[CONTRIBUTION FROM THE RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Phosphonation of Aromatic Compounds with Phosphorus Pentasulfide

BY H. Z. LECHER,[1] R. A. GREENWOOD, K. C. WHITEHOUSE AND T. H. CHAO

RECEIVED JANUARY 24, 1956

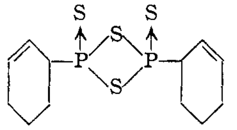
Phosphorus pentasulfide reacts with benzene, *o*-xylene, anisole, phenetole, naphthalene and 2-isopropylnaphthalene in specific temperature ranges with formation of dimeric arylthionophosphine sulfides $(ArPS_2)_2$. Reactions and some peculiar properties of this new type of aromatic phosphorus compounds are discussed. Hydrolysis gives phosphonic acids; chlorination, arylphosphonothioic dichlorides, $ArP(:S)Cl_2$, or aryltetrachlorophosphoranes, $ArPCl_4$.

In a preceding paper[2] the phosphonation of aromatic compounds with hexagonal phosphoric anhydride, P_4O_{10}, has been described and discussed. This reaction proceeds at high temperature (about 275 to 325°). One or two covalent P–O bonds are opened, the aryl group attaching itself to P, the hydrogen to O.

Since "phosphorus pentasulfide" (tetraphosphorus decasulfide), P_4S_{10}, has a structure analogous to that of P_4O_{10}, it seemed a natural sequel to our former work to investigate its behavior toward aromatic compounds at elevated temperatures. Obviously the aromatic compounds had to be free of polar substituents that would react with phosphorus pentasulfide.

While the phosphonation with phosphoric anhydride had been novel, reactions of aromatic compounds with the pentasulfide are not new. An extensive patent literature[3] describes reactions with hydrocarbons under a variety of conditions. The products obtained have been subjected to many empirical transmutations to make them suitable as additives to lubricating oils.[3] Notwithstanding their practical value, these patents have in no way elucidated the reactions nor described any well-characterized reaction product.

The only reliable scientific information about a reaction of phosphorus pentasulfide with a hydrocarbon was published when our work on the phosphonation of aromatic compounds was well under way. Fay and Lankelma[4] refluxed a large excess of cyclohexene with phosphorus pentasulfide and obtained in a very slow reaction Δ^2-cyclohexenylthionophosphine sulfide which they formulated as



since a molecular weight determination indicated a dimer.

In this investigation of reactions of aromatic compounds with P_4S_{10} we found, in the first place, that each compound has its own quite narrow optimum temperature range; at lower temperatures no reaction takes place and at higher temperatures resins are formed. It is important to work at the lowest feasible temperature. The reaction with P_4S_{10} occurs always at a temperature lower than that required for the reaction with P_4O_{10}.

In the second place we found, first in an empirical way, that a considerable excess of the aromatic compound is important in order to minimize undesirable side reactions.

At the beginning of this work we encountered difficulties in isolating pure reaction products of benzene and naphthalene. However, the investigation of the phosphonation of anisole clarified the picture and, therefore, shall be discussed first.

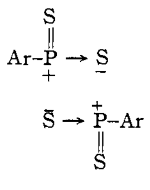
I. The Reaction with Anisole and Phenetole.—The reaction of anisole with phosphorus pentasulfide is a particularly smooth one. When the sulfide is heated with an excess of anisole at reflux temperature, *p*-anisylthionophosphine sulfide (I) is obtained in about 80% yield according to the equation

$$4\ CH_3O{\cdot}C_6H_5 + P_4S_{10} = 2\ \underset{\text{I}}{(CH_3O{\cdot}C_6H_4{\cdot}PS_2)_2} + 2H_2S$$

The sulfide I gives on long boiling with water an almost quantitative yield of *p*-anisylphosphonic acid[5]

$$(CH_3O{\cdot}C_6H_4{\cdot}PS_2)_2 + 6\ H_2O = 2\ CH_3O{\cdot}C_6H_4{\cdot}PO_3H_2 + 4\ H_2S$$

Cryoscopic molecular weight determinations in naphthalene or *p*-chloronitrobenzene indicated a dimer, supporting Fay and Lankelma's findings[4] for the cyclohexenyl compound. A four-membered covalent ring, however, would be unique among phosphorus compounds. Thus dimetaphosphoric acid or dimetaphosphates do not exist[6] nor does dimeric phosphonitridic dichloride. It seems more probable that the electrostatic attraction between semi-polar P→S bonds causes a bimolecular association in solution[7]



Also, the very low solubility of arylthionophosphine sulfides in organic solvents at room temperature suggests their polar nature.

