

POLYNUCLEAR AROMATIC COMPOUNDS FOR HIGH TEMPERATURE LUBRICANTS

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FOREWORD

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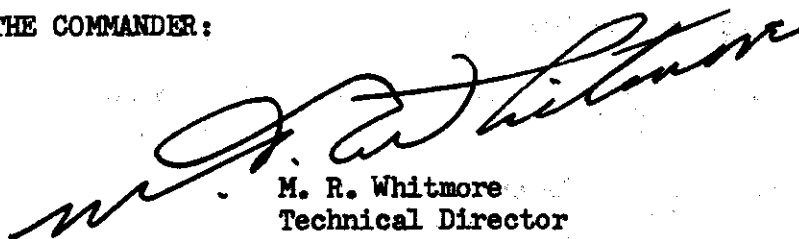
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ABSTRACT

The properties of triaryl esters of phosphoric acid were studied with regard to their suitability as high-temperature lubricants and related materials. It was found that naphthyl derivatives did not have sufficient thermal stability to compensate for the unwanted increase in viscosity and melting point. The 4-biphenyl group possessed all the advantages of the naphthyl group with much better thermal stability. One particular compound prepared, bis(o-chlorophenyl) 4-biphenyl phosphate had a thermal stability of over 510°C (950°F), by far the highest stability of any compound prepared under this contract. It was found that the chlorophenyl phosphates possessed outstanding thermal stability and seemed to be the most promising type of compound for further development. It was found possible to vary considerably the physical properties of a compound by incorporating three different groups. Finally, the pronounced volatilizing and viscosity-reducing effect of the trifluoromethylphenyl group was observed in several compounds which contained one or more of these groups. It was also found possible to compile a table of approximate thermal decomposition temperatures of numerous aromatic groups.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. Whitmore
Technical Director
Materials Laboratory
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Due to increased severity of operating conditions, in particular higher speeds which result in higher working temperatures, the lubricants and hydraulic fluids currently being used in aircraft and related equipment are becoming inadequate with respect to thermal and oxidative stability. It is also necessary, while striving for increased temperature stability, to refrain from excessive sacrifice of low-temperature fluidity. The approach to this problem in this case has been the investigation of aromatic phosphate esters.

This project had its start in August, 1952; the plan was to investigate the suitability of bi- and tricyclic liquid polynuclear aromatic compounds as high-temperature lubricants and related materials. A literature search was carried out, and from the 2400 compounds thus obtained, 14 were selected which seemed to be of the most promising type. These compounds were representative of ethers, esters, ketones, alkylated aromatics, etc. Subsequently three other compounds were added to the list.

After screening these compounds for desirable properties, in particular thermal stability, the conclusion was reached that by far the most promise lay in the class of aryl phosphate esters. The work has been devoted to this type of compound since then.

The original phosphates were diphenyl naphthyl phosphates. The compounds possessed remarkable thermal stability, over 460°C, but happened to be low-melting solids. The attempt was made to achieve a liquid state at room temperature or below, yet retain the good thermal stability of the parent compounds. This search led through the tolyl and quinolyl analogs and tris(o-chlorophenyl) phosphate. This work demonstrated that liquid compounds of high thermal stability could be prepared and pointed the way to further improvement in physical properties.

II. DISCUSSION

For the sake of convenience the compounds synthesized during the year have been grouped into arbitrary classes, each class having some feature in common. The chronological order of preparation of the compounds has been disregarded.

The listing of physical properties of all the compounds prepared is given in Table I. Those compounds which were considered to possess promising properties were subjected to further testing, the results of which

are shown in Table II. The approximate thermal decomposition temperatures of substituent groups are listed in Table III.

Class I consists of diphenyl phosphates in which the third group was varied. The intention, in this case, was to proceed from the original diphenyl naphthyl phosphates, and to vary the polynuclear group to determine the effect on the characteristics of the structure. The phenyl group is quite thermally stable, so that any instability of the third group could be easily observed. This class consists of the following compounds:

- ML0 9523 Diphenyl 5,6,7,8-tetrahydro-1-naphthyl phosphate
- ML0 9526 Diphenyl 2-chloro-1-naphthyl phosphate
- ML0 9532 Diphenyl 3-pyridyl phosphate
- ML0 9537 Diphenyl 2,4-dichloro-1-naphthyl phosphate
- ML0 9543 Diphenyl 5-indanyl phosphate
- ML0 9544 Diphenyl 4-indanyl phosphate
- ML0 9551 Diphenyl pentachlorophenyl phosphate
- ML0 9558 Diphenyl 3,4-dimethylphenyl phosphate
- ML0 9559 Diphenyl 3,5-dimethylphenyl phosphate
- ML0 9560 Diphenyl 4-biphenylyl phosphate

Compound ML0 9523, the tetralyl derivative, was prepared to study the effect on fluidity of hydrogenating one of the naphthyl rings. It was expected that a liquid phosphate would result, analogous to the fact that tetralin is a liquid and naphthalene is a solid and the two materials have a difference of some 110°C in their melting points. This proved to be the case, since the tetralyl compound was a viscous liquid having a pour point of 0°F. The thermal stability had dropped to 383°C (721°F). This could be due to lability of the hydrogen atoms on the saturated ring, causing reversion to the aromatic structure on heating. The viscosity slope was rather poor. Although this compound would not now be considered promising, at the time of its preparation its properties were considered sufficiently good to warrant carrying out secondary tests. As previously mentioned, the results of these secondary tests are given in Table II.

Continued

The effect of chlorinating the naphthyl group was shown in the next compound in the series, diphenyl 2-chloro-1-naphthyl phosphate, MLO 9526. In this instance, a liquid state was also achieved, although with a fairly high pour point, 25°F. It appeared that the chloronaphthyl group was considerably less thermally stable than the simple naphthyl group. The thermal decomposition temperature was 404°C (759°F) compared to 462°C (864°F) for the parent compound, diphenyl 1-naphthyl phosphate.

Since all previous attempts to prepare a dipyridyl phosphate had failed, an attempt was made to prepare a simple monopyridyl compound. The diphenyl 3-pyridyl phosphate, MLO 9532, was chosen and was prepared without difficulty. The pyridyl group imparted an unusual fluidity to the compound, which incidentally was quite subject to supercooling. The pour point was -30°F, although refrigeration slowly induced crystallization. The crystalline material melted at 33°C, somewhat lower than triphenyl phosphate, which melts at 49-50°C. The pyridyl group also caused a decrease in thermal stability, since the compound decomposed at 362°C (684°F). Although there appears to be no great possibility of this type of compound being suitable as a high-temperature lubricant, it is thought to offer a reasonable chance of being effective as a high-temperature antioxidant.

Another phosphate containing a chlorinated naphthyl group was diphenyl 2,4-dichloro-1-naphthyl phosphate, MLO 9537. This compound was prepared to ascertain if dichlorination of the naphthyl group would produce poorer thermal stability than monochlorination. It was found that the decomposition temperature had indeed dropped, from 404°C to 383°C. As might be expected, the compound was a solid. The indications were that halogenation of the naphthyl group resulted in unfavorable thermal stability.

It was possible to obtain large enough samples of 4-indanol and 5-indanol to prepare usable amounts of the corresponding diphenyl phosphates. Diphenyl 4-indanyl phosphate, MLO 9544, was a rather limpid liquid with a fair viscosity slope. The thermal decomposition temperature was mediocre, 394°C (741°F). The viscosity slope was fair, being 0.844 from 100-210°F.

Diphenyl 5-indanyl phosphate, MLO 9543, was a low-melting solid with viscosity characteristics quite similar to the 4-indanyl compound. The 5-indanyl phosphate, however, possessed excellent thermal stability, having a decomposition temperature of over 454°C (849°F).

Another compound in this class was diphenyl pentachlorophenyl phosphate, MLO 9551. Due to the intractability of tris(pentachlorophenyl) phosphate, discussed later, regarding the difficulty of determining physical constants, it was decided to prepare the diphenyl compound in order to study the characteristics of the pentachlorophenyl group. The compound had a rather high melting point, 120°C, and the pentachlorophenyl group appeared

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to be thermally stable only up to 372°C (702°F). There appeared to be little promise as far as potential use as a lubricant was concerned. The compound diphenyl 3,4-dimethylphenyl phosphate, MLO 9558, was prepared to observe whether it resembled its structural analog, diphenyl 5-indanyl phosphate, with reference to the latter's excellent thermal stability. This proved to be the case, since MLO 9558 was thermally stable above 444°C, which was higher than its normal boiling point of 431°C. The thermal stability of the 5-indanyl compound, which possesses one more carbon atom, was over 454°C, higher than its normal boiling point. The melting point of MLO 9558 was higher, being 48°C vs. 29°C for the indanyl compound. The viscosity characteristics were fair.

The next compound was also a dimethylphenyl derivative, diphenyl 3,5-dimethylphenyl phosphate, MLO 9559. It was desired to observe whether the excellent thermal stability of the 3,4-dimethylphenyl compound would also be achieved. In this case the positions of the methyl groups on the ring do not resemble a bicyclic ring. This compound was thermally stable above 431°C (808°F), which is higher than its normal boiling point of 419°C (786°F). The viscosity slope, 0.863 from 100-210°F, was fairly good, and the melting point was down to 32°C.

Although the thermal stability of the dimethylphenyl group appears to be quite good, there seems to be little reason to assume that the oxidation stability of the group should be better than tolyl, which is rather poor. Even so, the greatly increased thermal stability of the dimethylphenyl compounds over the monomethylphenyl compounds is surprising.

Since work on compounds which are discussed under other class headings had indicated a limit of thermal stability of the 2-biphenyl group of about 440-455°C, it was desired to observe whether the 4-biphenyl group would be more stable. In this case the para configuration was considerably more stable. The compound diphenyl 4-biphenyl phosphate, MLO 9560, did not decompose at its normal boiling point of 485°C (905°F). The melting point, 64°C, was rather high, but still surprisingly low considering the melting point of the intermediate 4-phenylphenol, which is 164°C. The viscosity slope was fair. The boiling and melting points are quite close to those of diphenyl 2-naphthyl phosphate, 471°C and 64°C respectively.

Class II is also derived directly from the original diphenyl naphthyl phosphates. In this class are all symmetrical compounds possessing a single naphthyl group. These are as follows:

MLO 9521 Bis(o-chlorophenyl) 1-naphthyl phosphate

MLO 9525 Bis(p-chlorophenyl) 1-naphthyl phosphate

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MLO 9535 Bis(2,4-dichlorophenyl) 1-naphthyl phosphate

MLO 9536 Bis(2-biphenyl) 1-naphthyl phosphate

Since the naphthyl group was found to be rather undesirable, this series received little attention in more recent work. The first compound, bis(o-chlorophenyl) 1-naphthyl phosphate, MLO 9521, was prepared as an analog of the diphenyl naphthyl phosphate in an attempt to obtain a liquid state. The compound was a rather viscous liquid with a fair viscosity slope and a pour point of 30°F, a reduction of about 100°F from that of the diphenyl compound. The material was quite thermally stable, decomposing at 477°C (890°F). It was found later that this decomposition could be attributed to the naphthyl group.

Concerning the next compound listed, bis(p-chlorophenyl) 1-naphthyl phosphate, MLO 9525, it was thought desirable to compare its properties with those of the corresponding o-chlorophenyl compound. The effect on the melting or pour point was particularly interesting, since p-chlorophenol melts about 40°C higher than o-chlorophenol. However, it was found that the p-chlorophenyl structure had a somewhat lower pour point and considerable lower viscosity, although it still was rather viscous. The viscosity slope was slightly poorer. The thermal decomposition temperature was also somewhat lower, being 468°C (872°F). The effect of dichlorinating the phenyl group was shown in bis(2,4-dichlorophenyl) 1-naphthyl phosphate, MLO 9535. This was a very viscous fluid with a fairly good thermal stability, decomposing at 432°C (810°F). The temperature range from about 430-440°C seems to be the decomposition point of the 2,4-dichlorophenyl group, as evidenced by the three compounds prepared which contained that group (MLO 9535, 9545, and 9550).

Compound MLO 9536, bis(2-biphenyl) 1-naphthyl phosphate, was a taffy-like liquid which slowly crystallized on standing. Here again the thermal stability was good, 440°C, although it did not approach the exceedingly high calculated normal boiling point of 545°C. There appeared to be little of immediate interest in this material.

Class III is composed of compounds having two naphthyl groups and a varying third group. These were:

MLO 9534 Bis(1-naphthyl) 3-pyridyl phosphate

MLO 9538 Bis(1-naphthyl) o-chlorophenyl phosphate

The pyridyl compound, MLO 9534, was made to determine if the pyridyl group

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would impart fluidity to a large grouping like the dinaphthyl phosphate, since this effect was observed with a diphenyl phosphate. The product was a very viscous oil; it appeared likely that the liquid was supercooled and that crystallization could be induced under the right conditions. The compound proved to be extremely susceptible to degradation, both thermal and oxidative; in fact, it carbonized to such an extent in the isoteniscope that the apparatus could not be used again.

The other compound, bis(1-naphthyl) o-chlorophenyl phosphate, MLO 9538, was also a molasses-like liquid. The thermal decomposition temperature was 417°C (783°F), a temperature range which seems to occur rather often in testing the various compounds. The combination of two naphthyl groups seemed to impair the thermal stability.

Class IV is that comprised of bis-phosphates of naphthalenediol. These were prepared in an attempt to reduce the average number of naphthyl groups per phosphate group. The two compounds were:

MLO 9528 1,6-Naphthylene bis(diphenyl phosphate)

MLO 9548 1,5-Naphthylene bis(diphenyl phosphate)

The first of these products, MLO 9528, was an exceedingly viscous liquid with poor thermal stability. Only a small amount of sample was obtained, probably due to hydrolytic or thermal decomposition during the purification process. The viscosity slope was rather good. The second compound, MLO 9548, was a fairly high-melting solid with the higher-than-average decomposition temperature of 441°C (826°F). The extrapolated normal boiling point was exceedingly high, being 620°C (1148°F). On the whole, however, the naphthylene class did not seem to offer any particular advantages.

