. Schurmann, *Ber.*, **47**, 1195 (1914).

[12] L. M. Long, *J. Am. Chem. Soc.*, 68, 2159 (1946).

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## Reaction of Phenols with Phosphorus Pentachloride[1]

A. G. PINKUS AND P. G. WALDREP

*Received January 6, 1959*

Although the reaction of alcohols with phosphorus pentachloride is a standard method for the preparation of alkyl chlorides, little is known concerning the mechanism.[2] Gerrard and Phillips have postulated the formation of $ROPCl_4$ as an intermediate in this reaction.[3] This intermediate can be used to explain the formation of the alkyl chloride and phosphorus-containing by-products which are also obtained.[3] Although such alkoxyphosphorus tetrachlorides have never been isolated to our

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[1] Presented at the Southwest Regional Meeting of the American Chemical Society, San Antonio, Tex., Dec. 4–6, 1958.

[2] For a comprehensive review of earlier work and further work on the mechanism, see W. Gerrard, *J. Chem. Soc.*, 741 (1946).

[3] W. Gerrard and R. J. Phillips, *Chem. & Ind. (London)*, 540 (1952).

knowledge, it is of interest that analogous aryloxy compounds from the reaction of phenols with phosphorus pentachloride have been obtained.[4] Aryloxyphosphorus tetrachlorides[5] can also be prepared by the reaction of aryloxyphosphorus dichlorides with chlorine.[4,6]

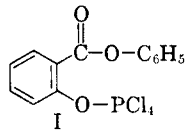
$$ArOH + PCl_5 \xrightarrow{-HCl} ArOPCl_4 \longleftarrow ArOPCl_2 + Cl_2$$

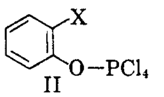
It is of considerable mechanistic interest that aryloxyphosphorus tetrachlorides decompose on heating to aryl chlorides and phosphorus oxychloride.[7,8]

$$ArOPCl_4 \longrightarrow ArCl + POCl_3$$

A thorough study of this decomposition would be of interest not only from the standpoint of mechanism, but also since this reaction furnishes a means for converting phenols into aryl chlorides.[9] The main drawback to such a study is the reported[4,6] instability of aryloxyphosphorus tetrachlorides with respect to moisture.

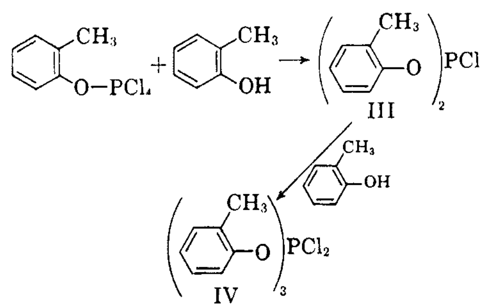
In this connection, the related product (I)[10] from the reaction of phenyl salicylate and phosphorus pentachloride was of interest since it was reported[8] to be quite stable. Thus, it was the initial object of the present investigation to prepare other *ortho*-substituted compounds of this type (II) in the expectation of obtaining a series of stable compounds suitable for use in the studies outlined above.


I


II

## RESULTS

*ortho-Substituted phenols.* When X was the aldehyde $(\overset{\overset{O}{\|}}{—CH})$ group, the product of the reaction was unstable to both moisture and oxygen since it hydrolyzed easily and turned a dark blood-red color on standing.[11] When X was phenyl or methyl, the product hydrolyzed rapidly in contact with air. With *ortho*-cresol, further reactions were carried out to determine whether more highly substituted compounds (III and IV) might be more stable; however, these compounds were also unstable to atmospheric moisture.