It was observed that the freezing point of solutions in molten naphthalene or *p*-chloronitrobenzene rose when such solutions were kept at about 80°, *i.e.*, a gradual further polymerization of the

---

[1] 1049 Kenyon Avenue, Plainfield, N. J.

[2] H. Z. Lecher, T. H. Chao, K. C. Whitehouse and R. A. Greenwood, THIS JOURNAL, **76**, 1045 (1954).

[3] G. G. Pritzker, *Nat. Petroleum News*, **37R**, 1001 (1945); this survey quotes 114 U. S. Patents.

[4] P. Fay and H. P. Lankelma, THIS JOURNAL, **74**, 4933 (1952).

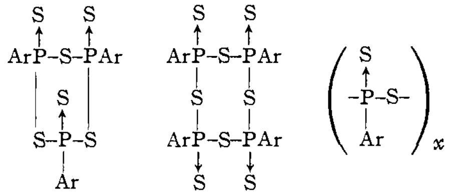
[5] A. Michaelis, *Ann.*, **293**, 251 (1896).

[6] J. P. Ebel, *Bull. soc. chim. France*, [5] **20**, 1091 (1953).

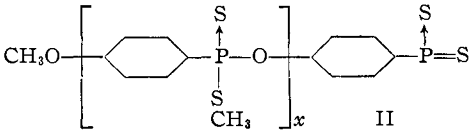
[7] Very probably certain arylimides of phosphorus associate in a similar manner. A. Michaelis, *Ann.*, **407**, 290 (1915), observed that several arylimides of phosphorous, phosphoric, phosphonothionic and arylphosphonic acids are dimeric in solution and postulated a four-membered ring structure. However, Michaelis' reactions, supporting this view, can be explained easily by a different mechanism.

dimer was taking place. Such polymerization is easily accomplished by heating this sulfide for a few hours above its melting point (228–229.5°). A transparent brittle resin results which is very soluble in organic solvents, in contrast to the polar, sparingly soluble dimer.

It is probable that the polymerization proceeds on two routes, one involving only the PS_2 groups, the other also the CH_3O groups. The first route leads probably to the more stable six- and eight-membered rings and possibly higher polymers[8] and



the second to polyesters of the type II.


II

Such reactions take place during the preparation of the *p*-anisylthionophosphine sulfide from anisole and P_4S_{10} and are partly responsible for the (about 20%) yield loss in the anisole mother liquor. The presence of compounds of type II is indicated by the formation of methylmercaptan in the hydrolysis of such mother liquors. Some attack of phosphorus pentasulfide or of the thionophosphine sulfide on the methoxy groups of anisole itself is also possible.

The lower phosphorus sulfides P_4S_3 and P_4S_7 do not react with boiling anisole, unless sulfur is present to convert them into P_4S_{10}.

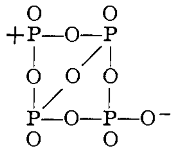
Phenetole behaves like anisole, but gives somewhat lower yields.

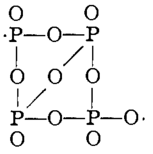
II. The Reactions with Aromatic Hydrocarbons.—The behavior of P_4S_{10} differs from that of P_4O_{10}. With the latter only the phosphorus, never the oxygen, becomes attached to the nucleus. With P_4S_{10} the phosphonation is still the main reaction, but some thionation of the nucleus also takes place; it is negligible with anisole but quite conspicuous with benzene and naphthalene. Simultaneously the pentasulfide is reduced to lower phosphorus sulfides. Since these lower sulfides do not react with the aromatic hydrocarbon and are sparingly soluble, they contaminate the equally insoluble thionophosphine sulfides.

The phosphonation of *naphthalene* with phosphorus pentasulfide proceeds best in a temperature range of 160 to 190°. The phosphorus enters the β-position and hydrolysis of the thionophosphine sulfide gives 2-naphthylphosphonic acid. Though this reaction is by far not as smooth as the one with anisole and gives annoying by-products, it is better suited for the preparation of the phosphonic acid than our phosphorus pentoxide method.[2] Large amounts of this acid have been prepared and a suitable process is described in the Experimental part.

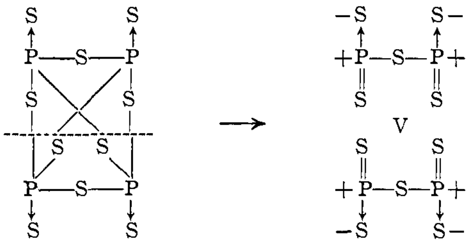
When a molecular ratio of 10 $C_{10}H_8$: 1 P_4S_{10} is used, the 2-naphthylthionophosphine sulfide is contaminated by a lower phosphorus sulfide. However, with a ratio 50:1 the pure thionophosphine sulfide is obtainable. This large excess of naphthalene does not act as a solvent for by-products; these additional 40 moles are of no help when added after the reaction in the ratio 10:1 has been finished. A reasonably pure 2-naphthylthionophosphine sulfide can be obtained with a ratio 10:1 if sulfur is present (which converts the lower phosphorus sulfides to P_4S_{10}).

