B. **Trifluoroethylene–Methanethiol Adducts.**—These isomers(IX and X) were separated with a 13' × 0.75'' column packed with a 3:7 mixture of Dow Corning Silicone 200 (50 centistokes) and 48–65 mesh fire brick. The column temperature was 80–90°.

Starting Materials.—2,2,2-Trifluoroethanethiol was prepared by the reductive thiolation of trifluoroacetaldehyde hydrate as described by Harris and Sheppard.[15]

(15) J. F. Harris, Jr., and W. A. Sheppard, *J. Org. Chem.*, **26**, in press (1961).

[Contribution from the Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.]

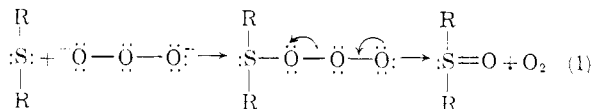# Ozone Oxidation of Nucleophilic Substances. I. Tertiary Phosphite Esters[1]

By Quentin E. Thompson

Received June 20, 1960

Triaryl and trialkyl phosphites were oxidized rapidly and quantitatively to the corresponding phosphates by ozone. Trialkyl phosphites showed exact 1:1 proportions at high ester dilution, but in concentrated solution two moles was oxidized by one mole of ozone. Similar 2:1 proportions were observed in all cases with triaryl phosphites provided ozone was added to the phosphite at temperatures above −5°. At −70°, ozone and triaryl phosphites formed 1:1 adducts. The n.m.r. spectrum of the P^{31} nucleus in (PhO)$_3$P–O$_3$ showed a shift of +63 ± 1 p.p.m. indicating probable pentacovalency. The cyclic structure III has been tentatively assigned. Treatment of the adduct with excess trialkyl phosphite gave one mole of triaryl phosphate and essentially two moles of trialkyl phosphate. Dimethyl sulfide and tributylphosphine were similarly oxidized. Utilization of more than one of the oxygen atoms in ozone was also observed upon addition of ozone to phosphines or dialkyl sulfides in concentrated solution.

The importance of ozone as a carbon–carbon double bond reagent has overshadowed its role as an oxidizing agent for other organic functional groups although nucleophilic substances such as organic amines, sulfides and phosphines are known to undergo facile ozone oxidation. Unselective oxidative decomposition of primary amines by ozone has been known for many years.[2,3] Generally, trialkylamines are converted to the corresponding amine oxides.[2–5] Dialkyl, arylalkyl and some diaryl sulfides are readily oxidized to their corresponding sulfoxides and sulfones.[4,6–10] Various other sulfur compounds are also oxidized smoothly with ozone.[10] Triphenylphosphine and triphenylarsine have been converted to their respective oxides in high yields.[4]

These reactions have in common as their initial step the electrophilic attack of ozone upon an unshared electron pair of the amine, sulfide, etc. The mechanism presently accepted[11] for this type of oxidation is shown as follows for dialkyl sulfides.[9] To the extent that a 1:1 relationship

occurs this formulation is satisfactory. When substantial deviation from this ratio is observed, *i.e.*, when more than one atom of oxygen per ozone molecule is placed upon the substrate, the adequacy of the present scheme comes under question.

In the case of sulfides, serious discrepancies are to be noted in ozone reaction proportions between the observation of Maggiolo[9] and Horner[4] on the one hand and Barnard[10] and Boer and Kooyman[8] on the other. The former have, under their experimental conditions, observed the 1:1 ratio upon which the simple mechanism 1 was based. The latter workers, and in particular Barnard,[10] have observed that significantly less ozone is required to effect the R$_2$S → R$_2$SO$_2$ transformation than the two moles required by 1. These discrepancies can now be accounted for as a result of observations made in this Laboratory while investigating the ozone oxidation of another class of nucleophilic compounds, namely, tertiary phosphite esters.[12]

Both triaryl and trialkyl phosphites were found to be rapidly and quantitatively oxidized to their corresponding phosphates under mild conditions. Unexpectedly, one, two or, in certain special cases with triaryl phosphites, essentially all three of the oxygen atoms of ozone could be utilized depending on experimental factors. Thus, the over-all proportions could in the various cases correspond to equations (2), (3) and (4)

$$(RO)_3P + O_3 \longrightarrow (RO)_3P{=}O + O_2 \qquad (2)$$
$$2(RO)_3P + O_3 \longrightarrow 2(RO)_3P{=}O + 1/2O_2 \qquad (3)$$
$$3(ArO)_3P + O_3 \longrightarrow 3(ArO)_3P{=}O \qquad (4)$$

When the lower trialkylphosphites (R = CH$_3$, *iso*-C$_3$H$_7$ and *n*-C$_4$H$_9$) were oxidized in the conventional manner by addition of an ozone–oxygen stream to a cold solution of the phosphite, uptake of ozone was rapid. Absorption ceased abruptly at the end of the reaction. Ozone consumption for the various oxidations amounted to 65–95 mole per cent. of that required on a 1:1 stoichiometric basis. It was apparent from these experiments that the proportions varied between 1:1 and 2:1 depending on the concentration of the

(1) A preliminary report of some of this work has appeared in *Chemistry & Industry*, 121 (1959).