The stoichiometry of the reaction with *ortho*-nitrophenol[12] was more complicated than a simple 1:1 reaction. When the reaction mixture was hydrolyzed, a mixture of products was obtained instead of the *ortho*-nitrophenyl phosphate (V) expected. From this mixture, it was possible to isolate the trisubstituted phosphate:tris(*ortho*-nitrophenyl)phosphate (VI). It would be expected that the mono- and disubstituted phosphates (V and VII) would also be present. Recrystallization of the crude product into pure compounds was not accomplished because of the unusual solubility characteristics of these compounds. In view of the experimental conditions used in carrying out the reactions (see experimental part) in which the formation of polysubstituted products was minimized by keeping phosphorus pentachloride in excess during the reaction, these results were somewhat surprising. Kosolapoff suggests[7] that disproportionation can take place during hydrolysis. Another possibility is the further reaction of ArOPCl$_4$ with the phenol to produce products which on hydrolysis would yield the corresponding mono- and diaryloxyphosphates (as outlined below). Because of the experimental procedure used in the present work, however, such reactions could only take place if the chlorines in ArOPCl$_4$ were more reactive than those in phosphorus pentachloride. The latter explanation seems plausible since the tris-compound was obtained *before* the hydrolysis was carried out (see experimental part). Furthermore, the latter explanation is substantiated by the work of Rydon and Tonge[4c] on disproportionation reactions of aryloxyphosphorus halides.

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(4) A summary of earlier work can be found in the following references: (a) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1950, p. 325; (b) D. G. Coe, S. R. Landauer, and H. N. Rydon, *J. Chem. Soc.*, 2281 (1954); (c) H. N. Rydon and B. L. Tonge, *J. Chem. Soc.*, 3043 (1956).

(5) In view of recent work showing (on the basis of conductivity studies) that various aryloxyphosphorus halides are dimeric [G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 3038 (1956) and ref. (4) (c)], it is probable that aryloxyphosphorus tetrahalides are also dimeric.

(6) R. Anschütz and W. D. Emery, *Ann.*, **239**, 301 (1887); R. Anschütz and C. D. Moore, *Ann.*, **239**, 314 (1887); L. Anschütz, F. Koenig, and H. Walbrecht, *Ann.*, **525**, 297 (1936).

(7) Ref. (4) (a), p. 328.

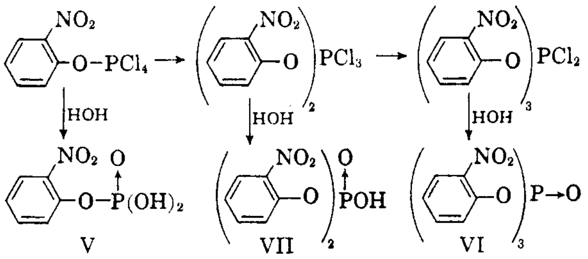
(8) A. Michaelis and W. Kerkhof, *Ber.*, **31**, 2172 (1898).

(9) After the work reported in this paper was complete, a method for accomplishing this in good yields by the thermal decomposition of tetraaryloxyphosphorus monohalides was reported: D. G. Coe, H. N. Rydon, and B. L. Tonge, *J. Chem. Soc.*, 323 (1957).

(10) See, however, A. G. Pinkus, P. G. Waldrep, and P. H. Ko, Abstracts, 134th meeting of the American Chemical Society, Chicago, Ill., Sept. 8–12, 1958.

(11) The authors wish to acknowledge the aid of Mr. Jack Goodwyn in carrying out this experiment.

(12) The authors acknowledge the aid of Mr. Luis Ramos in this experiment.



*Di-ortho-substituted phenols.* In view of the instability to moisture of the *ortho*-substituted phenols discussed above, it seemed that perhaps the more hindered 2,6-disubstituted phenols might form more stable compounds. One of the most hindered compounds of this type, 2,6-di-*tert*-butyl-*p*-cresol, was studied because of its ready availability.[13] However, even under vigorous reflux conditions in benzene or carbon tetrachloride, no reaction appeared to take place.

As further examples of di-*ortho*-substituted types, the reactions of 2,4,6-trihalophenols with phosphorus pentachloride were investigated. The trichlorophenol reacted at room temperature whereas the tribromo- and triiodophenols required heat. The products of these reactions appeared to be somewhat more stable to atmospheric moisture than the mono-*ortho*-substituted compounds previously investigated; however, the stability was not outstanding.

At the present time, in view of the more interesting results obtained in related work,[10] we do not contemplate any further work along the lines discussed in this paper.