The remarkable effect of the dilution with naphthalene requires some discussion, since it indicates a dissociation of P_4S_{10}. As stated in our preceding paper,[2] the reaction of hexagonal P_4O_{10} with aromatic compounds starts at a temperature at which the conversion of the former into orthorhombic macromolecules progresses at a reasonable rate. This conversion must start with the breaking of one of the covalent P–O bonds, which probably results in a hybrid ion III, less probably in a biradical IV. Then the cationic end of the former electrophilically substitutes the nucleus.


III


IV

Since sulfur is less electronegative than oxygen, P_4S_{10} might have a greater tendency to form a biradical of the type IV (substitute S for O). It would be this biradical which causes the thionation. A dissociation of P_4S_{10} into smaller particles, as indicated by the dilution effect, cannot produce biradicals, but would produce P_2S_5 with semi-polar $P\rightarrow S$ bonds (V); hence the electrophilic phosphonation would be favored and the thionation suppressed.



The reaction of *benzene* with phosphorus pentasulfide requires a temperature of about 225°. The phenylthionophosphine sulfide, $(C_6H_5PS_2)_2$, has been obtained, mixed with some P_4S_7. Taking this admixture into account, the determination of the molecular weight again indicated a dimer. The Experimental part describes also the phosphonation of *o-xylene* and of *2-isopropylnaphthalene* with phosphorus pentasulfide.

III. Chlorination of Arylthionophosphine Sulfides.—The sulfur in the arylthionophosphine sulfides is easily replaced by chlorine. Depending upon the amount and kind of chlorinating agent and

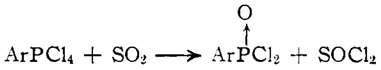
---

[8] The recently described C_6H_5PSO is trimeric, but forms also higher polymers; L. Anschütz and H. Wirth, *Naturwissenschaften*, **43**, 16 (1956).

other conditions, one or both sulfur atoms are replaced

$$\underset{}{(ArPS_2)_2} \longrightarrow \underset{VI}{2ArPSCl_2} \longrightarrow \underset{VII}{2ArPCl_4}$$

The arylphosphonothioic dichlorides VI starting materials for arylphosphonothionic esters, have so far been prepared from aryldichlorophosphines,[9] which in turn were obtained in a Friedel–Crafts reaction with phosphorus trichloride. The aryltetrachlorophosphoranes VII have been prepared in the past by chlorination of the aryldichlorophosphines.[10] They give on hydrolysis the phosphonic acids (which, of course, are more easily prepared by direct hydrolysis of the thionophosphine sulfides) and can be easily converted into the arylphosphonic dichlorides VIII, preferably by reaction with sulfur dioxide[11]



$$ArPCl_4 + SO_2 \longrightarrow Ar\overset{\overset{O}{\uparrow}}{P}Cl_2 + SOCl_2$$

VIII

We have used as chlorinating agents elemental chlorine, sulfuryl chloride, sulfur mono- and dichlorides, and phosphorus pentachloride. With the exception of sulfur monochloride, these agents can perform both steps. Sulfur monochloride, however, is unable, even at its boiling point, to replace the second sulfur atom by chlorine.

Acknowledgment.—We are indebted to Miss Z. F. Smith for the determinations of molecular weights; to Messrs. O. E. Sundberg and S. G. Redshaw and their associates for the analyses.

Experimental

Phosphorus Pentasulfide.—In some experiments we used a product obtained from Oldbury Electro-Chemical Co., m.p. 276–278° (softening at 269°). In other experiments we used a product from Victor Chemical Works. No difference in behavior or yield was observed.

Reaction of Anisole with Phosphorus Pentasulfide.—A mixture of 108 g. (1 mole) of anisole and 44.4 g. (0.1 mole) of P_4S_{10} was agitated and heated to reflux. Moisture was strictly excluded. When the temperature reached 145°, evolution of hydrogen sulfide began. The temperature gradually climbed to 150° where it remained for 1.5 hours; during this period the phosphorus pentasulfide completely disappeared and a clear light orange solution was formed. Shortly afterward a light yellow precipitate (*p*-anisylthiono phosphine sulfide) started to form. The temperature rose finally to 155–160°. After about 6 hours total refluxing time, the evolution of hydrogen sulfide had substantially ceased. On cooling, the bulk of the thionophosphine sulfide crystallized. The yield of solvent-free product was about 80% of theory.

p-Anisylthionophosphine sulfide is not indefinitely stable in boiling anisole but undergoes polymerization and other changes; see below. After 20.2 g. was refluxed with 100 cc. of anisole for 48 hours, on cooling only 11.8 g. was recovered. It follows that the heating should not be continued after the H_2S evolution has ceased; otherwise the yield drops considerably.