(2) W. Strecker and H. Thienemann, *Ber.*, **53**, 2096 (1920).

(3) W. Strecker and M. Baltes, *ibid.*, **54**, 2693 (1921).

(4) L. Horner, H. Schaefer and W. Ludwig, *ibid.*, **91**, 75 (1958).

(5) A. Maggiolo and S. Niegowski, *Advances in Chem. Ser.*, **21**, 202 (1959).

(6) H. Böhme and H. Fischer, *Ber.*, **75**, 1310 (1942); A. Meuwsen and H. Gebhardt, *ibid.*, **70**, 796 (1937).

(7) C. C. Price and O. H. Bullitt, *J. Org. Chem.*, **12**, 238 (1947).

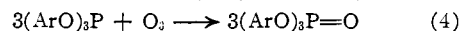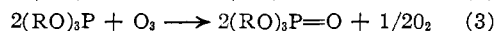(8) H. Boer and E. C. Kooyman, *Anal. Chim. Acta*, **5**, 550 (1951).

(9) A. Maggiolo and E. A. Blair, *Advances in Chem. Ser.*, **21**, 200 (1959).

(10) D. Barnard, *J. Chem. Soc.*, 4547 (1957).

(11) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

(12) Oxidations of tertiary phosphites to their corresponding phosphates have been effected by a variety of other oxidizing agents; *cf.* J. R. Cox and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5441 (1958), and references cited therein.

phosphite with the 2:1 ratio being favored at high phosphite concentration. This was proved by addition of a known amount of ozone (25 mmoles) to 100 mmoles of tributyl phosphite without solvent. Exactly 50 mmoles of phosphate was produced leaving 50 mmoles of phosphite unreacted. Obviously the stoichiometry up to the point of interruption corresponded to eq. 3. At high ester dilution, obtained by addition of tributyl phosphite to a continuous excess of ozone in methylene chloride at −75°, the ratio of ozone consumed to phosphite oxidized was exactly 1:1. To eliminate any possibility that the oxygen carrier gas might be involved, the experiment under concentrated conditions was repeated using oxygen-free ozone.[13] No significant change in stoichiometry resulted. This fact coupled with the known[14] sluggishness of trialkyl phosphites toward oxygen served to eliminate the latter as a factor affecting the stoichiometry.
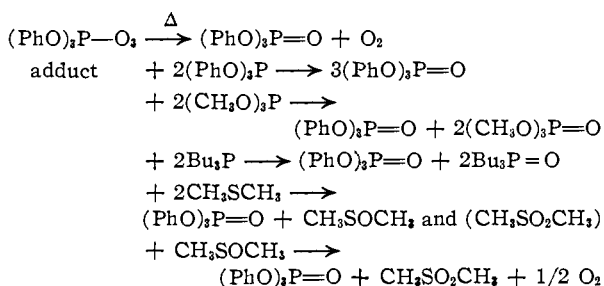
The triaryl phosphites (where Ar = phenyl, p-t-butylphenyl, p-tolyl) differed from the trialkyl esters in that 2:1 stoichiometry appeared to be the rule even under dilute conditions provided ozone was added to the phosphite at temperatures above −5°. Indeed, a slight concentration effect was observed, but in the case of triphenyl phosphite this effect was such that slightly more than two moles of ester in concentrated solution was oxidized by one mole of ozone. Use of oxygen-free ozone again did not change the stoichiometric results.

