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Autoxidation of Trialkylphosphines[1a]

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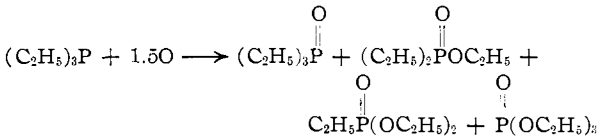
An investigation of the autoxidation of trialkylphosphines has resulted in the firm establishment of the nature of the products and a qualitative description of a number of factors which influence the reaction. The major products are the corresponding phosphine oxides and phosphinate esters, phosphonates and phosphates being formed in lesser amounts. Substances such as diphenylamine and hydroquinone effectively inhibit autoxidation for extended periods of time. A radical chain mechanism is proposed for this autoxidation process based on a variety of evidence. In this mechanism oxygen reacts with an intermediate hydrocarbon radical rather than directly at phosphorus.

The reaction of phosphines with oxygen is one with which workers in the field are unhappily familiar, but there has been no recent investigation of the subject despite its fundamental importance. In this investigation we have sought to provide qualitative information which would more closely define the nature of the autoxidation of trialkylphosphines in the liquid phase. This has resulted in the firm establishment of the nature of the products as well as a proposal for the route by which the reaction with molecular oxygen occurs.

Some information bearing on the liquid phase autoxidation of trialkylphosphines was provided by the investigations of Jorissen and Engler shortly before the turn of the century.[2] These workers reported that approximately 1.5 gram atoms of oxygen was taken up per mole of triethylphosphine and were, consequently, led to propose the formation of esters in addition to the usual phosphine oxide product; however, only the phosphine oxide was actually isolated. Since this time there have been many incidental observations made on the autoxidation of tertiary phosphines. It has come to be generally known that the order of reactivity of phosphines toward oxygen is benzyl > alkyl > aryl. The isolated products have consistently been tertiary phosphine oxides.



$$(C_2H_5)_3P + 1.5O \longrightarrow (C_2H_5)_3\overset{\overset{O}{\|}}{P} + (C_2H_5)_2\overset{\overset{O}{\|}}{P}OC_2H_5 + C_2H_5\overset{\overset{O}{\|}}{P}(OC_2H_5)_2 + \overset{\overset{O}{\|}}{P}(OC_2H_5)_3$$

Results and Discussion

Products.—Since there was some confusion in the literature as to what products result from trialkyl phosphine autoxidation, it was decided to make this the first point of investigation. Table I records the products we have observed in the autoxidation of tributyl- and tricyclohexylphosphines. These reactions were exothermic, clean and went rapidly very nearly to completion. It can be seen that the corresponding tertiary phosphine oxides and phosphinic acid esters are the major products and are formed in roughly equal amounts. These materials were isolated from the reaction mixtures by appropriate means and identified by comparison with authentic samples. The phosphonate and phosphate esters which are formed in lesser amounts were identified by vapor phase chromatography, again with the aid of authentic specimens. Thus, our findings completely substantiate the results and speculations of Jorissen and Engler[2] as to the nature of the products resulting from trialkylphosphine autoxidation.

TABLE I

PRODUCTS OF THE AUTOXIDATION OF TRIBUTYLPHOSPHINE AND TRICYCLOHEXYLPHOSPHINE

		Products, %[b]			
R_3P (wt., g.)	Solvent[a]	$R_3\overset{\overset{O}{\|}}{P}$	$R_2\overset{\overset{O}{\|}}{P}OR$	$R\overset{\overset{O}{\|}}{P}(OR)_2$	$\overset{\overset{O}{\|}}{P}(OR)_3$
$(n\text{-}C_4H_9)_3P$ (12.4)[c]	Hexane	42	49	6	3
$(n\text{-}C_4H_9)_3P$ (12.4)[d]	Acetone	57	40	2	1
$(\text{Cyclo-}C_6H_{11})_3P$ (5.6)[c]	Hexane	50	40	10[e]	

[a] Amount of solvent employed was 135 ml.; oxidations were carried out at 26°. [b] Determined by vapor phase chromatography. [c] Oxidized with air at a flow rate of 100 ml./min. for 2.5 hours. [d] Oxidized with air at a flow rate of 200 ml./min. for 2.0 hours. [e] The cyclohexyl phosphonate and phosphate esters were not resolved by the v.p.c. method employed. The 10% figure probably represents the amount of the mixture present.