Class V consists of phenylene derivatives; that is, derivatives of dihydroxy benzene. These were:

MLO 9524 1,3-Phenylene bis(diphenyl phosphate)

MLO 9527 1,3-(4-Chlorophenylene) bis(diphenyl phosphate)

MLO 9530 1,4-Phenylene bis(diphenyl phosphate)

MLO 9539 1,4-(2-Chlorophenylene) bis(diphenyl phosphate)

The resorcinol derivatives were first investigated since resorcinol esters

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seemed to have the lowest melting point. The compound which inspired interest in this class was MLO 9524, 1,3-phenylene bis(diphenyl phosphate). This material had an excellent viscosity slope compared to other phosphates, 0.750 from 100-210°F, and an extrapolated normal boiling point of 547°C (1017°F). The thermal stability was only fair, 416°C, and hydrolytic stability was relatively poor. The compound had a very high flash point, 618°F.

Compound MLO 9527 was a chloro-substituted derivative of MLO 9524. It was hoped to improve thermal stability in this way. However, the decomposition temperature dropped to 394°C (741°F) and the viscosity slope was poorer than 1,3-phenylene bis(diphenyl phosphate), as were almost all the other properties.

The next compound, MLO 9530, 1,4-phenylene bis(diphenyl phosphate) was a solid melting at 109°C, but was the most thermally stable phenylene derivative prepared, decomposing at 455°C (851°F). The viscosity slope was rather good. In common with all the phenylene compounds, the extrapolated normal boiling point was quite high (550°C).

In an attempt to achieve a liquid state, yet retain the good characteristics of MLO 9530, a chloro-derivative, 1,4-(2-chlorophenylene) bis(diphenyl phosphate), MLO 9539, was prepared. The melting point did indeed drop, to 78°C, but so also did thermal stability, to 417°C (783°F). It appeared that the phenylene group could not be chlorinated without serious loss of thermal stability.

Class VI is represented by only a single compound.

MLO 9533 4,4'-Biphenylene bis(diphenyl phosphate)

These compounds are derivatives of dihydroxy biphenyl, each ring bearing one hydroxyl group. The bond joining the two rings is considered to be extremely stable. Compound MLO 9533, although exceedingly high boiling (589°C calculated), was thermally unstable above 416°C. The melting point was 89°C, lower than might have been expected.

Class VII is a rather large one, consisting of tris-phosphates; that is, compounds having three identical groups joined to the phosphate radical. The purpose of preparing these compounds was to study the thermal stability of the groups themselves, disregarding the suitability of the material as a lubricant. In this case, the performance of the group is unobscured by outside influences, except where the physical properties of the compound are such as to make manipulation unduly difficult. Naturally, many of these materials are high-melting solids.

The compounds are as follows:

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MLO 9540 Tris(2-biphenyl)l) phosphate
MLO 9541 Tris(3-chloro-2-biphenyl)l) phosphate
MLO 9542 Tris(3-chloro-4-biphenyl)l) phosphate
MLO 9545 Tris(2,4-dichlorophenyl) phosphate
MLO 9547 Tris(o-bromophenyl) phosphate
MLO 9552 Tris(pentachlorophenyl) phosphate
MLO 9553 Tris(m-chlorophenyl) phosphate
MLO 9555 Tris(3,5-dimethylphenyl) phosphate
MLO 9556 Tris(3,4-dimethylphenyl) phosphate
MLO 9557 Tris(o-fluorophenyl) phosphate
MLO 9561 Tris(m-trifluoromethylphenyl) phosphate

The first compound, tris(2-biphenyl)l) phosphate, MLO 9540, was made in an attempt to determine the stability of the unsubstituted biphenyl group. This was quite high, 454°C (849°F) but did not nearly approach the normal boiling point of the compound, calculated to be 546°C. The melting point, 115°C, was rather high.

The effect of chlorinating the biphenyl nucleus was demonstrated by the next two compounds listed. In the case of tris(3-chloro-2-biphenyl)l) phosphate, MLO 9541, an exceedingly high melting point resulted (195°C) together with reduced thermal stability (417°C). The isomer, tris(3-chloro-4-biphenyl)l) phosphate, MLO 9542, decomposed at the same temperature (417°C) but melted considerably lower (154°C). The extrapolated normal boiling point appeared to be about 620°C, although this was only an approximation due to the anomalous shape of the curve.

Since tris(o-chlorophenyl) phosphate proved to have excellent thermal properties, the effect of the 2,4-dichlorophenyl group was studied. The addition of the second chlorine group to the benzene ring, in tris(2,4-dichlorophenyl) phosphate, MLO 9545, resulted in a decomposition temperature of 440°C (824°F), and a melting point of 93°C. The viscosity slope was rather poor. This compound was extremely susceptible to hydrolysis.

Also prepared as an analogy to the o-chlorophenyl phosphate was

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tris(o-bromophenyl) phosphate, MLO 9547. It was hoped to retain the fluidity and thermal stability of the chloro compound, yet achieve a higher boiling point. This expectation was not realized. The compound had poorer thermal stability, 429°C, and a higher melting point, 83°C. The bromine atom appeared not to have the firmness of attachment to the benzene ring exhibited by the chlorine atom.

Another compound in the series is an example of intractability due to high molecular weight. The compound, tris(pentachlorophenyl) phosphate, MLO 9552, precipitated from the reaction mixture and could be purified only by washing with ethanol. The substance melted with decomposition at about 230-240°C. It appeared to be insoluble in any of the ordinary solvents, which made it impossible to obtain a molecular weight value. This difficulty in handling was responsible for the preparation of diphenyl pentachlorophenyl phosphate, previously discussed.

The next compound, tris(m-chlorophenyl) phosphate, MLO 9553, was prepared to compare with the analogous o-chlorophenyl phosphate. This material had quite interesting properties including a thermal stability over 464°C (867°F), which was higher than its normal boiling point of 452°C (846°F). The pour point was very good, -20°F, and the viscosity at 100°F was only 28 cs. The secondary tests all gave very good results, including a better hydrolytic stability than the o-chlorophenyl compound. The compound tris(3,5-dimethylphenyl) phosphate, MLO 9555, was prepared to compare with diphenyl 3,5-dimethylphenyl phosphate. As might be expected, the melting point rose somewhat (14°C increase) as did the viscosity and boiling point. The thermal decomposition temperature was over 452°C. In this case, the effect of the higher molecular weight produced a straightforward change in properties.

The same holds true for tris(3,4-dimethylphenyl) phosphate, MLO 9556. In comparison to diphenyl 3,4-dimethylphenyl phosphate, the physical properties varied as might be expected from the increase in molecular weight. Thus, the boiling point, melting point and viscosity all were higher. The compound was quite thermally stable, not decomposing at 462°C (864°F).

The current general interest in fluorine-containing compounds led to the preparation of tris(o-fluorophenyl) phosphate, MLO 9557, to ascertain if the fluorine atom imparted any unique properties. This did not seem to be the case. Aside from a slightly low boiling point (417°C) for a molecular weight of 380, none of the other properties seemed noteworthy: melting point 79-81°C, thermal stability above the boiling point, mediocre viscosity slope. The compound was not considered interesting enough to examine at greater length.

The final compound of this series, tris(m-trifluoromethylphenyl)

phosphate, MLO 9561, is of considerable interest. The trifluoromethyl group sterically resembles methyl, but would be expected to have considerably better oxidation resistance. This phosphate, with a molecular weight of 530, possessed truly surprising volatility as shown by a boiling point of 366°C. By way of comparison, tris(o-chlorophenyl) phosphate, molecular weight 430, boils at 463°C, and triphenyl phosphate, molecular weight 326, boils at 385°C. The absolute viscosity values were quite low, e.g., 14 cs at 100°F; the viscosity slope from 100-210°F was rather poor (0.935). These low viscosities resulted in a pour point of -35°F; however, the compound could be induced to crystallize to a solid melting at 13°C. The compound was thermally stable above its boiling point. The unusual effect of the trifluoromethylphenyl group on the properties of the phosphate structure indicated that compounds containing this group deserved further investigation.

Class VIII was composed of phosphonates. These are compounds having one direct carbon-phosphorus bond, instead of the usual carbon-oxygen-phosphorus linkage. These compounds were:

MLO 9546 Diphenyl benzenephosphonate

MLO 9549 Bis(o-chlorophenyl) benzenephosphonate

MLO 9550 Bis(2,4-dichlorophenyl) benzenephosphonate

The first compound, diphenyl benzenephosphonate, MLO 9546, was stable above 429°C (804°F). This compound was a solid melting at 76°C, which is considerably higher than the analogous triphenyl phosphate. The thermal decomposition temperatures of the two compounds are quite similar.

The second compound was a liquid. This material, bis(o-chlorophenyl) benzenephosphonate, MLO 9549, was thermally stable above 444°C (831°F), but it had a rather poor viscosity slope. The 10°F pour point was fairly good.

The last compound, bis(2,4-dichlorophenyl) benzenephosphonate, MLO 9550, was made in an effort to obtain a still higher boiling phosphonate. However, the 2,4-dichlorophenyl group was thermally unstable above 429°C (804°F), so the limit of thermal stability of the phosphonate group remains at present unknown.

The compounds in Class IX were alike in that they contained the 4-biphenyl group. These were:

MLO 9560 Diphenyl 4-biphenyl phosphate

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ML0 9563 Bis(o-chlorophenyl) 4-biphenyl phosphate

ML0 9564 Bis(m-trifluoromethylphenyl) 4-biphenyl phosphate

It will be remembered that diphenyl 4-biphenyl phosphate was thermally stable above 485°C, but was a solid. The other two compounds listed represent an effort to retain that thermal stability, yet achieve a liquid state. In both cases, this was accomplished.

The compound bis(o-chlorophenyl) 4-biphenyl phosphate, ML0 9563, was a viscous liquid which was thermally stable above its normal boiling point of 510°C (950°F). This is by far the highest thermal stability observed up to the present time. This information also establishes the fact that when bis(o-chlorophenyl) 1-naphthyl phosphate, ML0 9521, decomposes at 477°C, it is the naphthyl group exhibiting instability. It had heretofore been impossible to determine this, since no other compound previously prepared, containing either the o-chlorophenyl or 1-naphthyl groups, could be tested above 477°C, either because the boiling point was too low or because the compound decomposed. In this case, of course, the o-chlorophenyl group was shown to be thermally stable above 510°C.

The third compound, bis(m-trifluoromethylphenyl) 4-biphenyl phosphate, ML0 9564, exhibited the pronounced effect of the trifluoromethylphenyl group in enhancing volatility. Compared to ML0 9563, the boiling point was 85°C lower while the molecular weight was 64 units higher. The compound was reasonably fluid, having a viscosity of 82 cs at 100°F, and was stable above its normal boiling point, 424°C.

Class X consisted of unsymmetrical phosphates, that is phosphates having three different groups attached to the phosphate radical. These compounds were:

ML0 9554 Phenyl o-chlorophenyl 1-naphthyl phosphate

ML0 9562 Phenyl m-trifluoromethylphenyl 1-naphthyl phosphate

The first compound, ML0 9554, was a somewhat viscous liquid which thermally decomposed at 470°C (878°F). The pour point (15°F) was fair, while the other properties were about average.

In the case of phenyl m-trifluoromethylphenyl 1-naphthyl phosphate, ML0 9562, the volatilizing influence of the trifluoromethylphenyl group is again shown. The boiling point was 421°C (790°F) and the pour point was 5°F.

It appears that this group also greatly promotes the solubility of phosphates in aliphatic naphtha. It seems quite feasible to vary such properties of a compound as boiling point, hydrolytic stability, viscosity and the like, by varying the three groups. The economics of production would, of course, have to be considered.

In Class XI were placed the miscellaneous compounds which do not fit in the other classes. These were:

ML0 9529 Bis(p-chlorophenyl) 2-chloro-1-naphthyl phosphate

ML0 9531 Triphenyl thiophosphate

The first of these, bis(p-chlorophenyl) 2-chloro-1-naphthyl phosphate, ML0 9529, exhibited the typical instability of the 2-chloro-1-naphthyl group, decomposing at 394°C (741°F). The material was a viscous liquid which could be induced to crystallize to a fairly high-melting solid.

The effect of substituting a sulfur atom for an oxygen atom in the phosphate radical is shown in triphenyl thiophosphate, ML0 9531. The melting point was slightly higher than that of triphenyl phosphate, while the thermal stability was considerably lower. The viscosity slope was poor. It is conceivable that compounds of this type might prove interesting as antioxidants.

Several other preparations were attempted but failed, due mostly to decomposition of the product during attempted purification. The compound, 1,2-phenylene bis(diphenyl phosphate) decomposed on distillation, with only triphenyl phosphate being recovered. A series of compounds containing the bis(di-p-chlorophenyl phosphate) structure decomposed on distillation to yield tris(p-chlorophenyl) phosphate. These compounds were 1,6-naphthylene bis(di-p-chlorophenyl phosphate), 1,3-phenylene bis(di-p-chlorophenyl phosphate) and 1,3-(4-chlorophenylene) bis(di-p-chlorophenyl phosphate). In a similar manner, an attempt to prepare 1,3,5-phenenyl tris(diphenyl phosphate) yielded only triphenyl phosphate. Another compound, which was prepared to study the properties of the nitro group, was tris(2-chloro-4-nitrophenyl) phosphate. This material decomposed rather vigorously after a period of refluxing, leaving a carbonized resin. Another compound, 4,4'-biphenylene bis(o-chlorophenyl) phosphate, was apparently hydrolyzed during the process of washing with water and dilute acid, and only the starting 4,4'-dihydroxybiphenyl was recovered.

The preparation of tris(o-nitrophenyl) phosphate failed due to decomposition of the product on attempted distillation. The same thing occurred in the case of diphenyl benzyl phosphate, diphenyl 2-phenylethyl

phosphate, 3,3'-dichloro-4,4'-biphenylene bis(di-o-chlorophenyl phosphate) and 3,3'-biphenylene bis(diphenyl phosphate). Two other attempted preparations, those of 2,3-naphthylene p-chlorophenyl phosphate and 2,3-naphthylene benzenephosphonate, gave products having molecular weights to which no definite structure corresponded.