Upon addition of ozone to a dilute solution of triphenyl phosphite (one mole) in methylene chloride at −75°, the reaction took an entirely unexpected course. Approximately 0.85 mole of ozone was absorbed. Allowing the reaction mixture to come to room temperature caused liberation of oxygen, beginning at about −15°, and formation of triphenyl phosphate in quantitative yield. This observation suggested that a relatively stable per-oxygenated intermediate had been formed which decomposed upon warming. Subsequent investigation proved this assumption substantially correct. Triphenyl phosphite and an ozone stream were added concurrently to methylene chloride at −70° in such a manner that excess ozone was always present in the reaction mixture. This resulted in exact 1:1 molar absorption of ozone. Upon removal of excess ozone and warming, one mole of oxygen was smoothly liberated and a mole of triphenyl phosphate was produced. If instead of warming, two or more moles of a trialkyl phosphite was added, a vigorous reaction occurred and approximately 1.7 to 1.8 moles of trialkyl phosphite was oxidized to the corresponding phosphate. One mole of triphenyl phosphate was also concurrently produced. Thus, ozone stoichiometry approaching 3:1 was being observed. Clearly, the trialkyl phosphite subsequently added was not oxidized by ozone itself but by a peroxygenated 1:1 adduct of ozone with triphenyl phosphite. Ozone adducts of tris-(p-t-butylphenyl) phosphite and tris-p-tolyl phosphite were also prepared. These behaved similarly in

their oxidizing properties. All appeared to be stable in solution below about −20°. Addition of other easily oxidizable materials such as tributylphosphine or dimethyl sulfide to a cold solution of the triphenyl phosphite–ozone adduct resulted in rapid oxidation of substantially more than one additional mole of the substrate. Reaction of the triphenyl phosphite–ozone compound with additional triphenyl phosphite proceeded more sluggishly and in two distinct steps. Oxidation of one mole of the added phosphite occurred readily at −40°. If the reaction was immediately terminated, a total of only two moles of triphenyl phosphate was obtained. If the mixture was held another 16 hr. at −40 to −50°, additional triphenyl phosphite was oxidized so that the total amount of triphenyl phosphate amounted to about 2.5 moles.[15]

Oxidation of dimethyl sulfoxide by the adduct also proceeded sluggishly and in this case only one mole could be oxidized. These results showing the course of the principal reactions which occur are summarized in Chart I.

CHART I

$$(PhO)_3P—O_3 \xrightarrow{\Delta} (PhO)_3P{=}O + O_2$$

adduct 　　$+ 2(PhO)_3P \longrightarrow 3(PhO)_3P{=}O$

　　$+ 2(CH_3O)_3P \longrightarrow$
　　　　　　$(PhO)_3P{=}O + 2(CH_3O)_3P{=}O$

　　$+ 2Bu_3P \longrightarrow (PhO)_3P{=}O + 2Bu_3P{=}O$

　　$+ 2CH_3SCH_3 \longrightarrow$
　　　　$(PhO)_3P{=}O + CH_3SOCH_3 \text{ and } (CH_3SO_2CH_3)$

　　$+ CH_3SOCH_3 \longrightarrow$
　　　　　$(PhO)_3P{=}O + CH_3SO_2CH_3 + 1/2\ O_2$

Triaryl phosphites appeared to be the only trivalent phosphorus compounds with the ability to form relatively stable compounds with ozone. All attempts to demonstrate the existence of similar intermediates with tributyl phosphite, tributylphosphine or triphenylphosphine were unsuccessful. When these materials were added to excess ozone at low temperature, 1:1 reaction occurred but no intermediate adduct could be detected. Presumably only simple oxidation of the substrate, i.e., reaction 1, had occurred.
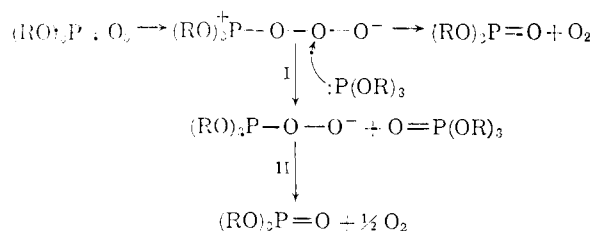
The question of formulating a mechanism accounting for the behavior of trialkyl phosphites on the one hand and that of triaryl phosphites on the other is not easily met. A simple extension of the previously accepted zwitterion mechanism (1) such as that shown in Chart II is sufficient to account for the results observed with trialkyl phosphites but is unsatisfactory for triaryl phosphites. Electrophilic attack of ozone upon the phosphite could give I which might either break up into phosphate and oxygen or be attacked further by another mole of trialkyl phosphite if the latter is present in high concentration. A somewhat analogous mech-

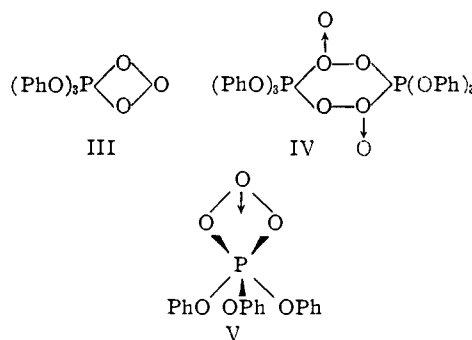(13) G. A. Cook, A. D. Kiffer, C. V. Klump, A. H. Malik and L. A. Spence, Advances in Chem. Ser., 21, 44 (1959).