## EXPERIMENTAL

*Reaction of phenols with phosphorus pentachlorides.* The general procedure used in all of the reactions is described. In order to minimize polysubstitution of phosphorus pentachloride and to favor the formation of the monosubstituted compound, the reactions were run in such a way as to keep the concentration of the phenol at a minimum at all times, and to keep phosphorus pentachloride in excess during the reaction. This was done by adding the phenol dropwise to the phosphorus pentachloride.

A solution of 0.100 mole of the phenol dissolved in approximately[14] 50 ml. of purified ACS grade benzene was added dropwise by means of a dropping funnel to a stirred suspension of 0.100 mole of phosphorus pentachloride in approximately 50 ml. of benzene in a three-neck flask. The flask was equipped with a condenser which was attached to a calcium chloride drying tube which led in turn to a safety bottle and then to a solution of sodium hydroxide for absorption of hydrogen chloride. By the completion of the addition, the phosphorus pentachloride had reacted and gone into solution. The reaction mixture was allowed to stir for about 1-3 hr. after the completion of addition. The benzene solution was then transferred to a one-neck flask and the solvent removed *in vacuo* to obtain the crude product.

Since the present investigation was an exploratory study, no elaborate precautions were taken to exclude atmospheric moisture in the handling of the compounds. Thus, the results are of a qualitative nature. Since the compounds prepared were very hygroscopic—some liquefying almost immediately on contact with atmospheric moisture—the melting points and analyses are not reported because of the questionable purity of the compounds. In order to obtain pure compounds for reliable melting points and analyses, rigorous dry box techniques are recommended.

With the exception of the compound obtained from salicylaldehyde, which was an oily liquid, all of the other compounds were white solids.

*Reaction of ortho-nitrophenol.* The reaction was carried out according to the general procedure above. After standing for several days, a solid deposited from the benzene solution (before removal of solvent). The benzene solution was decanted and the solid collected, tris(*ortho*-nitrophenyl)-phosphate (VI) and weighed 2.0 g. after drying. The melting point, after recrystallization from purified isopropyl alcohol, was 126.4–128.0° (total immersion thermometer) (lit.[15] 126°). The benzene solution from the decantation, was evaporated *in vacuo* leaving a solid mass weighing 13.4 g. The solid was unstable to moisture. It was hydrolyzed by adding ice. A vigorous reaction took place with evolution of hydrogen chloride and formation of a brown oil which solidified on standing for about 2 hr. The solid was collected by filtration and washed with water. The wash water appeared to hydrolyze and dissolve the solid on the Büchner funnel, since after drying over calcium chloride only 1.2 g. of the solid remained. A comparison of the ultraviolet spectrum of the yellow filtrate with that of an aqueous solution of *ortho*-nitrophenol confirmed the presence of this compound in the filtrate. Thus it would appear that the solid which is probably the mono- and diphosphate esters, is readily hydrolyzed by water into *ortho*-nitrophenol and phosphoric acid. The molybdate test for phosphate showed its presence in the filtrate. The solid from the hydrolysis melted 164.5–166.0°. Attempts made to recrystallize the compound were unsuccessful since the compound was either too soluble or too insoluble in the many solvents tried. No combination of mixed solvents was found to be satisfactory. The compound decomposed into *ortho*-nitrophenol during an attempted sublimation under reduced pressure. Chromatography over silica gel was unsuccessful.

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[13] The authors express thanks to Shell Chemical Corp. and to Koppers Co., Inc. for samples of this compound.

[14] If necessary to dissolve the phenol completely, larger volumes of benzene were occasionally used.

[15] A. Engelhardt and P. Latschinow, *J. Russ. Phys. Chem. Soc.*, **2**, 116; *Z. für Chemie*, **1870**, 230; (*Beilsteins Handbuch der Organischen Chemie, Band*, **6**, vierte auflage, Verlag von Julius Springer, Berlin, 1923, p. 222) prepared this compound by heating *ortho*-nitrophenol and phosphorus pentachloride and treating the reaction product with water.

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# Infrared Spectra of Acid Azides[1]

EUGENE LIEBER[2] AND EDWIN OFTEDAHL

*Received January 6, 1959*

Recent investigations[3,4] have demonstrated that reactions which theoretically should lead to thiocar-