III. EXPERIMENTAL

A. Apparatus and Methods

1. Thermal Stability. The method used for the determination of thermal stability involves the use of the isoteniscope to measure vapor pressure. In theory, the graph of log P (vapor pressure) versus the inverse of the absolute temperature is a straight line. When the compound starts to decompose, the vapor pressure increases non-uniformly, apparently due to the formation of volatile products, and departs from the straight line. This point of departure is taken as the thermal decomposition temperature. The isoteniscope is essentially a bulb attached to a U-tube manometer, and this to an air condenser. Both the method of determining thermal stability and the design of the isoteniscope were obtained from WADC TR 53-45 "Synthetic Lubricants", University of Michigan on WADC Contract No. W-33-038-ac-21457, dated December, 1952. By refluxing under vacuum the liquid being tested, the liquid accumulates in the U-tube, displacing the air present in the process. The isoteniscope is then cooled, and the liquid poured from the manometer back into the bulb, some liquid being allowed to remain to act as a liquid seal to exclude air. The process is repeated several times, to remove all traces of air. The temperature is then raised gradually, and the liquid legs in the manometer balanced by an applied external pressure. At a given temperature the applied pressure necessary to balance the manometer equals the vapor pressure. After considerable initial difficulty in eliminating sources of trouble in the apparatus, the method was found to be quite satisfactory, although tedious.

An air bath was tried at first for heating the isoteniscope, but was abandoned due to non-uniform temperature gradients. An aluminum block, heated by a flame, was found to give good results. The block is cylindrical, and surrounded by a glass shield; the block is provided with suitable recesses for inserting the isoteniscope and observing the manometer and bulb.

2. Viscosity at 400°F. In order to provide a 400°F bath for viscosity determinations, consideration must be given to the problems inherent in maintaining such a relatively high temperature. If a liquid medium heated by some external source is used, the main difficulty is selecting a medium of sufficiently satisfactory oxidative and thermal stability. Continued

transparency of the bath liquid is also necessary. Rather than use this method with its attendant complications, it was decided to use a refluxing liquid in an insulated chamber to provide the constant temperature. A drawing of the apparatus is shown in Wright Air Development Center Technical Report 53-337, November, 1953, p. 23. The body of the apparatus is a double-walled chamber with provisions for evacuating the annulus, if desired. A side-opening accepts a condenser. The viscosimeter is inserted into the central and large side holes in the plug and secured by rubber sleeves. The plug is equipped with an inlet and outlet for passage of a cooling medium to condense any vapor which might rise to the rubber sleeves. An expansion bellows at the bottom of the jacket relieves strain at high temperatures. It was found, at the barometric pressure prevailing in San Antonio, that tetralin gave a vapor temperature of 400°F.

3. Molecular Weight. This property was determined by the cryoscopic method using benzene as a solvent.

4. Flash and Fire Point. The ASTM open cup procedure No. D 92-52 was used, except that a miniaturized cup was used instead of the standard cup. The wall thickness of the standard cup was retained, but the volume was reduced by reducing the inside diameter of the cup, keeping the height, upper flange diameter and base diameter constant. Therefore, the cross-section of the small cup resembled a spool, with one end of the central opening closed. A sample of only about 20 cc is required, and results were in good agreement with the standard cup.

5. Solubilities. The solvent was added dropwise to a sample of about 2 gm of the material being tested. If the sample blended with the solvent under the continuing dilution, the sample was rated "infinitely soluble". If the sample did not blend with the solvent, a second technique was used. This method was to add the sample dropwise from a microburette to a given volume of solvent and observe the point where cloudiness occurs.

If, as in the case of water, the solubility of the sample were less than 0.01 gm of 150 cc of solvent, the sample was termed "insoluble".

6. Hydrolytic Stability. Ten grams of sample were added to 125 ml of distilled water in a 500-ml flask. The flask was agitated for sixteen hours at 100°F. A 100 ml sample of the water layer, centrifuged if necessary for clarification, was titrated with 0.1 N KOH. The hydrolytic stability was reported as mg KOH/gm sample.

7. Autogenous Ignition Temperature. A 125 ml Erlenmeyer flask was placed in a 4 in. porcelain evaporating dish containing about one-half its volume of molten lead. A thermocouple was immersed in the lead. The dish was heated with a gas-oxygen torch. The temperature was gradually raised

and at intervals a drop of sample was dropped into the flask. The temperature at which the liquid ignited was taken as the autogenous ignition temperature. A maximum workable temperature of about 1400°F can be attained by this method. This is above the softening point of Pyrex glass.

8. Vapor Pressure at 25°C and 100°C. These values were obtained by extrapolation of the vapor pressure-temperature curves obtained during the thermal stability test. An experimental spot check was made on bis(m-tolyl) 1-naphthyl phosphate at 100°C using the transpiration method. Since the experimental value was 2.1×10^{-4} mm, compared with 0.7×10^{-4} obtained by extrapolation, and since the experimental error in measuring these low vapor pressures is quite high, the extrapolation was considered to give satisfactory results.

B. Chemical Syntheses

(1). Bis(o-chlorophenyl) 1-naphthyl phosphate. MLO 9521.

a. 1-Naphthyl phosphoryl dichloride. In a 2-liter flask equipped with a thermowell and an 80 cm reflux condenser was placed 576.6 gm (4 moles) of 1-naphthol and 613.4 gm (4 moles) of POCl_3 . The mixture was brought, as quickly as possible, to 200°C; this required 27 hours. The reaction product was stripped of volatiles under aspirator vacuum up to 200°C flask temperature. Vacuum distillation gave 563 gm of 1-naphthyl phosphoryl dichloride, a somewhat viscous, refractive water-white liquid, boiling at 157°/4 mm, $n_D^{34.5}$ 1.5942. The yield was 54%.

b. Bis(o-chlorophenyl) 1-naphthyl phosphate. In a 2-liter flask was placed 261 gm (1 mole) of 1-naphthyl phosphoryl dichloride dissolved in 2 pounds of pyridine. To this solution was added dropwise with cooling 257 gm (2 moles) of redistilled o-chlorophenol.

After standing overnight the reaction mixture was diluted with 5 pounds of CCl_4 , then washed with two successive one-liter portions of water, one liter of 3% HCl, and one liter of water. After separation and drying of the organic layer, the volatile components were stripped off. Distillation of the residue gave 259 gm of bis(o-chlorophenyl) 1-naphthyl phosphate a viscous, greenish-yellow refractive oil, $n_D^{33.5}$ 1.6111, d_4^{25} 1.3525, boiling at 221°C/0.18 mm. The molecular weight was 448 (obsd.); 445 (calc.). The yield was 58%.

(2). Tris(o-chlorophenyl) phosphate. MLO 9522.

To 76.6 gm (0.5 moles) of POCl_3 in a 1-liter, 2-neck round bottom flask was added 192.8 gm (1.5 moles) of redistilled o-chlorophenol. The

flask was equipped with a reflux condenser and thermowell. To the reaction mixture was added 6.7 gm of powdered anhydrous $MgCl_2$ (prepared by heating $MgCl_2 \cdot 6H_2O$ until the original melt re-solidifies completely); the mixture was brought to $200^\circ C$ and refluxed there for 4 hours.

The reaction mixture, after dilution with one liter of CCl_4 , was then washed in turn with one-liter portions of water, 5% KOH, water, 3% HCl and water. After drying the organic layer and removing volatile materials, the residue was vacuum-distilled. The tris(o-chlorophenyl) phosphate was a water-white liquid, $n_D^{30.5}$ 1.5811, d_4^{25} 1.4076, boiling at $195^\circ C/0.13$ mm. The molecular weight was 379 (obsd.); 380 (calc.). The yield was 73%. This compound can be induced to crystallize to a solid melting at $34-35^\circ C$.

(3). Diphenyl 5,6,7,8-tetrahydro-1-naphthyl phosphate. MLO 9523.

a. 5,6,7,8-Tetrahydro-1-naphthol. This preparation followed the method of Papa and Schwenk (1). A solution was made of 100 gm of 1-naphthol in 3 liters of 10% NaOH solution. The solution was heated to $65-75^\circ C$ and then 300 gm of Raney Ni-Al alloy was added portionwise during three and one-half hours. The solution was allowed to stand overnight. During the reaction, it was found desirable to add Dow Corning Antifoam A to break the persistent foam which formed.

The solution was filtered from the nickel residue; then made strongly acid with conc. H_2SO_4 . The reaction mixture was divided into two portions, and each portion was extracted three times with 200 cc portions of ether. The ether solution was dried over anhydrous $MgSO_4$ and most of the ether distilled off. The residue was placed in an evaporating dish to allow the remaining ether to volatilize. The yield was about 30 gm of crude product, melting at $72^\circ C$. Tetrahydronaphthol melts at $71^\circ C$. In all, five lots of product were made, a total of 125-150 gm. The crude tetralol was steam-distilled, resulting in a white product melting at $71-72^\circ C$.

b. Diphenyl 5,6,7,8-tetrahydro-1-naphthyl phosphate. To 155.7 gm (0.58 moles) of diphenyl phosphoryl chloride dissolved in 1 pound of pyridine was added 87.4 gm (0.58 moles) of 1-tetralol. After reaction was complete, the mixture was diluted with five pounds of CCl_4 , then washed in the usual fashion with four one-liter portions of water, dried, and stripped of volatiles. The diphenyl 1-tetralyl phosphate distilled at $199^\circ C/0.14$ mm. The product, a yellow viscous oil, $n_D^{23.5}$ 1.5771, d_4^{25} 1.2197, weighed 136.3 gm, equivalent to a yield of 62%. The molecular weight was 379 (obsd.); 380 (calc.).

(4). 1,3-Phenylene bis(diphenyl phosphate). MLO 9524.

To a solution of 55.1 gm (0.5 moles) of resorcinol dissolved in

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one pound of pyridine was added 268.5 gm (1.0 mole) of diphenyl phosphoryl chloride. A considerable amount of heat was evolved. After standing for 15 hours, the mixture was diluted in the usual fashion with five pounds of CCl_4 , then washed successively with one-liter portions of water, 5% KOH, water, 3% HCl and water. The organic layer was then dried over anhydrous MgSO_4 and the volatile material distilled off. Distillation of the residue gave 152.1 gm of 1,3-phenylene bis(diphenyl phosphate), a water-white, fairly viscous liquid, b.p. $284^\circ\text{C}/0.09\text{ mm}$, n_D^{30} 1.5739, d_4^{25} 1.2916. The yield was 53%. In this case as in several others, the distillate appeared clear, while distilling, but had a hazy appearance in the receiver. The molecular weight checked well, being 575 (obsd.), 574 (calc.).

(5). Bis(p-chlorophenyl) 1-naphthyl phosphate. MLO 9525.

To a solution of 195.7 gm (0.75 moles) of 1-naphthyl phosphoryl dichloride in one pound of pyridine was added 192.5 gm (1.5 moles) of p-chlorophenol. After allowing the mixture to stand for 15 hours, it was diluted with five pounds of CCl_4 , then washed in succession with one-liter portions of water, 5% KOH, water, 3% HCl and water, then dried over anhydrous MgSO_4 . The volatiles were distilled off and the residue vacuum-distilled. The product, weighing 248.9 gm (74.6% yield), was a viscous yellow liquid, b.p. $229\text{--}237^\circ\text{C}/0.09\text{ mm}$, n_D^{25} 1.6110, d_4^{25} 1.3526. The observed molecular weight was 444, in good agreement with the calculated value of 445.

(6). Diphenyl 2-chloro-1-naphthyl phosphate. MLO 9526.

a. t-Butyl hypochlorite. Following the procedure of Irwin and Hennion (2), to a 5-liter flask equipped with a stirrer, inlet tube and outlet tube was charged 480 gm of approximately 30% NaOH and 148.2 gm (2 moles) of t-butyl alcohol. To the layered mixture was added water until the layers disappeared. This required dilution to about 2 liters. Chlorine gas was then bubbled through the solution until it was no longer absorbed. The reaction mixture was kept ice-cold during the process. The volatile, yellow oil which formed an upper layer was washed with 200 cc of saturated Na_2CO_3 solution, then dried over CaCl_2 . Safety precautions for handling this material are given in the reference.

b. 2-Chloro-1-naphthol. In accordance with the procedure of Ginsburg (3), a suspension of 246.4 gm (1.71 moles) of 1-naphthol in 900 cc of CCl_4 , contained in a 2-liter flask equipped with a stirrer, dropping funnel and condenser, was reacted with 185 gm (1.71 moles) of t-butyl hypochlorite added dropwise. The solution became warm and a dark-red color appeared. The naphthol dissolved. The reaction mixture was refluxed for 2 hours, then the volatiles were distilled off, up to a flask temperature of 150°C . Then three vacuum distillations gave 191 gm of product boiling between $117\text{--}128^\circ\text{C}/3.9\text{ mm}$. This product was obtained in five fractions having the follow-

ing observed molecular weights: 175.8, 176.4, 176.7, 179.1, 178.6. The calculated molecular weight of 2-chloro-1-naphthol is 178.5. The product was a white solid having a phenolic odor; it tended to turn pink on standing. The melting point was 54-56°C. The combined yield was 63%.

c. Diphenyl 2-chloro-1-naphthyl phosphate. To a solution of 95.0 gm (0.531 moles) of 2-chloro-1-naphthol dissolved in pyridine was added 142.6 gm (0.531 moles) of diphenyl phosphoryl chloride. After standing for 15 hours, the mixture was diluted with five pounds of CCl_4 , then washed in sequence with one-liter portions of water, 5% KOH, water, 3% HCl and water. After preliminary stripping, the residue was vacuum-distilled. The product, a viscous yellow liquid, had a boiling point of 207-208°C/0.1 mm, n_D^{20} 1.6153, d_4^{25} 1.3021. The weight was 147.9 gm, equivalent to a yield of 68%. The molecular weight was 412 (obsd.); 410 (calc.).

(7). 1,3-(4-chlorophenylene) bis(diphenyl phosphate). MLO 9527.

To a solution of 63 gm (0.435 moles) of 4-chlororesorcinol in one pound of pyridine was added 234 gm (0.87 moles) of diphenyl phosphoryl chloride, and the mixture allowed to stand for 15 hours. The reaction mixture was added to five pounds of CCl_4 and the solution washed successively with 1-liter portions of water, 5% KOH, 3% HCl and water. After the solution had been dried over anhydrous MgSO_4 , the volatile materials were removed by distillation up to 150°C (flask temperature) under aspirator vacuum. Two vacuum distillations gave 90.6 gm of product, a cloudy, fairly viscous liquid boiling at 285-289°C/0.2 mm, d_4^{25} 1.3297. The yield was 34%. Molecular weight; 613 (obsd.), 608.5 (calc.).

(8). 1,6-Naphthylene bis(diphenyl phosphate). MLO 9528.