The autoxidation of triphenylphosphine was investigated briefly. Only a minor amount of triphenylphosphine oxide was produced in a solution of triphenylphosphine in benzene which was blown with oxygen for three hours at the boiling point. A comparable experiment in which two mole % of 2,2'-azobis-(2-methylpropionitrile) was added resulted in the formation of 53% triphenylphosphine oxide, 41% of the triphenylphosphine being recovered.

Rate of Autoxidation.—Air was passed into solutions (10% by volume) of tributylphosphine in hexane and the uptake of oxygen was followed by measuring the oxygen concentration in the exit gas stream. It was found that the rate of autoxidation was quite fast at room temperature and independent of phosphine concentration up to 98% completion. Furthermore, the time required for reaction with pure oxygen was about one-fifth that with air at the same flow rate. Thus, it appears that oxygen uptake was diffusion controlled

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[1] (a) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961. (b) American Machine and Foundry Co., Springdale, Conn.

[2] W. P. Jorissen, *Ber.*, **29**, 1707 (1896); W. P. Jorissen, *Z. physik. Chem.*, **22**, 34 (1897); C. Engler and W. Wild, *Ber.*, **30**, 1669 (1897); C. Engler and J. Weissberg, *ibid.*, **31**, 3055 (1898).

under the conditions used. The total amount of oxygen consumed was in good agreement with that required by the observed products. An induction period of four minutes was noted at −20° but not at 26°. At −80° reaction with oxygen was very slow.

These findings differ considerably from those of Davies and Jones who reported that tributylphosphine is inert to molecular oxygen at room temperature.[3] They recommended boiling this phosphine (245°) in a stream of air to convert it to the phosphine oxide, the only oxidation product which was detected.

Effect of Medium and Conditions.—Examination of the autoxidation of tributylphosphine in various solvents and under differing conditions has given valuable information about the nature of the reaction. The effect of these variables on the ratio of the two major products is presented in Table II.

Experiments 2–5 demonstrate that changes in flow rate, oxygen concentration in the gas stream, initial phosphine concentration and temperature do not have a significant bearing on the relative amounts of the major products. On the other hand, experiments 5–14 indicate that the medium plays a role in the process which is product determining. The amount of tertiary phosphine oxide formed increases steadily as the solvent becomes more polar.

TABLE II

EFFECT OF VARIOUS CONDITIONS AND MEDIA ON THE AUTOXIDATION OF TRIBUTYLPHOSPHINE

Expt.	Solvent[a]	Temp., °C.	Air or oxygen flow rate, ml./min.	Mole ratio[b] $(n\text{-}C_4H_9)_3PO/(n\text{-}C_4H_9)_2\text{-}PO_2C_4H_9\text{-}n$
1	None	30	Air, 50	0.92
2	Hexane[c]	26	Air, 200	.80
3	Hexane	26	Air, 200	.81
4	Hexane	−20	Air, 210	.82
5	Hexane	26	O_2, 400	.83
6	*t*-Butylbenzene	26–70	O_2, 400	.95
7	Benzene	60–80	O_2. 400	1.06
8	Toluene	65–80	O_2, 400	1.11
9	Chlorobenzene	65–80	O_2, 400	1.15
10	Acetone	26	Air, 200	1.28
11	Acetonitrile	65	Air, 200	1.89
12	100% alcohol	26	O_2, 400	1.82[d]
13	95% alcohol	26	O_2, 400	1.96[e]
14	90% alcohol	26	O_2, 400	2.86[e]
15	Hexane[f]	26	O_2, 400	1.68
16	Hexane[g]	26	O_2, 400	0.95

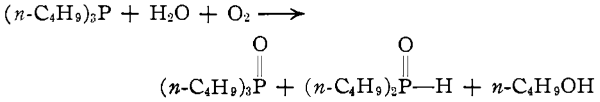
[a] Solutions of 12.4 g. of tributylphosphine in 135 ml. of the solvent except where otherwise noted. [b] Determined by v.p.c. using calibration curves. [c] Solution of 4.1 g. of tributylphosphine and 135 ml. of hexane. [d] Mole ratio $(n\text{-}C_4H_9)_3PO/(n\text{-}C_4H_9)_2PO_2C_2H_5$. [e] Mole ratio $(n\text{-}C_4H_9)_3PO/(n\text{-}C_4H_9)_2PHO$. [f] Thirteen grams of benzaldehyde added before oxidation. [g] Nine and six-tenths grams of inhibitor-free styrene added before oxidation.