***p*-Anisylthionophosphine Sulfide.**—When this product was washed with anisole, the solvent could not be completely removed by drying *in vacuo* over paraffin and phosphoric anhydride. A sample dried in this manner loses considerable amounts of anisole when heated to about 230°. Also, when the product was washed with benzene, the solvent—in this case benzene—could not be completely removed at room temperature; it was necessary to dry *in vacuo* at elevated temperature.

It seems that *p*-anisylthionophosphine sulfide forms clathrates with certain solvents. A sample recrystallized from *o*-dichlorobenzene, washed with benzene and dried *in vacuo* at 150° was analyzed.

Anal. Calcd. for $(C_7H_7OPS_2)_2$: C, 41.58; H, 3.46; P, 15.35; S, 31.68. Found: C, 41.8, 41.6; H, 3.81, 3.81; P, 15.9, 15.7; S, 30.3.

The compound was extremely sensitive to moisture, which factor accounts for the low sulfur value (loss of H_2S). The purest sample showed a m.p. of 228–229.5°.

For the determination of the molecular weight freshly prepared, solvent-free *p*-anisylthionophosphine sulfide was used. Moisture was carefully excluded. Cryoscopic determinations were made in *p*-chloronitrobenzene and in naphthalene. It was observed that the indicated molecular weight slowly increased at the fusion temperature of the solvent, particularly in naphthalene.

Anal. Calcd. for $(C_7H_7OPS_2)_2$: mol. wt., 404. Found: (A) in *p*-chloronitrobenzene, concn. 1.6%, first reading 423, second reading 469; concn. 1.1%, first reading 415, second reading 467. (B) in *p*-chloronitrobenzene, concn. 2%, first reading 436, after 2.75 hours 453, after 3 hours 458, after 4.5 hours 495–548. B in naphthalene, concn. 1.4% first reading 491, after 3 hours 734, after 5 hours 985.

These determinations show that *p*-anisylthionophosphine sulfide is a dimer and that it polymerizes slowly in solution at about 80–85°, more rapidly in a non-polar than in a polar solvent.

***p*-Anisylphosphonic Acid.**—Though the *p*-anisylthionophosphine sulfide decomposes in humid air with evolution of hydrogen sulfide, its complete hydrolysis to the phosphonic acid required long boiling with water, preferably in the presence of a wetting agent. After 18 hours of refluxing with 10 parts of water, a clear solution was formed. On cooling, the phosphonic acid crystallized and a second crop was obtained by concentrating the mother liquor; yield nearly quantitative, m.p. 179–179.5°.[12]

Polymerization of *p*-Anisylthionophosphine Sulfide.—A sample was heated in an atmosphere of dry nitrogen at 200–213° for 5 hours, then chilled in a bath of Dry Ice and acetone. The polymer thus obtained was a transparent brittle resin, very soluble in organic solvents, in contrast to the sparingly soluble dimer.

Anal. Calcd. for $(C_7H_7OPS_2)_x$: C, 41.58; H, 3.46; P, 15.35; S, 31.68. Found: C, 39.7, 39.7; H, 3.25, 3.45; P, 14.5, 14.9; S, 29.8, 29.8.

Hydrolysis of this polymer with boiling water gave a poor yield of impure *p*-anisylphosphonic acid; methyl mercaptan was formed; no phenol could be detected. A water-insoluble, alkali-soluble oil was also formed but could not be purified and identified.

Another polymerization was carried out at 245–250° for 4 hours and the melt was poured into a steel vessel chilled with Dry Ice. The molecular weight of the sample was determined by the cryoscopic method in *p*-chloronitrobenzene. At concentrations of 2.7, 3.75, 4.2%, average molecular weights of 658, 677, 676, respectively, were found. There was no trend to further polymerization on repeated readings, as was observed with the dimeric thionophosphine sulfide.