In a 1-liter flask was placed 80.1 gm (0.5 mole) of 1,6-naphthalenediol (Eastman, Pract.) dissolved in one pound of pyridine and 268.6 gm (1.0 mole) of diphenyl phosphoryl chloride. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 and washed with 1-liter portions of water, 5% KOH, water, 3% HCl and water. After heating to 200°C under aspirator vacuum to remove volatiles, the residue was vacuum-distilled. The product appeared to decompose somewhat on distillation. A yield of 55.2 gm (17.7% of theory) of viscous liquid was obtained, b.p. 265-275°C/0.21 mm, $n_D^{21.5}$ 1.5998, d_4^{25} 1.2950, molecular weight (obsd.) 586. The calculated molecular weight was 624.

(9). Bis(p-chlorophenyl) 2-chloro-1-naphthyl phosphate. MLO 9529.

a. Di-p-chlorophenyl phosphoryl chloride. In a 5-liter round bottom flask equipped with a reflux condenser and thermowell was placed 1075 gm

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(7 moles) of POCl_3 and 1800 gm (14 moles) of p-chlorophenol. The mixture was heated to 200°C and kept there for 7 hours. After distillation to a flask temperature of 150°C under aspirator vacuum, the residue was vacuum-distilled. The final product, a water-white refractive liquid, weighed 1111 gm, a yield of 46.8%. The product had a boiling point of $212^\circ\text{C}/5$ mm, molecular weight 337 (obsd.); 339 (calc.).

Also obtained as a by-product was 189.5 gm of p-chlorophenyl phosphoryl dichloride, b.p. $143^\circ\text{C}/17$ mm, which is equivalent to a yield of 11% based on POCl_3 .

b. Bis(p-chlorophenyl) 2-chloro-1-naphthyl phosphate. In a 1-liter Erlenmeyer flask was placed a solution of 80.0 gm (0.448 moles) of 2-chloro-1-naphthol in one pound of pyridine. To this solution was added 150.6 gm (0.448 moles) of di-p-chlorophenyl phosphoryl chloride. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 and washed in the usual sequence with 1-liter portions of water, 5% KOH, 3% HCl and water. After drying the solution over MgSO_4 , the volatiles were removed by heating to 150°C under aspirator vacuum. Two vacuum distillations then gave 132.9 gm of a viscous orange-yellow liquid boiling from 232 - $237^\circ\text{C}/0.1$ mm. The liquid could be induced to crystallize to a solid melting at 80 - 81°C . The yield was 62%. The observed molecular weight was 465; the calculated value was 479.5.

(10). 1,4-Phenylene bis(diphenyl phosphate). MLO 9530.

In a 1-liter flask was placed 55.1 gm (0.5 mole) of hydroquinone dissolved in one pound of pyridine and 268.6 gm (1.0 mole) of diphenyl phosphoryl chloride. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 , and washed successively with 1-liter portions of water, 5% KOH, water, 3% HCl and water. A considerable amount of white granular material precipitated out of solution. The solid was filtered off, and the CCl_4 solution was dried over anhydrous MgSO_4 . Removal of the CCl_4 left very little residue. The white solid previously filtered off was recrystallized from dioxane. The melting point was 105°C and the molecular weight was 543. The calculated molecular weight for 1,4-phenylene bis(diphenyl phosphate) was 574. Vacuum distillation of this material gave 102.3 gm of product, a white solid melting at 109°C , b.p. 288 - $290^\circ\text{C}/0.13$ mm, molecular weight 575 (obsd.); 574 (calc.). The yield was 35.6%.

(11). Triphenyl thiophosphate. MLO 9531.

Into a 1-liter flask fitted with a thermowell and 80 cm reflux condenser was placed 338.8 gm (2 moles) of thiophosphoryl chloride and 376.4 gm (4 moles) of phenol. Refluxing for 38 hours resulted in little

apparent reaction, the reflux temperature reaching only 147°C. The reaction mixture was cooled, and 6.8 gm (2 wt.% based on PSCl_3) of PCl_3 was added to catalyze the reaction (4). The temperature was then brought to 200°C in 2 hours and reflux was continued for 4 hours. After repeated fractionations, there was obtained 192.9 gm of triphenyl thiophosphate, a white solid melting at 53-54°C, b.p. 212°C/4 mm, $n_D^{30.5}$ 1.5897 (supercooled liquid), molecular weight 343 (obsd.); 342 (calc.). The product had a strong H_2S odor.

(12). Diphenyl 3-pyridyl phosphate. MLO 9532.

To a solution of 95.1 gm (1 mole) of 3-pyridol dissolved in one pound of pyridine was added 268.5 gm (1 mole) of diphenyl phosphoryl chloride. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 and washed with 1-liter quantities of water, 5% KOH, 3% HCl and water. After drying over anhydrous MgSO_4 , the CCl_4 and other volatile materials were removed by heating at atmospheric pressure and under aspirator vacuum to a flask temperature of 150°C. Two subsequent distillations gave 194.3 gm of diphenyl 3-pyridyl phosphate, a fairly mobile yellow liquid, b.p. 183-185°C/0.10 mm, n_D^{22} 1.5672. Upon prolonged refrigeration, the liquid crystallized to a solid, m.p. 33°C. The pour point of the liquid was -30°F. The yield was 56.6%. Molecular weight 331 (obsd.); 328 (calc.).

(13). 4,4'-Biphenylene bis(diphenyl phosphate). MLO 9533.

To a solution of 93.1 gm (0.5 mole) of 4,4'-dihydroxybiphenyl in one pound of pyridine was added 268.5 gm (1.0 mole) of diphenyl phosphoryl chloride, and the mixture allowed to stand for 60 hours. After adding five pounds of CCl_4 , and washing successively with 1-liter portions of water, 5% KOH, 3% HCl and water, the solution was dried over anhydrous MgSO_4 . After removal of volatiles by heating under aspirator vacuum to a temperature of 150°C, the residue was vacuum-distilled. The product was a white solid, m.p. 89°C, which boiled at 339-343°C/0.14 mm. The molecular weight was 650 (obsd.); 650 (calc.). The yield was 145.2 gm or 44.7%.

(14). Bis(1-naphthyl) 3-pyridyl phosphate. MLO 9534.

To 184.3 gm (0.5 mole) of dinaphthyl phosphoryl chloride dissolved in one-half pound of pyridine was added 47.5 gm (0.5 mole) of 3-hydroxypyridine. After standing for about 36 hours, the reaction mixture was diluted with five pounds of CCl_4 and washed with 1-liter portions of water, 5% KOH and water. After stripping off volatiles by heating to 150°C under aspirator vacuum, the reaction product was vacuum-distilled. The product was a very viscous orange liquid, n_D^{27} 1.6372, b.p. 243-248°C/0.11 mm. The mole-

cular weight was 432 (obsd.); 427 (calc.).

(15). Bis(2,4-dichlorophenyl) 1-naphthyl phosphate. MLO 9535.

To 163 gm (1 mole) of 2,4-dichlorophenol dissolved in one pound of pyridine was added 130.5 gm (0.5 mole) of 1-naphthyl phosphoryl dichloride. After standing for 15 hours, the product was worked up in the usual manner by addition of five pounds of CCl_4 , washing with 1-liter portions of water, 5% KOH, 3% HCl and water, then drying the solution over anhydrous MgSO_4 and distilling off the volatiles under aspirator vacuum up to 150°C . Two vacuum distillations gave 103.4 gm of bis(2,4-dichlorophenyl) 1-naphthyl phosphate, a very viscous yellow liquid, n_D^{25} 1.6210, boiling at $248-249^\circ\text{C}/0.16$ mm. The molecular weight was 514 (obsd.); 514 (calc.).

(16). Bis(2-biphenyl) 1-naphthyl phosphate. MLO 9536.

To 170.2 gm (1 mole) of o-phenylphenol dissolved in one pound of pyridine was added 130.5 gm (0.5 moles) of 1-naphthyl phosphoryl dichloride. After standing 15 hours, the mixture was heated to 110°C and kept there for 1 hour to insure complete reaction. The mixture was cooled, diluted with five pounds of CCl_4 , and washed successively with 1-liter portions of water, 5% KOH, 3% HCl, and water, dried over anhydrous MgSO_4 , and stripped of volatiles by heating to 150°C under aspirator vacuum. Vacuum distillation gave 173.9 gm (66.4% yield) of product, a glassy liquid boiling at $271^\circ\text{C}/0.1$ mm. Upon crystallization of the liquid, a solid melting at $78-79^\circ\text{C}$ was obtained. The molecular weight was 529 (obsd.); 524 (calc.).

(17). Diphenyl 2,4-dichloro-1-naphthyl phosphate. MLO 9537.

To 106.5 gm (0.5 mole) of 2,4-dichloro-1-naphthol dissolved in one pound of pyridine was added 134.5 gm (0.5 mole) of diphenyl phosphoryl chloride. The mixture was heated to 110°C and refluxed at that temperature for 1 hour. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 and washed successively with 1-liter portions of water, 5% KOH, 3% HCl and water. Removal of volatiles by stripping under aspirator vacuum up to 150°C left a residue which was vacuum-distilled. The product, diphenyl 2,4-dichloro-1-naphthyl phosphate, weighing 105.3 gm, was a red, viscous liquid, boiling at $236^\circ\text{C}/0.11$ mm, which slowly crystallized to a solid melting at $64-65^\circ\text{C}$. The molecular weight was 443 (obsd.); 445 (calc.). The yield was 47.3%.

(18). Bis(1-naphthyl) o-chlorophenyl phosphate. MLO 9538.

To 92.3 gm (0.25 moles) of di-1-naphthyl phosphoryl chloride dissolved in one pound of pyridine was added 32.2 gm (0.25 moles) of o-chloro-

phenol. The mixture was heated to 110°C for 1 hour to insure complete reaction, then allowed to cool. To the reaction mixture was added five pounds of CCl₄ and the solution was washed in turn with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution was dried over anhydrous MgSO₄ and stripped of volatiles by heating to 150°C under aspirator vacuum. The residue was then vacuum-distilled. The product was an extremely viscous orange liquid, b.p. 248-250°C/0.13 mm, molecular weight 462 (obsd.); 460.5 (calc.). The weight of product was 173.9 gm, equivalent to a yield of 66.4%.

(19). 1,4-(2-Chlorophenylene) bis(diphenyl phosphate). MLO 9539.

To 100.0 gm (0.69 moles) of chlorohydroquinone dissolved in one pound of pyridine was added 371.0 gm (1.38 moles) of diphenyl phosphoryl chloride. The reaction mixture was heated to reflux, then allowed to cool. After the addition of five pounds of CCl₄, the mixture was washed in turn with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution was then dried over anhydrous MgSO₄ and stripped by heating to 150°C under aspirator vacuum. Vacuum distillation gave 234.5 gm of product boiling at 285-288°C/0.14 mm. The yield was 54.9%. The product solidified on standing and, when recrystallized twice from ethanol, melted at 71-72°C. The molecular weight of the recrystallized material was 572 (obsd.); 608.5 (calc.), being a deviation of 6%. Probably some solvent retention occurred.

(20). Tris(2-biphenyl) phosphate. MLO 9540.

In a 2-neck, 500 cc round-bottom flask equipped with a thermowell and spiral condenser was placed 255.3 gm (1.5 moles) of *o*-phenylphenol and 76.7 gm (0.5 mole) of POCl₃. After the addition of 8.3 gm of anhydrous MgCl₂, the mixture was heated to 200°C and kept at that temperature until reflux had stopped. After cooling, the product was poured into a 2-liter Erlenmeyer flask and dissolved in warm ether-benzene. The solution was washed with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution was then dried over anhydrous MgSO₄ and stripped of volatiles up to 150°C under aspirator vacuum. Vacuum distillation gave 183.7 gm of product, a white solid. The boiling point was 275-278°C/0.18 mm. After recrystallization from ethanol, the m.p. was 114.5-115°C. The molecular weight was 537 (obsd.); 554 (calc.). Here again, it is thought that a small amount of solvent was retained.

(21). Tris(3-chloro-2-biphenyl) phosphate. MLO 9541.

A mixture of 307.1 gm (1.5 moles) of 2-chloro-6-phenylphenol, 76.5 gm (0.5 mole) of POCl₃ and 11.2 gm of anhydrous MgCl₂ was heated until the temperature reached 200°C. The reaction mixture was then cooled, dissolved in about 3 liters of benzene, and washed successively with 1-liter portions of water, 5% KOH, 3% HCl and water. It was dried over anhydrous

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MgSO₄, then stripped of volatile material by heating to 150°C under aspirator vacuum. The product, a white solid boiling at 278-280°C/0.23 mm, was then obtained by vacuum distillation of the residue. The yield was 102.9 gm, equivalent to 31.3%. Upon recrystallization of the solid from ethanol with some benzene added, the melting point was 194-195.5°C. Due to low solubility in ordinary cryoscopic solvents, no molecular weight was determined.

(22). Tris(3-chloro-4-biphenyl) phosphate. MLO 9542.

A mixture of 307.1 gm (1.5 moles) of 2-chloro-4-phenylphenol, 46.5 gm (0.5 mole) of POCl₃ and 11.2 gm of anhydrous MgCl₂ was heated to 200°C, then allowed to cool. The reaction product was dissolved in about three pounds of benzene and washed with 1 liter of water. A curdy emulsion formed which was broken by the addition of one pound of ether. The solution was then washed twice with 500 cc portions of 5% KOH, then twice with 500 cc portions of 3% HCl. A final water wash caused the re-formation of the curdy solid. The addition of ethylene dichloride did not dissolve the solid. After standing, the solid had settled out, leaving a dark supernatant organic layer. The solid was removed by filtration and dried. The liquid was dried over anhydrous MgSO₄, then stripped. Very little residue was left. The solid was combined with the residue, and the mixture vacuum-distilled. The product was a solid weighing 158.9 gm, boiling at 337-340°C/0.12 mm. The yield was 48.3%. The product, recrystallized twice from ethanol-benzene, melted at 153-154.5°C. The slight solubility of the product in benzene made a molecular weight determination difficult. A value of 607 (obsd.); 657.5 (calc.) was obtained on a very dilute solution.

(23). Diphenyl 5-indanyl phosphate. MLO 9543.