Aromatic solvents had an unexpected effect on the autoxidation reaction. Tributylphosphine reacted very slowly with oxygen in benzene, toluene or chlorobenzene solution at temperatures below 60°. At this temperature or slightly above, a spontaneous reaction commenced and the normal products were observed. In *t*-butylbenzene solution a moderate reaction took place at room temperature which accelerated as the temperature was raised. The presence of two molar equivalents of benzene in hexane solution was insufficient to inhibit the autoxidation reaction. Since the ultraviolet spectrum of benzene in the presence of excess tributylphosphine was normal as was the phosphorus n.m.r. spectrum of the phosphine in benzene solution, no unusual interaction of these materials is indicated. Thus, the aromatic solvents probably exert their inhibiting influence on some autoxidation intermediate.

Tributylphosphine oxide was one of the major products in ethanol and aqueous ethanol solutions as in other solvents, but the nature of the product resulting from cleavage of a P–C bond was different in each case. Ethyl dibutylphosphinate was formed in a large excess of dry ethanol almost to the exclusion of the butyl phosphinate ester. It was shown that this ethyl ester was not formed at the expense of the butyl ester by oxidizing a mixture of the latter and tributylphosphine in absolute ethanol. Analysis of the resulting mixture demonstrated that an amount of butyl ester was present equal to that added initially. When tributylphosphine was oxidized in the presence of a modest excess of dry ethanol, both esters were produced along with 1-butanol in an amount equivalent to the ethyl ester.

$$(n\text{-}C_4H_9)_3P + C_2H_5OH + O_2 \longrightarrow (n\text{-}C_4H_9)_3PO + (n\text{-}C_4H_9)_2PO_2(n\text{-}C_4H_9) + (n\text{-}C_4H_9)_2PO_2C_2H_5 + n\text{-}C_4H_9OH$$

In aqueous ethanol the products were 1-butanol, tributylphosphine oxide and dibutylphosphine oxide. The formation of this last-mentioned product is particularly significant since it is suggestive of a reactive intermediate of lower oxidation state than the usual P–C cleavage product which is susceptible to nucleophilic attack.



$$(n\text{-}C_4H_9)_3P + H_2O + O_2 \longrightarrow (n\text{-}C_4H_9)_3\overset{\overset{\displaystyle O}{\|}}{P} + (n\text{-}C_4H_9)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{—}H + n\text{-}C_4H_9OH$$

Effect of Additives.—It was found that small amounts (0.02–0.10 mole %) of substances such as diphenylamine and hydroquinone effectively inhibit the autoxidation of tributylphosphine and similar tertiary phosphines. For example, 90% of the initial amount of tributylphosphine was recovered from a hexane solution containing 0.1 mole % of diphenylamine which had been blown with air for 24 hours. In the absence of the inhibitor, this phosphine was completely oxidized in less than one hour.

Inhibitors of this type also had some effect in suppressing the air oxidation of typical primary and secondary phosphines, but it was of shorter duration. Inhibition was generally noted for about one hour when exposure to air was continuous. After this period oxidation commenced, although at a moderated rate. It is felt that such inhibitors could materially facilitate the handling and storage of phosphines in laboratory and commercial usage.

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(3) W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929).

The autoxidation of tributylphosphine also was inhibited by less than molar amounts of diphenyl disulfide, thiophenol, sodium ethoxide and sodium hydroxide. Metal salts such as ferric and cuprous chlorides had no important effect. Surprisingly, triphenylphosphine functioned as an inhibitor in equimolar amounts or somewhat less.

The presence of molar amounts of either benzaldehyde or styrene did not greatly influence the rate or products of tributylphosphine autoxidation in hexane (Table II, expt. 15 and 16), nor were these additives altered thereby to a significant degree. No trace of benzoic acid was detected in the first case and benzaldehyde was recovered nearly quantitatively when just enough air was added to react completely with the phosphine. About 90% of the styrene was recovered in the latter experiment.