Elsewhere we have described the preparation of *p*-anisylthionophosphine sulfide by heating anisole and phosphorus pentasulfide at about 150° for approximately 6 hours. In this process some polymerization must occur and obviously the polymer would be in the mother liquor of the rather insoluble thionophosphine sulfide. A considerable amount of accumulated mother liquor was freed from anisole and the sticky residue was refluxed with water. A small amount of methyl mercaptan was formed and identified as mercury salt and as 2,4-dinitrophenyl derivative. Some *p*-anisylphosphonic acid and a viscous unidentifiable oil were also obtained.

Anisole and Lower Sulfides of Phosphorus.—Tetraphosphorus heptasulfide, P_4S_7, 34.8 g., was added to 109 cc. of anisole. The mixture was refluxed for 5 hours with stirring. The sulfide did not dissolve, and there was no noticeable evolution of hydrogen sulfide. All P_4S_7 was recovered. Reaction did occur when P_4S_7 + 3S was used; it was, however, not as clean-cut as with pre-formed P_4S_{10}.

Tetraphosphorus trisulfide, P_4S_3, 22.0 g., was added to 109 cc. of anisole. The mixture was refluxed with stirring

---

[9] Fr. Guichard, *Ber.*, **32**, 1572 (1899).

[10] A. Michaelis, *ibid.*, **6**, 816 (1873)

[11] A. Michaelis, *Ann.*, **181**, 297 (1876).

[12] V. L. Bell, Jr., and G. M. Kosolapoff, This Journal, **75**, 4901 (1953); m.p. 179°.

for 6.5 hours. The sulfide dissolved at 110–120° but only traces of hydrogen sulfide were formed. Reaction did occur when $P_4S_3 + 7S$ was used; the yield of *p*-anisylphosphonic acid was less than one-half of that obtained with pre-formed P_4S_{10}.

Anisole and Sulfur.—Sulfur, 25.6 g., was added to 109 cc. of anisole. On heating, the sulfur dissolved. The solution was refluxed for 17 hours. There was no evolution of hydrogen sulfide, and all of the sulfur was recovered.

Phenetole and Phosphorus Pentasulfide. *p*-Phenetylthionophosphine Sulfide and *p*-Phenetylphosphonic Acid.—P_4S_{10}, 44.4 g. (0.1 mole), and 122 g. (1 mole) of phenetole were heated with stirring to reflux. The sulfide dissolved and hydrogen sulfide was evolved. The mixture was kept at about 165° for 5 hours. On cooling, the thionophosphine sulfide crystallized out, was filtered and washed with benzene; crude, 54.7 g., m.p. 219–224.5° (after softening at 215°). For the analysis the substance was dried *in vacuo* at 80° for 5 days.

Anal. Calcd. for $(C_8H_9OPS_2)_2$: C, 44.4; H, 4.16; P, 14.3; S, 29.6. Found: C, 42.9, 43.1; H, 4.06, 4.16; P, 14.9; S, 28.2.

Thirty-two and seven-tenths grams was hydrolyzed by boiling with 100 cc. of water for 18 hours. The clear solution obtained separated on cooling; 21.66 g. of *p*-phenetylphosphonic acid, m.p. 173–173.5°.[13]

From the mother liquor an additional 5.42 g. of low purity was obtained.

Anal. Calcd. for $C_8H_{11}O_4P$: C, 47.5; H, 5.45; P, 15.3. Found: C, 47.5; H, 5.58; P, 15.4, 15.5.

Reaction of Naphthalene with Phosphorus Pentasulfide[14] Preparation of 2-Naphthylphosphonic Acid.—The following procedure has been found advantageous for the preparation of large amounts of the phosphonic acid. Seven hundred ten grams (1.6 moles) of P_4S_{10} was added to 2,048 g. (16 moles) of molten naphthalene. The yellow slurry was stirred and heated at 180°. The phosphorus sulfide dissolved and hydrogen sulfide was copiously evolved. Performing the reaction in a current of nitrogen did not offer advantages since the H_2S provides an inert atmosphere anyway. Heating was continued until the evolution of hydrogen sulfide substantially ceased (about 22 hours). The reaction mixture was allowed to cool to about 100° whereupon 640 cc. of water was added; this addition had to be slow at the start because the hydrolysis is exothermic and produces huge amounts of H_2S. After all the water had been added the mixture was heated at 95–100° for about 24 hours to complete the hydrolysis. At this stage the hot molten upper naphthalene layer (about 1200 g.) was separated; undesirable by-products were removed in this layer. The lower layer consisted at 90–100° of a homogeneous mixture of phosphonic acid, naphthalene, water and phosphoric acid. The naphthalene (about 300 g.) was recovered from it by steam distilling and the residue was diluted with hot water to a volume of 4 l. On cooling, the 2-naphthylphosphonic acid crystallized, was isolated by filtration and washed with water; yield about 550 g. or about 41–42% (based on P_4S_{10}). The acid prepared in this manner was quite pure and melted at its worst only a few degrees below the melting point of pure 2-naphthylphosphonic acid (193–194°).