To a solution of 51.2 gm (0.382 mole) of 5-indanol (research sample furnished by Carbide and Carbon Chemicals Company) in one pound of pyridine was added 102.7 gm (0.382 moles) of diphenyl phosphoryl chloride. The solution was heated to reflux, then allowed to cool. After standing for 15 hours, the solution was mixed with five pounds of CCl₄ and washed in the usual sequence with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution was dried over anhydrous MgSO₄, then the volatiles were distilled off. Two vacuum distillations gave 90.2 gm of product, a water-white liquid boiling at 199-201°C/0.21 mm, crystallizing to a solid melting at 29°C. The molecular weight was 356 (obsd.); 366 (calc.). Other properties were: d_4^{25} 1.2224, n_D^{19} 1.5770. The yield was 49.3%.

(24). Diphenyl 4-indanyl phosphate. MLO 9544.

To a solution of 50.6 gm (0.378 moles) of 4-indanol (a research

Continued

sample supplied by Carbide and Carbon Chemicals Company) in one pound of pyridine was added 101.5 gm (0.378 moles) of diphenyl phosphoryl chloride. The solution was heated to reflux and allowed to cool. To the reaction mixture was added five pounds of CCl_4 , after which it was washed with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution was dried over anhydrous MgSO_4 , then distilled up to 150°C under aspirator vacuum. Two subsequent vacuum distillations gave 95.9 gm (52.4% yield) of product, a colorless fairly viscous liquid boiling from $194\text{--}196^\circ\text{C}/0.16$ mm, d_4^{25} 1.2227, n_D^{20} 1.5753. The molecular weight was 362 (obsd.); 366 (calc.).

(25). Tris(2,4-dichlorophenyl) phosphate. MLO 9545.

A mixture of 244.5 gm (1.5 moles) of 2,4-dichlorophenol and 76.5 gm (0.5 mole) of POCl_3 plus 8.0 gm of anhydrous MgCl_2 was heated to 200°C and kept there for 4 hours. The reaction mixture was stripped up to 180°C under aspirator vacuum. Two vacuum distillations then gave 143.3 gm (a 54.3% yield) of product, a white crystalline solid, b.p. $242\text{--}246^\circ\text{C}/0.14$ mm, m.p. $92.5\text{--}94^\circ\text{C}$, molecular weight 528 (obsd.); 533 (calc.).

(26). Diphenyl benzenephosphonate. MLO 9546.

To a solution of 188 gm (2 moles) of phenol dissolved in one pound of pyridine was added 195 gm (1 mole) of dichlorophenylphosphine oxide (Eastman, Pract.; redistilled, b.p. $116\text{--}120^\circ\text{C}/6$ mm). A large amount of heat was liberated, requiring intermittent cooling of the reaction flask. After standing for 15 hours, the reaction mixture was diluted with five pounds of CCl_4 , then washed in turn with 1-liter portions of water, 5% KOH, 3% HCl and water. After the solution was dried over anhydrous MgSO_4 , the volatile components were removed by heating to 150°C under aspirator vacuum. Subsequent vacuum distillation gave 238 gm of diphenyl benzenephosphonate, b.p. $170\text{--}174^\circ\text{C}/0.14$ mm, m.p. 76°C , molecular weight 314.5 (obsd.); 310 (calc.). The yield was 76.8%.

(27). Tris(o-bromophenyl) phosphate. MLO 9547.

A mixture of 249.1 gm (1.44 moles) of o-bromophenol and 73.6 gm (0.48 mole) plus 8.1 gm of anhydrous MgCl_2 was heated to 200°C and kept there until reflux had stopped. The mixture was then cooled, diluted with five pounds of CCl_4 , and washed with 1-liter portions of water, 5% KOH, 3% HCl and water. After drying the solution over anhydrous MgSO_4 and removing the volatiles by heating the 160°C under aspirator vacuum, the residue was vacuum-distilled. The product, a white crystalline solid weighing 103.2 gm (a yield of 38.3%) had the following properties: b.p. $225\text{--}228^\circ\text{C}/0.22$ mm, m.p. $83\text{--}84^\circ\text{C}$, molecular weight 554 (obsd.); 563 (calc.).

(28). 1,5-Naphthylene bis(diphenyl phosphate). MLO 9548.

To a solution of 71.6 gm (0.447 mole) of 1,5-naphthalenediol (Eastman, Pract.) in one pound of pyridine, was added 240.2 gm (0.894 mole) of diphenyl phosphoryl chloride and the mixture allowed to stand for 70 hours. After the addition of five pounds of CCl_4 to the reaction mixture, it was washed successively with 1-liter portions of water, 5% KOH, 3% HCl and water. A brown crystalline precipitate settled out and was removed. The solution was dried over anhydrous MgSO_4 and allowed to stand for 15 hours, upon which more precipitate settled out. This was filtered off, washed with water to remove MgSO_4 and dried. The filtrate was distilled, but very little residue was obtained. The brown precipitate previously obtained was recrystallized several times, finally from benzene, giving a white powder, m.p. 144-145°C. The weight was 95 gm, a yield of 34.1%. The molecular weight was not determined due to the insolubility of the compound in freezing benzene.

(29). Bis(o-chlorophenyl) benzenephosphonate. MLO 9549.

To a solution of 257.2 gm (2 moles) of o-chlorophenol in one pound of pyridine was added 195 gm (1 mole) of dichlorophenylphosphine oxide. The reaction vessel was cooled in an ice-bath. After the reaction mixture had stood for about 50 hours, it was diluted with five pounds of CCl_4 , then washed successively with 1-liter portions of water, 5% KOH, 3% HCl and water. The solution, after drying over anhydrous MgSO_4 , was stripped of solvent and other volatile materials by heating to 150°C under aspirator vacuum. Subsequent vacuum distillation gave 287.4 gm of product, a colorless, fairly viscous oil, b.p. 194-197°C/0.24 mm, d_4^{25} 1.3378, n_D^{21} 1.5965, molecular weight 375 (obsd.); 379 (calc.). The yield was 75.8%.

(30). Bis(2,4-dichlorophenyl) benzenephosphonate. MLO 9550.

To a solution of 97.8 gm (0.6 mole) of 2,4-dichlorophenol dissolved in one pound of pyridine was added 58.5 gm (0.3 mole) of dichlorophenylphosphine oxide. An ice-bath was used to moderate the reaction. After reaction was complete, the pyridine hydrochloride formed by the reaction was filtered off, and the filtrate stripped of volatiles by heating to 150°C under aspirator vacuum. Subsequent vacuum distillation gave 77.4 gm (57.6% yield) of product, a solid, b.p. 220-223°C/0.2 mm, m.p. 117-118.5°C, molecular weight 448 (obsd.); 448.5 (calc.).

(31). Diphenyl pentachlorophenyl phosphate. MLO 9551.

To a solution of 133.2 gm (0.5 moles) of pentachlorophenol in one pound of pyridine was added 134.3 gm (0.5 moles) of diphenyl phosphoryl

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chloride. After the initial heat of reaction had subsided the solution was reheated to reflux temperature then allowed to cool. The reaction mixture was filtered, then distilled at atmospheric pressure to remove the pyridine, up to a flask temperature of 150°C. After a further stripping up to 150°C under aspirator vacuum, the reaction product was vacuum-distilled. The product was a white solid weighing 76.3 gm, b.p. 220-226°C/0.16 mm, m.p. 120-121.5°C. The molecular weight was 487 (obsd.); 498.5 (calc.). The yield was 30.6%.

(32). Tris(pentachlorophenyl) phosphate. MLO 9552.

To a solution of 217.3 gm (0.82 moles) of pentachlorophenol in one pound of pyridine was added 41.6 gm (0.27 moles) of POCl₃ dissolved in one-half pound of pyridine. The addition was portion-wise. The reaction was exothermic. As soon as the POCl₃ solution contacted the pentachlorophenol solution crystals formed and gradually increased in amount. After standing overnight, the mass of white crystals was vacuum-filtered, then washed with ethanol. The crystals were then dispersed in ethanol, allowed to stand for several hours with frequent swirling, then re-filtered. After two washings on the filter with ethanol, the crystals were again dispersed in ethanol, allowed to stand, filtered and washed twice as before, then dried in a desiccator. The weight of product was 141 gm, a yield of 62%. The melting point was 230-240°C with darkening. The material seemed slightly soluble in boiling pyridine; insoluble in ether, dioxane, benzene, chloroform, carbon tetrachloride, methanol, isopropyl alcohol, butanol, heptane and ethyl acetate.

(33). Tris(m-chlorophenyl) phosphate. MLO 9553.

A mixture of 150 gm (1.17 moles) of m-chlorophenol and 59.9 gm (0.39 moles) of POCl₃, together with 5.2 gm of anhydrous MgCl₂ was heated to 200°C and refluxed for 3 hours. The reaction mixture was then stripped by distillation to 150°C at atmospheric pressure followed by heating under aspirator vacuum to 150°C. Subsequent vacuum distillation gave 120.7 gm of product, a water-white liquid, b.p. 196-197°C/0.12 mm, n_D^{21} 1.5820, d_4^{25} 1.4031. The molecular weight was 430 (obsd.); 429.5 (calc.). The yield was 72.1%.

(34). Phenyl o-chlorophenyl 1-naphthyl phosphate. MLO 9554.

a. Phenyl 1-naphthyl phosphoryl chloride. A mixture of 320.8 gm (1.23 moles) of 1-naphthyl phosphoryl chloride and 115.7 gm (1.23 moles) of phenol was heated to reflux. The flask temperature rose gradually until at 265°C there was practically no reflux. This heating required three hours. The reaction mixture was cooled, then stripped by heating to about

230°C under aspirator vacuum. The residue was then vacuum-distilled. The product was a white refractive liquid, b.p. 178-179.5°C/0.11 mm, n_D^{20} 1.6000, d_4^{25} 1.3078. The molecular weight was 322 (obsd.); 318.5 (calc.).

b. Phenyl o-chlorophenyl 1-naphthyl phosphate. To 50.6 gm (0.392 moles) of o-chlorophenol dissolved in one-half pound of pyridine was added 125.0 gm (0.392 moles) of phenyl 1-naphthyl phosphoryl chloride. This flask was rinsed with one-half pound of pyridine which was added to the reaction vessel. The reaction mixture was heated to reflux and allowed to cool.

The pyridine hydrochloride was filtered off and the filtrate was concentrated by heating to 150°C at atmospheric pressure then reheating to 150°C under aspirator-vacuum. Vacuum-distillation then gave 113.5 gm of the product, an almost colorless, somewhat viscous liquid, b.p. 225-227°C/0.31 mm, $n_D^{21.5}$ 1.6091, d_4^{25} 1.3003. The molecular weight was 409 (obsd.); 410.5 (calc.). The yield was 70.5%.

(35). Tris(3,5-dimethylphenyl) phosphate. MLO 9555.

A mixture of 183.3 gm (1.5 moles) of 3,5-dimethylphenol and 76.8 gm (0.5 moles) of POCl_3 in the presence of 6.5 gm of anhydrous MgCl_2 was heated to 200°C and held there for 7 hours. Then the volatiles were removed by heating to 150°C, first under atmospheric pressure, then under aspirator vacuum. Vacuum distillation of the residue gave 151.9 gm of the product, a colorless liquid, b.p. 200-202°C/0.18 mm, n_D^{22} 1.5529, d_4^{25} 1.1274, which crystallized to a solid melting at 46-46.5°C. The molecular weight was 407 (obsd.); 410 (calc.). The yield was 74.1%.

(36). Tris(3,4-dimethylphenyl) phosphate. MLO 9556.

A mixture of 183.3 gm (1.5 moles) of 3,4-dimethylphenol, 76.8 gm (0.5 moles) of POCl_3 and 6.5 gm of anhydrous MgCl_2 was heated to 200°C and refluxed there for 6 hours. The reaction mixture was then heated to 150°C under aspirator vacuum to remove volatile material. Subsequent vacuum distillation gave 140.2 gm of product, a solid boiling at 213-215°C/0.19 mm, m.p. 71.5-72.5°C. The molecular weight was 397 (obsd.); 410 (calc.).

(37). Tris(o-fluorophenyl) phosphate. MLO 9557.

A mixture of 134.4 gm (1.2 moles) of o-fluorophenol, 61.4 gm (0.4 moles) of POCl_3 and 4.9 gm of anhydrous MgCl_2 was heated to 200°C. The reaction started quite vigorously upon initial application of heat, but soon moderated. After the reaction was complete the volatile material was removed by heating to 200°C under aspirator vacuum. Vacuum distillation gave 107.3 gm of product, a white solid melting at 79-81°C. The molecular weight

values were 388 (obsd.); 380 (calc.). The yield was 70.6%.

(38). Diphenyl 3,4-dimethylphenyl phosphate. MLO 9558.

To a solution of 61.0 gm (0.5 moles) of 3,4-dimethylphenol in one pound of pyridine was added 134.0 gm (0.5 moles) of diphenyl phosphoryl chloride. Then the mixture was heated to reflux, cooled and refrigerated for 65 hours. The pyridine hydrochloride which crystallized out was removed by vacuum filtration. After removing volatiles by heating to 170°C, finally under aspirator vacuum, the product was obtained by vacuum distillation of the residue. The product was a white solid, b.p. 183-184°C/0.13 mm, m.p. 48-49°C. The weight of product was 125.5 gm, which was equivalent to 70.9% of the theoretical.

(39). Diphenyl 3,5-dimethylphenyl phosphate. MLO 9559.

To a solution of 61.0 gm (0.5 moles) of 3,5-dimethylphenol in one pound of pyridine was added 134.0 gm (0.5 moles) of diphenyl phosphoryl chloride. The mixture was refrigerated for 15 hours, after heating to reflux and allowing to cool. The pyridine hydrochloride crystals were filtered off, and the filtrate stripped by the usual process of distillation at atmospheric pressure to a flask temperature of 150°C followed by distillation up to 200°C under aspirator vacuum. The product then obtained by vacuum distillation was a low-melting solid, b.p. 181-183°C/0.1 mm, m.p. 32-33°C, molecular weight 350 (obsd.); 354 (calc.). The yield was 89.9 gm, 50.8% of theory.

(40). Diphenyl 4-biphenylyl phosphate. MLO 9560.