Coöxidation of Tributylphosphine and Tricyclohexylphosphine.—Coöxidation of equimolar amounts of these phosphines in hexane solution gave further information bearing on the reaction mechanism. In addition to the usual amounts of tertiary phospine oxides, four other major products were formed in this experiment. These proved to be the "normal" and "mixed" phosphinic acid esters as indicated in the following equation (R = *n*-C_4H_9, R′ = cyclo-C_6H_{11}; the figures in parentheses are area % by v.p.c. analysis).

$$R_3P + R'_3P \xrightarrow{O_2} R_3PO(29) + R'_3PO(23) + R_2PO_2R(14) + R'_2PO_2R'(7) + R_2PO_2R'(12) + R'_2PO_2R \quad (12)$$

It was shown that the "mixed" esters were not produced by exchange reactions after oxidation by combining the crude oxidation mixtures obtained from the individual phosphines and subjecting this mixture to the conditions of the coöxidation experiment.

Mechanism.—Based on the results we have obtained, the following mechanism is proposed for the autoxidation of trialkyl phosphines.

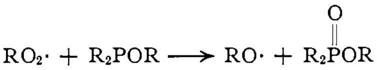
$$\text{Initiation} \longrightarrow R\cdot(RO\cdot, RO_2\cdot) \quad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (2)$$

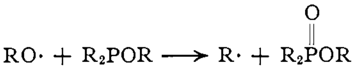
$$RO_2\cdot + R_3P \longrightarrow RO\cdot + R_3P{=}O \quad (3)$$

$$RO\cdot + R_3P \longrightarrow R\cdot + R_3P{=}O \quad (4a)$$

$$RO\cdot + R_3P \longrightarrow R\cdot + R_2POR \quad (4b)$$

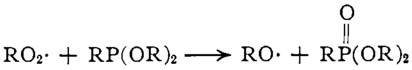


$$RO_2\cdot + R_2POR \longrightarrow RO\cdot + R_2\overset{\overset{O}{\|}}{P}OR \quad (5)$$

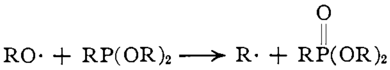


$$RO\cdot + R_2POR \longrightarrow R\cdot + R_2\overset{\overset{O}{\|}}{P}OR \quad (6a)$$

$$RO\cdot + R_2POR \longrightarrow R\cdot + RP(OR)_2 \quad (6b)$$



$$RO_2\cdot + RP(OR)_2 \longrightarrow RO\cdot + R\overset{\overset{O}{\|}}{P}(OR)_2 \quad (7)$$



$$RO\cdot + RP(OR)_2 \longrightarrow R\cdot + R\overset{\overset{O}{\|}}{P}(OR)_2 \quad (8a)$$

$$RO\cdot + RP(OR)_2 \longrightarrow R\cdot + P(OR)_3 \quad (8b)$$

$$RO_2\cdot + P(OR)_3 \longrightarrow RO\cdot + O{=}P(OR)_3 \quad (9)$$

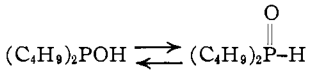
The salient features of this radical chain mechanism are that oxygen reacts with a hydrocarbon radical rather than directly at phosphorus, as might be supposed from the nature of the products, and that the relative amounts of phosphine oxide and phosphorus ester produced are determined by the competitive reactions 4a and 4b. The nature of the initiation process is not clear, but it may be related to the much slower reactions with oxygen which occur in very dilute solutions or in the presence of inhibitors.