The optimum reaction temperature is about 160–190°. Under 160° the reaction is too slow and over 200° the yield decreases.

In our early experiments we steam distilled the naphthalene off before or during the hydrolysis. Some oily by-products went over with and after it, but some stayed behind with the aqueous still residue and became a nuisance in the isolation of the phosphonic acid, since they are somewhat soluble in a concentrated aqueous solution of that acid but separate on dilution with water.

Reaction of Naphthalene with Phosphorus Pentasulfide. Isolation of 2-Naphthylthionophosphine Sulfide.—A mixture of 88.8 g. (0.2 mole) of P_4S_{10} and 236 g. (2.0 moles) of molten naphthalene was stirred and heated to about 190° and kept there for 24 hours. The phosphorus sulfide dissolved and hydrogen sulfide was evolved. At a later stage some of the thionophosphine sulfide started to crystallize. After the reaction was complete the mixture was cooled to about 100° and diluted with 250 cc. of benzene. The slurry was filtered and the filter cake thoroughly washed with benzene; pale yellow crystalline powder, after drying *in vacuo*, 77 g., m.p. unsharp 210–245°. This product was badly contaminated by lower sulfides of phosphorus. Also, recrystallization from *o*-dichlorobenzene did not give a pure product.

A pure 2-naphthylthionophosphine sulfide was obtained when a very great excess of naphthalene was used. P_4S_{10}, 22.2 g. (0.05 mole), was added to 320 g. (2.5 moles) of molten naphthalene. The charge was heated with stirring to 170–180° and kept there for about 24 hours. After it had been cooled to 85°, 350 cc. of dry benzene was added. The yellow thionophosphine sulfide was filtered at 50°, washed with benzene and dried *in vacuo;* yield 16.4 g.; recrystallized from *o*-dichlorobenzene, m.p. (pre-heated bath) 268–271° (after softening at 263°).

Anal. Calcd. for $(C_{10}H_7PS_2)_2$: C, 54.0; H, 3.05; S, 28.8. Found: C, 53.3, 53.1; H, 3.18, 3.20; S, 28.7, 28.7.

Pure 2-naphthylthionophosphine sulfide, 9.0 g., was hydrolyzed by refluxing with 100 cc. of water for 23 hours. Hydrogen sulfide was formed. The clear solution deposited at 0–5°, 6.76 g. of pure 2-naphthylphosphonic acid; evaporation of the mother liquor (which contained also a little phosphoric acid) gave 1.4 g. of crude phosphonic acid.

The following experiment shows that the great excess of naphthalene used in the former did not act merely as a solvent for impurities, but influenced the course of the reaction. Naphthalene, 128 g. (1 mole), and 44.4 g. (0.1 mole) of P_4S_{10} was used and the reaction performed as in the former experiment. After the heating period 512 g. (4 moles) of naphthalene was added to produce a clear solution at 110°. At 80°, 700 cc. of dry benzene was added and the reaction product filtered at 45° and washed with 200 cc. of benzene; yield only 16.4 g. (one-half of the yield of the former experiment) of a very impure thionophosphine sulfide which could not be purified by recrystallization from *o*-dichlorobenzene.

Since the contamination of the thionophosphine sulfide (when an insufficient excess of naphthalene is used) consists of lower sulfides of phosphorus, the reaction was repeated in the presence of sulfur which would reconvert them into P_4S_{10}: starting materials, 128 g. (1 mole) of naphthalene, 44.4 g. (0.1 mole) of P_4S_{10}, 6.4 g. (0.2 mole) of sulfur, temperature 185–190°. The reaction was faster than usual and heating was interrupted after 5 hours. Working up as in the other experiments gave 28.5 g. of crude thionophosphine sulfide which, however, was pure after two recrystallizations from *o*-dichlorobenzene.

Reaction of Benzene with Phosphorus Pentasulfide. Phenylthionophosphine Sulfide and Phenylphosphonic Acid.—Two hundred cc. (2.2 mole) of dry benzene and 48.8 g. (0.11 mole) of P_4S_{10} were heated in an agitated stainless steel autoclave at 225° for 24 hours. The yellow solid was filtered and washed with 200 cc. of benzene; 34.4 g. dry. From the wash liquors 9 g. of crude product was isolated. After two recrystallizations from *o*-dichlorobenzene, m.p. very unsharp 203–215° (after softening at 198°). *Anal.* Calcd. for $4\ (C_7H_5PS_2)_2 + 1\ P_4S_7$: C, 33.36; H, 2.34; P, 21.58; S, 42.73; mol. wt., 345. Found: C, 33.1; H, 2.05; P, 22.04; S, 42.1; mol. wt. (cryoscopic in naphthalene), 340.