To 85.1 gm (0.5 moles) of p-phenylphenol dissolved in one-half pound of pyridine was added 134.3 gm (0.5 moles) of diphenyl phosphoryl chloride. The mixture was heated to the boiling point, then allowed to cool and stand for 15 hours. The crystals were filtered off, and the pyridine was stripped by heating the solution to 150°C, first at atmospheric pressure, then under aspirator vacuum. The product, upon vacuum distillation, was a white solid, b.p. 216-222°C/0.07 mm, m.p. 64-65°C, molecular weight 396 (obsd.); 402 (calc.). The product weighed 117.5 gm, a yield of 58.5%.

(41). Tris(m-trifluoromethylphenyl) phosphate. MLO 9561.

a. m-Trifluoromethylphenol. A 500 gm (3.1 moles) portion of m-trifluoromethylaniline (Halogen Chemicals, Inc., Columbia, S. C.) was added gradually with stirring to a warm solution of 259 ml of conc. H₂SO₄ (4.65 moles) in 2 liters of water contained in a 4-liter beaker. The amine sul-

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fate was dispersed as it formed. The mixture was cooled to 3°C in an ice bath and a solution of 248 gm of NaNO₂ (3.6 moles) in 500 ml of water was added with stirring over a 15 minute period. About 6 or 7 handfuls of crushed ice were added directly to the reaction mixture during the addition of NaNO₂. After completion of the addition (during which the temperature rose to 11.5°C) the solution was stirred an additional 20 minutes. The diazonium solution was removed from the ice bath, and urea was added until there was a negative test for HONO using starch-iodide paper. Then the solution (about 4 liters) was placed in a 5-liter flask and heated to about 95°C, at which temperature reflux occurred. On heating, the solution turned red and a layer of dark red liquid collected on the bottom of the flask. After about 5 minutes heating, the heating mantle was removed and the solution was allowed to stand for about one-half hour, during which time nitrogen was evolved. The reaction mixture was then heated to reflux a few more minutes, then allowed to cool.

Most of the aqueous layer was decanted off. The red oil was taken up in ether, then the aqueous layer was saturated with NaCl and extracted twice with ether. The ether extracts were combined, dried over anhydrous MgSO₄. After distilling off the ether, the residue was fractionated. A crude product, b.p. 172-187°C, weighing 222.2 gm was obtained. This was dissolved in about an equal volume of ether, extracted twice with 250 ml portions of saturated NaCHO₃ solution to remove HF present and dried over anhydrous MgSO₄. After removal of the ether and fractionation, a product was obtained, boiling at 171-185°C, weighing 178.3 gm. The phenol was a yellow-orange oil. The yield was 35%.

A better preparation of *m*-trifluoromethyl phenol has been used by Dr. M. S. Carpenter of the Givaudan Corporation and is quoted here, with his kind permission, as an item of general interest.

120 gm of *m*-aminobenzotrifluoride was added with agitation to a previously prepared solution of 462 gm 93% H₂SO₄ in 1575 gm of water. The mixture was warmed to 60°, at which point the sulfate went into solution. The solution was then cooled, maintaining agitation. At 30° the sulfate precipitated out in finely divided form. The mixture was cooled to -5° and a solution of 54 gm NaNO₂ in 100 gm water was added during 20 minutes. The resulting clear solution was held at -5° to -6° for 10 minutes longer and a little urea was added to destroy nitrous acid.

A vigorous current of steam was passed into a solution of 75 gm of 93% H₂SO₄ in 370 gm water and the cold

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diazonium solution was dropped in during 20 minutes. Steam distillation was continued until no more oil passed over. The oil layer was removed and the aqueous layer extracted with benzene. The combined oil and extracts from four such operations were combined and distilled.

Fract. I	to 56°/3mm	1 gm
Fract. II	56-57°/3mm	430 gm
Residue		7 gm

d_{25}^{25} 1.3458 n_D^{20} 1.4570

b. Tris(m-trifluoromethylphenyl) phosphate. A mixture of 133.5 gm (0.825 moles) of m-trifluoromethylphenol, 42.2 gm (0.275 moles) of POCl_3 and 4.4 gm of anhydrous MgCl_2 was heated to 200°C and kept there for four hours. The mixture was stripped by heating to 150°C under aspirator vacuum, then vacuum-distilled. The product was a thin yellow liquid, b.p. 151-154°C/0.15 mm, m.p. 13°C, n_D^{26} 1.6790, d_4^{25} 1.4576. The molecular weight was 529 (obsd.); 530 (calc.). The yield was 103.5 gm, equivalent to 71%.

(42). Phenyl m-trifluoromethylphenyl 1-naphthyl phosphate. MLO 9562.

To 44.5 gm (0.275 moles) of m-trifluoromethylphenol in three-fourths pound of pyridine was added 87.5 gm (0.275 moles) of phenyl 1-naphthyl phosphoryl chloride. The mixture was heated to reflux, allowed to cool and stored under refrigeration for 15 hours. Then the pyridine hydrochloride was filtered off and the filtrate was stripped of volatiles, first under atmospheric pressure, then under aspirator vacuum. The product, obtained by vacuum distillation of the residue, was a pale yellow, somewhat viscous oil, b.p. 198-205°C/0.25 mm, n_D^{25} 1.5642, d_4^{25} 1.3215, molecular weight 437 (obsd.); 444 (calc.). The weight of product was 77.1 gm, a yield of 63%.

(43). Bis(o-chlorophenyl) 4-biphenyl phosphate. MLO 9563.

a. Di-o-chlorophenyl phosphoryl chloride. In a 3-liter, 2-neck flask was placed 1708.7 gm (13.3 moles) of o-chlorophenol and 1019.0 gm (6.65 moles) of POCl_3 . To the mixture was added 185.6 gm (3.32 moles) of degreased cast iron filings (5). The mixture was then refluxed until the flask temperature reached 250°C. It was then allowed to cool. After filtering off the insoluble residue the reaction mixture was stripped under aspirator vacuum to 150°C. A series of vacuum-distillations gave 997.9 gm of product, a pungent, slightly yellow liquid, b.p. 156-158°C/0.07 mm, n_D^{18} 1.5686. The yield was 44.5%.

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b. Bis(o-chlorophenyl) 4-biphenyl phosphite. To 85.1 gm (0.5 moles) of p-phenylphenol dissolved in one pound of pyridine was added 168.8 gm (0.5 moles) of di-o-chlorophenyl phosphoryl chloride. When the initial heat of reaction had subsided the mixture was heated to reflux, allowed to cool, then refrigerated for 15 hours. The mixture was then filtered, and freed of solvent by distillation to 150°C, first at atmospheric pressure, then under aspirator vacuum. The product was obtained by vacuum distillation. This was a colorless viscous oil, somewhat cloudy, b.p. 261-267°C/0.35 mm, n_D^{31} 1.6085, d_4^{25} 1.3286, molecular weight 468 (obsd.); 474 (calc.). The weight of product was 145.0 gm, a yield of 61.6%.

(44). Bis(m-trifluoromethylphenyl) 4-biphenyl phosphite. MLO 9564.

a. 4-Biphenyl phosphoryl dichloride. In a 1-liter, 2-neck flask was placed 255.3 gm (1.5 moles) of 4-phenylphenol, 345.2 gm of POCl₃ (2.25 moles) and 60 gm (ca. 1 mole) of degreased iron filings. The mixture was then refluxed for 4 hours. The maximum temperature attained was 146°C. The reaction mixture was distilled to 150°C at atmospheric pressure followed by distillation to 150°C under aspirator vacuum. In this way the excess POCl₃ was removed. Vacuum-distillation then gave 260.5 gm of product, a white solid, b.p. 180-184°C/4 mm, m.p. 83-84°C. The yield was 60.5%.

b. Bis(m-trifluoromethylphenyl) 4-biphenyl phosphite. To 71.8 gm (0.25 moles) of 4-biphenyl phosphoryl dichloride dissolved in one-half pound of pyridine was added 81 gm (0.5 moles) of m-trifluoromethylphenol. The mixture became quite warm. It was heated to reflux temperature and then left standing for 15 hours. The mixture was filtered and distilled at atmospheric pressure to 150°C (flask temperature) followed by heating to 150°C under aspirator vacuum. Subsequent vacuum-distillation gave 70.4 gm of product, a fairly viscous, yellow liquid, b.p. 230-231°C/0.18 mm, $n_D^{31.5}$ 1.5349, d_4^{25} 1.3684, molecular weight 537 (obsd.); 538 (calc.). The yield was 70.4 gm, or 52.3% of the theoretical.

Unsuccessful Preparations

(45). 1,2-Phenylene bis(diphenyl phosphite).

In a 1-liter flask was placed a solution of 55.1 gm (0.5 mole) of catechol dissolved in pyridine and 268.5 gm (1.0 mole) diphenyl phosphoryl chloride. The reaction mixture became quite hot and was allowed to stand. It was then diluted with five pounds of CCl₄ and washed with 1-liter portions of water, 5% KOH, water, 3% HCl and water. During the washing procedure, a white, rubbery precipitate settled out. This material had a melting point over 200°C. The CCl₄ solution was dried and stripped of volatiles. Upon vacuum distillation of the residue, 97.2 gm

of a fraction boiling at 159-160°C/0.12 mm, m.p. 49-50°C, was obtained. The molecular weight of this fraction was 327 (obsd.). Triphenyl phosphate has a m.p. of 49-50°C, molecular weight of 326 (calc.) and gave no depression of melting point when mixed with the product fraction.

(46). 1,3,5-Phenyl tris(diphenyl phosphate).

To a solution of 50.4 gm (0.4 mole) of phloroglucinol in one pound of pyridine was added 322.2 gm (1.2 moles) of diphenyl phosphoryl chloride. After standing, the reaction mixture was diluted with five pounds of CCl_4 , and washed with 1-liter portions of water, 5% KOH, 3% HCl and water. After the usual stripping procedure, a vacuum distillation was attempted, the head temperature reaching 324°C/0.20 mm. A second distillation gave a relatively low-boiling material melting at 49.5°C, molecular weight 325 (obsd.). The mixed melting point was triphenyl phosphate, molecular weight 326 (calc.) exhibited no depression. It seems possible that triphenyl phosphate was split out between two bis(diphenyl phosphate) groups on separate rings, leaving a $-\text{O}-\text{PO}(\text{O})-\text{O}-$ linkage joining the rings.

(47). 1,6-Naphthylene bis(di-p-chlorophenyl phosphate).

(48). 1,3-Phenylene bis(di-p-chlorophenyl phosphate).

(49). 1,3-(4-Chlorophenylene) bis(di-p-chlorophenyl phosphate).

These compounds are discussed as a group since the same behavior was shown by all of them. To a solution of 0.4 moles of the appropriate diol in pyridine was added 0.8 moles of di-p-chlorophenyl phosphoryl chloride. After addition of CCl_4 , and washing the solution in the usual manner, the volatiles were distilled off and the residue vacuum-distilled. In each case, the product was tris(p-chlorophenyl) phosphate, characterized by its melting point, 117°C, molecular weight, 429.5 (calc.) and mixed melting point.

(50). Tris(2-chloro-4-nitrophenyl) phosphate.

A mixture of 250.0 gm (1.44 moles) of 2-chloro-4-nitrophenol and 73.6 gm (0.48 mole) of POCl_3 plus 8.1 gm of anhydrous MgCl_2 , was heated to 200°C. The mixture was refluxed at this temperature for about 1.5 hours, when it was observed that the temperature was rising. The heat input was reduced, but an auto-catalytic decomposition had started. The mixture boiled out of the flask, turning to a carbonized resin.

(51). 4,4'-Biphenylene bis(o-chlorophenyl phosphate).

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To 71.6 gm (0.384 moles) of 4,4'-dihydroxybiphenyl dissolved in one pound of pyridine was added 129.8 gm (0.384 moles) of di-o-chlorophenyl phosphoryl chloride. The mixture, after subsidence of the initial heat of reaction, was heated to the boiling point and allowed to cool. The mixture was diluted with CCl_4 and washed in the usual way, upon which a large quantity of precipitate settled out. This precipitate melted above 270°C and probably was 4,4'-dihydroxybiphenyl. Working up the CCl_4 solution gave a small amount of the diol. It seems likely that the product hydrolyzed during the washing process.

(52). Tris(o-nitrophenyl) phosphate.

To 209 gm (1.5 moles) of o-nitrophenol dissolved in one-half pound of pyridine was added 76.5 gm (0.5 moles) of POCl_3 dissolved in one-half pound of pyridine. The addition was portionwise. Heat was liberated and crystals began forming. After allowing the reaction mixture to stand overnight (15 hours) the crystals were filtered off and discarded, and the volatiles were removed by distillation to 150°C (flask temperature), first at atmospheric pressure then under aspirator vacuum.

The residue at this point was a brownish-black liquid. This was distilled at 1.6 mm pressure. The first fraction consisted of a yellow liquid distilling at a head temperature of 72°C and a flask temperature of 80°C . However, as the temperature was gradually raised a brownish-black liquid distilled over at about $125^\circ/2-3$ mm. Then the temperature began to climb rapidly and a copious distillate came over at a b.p. of $150-160^\circ\text{C}$ with the flask temperature at about 220°C . At this point the contents of the flask erupted, demolishing the distilling head and spraying tarry liquid and very light, fluffy black ash.

(53). 2,3-Naphthylene p-chlorophenyl phosphate.

To a solution of 100 gm (0.625 moles) of 2,3-naphthalenediol dissolved in one pound of pyridine was added 153.4 gm (0.625 moles) of p-chlorophenyl phosphoryl dichloride. After standing for 15 hours the mixture was filtered and the filtrate was distilled at atmospheric pressure to a flask temperature of 150°C . Then the stripping was completed by distillation to 200°C under aspirator vacuum. When the residue was vacuum-distilled, a product was obtained, a white solid, b.p. $200-201^\circ\text{C}/0.15$ mm, weighing 70.7 gm. The melting point after recrystallization from ethanol was $97-98^\circ\text{C}$. The molecular weight of the recrystallized product was 388.

(54). 2,3-Naphthylene benzenephosphonate.

To a solution of 100 gm (0.625 moles) of 2,3-naphthalenediol dis-

Contrails

solved in one pound of pyridine was added 121.9 gm (0.625 moles) of dichlorophenylphosphine oxide. Considerable heat was liberated, and crystals formed. After standing overnight the reaction mixture was filtered and the filtrate stripped by distilling at atmospheric pressure to a flask temperature of 200°C. This was followed by distillation to 150°C under aspirator vacuum and vacuum-distillation. The product was an orange solid, b.p. 195-197°C/0.15 mm, weight 62.7 gm. After two recrystallizations from ethanol, the now-white product melted at 132-133.5°C and had a molecular weight of 511.