It is obvious how this scheme accounts for most of the results obtained including the nature of the products and the free radical features such as an induction period and inhibition by trace quantities of certain materials. The formation of "mixed" esters in the coöxidation of two phosphines is accounted for by reaction 4b, since a given alkoxy radical could react with a phosphine having the same or different substituents. Solvent polarity could influence the ratio of major products resulting from the product-determining steps, 4a and 4b. More polar solvents could favor the formation of the more polar phosphine oxide (4a). The role of aromatic solvents as weak inhibitors is probably related to their known function in other free radical reactions, complexing and moderating the reactivity of electrophilic radicals.[4]

The new P–C bond cleavage products observed in dry and aqueous ethanol are accounted for nicely on the basis of the reactions of these solvents with the key intermediate, R_2POR. Butyl dibutylphosphinite, the suspected intermediate in tributylphosphine autoxidation, was prepared independently and found to equilibrate rapidly with ethanol, and to undergo a fast reaction with water in aqueous ethanol to give dibutylphosphine oxide.

$$(C_4H_9)_2POC_4H_9 + C_2H_5OH \rightleftarrows (C_4H_9)_2POC_2H_5 + C_4H_9OH$$

$$(C_4H_9)_2POC_4H_9 + H_2O \longrightarrow (C_4H_9)_2POH + C_4H_9OH$$



$$(C_4H_9)_2POH \rightleftarrows (C_4H_9)_2\overset{\overset{O}{\|}}{P}{-}H$$

Under the autoxidation conditions, the ethyl phosphinite ester which would predominate in excess ethanol would then be oxidized to the phosphinate stage; however, since the secondary phosphine oxide formed in the reaction with water exists mainly in the "keto" form, it would resist further oxidation.[5]

Supporting Evidence.—The chief objection to the mechanism proposed here for the autoxidation of trialkylphosphines is the requirement that reaction 4b predominate over 4a in order to account for the product distribution. There can be no doubt that path 4a, the oxide-forming process, is favored thermodynamically. Further, it has been reported that *t*-butoxy radicals react with triphenylphosphine to give the oxide exclusively.[6]

$$t\text{-}C_4H_9O\cdot + (C_6H_5)_3P\cdot \longrightarrow t\text{-}C_4H_9\cdot + (C_6H_5)_3PO$$

Two items of additional information were obtained which serve to overcome this objection. A brief study of the reaction of *t*-butoxy radicals with

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(4) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987, 4997, 5002 (1958); *J. Org. Chem.*, **24**, 300 (1959).

(5) M. M. Rauhut and H. Currier, *J. Org. Chem.*, **26**, 4626 (1961).

(6) C. Walling, O. H. Basedow and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 2181 (1960).

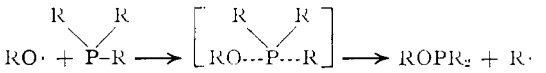
tri-*n*-butylphosphine demonstrated that P–C bond cleavage is the major reaction in this case where an alkyl rather than an aryl radical is ejected. Under conditions such that all the phosphine was consumed, the major product was a mixture of phosphorus acids. Using a deficiency of *t*-butoxy radicals so that only about half the phosphine had reacted, the major product was identified as *t*-butyl di-*n*-butylphosphinite (80%), the minor product being the phosphine oxide (20%).

$$t\text{-}C_4H_9O\cdot + (n\text{-}C_4H_9)_3P \longrightarrow t\text{-}C_4H_9OP(\text{-}n\text{-}C_4H_9)_2 + n\text{-}C_4H_9\cdot\ (80\%)$$

$$t\text{-}C_4H_9O\cdot + (n\text{-}C_4H_9)_3P \longrightarrow (n\text{-}C_4H_9)_3PO + t\text{-}C_4H_9\cdot\ (20\%)$$

Although attempts to synthesize this particular phosphinite ester independently were fruitless, a satisfactory identification was provided by physical evidence.

This result supports the proposed reaction scheme, but the reason for kinetic rather than thermodynamic control of products is still open to question. The explanation could lie in a radical displacement process in which breaking of the P–C bond is concerted with formation of the O–P bond. This would contrast with other trivalent phosphorus free radical processes for which a pentacovalent phosphoranyl intermediate has been proposed.[7] However, the phosphoranyl route cannot be excluded since it is conceivable that a particular geometry would be favored, and that this in turn would control the products formed.



Other evidence strongly favoring the mechanism advocated here was obtained from a study of the product distribution in neat samples of tributylphosphine to which limited amounts of oxygen had been added. As anticipated, significant amounts of the intermediate lower phosphinite ester were detected, and the formation of the phosphinate ester lagged behind that of the oxide in these early stages of reaction, although approximately equal amounts were present when autoxidation was complete. This pattern is obvious from the data presented in Table III.