The benzene mother liquor contained some benzene-1,2-dithiol, identified as *o*-phenylene trithiocarbonate, m.p. 167–167.5°.[15]

The combined crude phenylthionophosphine sulfide was hydrolyzed by refluxing with 200 cc. of water for 12 hours. The clarified solution was concentrated to a volume of 50 cc. and deposited on cooling 23.0 g. of crude phenylphosphonic acid, m.p. after recrystallization from water 164.5–166°. The aqueous mother liquor gave a strong phosphate test with ammonium phosphomolybdate which turned blue, indicating the presence of a reducing agent.

The temperature of the reaction of benzene with phosphorus pentasulfide is critical: 225° is about the optimum.

Reaction of *o*-Xylene with Phosphorus Pentasulfide. *o*-Xylylphosphonic Acid.—*o*-Xylene, 106 g. (1 mole), and

---

[13] A. Michaelis, *Ann.*, **293**, 258 (1896); m.p. 165°.

[14] J. May, *Ber.*, **44**, 1229 (1911), has allegedly prepared P_4S_{10} from P_4S_3 and sulfur in naphthalene at 175–180°; he has not observed that P_4S_{10} reacts with naphthalene. I. H. Derby and O. D. Cunningham, U. S. 1,772,386 (1930) caused P_4S_{10} (prepared from phosphorus and sulfur *in situ*) to react with naphthalene under conditions otherwise similar to ours; they formulated their reaction product as 1,8-naphthylene-bis-(thionophosphine sulfide). We found no indication of an 1- or disubstituted naphthalene.

[15] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1826 (1926), m.p. 165°.

TABLE I

Starting material	Chlorinating agent	Solvent	Conditions	Reaction product	Yield, g.	B.p., °C.	Mm.
$(CH_3O{\cdot}C_6H_4{\cdot}PS_2)_2$							
68 g.	Excess Cl_2	300 cc. CCl_4	8 hr. room temp., 8 hr. SO_2	$CH_3O{\cdot}C_6H_4{\cdot}POCl_2$[a]	63	149–153	6–7
91.7 g.	32 g. Cl_2	50 cc. CCl_4	16 hr. room temp.	$CH_3O{\cdot}C_6H_4{\cdot}PSCl_2$	92.7	124–128	1
11 g.	14 g. PCl_5	50 cc. $POCl_3$	1 hr. reflux, then SO_2	Same[b]	8.8	155–157	8
10 g.	6.6 cc. SO_2Cl_2	50 cc. CCl_4	Room temp.	Same	7.5	156–157	8
18.5 g.	67.5 g. S_2Cl_2[c]	50 cc. CCl_4	5 hr. reflux	Same	19.9		
$(C_{10}H_7PS_2)_2$							
12.15 g.	Cl_2 until sol.	75 cc. CCl_4	Room temp.	$C_{10}H_7{\cdot}PSCl_2$[d]	13.2	173–174	4
$(C_6H_5PS_2)_2 + P_4S_7$							
7.0 g.	13.0 g. PCl_5	50 cc. $POCl_3$	2 hr. reflux	$C_6H_5PSCl_2$[e]	5.5	120	12
$C_6H_5PSCl_2$							
12.0 g.	Excess Cl_2	25 cc. CCl_4	Room temp., then SO_2	$C_6H_5POCl_2$[f]	8.1	105–106	5

[a] *Anal.* Calcd. for $C_7H_7O_2Cl_2P$: C, 37.3; H, 3.1; Cl, 31.5; S, 0.0. Found: C, 36.6, 36.7; H, 3.23, 3.23; Cl, 31.5; S, 0.46. [b] *Anal.* Calcd. for $C_7H_7Cl_2OPS$: C, 34.8; H, 2.9; Cl, 29.4; S, 13.25. Found: C, 34.3; H, 2.81; Cl, 29.2; S, 13.1. [c] In a separate experiment it was determined that sulfur monochloride does not further chlorinate the phosphonothioic dichloride. The latter was heated to reflux for five hours with an excess of sulfur monochloride; 87% of the phosphonothioic dichloride was recovered by distillation under reduced pressure and only a negligible amount of sulfur was detected. [d] *Anal.* Calcd. for $C_{10}H_7Cl_2PS$: C, 46.0; H, 2.68; Cl, 27.2; P, 11.9; S, 12.4. Found: C, 45.2; H, 2.57; P. 11.7; S, 10.2; Cl, 28.7. [e] *Anal.* Calcd. for $C_6H_5Cl_2PS$: C, 34.1; H, 2.36; Cl, 33.6; P, 14.7; S, 15.18. Found: C, 33.8; H, 2.55; Cl, 33.8; P, 16.03; S, 14.3. [f] *Anal.* Calcd. for $C_6H_5Cl_2OP$: C, 36.9; H, 2.56; Cl, 36.4; P, 15.90. Found: C, 37.2; H, 2.80; Cl, 36.4, 36.7; P, 17.17.