(14) C. Zimmerman, Ann., 175, 1 (1875).

(15) In an earlier communication (footnote 1), it was reported that a total of three moles of phosphate was produced. This figure was obtained by analysis of unreacted triphenyl phosphite in the reaction mixture. Subsequent investigation has shown that the analytical procedure (see analytical method in Experimental) was, in this case, unreliable and gave low results. Actual isolation of triphenyl phosphate indicated that the maximum amount produced per mole of ozone was about 2.5 moles.
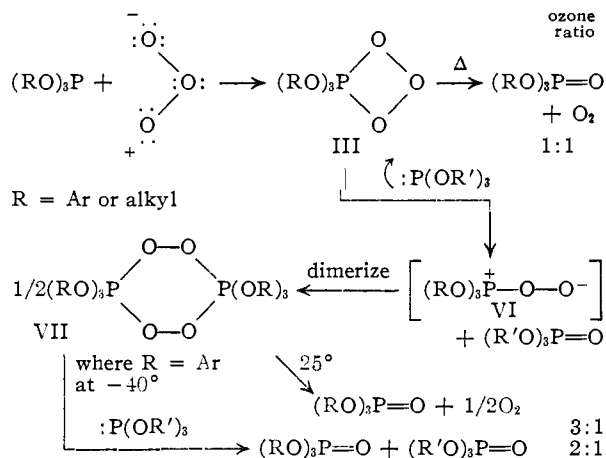
CHART II

$$(RO)_3P : O_2 \longrightarrow (RO)_3^+P\!-\!O\!-\!O\!-\!O^- \longrightarrow (RO)_3P\!=\!O + O_2$$

$$I \quad \searrow :P(OR)_3$$

$$(RO)_3P\!-\!O\!-\!O^- + O\!=\!P(OR)_3$$

$$II$$

$$(RO)_3P\!=\!O + \tfrac{1}{2} O_2$$

anism has been postulated by Bartlett and Meguerian[16a,b] for the reaction of triphenylphosphine with sulfur. On the other hand, compelling evidence was obtained from low temperature nuclear magnetic resonance measurements indicating that zwitterion structures analogous to those of Chart II could not adequately represent the important intermediate(s) observed in triaryl phosphite oxidation. The spectrum[17] of the P^{31} nucleus in the (PhO)$_3$P-O$_3$ adduct showed a chemical shift $\delta_{H_3PO_4} = +63 \pm 1$ p.p.m. in methylene chloride at $-60°$. When one molar equivalent of triphenyl phosphite was added and the oxidation of this was allowed to proceed, the spectrum then showed the expected peak of triphenyl phosphate at 18.5 ± 1 p.p.m.[18] and a second signal at 62 ± 1 p.p.m. The large positive shifts suggested strongly that the phosphorus nucleus of the unknown intermediate(s) must be bound to more than four oxygen nuclei.[18,19] This being the case, cyclic structures such as III, IV or possibly V would better represent the low-temperature adducts.[20] In the absence of further definitive information, III appears to be the most logical choice based on analogy with other known pentacovalent phosphorus compounds[21] and the observation that participation by phosphorus in four-membered ring transition intermediates is not uncommon.[21a] With this as a

(16) (a) P. D. Bartlett and G. Meguerian, J. Am. Chem. Soc., **78**, 3710 (1956). (b) A zwitterion intermediate of a structure similar to I but involving pyridine and ozone has been postulated by G. Slomp and J. L. Johnson, ibid., **80**, 915 (1958).

(17) We are indebted to Drs. C. F. Callis and M. M. Crutchfield and their assistants at the Inorganic Chemicals Division, Monsanto Chemical Co., for these spectra and for guidance in their interpretation.

(18) J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, J. Am. Chem. Soc., **78**, 5715 (1956).