(55). Diphenyl benzyl phosphate.

In a 500 ml flask equipped with a dropping funnel, stirrer and condenser was placed 210.6 gm (0.784 moles) of diphenyl phosphoryl chloride. To this was added dropwise 84.8 gm (0.784 moles) of benzyl alcohol during the course of 1.5 hours. No evidence of reaction was apparent. This mixture was then placed in a dropping funnel and added slowly with stirring to one pound of pyridine in a 1-liter flask. The mixture was refrigerated for about 60 hours.

The crystals which had formed were filtered off and the filtrate was freed of solvent by distillation to 150°C, first at atmospheric pressure, then under aspirator vacuum. On attempted distillation the product decomposed, and only relatively low-boiling material was obtained.

(56). Diphenyl 2-phenylethyl phosphate.

To 134.3 gm (0.5 moles) of diphenyl phosphoryl chloride dissolved in one pound of pyridine was added dropwise 61.1 gm (0.5 moles) of 2-phenylethanol. The mixture became hot and crystals formed. It was again heated to reflux and allowed to stand overnight (15 hours). The reaction mixture was then filtered and the filtrate was stripped by distillation to 150°C (flask temperature), first at atmospheric pressure then under aspirator vacuum. Upon attempted vacuum-distillation, the product apparently decomposed, with only low-boiling liquid and gas coming over.

(57). 3,3'-Dichloro-4,4'-biphenylene bis(di-o-chlorophenyl phosphate).

a. t-Butyl hypochlorite. In a 5-liter flask equipped with a stirrer, reflux condenser and gas inlet tube was placed 160 gm (4 moles) of NaOH dissolved in 2 liters of water. To this solution was added 148.2 gm (2 moles) of t-butyl alcohol, and the flask was placed in an ice bath. Chlorine gas was then passed into the solution until it was no longer absorbed. The oily layer was separated off and washed with 200 cc of saturated Na₂CO₃. It was placed over CaCl₂ and stored overnight (15 hours) under refrigeration. The yield was 193.3 gm (1.78 moles), or 89%.

b. 3,3'-Dichloro-4,4'-dihydroxybiphenyl. In a 2-liter flask equipped with a dropping funnel, mercury-sealed stirrer and reflux condenser was placed 165.7 gm (0.89 moles) of 4,4'-dihydroxybiphenyl suspended in about one liter of CCl_4 . To this suspension 193.3 gm (1.78 moles) of t-butyl hypochlorite was added dropwise. The reaction mixture warmed to the reflux temperature of CCl_4 . After the addition was complete the mixture was refluxed for 2 hours. A white solid layer was present so the mixture was again refluxed for two hours and allowed to cool.

The solid layer was filtered off. After recrystallization from boiling water, its melting point was over 232°C . The melting point of the starting material was $278-281^\circ\text{C}$. This solid was no doubt the original 4,4'-dihydroxybiphenyl.

The CCl_4 was distilled off at atmospheric pressure. When only a part of the solvent had been removed a second crop of crystalline solid precipitated. This was filtered off and the removal of CCl_4 completed, leaving a third quantity of solid in the flask.

The second crystal crop was purified by leaching with boiling water. Three small crystal crops were obtained from the water, having melting points of $127.5-128^\circ\text{C}$, $129-130^\circ$, $129-130^\circ\text{C}$. This material was apparently 3,3'-dichloro-4,4'-dihydroxybiphenyl (literature value 124° from water; Beilstein, VI, 992; 1st supp. VI, 484). Soxhlet extraction of the residue from the water leaching gave an additional 10 gm of crystals, m.p. $129-132^\circ\text{C}$. The combined weight of all crops, including those recovered from the third quantity of solid, was 45.7 gm. The residue from the Soxhlet extraction, upon recrystallization from aqueous alcohol, melted at $170-177^\circ\text{C}$. The weight was 24.5 gm. This substance was probably 3,3',5-trichloro-4,4'-dihydroxybiphenyl (literature m.p. 179° ; Beilstein, VI, 992; 1st supp. VI, 484).

The third quantity of solid material appeared to be a mixture of the dichloro and trichloro compounds. A lengthy process of fractional crystallization gave only minor amounts of relatively pure dichloro compound. No other component was detected. The yield of dichloro compound was 16%.

c. 3,3'-Dichloro-4,4'-biphenylene bis(di-o-chlorophenyl phosphate). To 44.3 gm (0.17 moles) of 3,3'-dichloro-4,4'-dihydroxybiphenyl dissolved in one pound of pyridine was added 114.8 gm (0.34 moles) of di-o-chlorophenyl phosphoryl chloride. The mixture was heated and left to stand overnight (15 hours). The reaction mixture was then filtered, and distilled at atmospheric pressure, then under aspirator vacuum, the flask temperature being taken to 150°C in each case. A small fraction b.p. $353-365^\circ\text{C}$ /

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0.2-0.14 mm was obtained on initial distillation, with evidence of decomposition. On attempted redistillation a constant-boiling fraction could not be obtained and decomposition was obvious.

(58). 3,3'-Biphenylene bis(diphenyl phosphate)

a. 3,3'-Dimethoxybiphenyl (6). To a boiling solution of 194 ml of conc. HCl in two liters of water contained in a 4-liter beaker was added 250 gm (1.025 moles) of o-dianisidine (EKC, Technical grade) in several portions with stirring. The suspension was reheated for 5-10 minutes with stirring. A solid layer remained at the bottom of the beaker. The mixture was then cooled in an ice-bath and to it was added 219 ml of conc. HCl with continued stirring. This was followed by the addition of a solution of 146 gm (2.1 moles) of NaNO₂ in 313 ml of water over a period of 10-15 minutes. The contents of the beaker were then stirred for 20 minutes. The original suspension upon diazotization gave a clear, dark-brown solution. The solution was divided in half and each half was filtered separately. The total filtrate was divided into 4 portions, (each of about 680 ml) and each portion poured rapidly into a precooled 500 ml portion of hypophosphorous acid (H₃PO₂, 30%) contained in a 2-liter flask. Nitrogen evolved; the reaction mixture was refrigerated (20°F) for about 17 hours, then allowed to stand at room temperature for about 6 hours. The solid which had formed was separated from the water phase. The water phase was extracted twice with 200 ml portions of ether. The solid material previously obtained was dissolved in the combined ether layers, which were then extracted twice with 200 ml portions of 20% NaOH. The aqueous layer contained a brownish oil or solid, while the ether layer was dark red. The ether solution was dried over anhydrous K₂CO₃.

This deamination procedure was repeated with three more 250 gm portions of o-dianisidine. The storage periods under refrigeration varied, but did not appear to affect the reaction. The solid formed in each case varied in color from bluish-green to dark brown. In each case the ether solution was red.

The ether was stripped off the combined product at atmospheric pressure followed by concentration under aspirator vacuum, with flask temperature being taken to 190°C. Upon vacuum distillation, the product was obtained, b.p. 165-176°C/4.1 mm, m.p. 42.5-43°C. The product was a clear yellow liquid which slowly solidified on standing. The weight of product was 699.4 gm, a yield of 79.6%.

b. 3,3'-Dihydroxybiphenyl (7). Twelve pounds of reagent grade hydriodic acid (47-47.5%) was distilled at atmospheric pressure with a stream of N₂ bubbling through the solution. The azeotrope boiling at 124-127°C was collected. This fraction (colorless, but rapidly turning

yellow on exposure to air) was placed in a 5-liter round bottom flask and to it was added 699 gm (3.26 moles) of molten 3,3'-dimethoxybiphenyl, forming an upper layer. The mixture was refluxed about 20 hours, distilling off methyl iodide about every three hours. Considerable amounts of CH₃I were no doubt lost through the reflux condenser during refluxing. A total of 311 gm (2.19 moles) of CH₃I was collected. The distillation each time was continued until a head temperature of 107°C was reached (at this temperature a constant-boiling aqueous phase distilled); at the end of 20 hours only aqueous liquid distilled over. On cooling the 2-phase reaction mixture, the top layer solidified; a small sample, on recrystallization from water, melted at 126.5-128°C.

The solid material was dissolved in ca. 2 liters of 6N NaOH; the solution was extracted twice with petroleum ether. Acidification of the aqueous phase precipitated the phenol. Attempts to further purify the product by recrystallization gave whiter crystals (the precipitated compound was orange) but did not appreciably change the melting point, which was 126-128°C. Therefore the material was used in this form. The weight of product was 582.3 gm, a yield of 95.8%.

c. 3,3'-Biphenylene bis(diphenyl phosphate). To 46.5 gm (0.25 moles) of 3,3'-dihydroxybiphenyl dissolved in one pound of pyridine was added 134.3 gm (0.5 moles) of diphenyl phosphoryl chloride. The mixture became quite warm. After the initial heat of reaction had subsided the solution was heated to reflux and allowed to cool. After standing 15 hours the solution was filtered and stripped of solvent by distillation to 150°C, first at atmospheric pressure, then under aspirator vacuum. On attempted vacuum distillation of the residue only volatile material and gas came over. A yellow gum remained in the flask.

Continued
IV. NOTEBOOK REFERENCES

The data from which this report was compiled are contained in Southwest Research Institute Notebooks Nos. 124, 125, 126, 521, 535, 550 and 551.

- (1). Papa, D. and Schwenk, E. Process for Hydrogenation of Naphthalene Compounds. Issue date July 12, 1949. U. S. Patent 2,475,718.
- (2). Irwin, C. F. and Hennion, G. F. Chlorination of Olefins in Reactive Solvents with t-Butyl Hypochlorite. Journal of the American Chemical Society. Volume 63. March 1941. p. 858.
- (3). Ginsburg, D. The Action of t-Butyl Hypochlorite on Organic Compounds. III. Phenols. Journal of the American Chemical Society. Volume 73. June 1951. p. 2723.
- (4). Gottlieb, H. B. Sulfur Addition with the Aid of Thiophosphoryl Chloride and the Catalysis of Triaryl Thiophosphate Formation. Journal of the American Chemical Society. Volume 54. February 1932. p. 748.
- (5). Zenftman, H. and McGillwray, R., Aryloxyphosphoryl Chlorides. Issue date April 4, 1951. British Patent 651,656. Chemical Abstracts. Volume 45. October 25, 1951. p. 9081.
- (6). Drake, N. L. (Editor). Organic Syntheses. John Wiley and Sons, Inc. New York. 1941. Volume 21. p. 30.
- (7). Mascarelli, I. and Vinsintin, B. Researches on Bipicric Acid and its Optical Resolution. Gazzetta Chimica Italiana. Volume 62. 1932. pp. 358-368. Chemical Abstracts. Volume 26. September 20, 1932. p. 4809.

A P P E N D I X

TABLE I. PHYSICAL PROPERTIES OF COMPOUNDS PREPARED

Compound	MLO Number	B.P., °C/mm (obsd.)	Calc. NBP ^a °C (°F)	η_D^{25}	Therm. Decomp. Temp. °C (°F)	Viscosity, cs $\frac{100^\circ\text{F}}{210^\circ\text{F}}$ $\frac{100^\circ\text{F}}{400^\circ\text{F}}$	ASTM Slope $\frac{100^\circ-210^\circ\text{F}}{210^\circ-400^\circ\text{F}}$	M.p. or $\frac{^\circ\text{C}}{^\circ\text{F}}$	Pour Pt., °F	Mol. Wt. $\frac{\text{obsd.}}{\text{calc.}}$
Diphenyl 1-naphthyl phosphate ^b	9515	201-207/0.12	162(864)	1.2468	> 162(864)	-- 5.94 1.27	-- 0.883	53.5(128)	--	--
Diphenyl 2-naphthyl phosphate	9516	203-210/0.14	171(880)	1.2395	> 171(880)	-- 5.58 1.24	-- 0.856	64-65(147-149)	--	--
Bis(m-tolyl) 1-naphthyl phosphate	9518	207-210/0.085	147(836)	1.2946	373(703)	105 7.19 1.41	0.945	0.867	5	410 (404)
Bis(p-tolyl) 1-naphthyl phosphate	9519	226-228/0.16	173(883)	1.2059	394(740)	127 7.39 1.38	0.932	0.880	10	410 (404)
Diphenyl 8-quinolyl phosphate	9520	211-218/0.12	149(840)	1.2801	330(626)	226 10.4 1.65	0.898	58-59(136-138)	--	--
Bis(o-chlorophenyl) 1-naphthyl phosphate	9521	217/0.13	193(919)	1.3525	1611(33.5)	292 10.5 1.65	0.947	0.883	30	448 (445)
Tris(o-chlorophenyl) phosphate	9522	195-196/0.13	163(865)	1.4076	1581(29.0)	65.3 5.95 1.26	0.883	34-35(93-95)	5	422 (430)
Diphenyl 5,6,7,8-tetrahydro-1-naphthyl phosphate	9523	199/0.14	139(822)	1.2197	1577(23.5)	73.8 6.21 1.08	0.891	0.996	0	379 (380)
1,3-Phenylene bis(di-phenyl phosphate)	9524	284/0.09	547(1017)	1.2916	1573(30.0)	114 9.98 1.90	0.750	0.752	0	575 (574)
Bis(p-chlorophenyl) 1-naphthyl phosphate	9525	229-237/0.09	502(936)	1.3526	1611(25.0)	211 8.18 1.38	0.990	0.914	25	444 (445)
Diphenyl 2-chloro-1-naphthyl phosphate	9526	207-208/0.10	176(889)	1.3021	1615(20.0)	206 9.26 1.51	0.931	0.891	25	412 (410)
1,3-(4-chlorophenylene) bis(di-phenyl phosphate)	9527	285-289/0.20	550(1022)	1.3297	1577(27.0)	170 11.5 2.01	0.798	0.758	10	613 (609)
1,6-Naphthylene bis(di-phenyl phosphate)	9528	265-275/0.20	556(1033)	1.2950	1599(21.5)	542 19.6 2.70	0.814	0.733	35	586 (624)
Bis(p-chlorophenyl) 2-chloro-1-naphthyl phosphate	9529	232-237/0.10	193(919)	--	394(741)	1130 13.3 1.62	1.08	0.946		465 (480)
1,4-Phenylene bis(di-phenyl phosphate)	9530	288-290/0.13	550(1022)	--	455(851)	-- 11.9 2.09	--	0.743	578	(574)
Triphenyl thiophosphate	9531	212/4	142(774)	--	1589(30.5)	20.1 3.28 0.89	0.892	53-54(127-129)		343 (342)
Diphenyl 3-pyridyl phosphate	9532	183-185/0.10	104(759)	--	1557(22.0)	18.9 3.38 0.93	0.838 ^b	33(91)	-30	331 (328)
4,4'-Biphenylene bis(di-phenyl phosphate)	9533	339-343/0.14	589(1092)	--	1416(781)	-- 30.3 3.70	--	0.680		650 (650)
Bis(1-naphthyl) 3-pyridyl phosphate	9534	243-248/0.11	510(950)	--	298(568)	-- 17.9 2.01	--	0.881	55	432 (427)
Bis(2,4-dichlorophenyl) 1-naphthyl phosphate	9535	248-249/0.16	511(952)	--	432(810)	-- 17.1 1.67	--	0.994	65	514 (511)