TABLE III

MATERIALS PRESENT IN TRIBUTYLPHOSPHINE SAMPLES TO WHICH LIMITED AMOUNTS OF OXYGEN HAVE BEEN ADDED

% of total O_2 uptake	% R_3P	% R_2POR	% $R_2\overset{O}{\overset{\vert}{P}}OR$	% $R_3P{=}O$
10	90	5	0	5
15	86	7	0	8
30	77	6	4	13

The autoxidation of organometallics and metalloids (Mg, B, Al, Li, Hg, Zn, etc.) bears a superficial similarity to that of trialkyl phosphines in the cleavage reactions and fast uptake of oxygen which occur in both cases. However, it appears that fundamentally they are quite different since the former are not chain reactions and are thought to involve initial complexation of oxygen with the metal and then rearrangement of a substituent group.[8]

$$RM + O_2 \longrightarrow [RM\cdot O_2] \longrightarrow ROOM$$

$$ROOM + RM \longrightarrow 2ROM$$

Finally, it should be pointed out that the new information provided here on reactions of alkoxy radicals with phosphines raises some interesting general questions about the nature of phosphorus free radical reactions. Other recent reports indicate that reactions of this type are exceptionally fast.[6,9] There is reason for suspecting that polar factors in the attacking radical and phosphorus substituents will prove to be of importance in determining the course and rate of these reactions.

Experimental[10]

Materials.—The tributylphosphine was Food Machinery and Chemical Corp. material which was distilled *in vacuo*. The center cut, b.p. 82° (1.0 mm.), which was used contained no volatile impurities as indicated by v.p.c. analysis. Tricyclohexylphosphine was prepared by Dr. W. A. Henderson, Jr., by the method of Issleib and Brack[11] and was of analytical purity, m.p. 73–75°. Triphenylphosphine was an Eastman Chemical and was recrystallized from ethanol before use. The solvents were the best available commercial grades. The hexane was extracted repeatedly with sulfuric acid, then water and finally dried and distilled. Benzene was extracted with sulfuric acid by mechanical stirring, washed with water, passed through an alumina column and distilled before use.

The authentic samples of compounds required for identification of products by vapor phase chromatography[12] and by other means are indicated below. Details of the preparations are presented only where it is considered desirable. Tri-*n*-butylphosphine oxide was prepared by oxidation of the phosphine in ethanol with the stoichiometric amount of hydrogen peroxide; m.p. 67–69° (after low temperature recrystallization from ether). Dibutyl butylphosphonate was obtained by the method of Kosolapoff[13]; b.p. 113–114° (0.3 mm.). Tributyl phosphate was an Eastman Chemical. Tricyclohexylphosphine oxide,[11] m.p. 155–157°, tricyclohexylphosphate,[14] m.p. 63–64°, and dibutylphosphine oxide[5], m.p. 65–66°, were prepared by the indicated known procedures.

Butyl Dibutylphosphinate.—A solution of 20.0 g. (0.112 mole) of dibutylphosphinic acid in 100 ml. of thionyl chloride was heated under reflux for 0.5 hr. and evaporated *in vacuo*. To the residual oil was added a mixture of 18 ml. of 1-butanol and 15 ml. of pyridine with cooling. After heating at 100° for 1 hr., 100 ml. of petroleum ether was added and the mixture was filtered. The filtrate was extracted with water, evaporated and the residual liquid distilled to give 14.1 g. (56%) of ester, b.p. 131–133° (0.5 mm.). Redistillation furnished a center cut with b.p. 105° (0.05 mm.), $n^{27}D$ 1.4422.

Anal. Calcd. for $C_{12}H_{27}O_2P$: C, 61.51; H, 11.62; P, 13.22. Found: C, 61.70; H, 12.01; P, 12.80.

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(7) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957).

(8) C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955); M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, 429, 438 (1959); A. G. Davies, D. G. Hare and R. F. M. White, *ibid.*, 341 (1961); H. Hock and F. Ernest, *Ber.*, **92**, 2716, 2723, 2732 (1960); G. A. Razuvaev, G. G. Petukhov, S. F. Zhiltsov and L. F. Kudriavtsev, *Doklady Akad. Nauk S.S.S.R.*, **135**, 87 (1960); S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961).