(19) Compounds with five oxygen atoms attached to phosphorus are known. V. A. Kukhtin, Doklady Akad. Nauk S.S.S.R., **121**, 466 (1958); C. A., **53**, 1105 (1959); and G. H. Birum and J. L. Dever, Abstracts of the 134th A.C.S. Meeting, Chicago, Ill., Sept., 1958, p. 101-P, have obtained products of the structure i by reaction of tertiary phosphite esters with α-diketones. It is significant that the latter workers report n.m.r. shifts of +67.5 p.p.m. for the compound where R = C$_6$H$_5$, R' = CH$_3$ and +62.5 p.p.m. where R = R' = C$_6$H$_5$. See also R. Ramirez, et al., J. Am. Chem. Soc., **82**, 2651, 2652 (1960).

$$(RO)_3P \begin{array}{c} O \\ \diagdown \\ O \end{array} \begin{array}{c} R' \\ C \\ \| \\ C \\ R' \end{array}$$

i

(20) A referee has correctly pointed out that our evidence does not exclude (PhO)$_3$P$\diagdown^{O}_{O\rightarrow O}$ as a possible structure. This, however, differs only from V in that no d-orbital overlap between the third oxygen and the central phosphorus atom is postulated. If d-orbital overlap is to be postulated for the apex oxygen, it would also then seem probable for the end oxygen.

(21) R. J. Gillespie and R. J. Nyholm, Quart. Revs., **11**, 339 (1957).

$$(PhO)_3P\begin{array}{c}O\\ \diagup \diagdown \\ O \quad \;\; O \\ \diagdown \diagup \\ O\end{array}$$

III

$$(PhO)_3P\begin{array}{c}O\!-\!O\\ \diagup \quad\quad \diagdown \\ \quad\quad\quad\quad P(OPh)_3 \\ \diagdown \quad\quad \diagup \\ O\!-\!O\end{array}$$

IV   O

$$\begin{array}{c} O \\ \diagup \downarrow \diagdown \\ O \quad\quad O \\ \diagdown \quad \diagup \\ P \\ \diagup | \diagdown \\ PhO \;\; OPh \;\; OPh \end{array}$$

V

starting point, the steps shown in Chart III provide a logical, though by no means exclusive, explanation of the experimental results.

CHART III

$$(RO)_3P + \begin{array}{c}:O:\\ \diagdown \\ \quad :O: \\ \diagup \\ O \\ +\end{array} \longrightarrow (RO)_3P\begin{array}{c}O\\ \diagup \diagdown \\ \quad\quad O \\ \diagdown \diagup \\ O\end{array} \xrightarrow{\Delta} (RO)_3P\!=\!O + O_2$$

III   ozone ratio 1:1

R = Ar or alkyl

$| \quad (:P(OR')_3$

$$1/2(RO)_3P\begin{array}{c}O\!-\!O\\ \diagup \quad\quad \diagdown \\ \quad\quad\quad P(OR)_3 \\ \diagdown \quad\quad \diagup \\ O\!-\!O\end{array} \xleftarrow{\text{dimerize}} \left[(RO)_3\overset{+}{P}\!-\!O\!-\!O^-\right] + (R'O)_3P\!=\!O$$

VII   VI

where R = Ar at $-40°$ $\searrow 25°$

:P(OR')$_3$ $(RO)_3P\!=\!O + 1/2O_2$ 3:1

$\longrightarrow (RO)_3P\!=\!O + (R'O)_3P\!=\!O$ 2:1

The primary product of ozone attack on the phosphite, whether aryl or alkyl, is presumed to be III.[22]

In the case of trialkyl phosphites, III has little stability and rapidly decomposes into one mole each of phosphate and oxygen giving over-all 1:1 ozone stoichiometry. However, in the presence of appreciable excess trialkyl phosphate or where R = aryl, III has sufficiently long life so that it suffers attack[23] by another molecule of phosphite

(21a) See A. W. Johnson and R. B. LaCount, Tetrahedron, **9**, 130 (1960), for a recent discussion of the mechanism of the Wittig reaction. Similar intermediates probably occur in the deoxygenation of epoxides by phosphites [C. B. Scott, J. Org. Chem., **22**, 1118 (1957)] or phosphines [M. S. Boskin and D. B. Denney, Chemistry & Industry, 330 (1959)].