44.4 g. (0.1 mole) of P_4S_{10} were heated in a 1-l. stainless steel shaking autoclave at 185° for 24 hours. The contents consisted of a yellow solid and an orange-brown liquid. Water, 150 cc., was added gradually. Since this hydrolysis is slow, the mixture was refluxed for 42 hours. The bulk of the organic layer was decanted off. The remaining mixture was reheated, the water layer adjusted to a volume of about 500 cc. and the rest of the xylene layer separated. The hot aqueous solution was treated with decolorizing carbon, clarified and cooled. *o*-Xylylphosphonic acid, 35.5 g., m.p. 149–152°, crystallized out. It was identical with the phosphonic acid previously obtained from xylene and phosphoric anhydride. The m.p. of the pure acid is 153–153.5°. From the aqueous mother liquor a pure phosphonic acid could not be isolated.

Reaction of 2-Isopropylnaphthalene with Phosphorus Pentasulfide. 2-Isopropyl-x-naphthylphosphonic Acid.—179 g. (1 mole) of 95% 2-isopropylnaphthalene and 44.4 g. (0.1 mole) of P_4S_{10} were heated with stirring at 170–175° for 18 hours. Hydrogen sulfide was evolved and the phosphorus sulfide which dissolved produced an orange-brown solution. The charge was cooled to 80° and 50 cc. of water was cautiously added. Hydrolysis was accomplished by refluxing for 20 hours. The layers were separated hot. The (water-insoluble) phosphonic acid crystallized from the organic layer, was filtered and washed with benzene; yield 11.0 g. of crude product, m.p. 210–212° after recrystallization from 80% alcohol.

Anal. Calcd. for $C_{13}H_{15}O_3P$: C, 62.4; H, 6.0; P, 12.4; neut. equiv., first break, 250, second break, 125. Found: C, 61.8; H, 5.66; P, 13.29, 13.14; neut. equiv., first break, 240.7, second break, 117. The sample was not quite pure.

The 2-isopropyl-x-naphthylphosphonic acid has considerable wetting power, but forms insoluble calcium and magnesium salts.

Chlorination Experiments.—These are summarized in Table 1.

In these reactions sulfur is removed as elemental sulfur when sulfur monochloride is used. When phosphorus pentachloride is used, thiophosphoryl chloride is formed. When chlorine, sulfur dichloride or sulfuryl chloride are employed, it depends upon the ratio of the reactants whether the removed sulfur appears as such or as sulfur mono- or dichloride; in the case of sulfuryl chloride, sulfur dioxide and thionyl chloride are formed. These inorganic chlorides boil much lower than the desired organophosphorus compounds and are easily removed by distillation.

BOUND BROOK, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE A. M. TODD CO.]

A New Ketone from Oil of *Mentha rotundifolia*

BY ROBERT H. REITSEMA

RECEIVED APRIL 9, 1956

A new ketone has been isolated from oil of *Mentha rotundifolia*. The structure of 1,2-epoxypulegone (piperitenone oxide) is proposed on the basis of spectra and degradation work. It is indicated that this ketone is the same as has been isolated from Indian "spearmint" and from species of *Lippia* oils. Previous conversions of the material have been reinterpreted by the use of the new structure.

Over half of the essential oil from *Mentha rotundifolia* has been found to consist of an unusual terpene, $C_{10}H_{14}O_2$.[1] Isolation of the ketone by freezing, or by preparation of the semicarbazone, was possible either from the whole oil or from fractions rich in the material. Interesting properties of hybrids from *M. rotundifolia* crossed to other mint species made the study of this new compound valuable.

Although this is an unusual terpene in an essential oil, one with the same analysis, designated lippione, has been isolated from *Lippia* genus oils.[2] More recently another report has appeared indicating the

[1] R. H. Reitsema, *J. Am. Pharm. Assoc.* (*Sci. Ed.*), **43**, 414 (1954).

[2] G. A. Fester, E. A. Martinuzzi and A. I. Ricciardi, *Rev. fac. ing. quim.* (*Sante Fe, Arg.*), **20**, 43 (1951), *Anal. assoc. quim. Argentina*, **42**, 43 (1954).