(9) F. R. Mayo, Abstracts of Papers Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 41-Q.

(10) Melting points and boiling points are uncorrected. Microanalyses were carried out in these laboratories under the supervision of Dr. J. Kuck.

(11) K. Issleib and A. Brack, *Z. anorg. allgem. Chem.*, **277**, 258 (1954).

(12) Details of the techniques developed for v.p.c. analyses of phosphorus compounds will be published elsewhere with R. Feinland and J. Sass.

(13) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

(14) R. T. K. Cornwell, U. S. Patent 2,770,555 (1956).

Ethyl dibutylphosphinate was prepared by the procedure outlined above using 10 ml. of absolute ethanol in place of the butanol. The product was obtained in 67% yield, b.p. 96° (1.2 mm.) (center cut).

Cyclohexyl dibutylphosphinate was obtained in a similar fashion using cyclohexanol; b.p. 139° (0.7 mm.), n^{25}D 1.4650.

Anal. Calcd. for $C_{14}H_{29}O_2P$: C, 64.58; H, 11.23; P, 11.90. Found: C, 64.40; H, 11.31; P, 11.95.

Cyclohexyl Dicyclohexylphosphinate.—To a solution of sodium cyclohexoxide prepared from 0.4 g. of sodium and 15 ml. of cyclohexanol was added a solution of 3.7 g. (0.015 mole) of dicyclohexylphosphinyl chloride[11] in 20 ml. of hot diglyme. The mixture was heated at 115° for 3.5 hr., then at 165° for 0.5 hr., cooled, filtered and evaporated *in vacuo*. The residue was taken up in petroleum ether, filtered and chromatographed on alumina with petroleum ether. From the first fractions there was obtained 0.9 g. (19%) of crude ester, m.p. 75–80°. The analytical sample had m.p. 85–86° (low temperature recrystallization from petroleum ether).

Anal. Calcd. for $C_{18}H_{33}O_2P$: C, 69.20; H, 10.65; P, 9.92. Found: C, 68.86; H, 10.89; P, 10.02.

Dicyclohexyl Cyclohexylphosphonate.—To a hot solution of sodium cyclohexoxide prepared from 2.3 g. of sodium and 100 ml. of cyclohexanol was added 9.0 g. of cyclohexylphosphonyl dichloride.[15] The mixture was stirred at 110° for 4 hr., cooled, filtered, and evaporated *in vacuo*. A portion of the residue was chromatographed on alumina using petroleum ether, then ether. The product was recovered from the ether fractions; m.p. 58–60°. Low temperature recrystallization from petroleum ether raised the m.p. to 59–60°.

Anal. Calcd. for $C_{18}H_{33}O_3P$: C, 65.82; H, 10.13; P, 9.43. Found: C, 66.04; H, 9.91; P, 9.41.

Butyl Dicyclohexylphosphinate.—To a solution of sodium butoxide prepared from 1.4 g. of sodium and 60 ml. of 1-butanol was added 15.0 g. (0.06 mole) of dicyclohexylphosphinyl chloride in 30 ml. of benzene. After heating at 100° for 3 hr., the mixture was cooled, filtered, washed with water and evaporated *in vacuo*. The residue was distilled to give 13.7 g. (80%) of ester, b.p. 132–135° (0.3 mm.). The analytical sample was a center cut, b.p. 134° (0.3 mm.), n^{24}D 1.4900.

Anal. Calcd. for $C_{16}H_{31}O_2P$: C, 67.10; H, 10.91; P, 10.98. Found: C, 66.96; H, 10.97; P, 10.59.

Butyl Dibutylphosphinite.—To a solution of 15.0 g. (0.083 mole) of dibutylchlorophosphine[16] in 100 ml. of hexane was added a mixture of 6.7 g. of 1-butanol and 6.6 g. of pyridine. The mixture was stirred for 0.5 hr. and filtered under nitrogen. The filtrate was evaporated, then distilled to furnish 13.9 g. (78%) of product, b.p. 78–83° (0.5 mm.). A center cut had b.p. 80° (0.5 mm.), n^{26}D 1.4453. This compound is quite sensitive to atmospheric oxygen and moisture.