(22) This primary intermediate has a formal analogy to the long sought for molozonide of the olefin–ozone system. Cf. P. S. Bailey (footnote 11) and the recent work of R. Criegee, Angew. Chem., **71**, 525 (1959), and Ber., **93**, 689 (1960), for a discussion of recent developments.
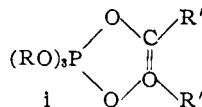
(23) A referee has objected to formulation of a nucleophilic approach by phosphite at an oxygen having a full electron octet. This argument has questionable validity in view of the demonstrated susceptibility of –O–O– bonds to nucleophilic attack not only by phosphorus but by other nucleophiles. D. B. Denny, W. F. Goodyear and B. Goldstein, J. Am. Chem. Soc., **82**, 1393 (1960), have shown unequivocally that the reduction of hydroperoxides, which can occur even at $-40°$, proceeds by a nucleophilic attack of trivalent phosphorus at the RO–OH bond. A similar result was obtained by D. B. Denney and M. A. Greenbaum, ibid., **79**, 979 (1957), for the reduction of aroyl peroxides to anhydrides by tributylphosphine. Many other examples of nucleophilic cleavage of –O–O– bonds are to be found in the literature. These include such well known reactions as the conversion of tertiary amines to amine oxides and dialkyl sulfides to sulfoxides and sulfones by peracids or peroxides.

yielding a mole of phosphate and a zwitterion VI, Where 2:1 ozone proportions are observed, another mole of phosphate must be produced along with half a mole of oxygen. This can be accomplished if VI dimerizes to the cyclic peroxide VII which can break down readily into the required number of phosphate and oxygen molecules.

In the special case of triaryl phosphites, III has unusual stability—so much so in fact that it does not react appreciably with added triphenyl phosphite until warmed to about −40°. This reaction results in the formation of one mole of phosphate and VII. The latter structure should be appreciably less active as an oxidizing agent but still be sensitive to thermal decomposition. Experimentally this was observed since oxidation of the second mole of added triphenyl phosphite proceeded sluggishly and was accompanied by appreciable loss of molecular oxygen giving over-all ozone stoichiometry of no more than 2.5 to 1. Intermediates III and VII are presumed to be those observed in the low temperature n.m.r. measurements—their shifts being essentially identical.

Regardless of mechanistic detail, the fact that the initial product of ozone attack, whatever its structure, can react further with the nucleophilic substrate remains the important consideration and represents an important extension of previous thinking.[24]

That this behavior is not confined to phosphite esters was shown by some ancillary experiments with phosphines and sulfides where again it appeared that ozone stoichiometry was dependent upon substrate concentration. Addition of tributylphosphine to excess ozone (using an N_2–O_3 stream) resulted in exact 1:1 stoichiometry whereas addition of ozone to the phosphine resulted in the consumption of only 0.55 mole of ozone. Presumably exact 2:1 proportions would have been observed had the reaction not been carried to completion. Similarly, addition of ozone to a fairly concentrated solution of triphenylphosphine in methylene chloride required only 0.64 mole of ozone to effect complete oxidation. A mechanism similar to that shown on Chart III is probably operative for phosphines. The presence of no relatively long lived intermediate corresponding to III could be detected. In the case of sulfides, diethyl and dibutyl sulfides (200 mmoles each) were treated with 73 and 74 mmoles of ozone, respectively. The amount of oxygen introduced onto the sulfur, giving both sulfoxide and sulfone, was found to be 203 and 202 milliatoms, respectively, indicating the utilization of approximately 2.75 of the three oxygen atoms in ozone. This suggests a more complex series of intermediate steps than in the case of phosphines.

These observations demonstrate that ozone attack at a nucleophilic center does not necessarily result in oxidation on a simple 1:1 stoichiometric basis. Instead, one or more intermediates may be

formed. These, being themselves oxidizing agents, may decompose or, under the proper conditions, oxidize additional substrate. The net effect is the utilization of one, two, or in some cases, all of the oxygen atoms in ozone.

Experimental[25]

Apparatus and Procedure.—Ozone was generated using a Welsbach T-23 laboratory ozonizer. The extreme sensitivity of certain phosphite esters to moisture necessitated rigorously anhydrous conditions. Before entering the ozonizer the oxygen stream was put through drying traps of Drierite and calcium chloride and finally a Dry Ice trap. On emerging from the ozonizer the stream was passed through a Welsbach model C ozone meter, a flow meter and finally through a 50-ml. bubbler of methylene chloride at −78°. Reactions were run in an Ace Glass Mini-lab. reactor (Cat. No. 10104) with 50-, 100- or 150-ml. reactor flasks. In all runs requiring a standardized ozone stream, standardization was carried out immediately before and after the run. When significant change in rate had occurred the reaction was repeated. The ozone meter was not used for determining the amount of ozone delivered but did serve as a convenient monitor of the gas stream—giving indication of change in ozone composition. With practice and careful attention to voltage, pressure and flow adjustments, a standardized gas stream could be delivered to the reactor with no significant change for several hours. In most of the work, the flow rate was about 0.5-0.6 l./min. with ozone delivery standardized in the range of 0.5-0.75 mmole/min. In all cases, the off-gas was put through neutral potassium iodide solution to determine unreacted ozone. By this method, the amount of ozone added to and absorbed by a reaction mixture could be determined at any time.