^a Normal boiling point

^b Viscosity at 20°F, 449 cs Slope 20°-100°F, 0.927

TABLE I. PHYSICAL PROPERTIES OF COMPOUNDS PREPARED
(Continued)

MLC Number	Compound	B.P., °C/mm (obsd.)	Calc. NBp ^a °C (°F)	d_4^{25}	n_D^{25}	Therm. Decomp. Temp. °C (°F)	Viscosity, cs 100°F 210°F 100°F	ASTM Slope 100°-210°F 210°-100°F	M.p., °C (°F) or P.L., °F	Pour P.L., °F	Mol. Wt. Obsd. Calc.
9536	Bis(2-biphenyl) 1-naphthyl phosphate	271/0.10	545(1013)	--	--	440(824)	-- 62.7 3.16	-- 0.908	78-79(172-174)	--	529 (524)
9537	Diphenyl 2,4-dichloro-1-naphthyl phosphate	236/0.11	487(909)	--	--	383(721)	-- 12.5 1.61	-- 0.934	64-65(147-149)	--	443 (445)
9538	Bis(1-naphthyl) 2-chloro-phenyl phosphate	248-250/0.13	508(946)	--	1.6389 ^{27.0}	417(783)	-- 20.0 2.13	-- 0.877	--	55	462 (461)
9539	1,4-(2-chlorophenylene) bis(diphenyl phosphate)	285-288/0.14	553(1027)	--	--	417(783)	-- 11.8 2.02	-- 0.761	71-72(160-162)	--	572 (609)
9540	Tris(2-biphenyl) phosphate	275-278/0.18	546(1015)	--	--	454(849)	-- -- 3.47	-- --	114-115(237-239)	--	537 (554)
9541	Tris(3-chloro-2-biphenyl) phosphate	278-280/0.23	550(1022)	--	--	417(783)	-- --	-- --	194-195.5(381-384)	--	--
9542	Tris(3-chloro-4-biphenyl) phosphate	337-340/0.12	620(1148)	--	--	417(783)	-- 5.44	-- --	153-154.5(307-310)	--	607 (658)
9543	Diphenyl 5-indanyl phosphate	199-201/0.21	441(826)	1.2224	1.5770 ^{19.0}	> 454(849)	37.4 5.02 1.16	0.816	29(84)	--	356 (366)
9544	Diphenyl 1-indanyl phosphate	194-196/0.16	439(822)	1.2227	1.5753 ^{20.0}	394(741)	39.5 ^c 4.93 1.24	0.844	--	-15	362 (366)
9545	Tris(2,4-dichloro-phenyl) phosphate	242-246/0.14	496(925)	--	--	440(824)	-- 11.5 1.38	-- 1.020	92.5-94(199-202)	--	528 (533)
9546	Diphenyl benzene-phosphonate	170-174/0.14	417(783)	--	--	> 429(804)	-- 3.92 0.97	-- 0.920	76(169)	--	315 (310)
9547	Tris(2-bromophenyl) phosphate	225-228/0.22	481(898)	--	--	429(804)	-- 8.50 1.50	-- 0.864	83-84(181-183)	--	554 (563)
9548	1,5-Naphthylene bis(diphenyl phosphate)	--	620(1148)	--	--	441(826)	-- --	-- --	144-145(291-293)	--	--
9549	Bis(2-chlorophenyl) benzene-phosphonate	194-197/0.24	444(831)	1.3378	1.5965 ^{21.0}	> 444(831)	93.6 6.37 1.27	0.841	--	10	375 (379)
9550	Bis(2,4-dichlorophenyl) benzene-phosphonate	220-223/0.20	467(873)	--	--	429(804)	-- -- 1.30	-- --	117-118.5(243-246)	--	448 (449)
9551	Diphenyl pentachloro-phenyl phosphate	220-226/0.16	464(867)	--	--	372(702)	-- -- 1.54	-- --	120-121.5(248-251)	--	487 (499)
9552	Tris(pentachlorophenyl) phosphate	--	--	--	--	ca. 230(446)	-- --	-- --	230-240(446-464)	--	--
9553	Tris(p-chlorophenyl) phosphate	196-197/0.12	452(846)	1.4031	1.5820 ^{21.0}	> 464(867)	27.6 ^d 3.92 1.01	0.867	--	-20	430 (430)
9554	Phenyl 2-chlorophenyl 1-naphthyl phosphate	225-227/0.31	473(883)	1.3003	1.6091 ^{21.5}	470(878)	109 7.54 1.43	0.896	--	15	409 (411)
9555	Tris(3,5-dimethyl-phenyl) phosphate	200-202/0.18	439(822)	1.1274	1.5599 ^{22.0}	> 452(846)	91.7 6.38 1.25	0.938	46-46.5(115-116)	--	407 (410)

^aNormal Boiling Point
viscosity at 20°F, 3209 cs Slope 20°-100°F, 1.006
viscosity at 20°F, 1565 cs Slope 20°-100°F, 1.004

TABLE I. PHYSICAL PROPERTIES OF COMPOUNDS PREPARED
(Continued)

Compound	MLG Number	B.p., °C/mm (obsd.)	Cal., NBFA ^a °C (°F)	d ₂₅ g/ml	n _D ^t	Therm. Decomp. Temp. °C (°F)	Viscosity, cs 100° 210° 400° F	ASTM Slope 100°-210° F 210°-400° F	M.p. °C (°F) or Pt, °F	Pour Pt, °F	Mol. Wt. obsd. (calc.)
Tris(3,4-dimethyl-phenyl) phosphate	9556	213-215/0.19	462(864)	--	--	> 462(864)	-- 7.44 1.38	-- 0.874	71.5-72.5(161-163)	--	397 (410)
Tris(o-fluorophenyl) phosphate	9557	175-177/0.21	417(783)	--	--	> 428(802)	-- 3.76 0.98	-- 0.897	79-81(174-178)	--	388 (380)
Diphenyl 3,4-di-methylphenyl phosphate	9558	183-184/0.13	431(808)	--	--	> 444(831)	-- 3.75 1.00	-- 0.886	48-49(118-120)	--	350 (354)
Diphenyl 3,5-di-methylphenyl phosphate	9559	181-183/0.10	419(786)	--	--	> 431(808)	22.3 3.64 0.96	0.863	32-33(90-91)	--	350 (354)
Diphenyl 4-biphenyl phosphate	9560	216-222/0.07	485(905)	--	--	> 485(905)	-- 7.52 1.45	-- 0.847	64-65(147-149)	--	396 (402)
Tris(m-trifluoromethyl-phenyl) phosphate	9561	151-154/0.15	366(691)	1.4576	1.6790 ^{26.0}	> 376(709)	14.0 ⁶ 2.56 0.72	0.935	13(55)	-35	529 (530)
Phenyl m-trifluoro-methylphenyl 1-naphthyl phosphate	9562	198-205/0.25	421(790)	1.3215	1.5642 ^{25.0}	> 429(804)	50.4 ^f 4.96 1.10	0.922	--	5	437 (444)
Bis(o-chlorophenyl) 4-biphenyl phosphate	9563	261-267/0.35	510(950)	1.3286	1.6085 ^{31.0}	> 510(950)	379 12.2 1.79	0.932	--	45	468 (474)
Bis(m-trifluoromethyl-phenyl) 4-biphenyl phosphate	9564	230-231/0.18	424(795)	1.3684	1.5349 ^{31.5}	> 429(804)	82.0 6.14 1.20	0.924	--	15	537 (538)

^aNormal Boiling Point
viscosity at 20°F, 356 cs Slope 20°-100°F, 1.006
viscosity at 20°F, 11,200 cs Slope 20°-100°F, 1.104

TABLE II. SECONDARY PROPERTIES OF PROMISING COMPOUNDS

Compound	MLC Number	Flash Pt, °F	Fire Pt, °F	Autogenous Ign. Temp., °F	Hydrolytic Stability mgKOH/gm Sample	Vapor Pressure, mm		CCl ₄	C ₆ H ₆	C ₂ H ₅ OH	Solubilities, gm/100 gm		H ₂ O (hot)	Aliph. Naphtha
						25°C	100°C				Trichloroethylene	H ₂ O (cold)		
Bis(m-tolyl) 1-naphthyl phosphate	9518	575	720	> 1400	0.00	1.4x10 ⁻⁸	7.0x10 ⁻⁵	inf.	inf.	inf.	inf.	ins.	ins.	26.4
Bis(p-tolyl) 1-naphthyl phosphate	9519	530	685	> 1400	0.05	5.0x10 ⁻⁸	1.2x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	22.6
Bis(o-chlorophenyl) 1-naphthyl phosphate	9521	585	756	> 1400	0.15	7.0x10 ⁻⁸	1.8x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	10.2
Tris(o-chlorophenyl) phosphate	9522	540	676	> 1400	0.60	2.9x10 ⁻⁶	2.0x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	15.5
Diphenyl 5,6,7,8-tetrahydro-1-naphthyl phosphate	9523	525	748	1053-1118	0.00	2.3x10 ⁻⁷	4.3x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	25.3
1,3-Phenylene bis(diphenyl phosphate)	9524	618	> 760	> 1400	1.02	2.7x10 ⁻⁹	1.2x10 ⁻⁵	inf.	inf.	inf.	inf.	ins.	ins.	1.7
Bis(p-chlorophenyl) 1-naphthyl phosphate	9525	565	> 760	> 1400	0.04	6.4x10 ⁻⁸	1.2x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	44.2
Diphenyl 2-chloro-1-naphthyl phosphate	9526	565	> 760	> 1400	0.19	5.5x10 ⁻⁷	6.0x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	7.9
1,3-(4-chlorophenylene) bis(diphenyl phosphate)	9527	675	> 760	> 1400	2.44	5.8x10 ⁻⁸	5.4x10 ⁻⁶	inf.	inf.	inf.	inf.	ins.	ins.	1.5
1,6-Naphthylene bis(diphenyl phosphate)	9528	-	-	> 1400	4.60	7.0x10 ⁻⁶	2.5x10 ⁻⁴	inf.	inf.	inf.	inf.	ins.	ins.	ins.
Diphenyl 5-indanyl phosphate	9543	535	> 760	1026-1118	0.09	2.4x10 ⁻⁴	1.0x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	16.7
Bis(o-chlorophenyl) benzenephosphonate	9549	515	> 760	1319-1418	0.53	1.1x10 ⁻⁴	3.2x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	15.5
Tris(m-chlorophenyl) phosphate	9553	540	760	> 1400	0.39	7.0x10 ⁻⁵	2.2x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	inf.
Phenyl o-chlorophenyl 1-naphthyl phosphate	9554	530	760	> 1400	1.23	3.6x10 ⁻⁵	1.2x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	8.4
Tris(m-trifluoromethylphenyl) phosphate	9561	430	670	> 1400	2.31	2.0x10 ⁻³	4.5x10 ⁻²	inf.	inf.	inf.	inf.	ins.	ins.	inf.
Phenyl m-trifluoromethylphenyl 1-naphthyl phosphate	9562	485	> 760	> 1400	2.73	6.0x10 ⁻⁴	2.5x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	inf.
Bis(o-chlorophenyl) 4-biphenyl phosphate	9563	485	> 760	> 1400	2.27	6.5x10 ⁻⁵	2.5x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	5.9
Bis(m-trifluoromethylphenyl) 4-biphenyl phosphate	9564	520	710	> 1400	0.92	5.0x10 ⁻⁴	2.0x10 ⁻³	inf.	inf.	inf.	inf.	ins.	ins.	inf.

TABLE III. APPROXIMATE THERMAL DECOMPOSITION TEMPERATURES OF FUNCTIONAL GROUPS

Group	Temperature °C (°F)	Group	Temperature °C (°F)
Phenyl	> 485 (905)	5-Indanyl	> 455 (850)
m-Tolyl	370 (705)	1-Naphthyl	475 (890)
p-Tolyl	395 (740)	2-Naphthyl	470 (880)
m-Trifluoromethylphenyl	> 430 (805)	5,6,7,8-Tetrahydro-1-naphthyl	385 (720)
3,4-Dimethylphenyl	> 460 (860)	2-Chloro-1-naphthyl	395-405 (740-760)
3,5-Dimethylphenyl	> 450 (840)	2,4-Dichloro-1-naphthyl	385 (720)
o-Fluorophenyl	> 430 (805)	1,5-Naphthylene	440 (825)
o-Chlorophenyl	> 510 (950)	1,6-Naphthylene	385 (720)
m-Chlorophenyl	> 465 (870)	Bis(1-naphthyl)	415 (785)
p-Chlorophenyl	> 470 (880)	2-Biphenyl	440-455 (820-850)
o-Bromophenyl	430 (805)	4-Biphenyl	> 510 (950)
2,4-Dichlorophenyl	430-440 (805-825)	3-Chloro-2-biphenyl	415 (785)
Pentachlorophenyl	370 (700)	3-Chloro-4-biphenyl	415 (785)
1,3-Phenylene	415 (780)	4,4'-Biphenylene	415 (785)
1,4-Phenylene	455 (850)	3-Pyridyl	300-360 (570-685)
1,3-(4-Chlorophenylene)	395 (740)	8-Quinolyl	330 (625)
1,4-(2-Chlorophenylene)	415 (780)	Benzenephosphonate	> 445 (830)
4-Indanyl	395 (740)	Thiophosphate	380 (720)