Anal. Calcd. for $C_{12}H_{22}OP$: P, 14.19. Found: P, 13.66.

Rate and Quantity of Oxygen Uptake by Tributylphosphine.—A Beckman oxygen analyzer was used to measure the percentage oxygen by volume in the gas stream exiting from the reaction vessel. The volume of gas was measured with a wet test meter. The reaction vessel was a cylinder 25 cm. high and 3.3 cm. in diameter. Solutions of 12.4 g. (0.061 mole) of tributylphosphine in 135 ml. of hexane were placed in the nitrogen-flushed vessel and air was passed in at the bottom at the desired rate through a medium fritted disk after the desired temperature had been attained.

In a typical experiment conducted at 26° and an air flow of 100 ml./min., the percentage O_2 in the exit stream remained constant from the start until 98% of the total O_2 had been taken up (99 min.). At this point the percentage O_2 in the gas stream rose sharply and a very slow uptake of oxygen continued for an additional 55 min. The total O_2 uptake corresponded to 0.0513 mole. The solvent was evaporated and the colorless liquid residue was analyzed by v.p.c. The amount of O_2 required by the mixture (Table I) was 0.0518 mole.

Other Autoxidation Experiments.—All other autoxidation experiments were conducted in a 300-ml. round-bottom flask fitted with a fritted gas inlet tube and a condenser. Isolation or identification of the products was carried out after evaporation of the solvent *in vacuo*. Generally, when the exothermic reaction had subsided, the air or oxygen flow was continued until a spot test was negative, carried out by adding 1 drop of solution to 1 ml. of carbon disulfide. A red coloration could be detected visually with as little as three parts per thousand of phosphine.

Isolation of Major Products from Tributylphosphine Autoxidation.—After evaporating the solvent, the residue from experiment 3, Table II, was distilled. Two major fractions were obtained: I, 5.1 g., b.p. 115–117° (0.25 mm.); and II, 5.5. g., b.p. 121–125° (0.25 mm.) (solidified on cooling). Fractions I and II were identified as butyl dibutylphosphinate and tributylphosphine oxide, respectively, by infrared.

Isolation of Major Products from Tricyclohexylphosphine Autoxidation.—The residue from the autoxidation of this phosphine (Table I) was taken up in 25 ml. of petroleum ether. The solid which deposited was collected and recrystallized from heptane to give crystalline tricyclohexylphosphine oxide, m.p. 156–157°. The petroleum ether filtrate was chilled to −75° and the supernatant solution separated and chromatographed on alumina. A trace amount of solid, m.p. 177–182°, was obtained from the first fractions. Later fractions contained cyclohexyl dicyclohexylphosphinate of m.p. 85–86° after low temperature recrystallization from petroleum ether.

Autoxidation of Triphenylphosphine.—A solution of 10.5 g. of triphenylphosphine and 0.13 g. of 2,2′-azobis-(2-methylpropionitrile) in 95 ml. of benzene was prepared and oxygen was passed in while maintaining a temperature of 78°. The reaction was discontinued after 3 hr. although slow oxygen uptake was still observed. The dark red solution was treated with charcoal, filtered and evaporated. The residue was treated with 100 ml. of petroleum ether and filtered to give 5.9 g. of triphenylphosphine oxide, m.p. 146–149° (154–155° after recrystallization from benzene–cyclohexane). From the filtrate there was recovered 4.3 g. of unreacted triphenylphosphine, m.p. 79–81°.

Reaction of Tributylphosphine with Di-*t*-butyl Peroxide.—A mixture of 5.55 g. (0.028 mole) of tributylphosphine and 3.65 g. (0.025 mole) of di-*t*-butylperoxide was heated at 130 ± 1° for 8 hr. in a nitrogen atmosphere. Analysis by v.p.c. and n.m.r. showed that there were two major phosphorus products in the ratio of 4:1. The minor component was identified as tributylphosphine oxide. After treatment with water the spectral characteristics due to the major product were absent and in their place there was observed the properties of dibutylphosphine oxide in the v.p.c., n.m.r. and infrared (strong P–H) spectra. This information serves to identify the major product of the reaction as *t*-butyl di-*n*-butylphosphinite.

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