Oxygen-free ozone was prepared using the silica gel absorption method described by Cook, et al.[13] A known amount of ozone was absorbed on a cold (−75°) silica gel column. The column was swept with a slow nitrogen stream for 3–5 minutes with the off-gas going through an iodide trap to detect any ozone loss. The stream was then switched to the reactor and the silica gradually warmed until the desired amount of ozone had been eluted and swept into the reaction mixture. Unreacted ozone both from the reactor and silica gel column was then determined iodimetrically.

With the exception of tris-(p-t-butylphenyl) phosphite, which was prepared by reaction of the phenol with phosphorus trichloride, all of the phosphites used were commercially available and were carefully distilled before use. Methylene chloride, used as a solvent in many of the oxidations, was dried by overnight stirring with, and distillation from, phosphorus pentoxide.
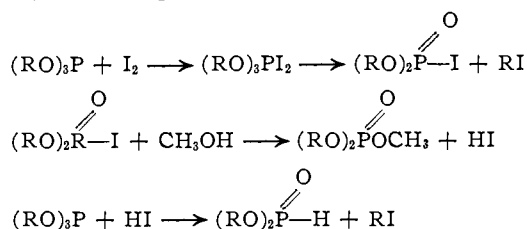
Analytical.—Ozone was determined iodimetrically by standard procedures.[26] Trialkyl phosphites and phosphines (both triaryl and trialkyl) were determined by titration with a standard solution of iodine in methanol.[27] This method made use of the fact that iodine reacts rapidly with trialkyl

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(24) The ozone oxidation of sulfur dioxide according to the reaction $3SO_2 + O_3 \rightarrow 3SO_3$ reported by E. H. Riesenfeld, German Patent 229,274 (1910); Zentr., 16, 178 (1911), appears not to be mechanistically comparable to our results since E. Briner, et al., Helv. Chim. Acta, 14, 804 (1931), have shown that the Riesenfeld oxidation was an ozone-catalyzed autocatalytic process.

(25) All melting and boiling points are uncorrected. Infrared spectra were run on a Perkin–Elmer recording spectrophotometer, model 21. The n.m.r. measurements were made with a Varian model V-4300B high resolution nuclear magnetic resonance spectrometer at a frequency of 16.2 Mc. and a magnetic field strength of approximately 9400 gauss (see footnote 17). A sample temperature of approximately −60° was maintained using a Varian temperature accessory and a regulated stream of nitrogen-cooling gas passed through a liquid nitrogen heat exchanger.

(26) See Welsbach Corp. "Basic Manual of Applications and Laboratory Ozonization Techniques," 1st Revision, p. 20, and G. Slomp [J. Org. Chem., 22, 1277 (1957)] for valuable discussion of the iodimetric method for determination of ozone.

(27) A procedure similar to this was used by Bartlett and Meguerian (footnote 16) to determine triphenylphosphine. The general method, however, was first developed at Shell Development Laboratories by Drs. G. A. Stenmark and F. T. Weiss (private communication), a modification of which appeared in P.B. 110895 No. S-13305, Technical report No. VIII, Office of Naval Research, Project No. NR 05525, 1951. In this report commercially prepared Karl Fischer reagent was used as the source of the standardized iodine.

phosphites[28] in the presence of methanol giving stoichiometry conforming to the reactions

$$(RO)_3P + I_2 \longrightarrow (RO)_3PI_2 \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\!\!-\!\!I + RI$$

$$(RO)_2\overset{O}{\overset{\|}{R}}\!\!-\!\!I + CH_3OH \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}OCH_3 + HI$$

$$(RO)_3P + HI \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\!\!-\!\!H + RI$$

The net effect is that one I_2 destroys two phosphites before the brown color of excess iodine is apparent. If pyridine is present, the reaction is arrested at the second stage and only one phosphite is consumed per molecule of I_2 added. The latter stoichiometry is also obtained for phosphines.[16]

In practice a solution of iodine (120 g.) in about 2 liters of methanol was prepared and standardized against thiosulfate. The methanol solution containing 0.261 mmole of I_2 per ml. was then used to determine trialkylphosphites and phosphines. Alternatively, standardization against good quality phosphite could be used. The titer of the solution did not change on long standing. For a determination, the unknown was dissolved in a few ml. of dry methanol, about 3 ml. of dry pyridine was added and the sample titrated rapidly to a brown end-point. An attempt was made to use this method to estimate triaryl phosphites taking advantage of the rapid alcoholysis of the latter in methanol. When pure triphenyl phosphite or a mixture with phosphate was dissolved in a 25-fold excess of dry methanol and the solution allowed to stand for 4 hr. or longer, 93–95% of the true value of phosphite could be determined consistently. The method failed to give reliable results, however, when used to determine excess unreacted triphenyl phosphite in an actual reaction mixture.[16]

Ozone Oxidation of Trialkylphosphites. (a) Preliminary Experiments.—Before the question of ozone proportions was investigated, numerous oxidations of the lower trialkyl phosphites, $(RO)_3P$ where R = methyl, isopropyl and n-butyl, were carried out to establish the course of the reaction and the identity of the products. The general procedure was as follows. One hundred mmoles of the freshly distilled phosphite was dissolved in 50–100 ml. of dry methylene chloride and the solution was cooled (usually to $-70°$). An ozone stream standardized in mmoles of ozone/min. was added until a slight blue color of excess ozone was apparent in the solution. The off-gases were passed through one or more traps containing neutral potassium iodide solution.

The reaction mixture was then sparged with nitrogen to carry excess ozone into the trap. Unreacted ozone was subtracted from the total delivered to the reaction mixture. The results of some specific experiments are summarized.

Trimethyl Phosphate.—Trimethyl phosphite (100 mmoles) in 50 ml. of methylene chloride at $-70°$ required 78 mmoles of ozone for completion. A similar experiment run in methanol required 83 mmoles of ozone. The batches were combined and solvents removed *in vacuo*. The clear colorless residue was distilled under reduced pressure giving a main cut of trimethyl phosphate, b.p. 103–105° (38 mm.), $n^{25}D$ 1.3939 (lit.[29] b.p. 97° at 35 mm. and $n^{25}D$ 1.3950) amounting to 26.5 g. (95%).

Triisopropyl Phosphate.—Triisopropyl phosphite (20.8 g. or 100 mmoles) in 100 ml. of methylene chloride at $-70°$ required only 66 mmoles of ozone for completion. Exactly the same amount was consumed when the reaction was repeated at 0°. Removal of solvent and distillation of the combined samples gave 41.7 g. (93%), b.p. 125–126° (41 mm.), $n^{25}D$ 1.4036 (lit.[29] b.p. 136° (68 mm.), $n^{20}D$ 1.4057) of colorless phosphate.

Tributyl Phosphate.—Tributyl phosphite (25 g. or 100 mmoles) in 100 g. of methylene chloride at $-15°$ required 64 mmoles of ozone to complete the oxidation. In a second experiment, 100 ml. of methylene chloride was saturated at $-10°$ with ozone (about 1.5 mmoles dissolved) before any phosphite was added. To this was then added 4.45 g.

(17.8 mmoles) of tributyl phosphite and the ozone flow continued until oxidation was complete. Subtraction of the ozone going through the reaction mixture from the total delivered indicated that 16 mmoles or 90% of that required on a 1:1 basis had been consumed.

Finally, in a third experiment, 40 g. (160 mmoles) of tributyl phosphite was completely oxidized at $-60°$ using no solvent. The total ozone consumption was 96 mmoles or 60% of that calculated on a 1:1 basis. Distillation of this material gave 40.6 g. (95.5%) of good quality tributyl phosphate, b.p. 120–121° (3 mm.), $n^{25}D$ 1.4226 (lit.[29] b.p. 135° (5 mm.), $n^{25}D$ 1.4224).

(b) Oxidation of Tributyl Phosphite under Conditions Giving Exact Stoichiometry.—Experiments previously described indicated that at low phosphite concentration the over-all stoichiometry approached 1:1 whereas at higher concentration nearly two moles of phosphite could be oxidized by one of ozone. These points were established conclusively by the following experiments.

To 100 ml. of dry methylene chloride at $-70°$ was added a standardized ozone–oxygen stream at the rate of 0.625 mmole of ozone per minute. At the same time a methylene chloride solution of tributyl phosphite (1.0 M) was added from a buret at a slightly slower rate so that the blue color of excess ozone was present in the reaction mixture at all times. When 15.0 mmoles of tributyl phosphite had been added, ozone flow was stopped and excess ozone in the reaction vessel was swept out with a stream of dry nitrogen. During the time of the reaction (30 min.) a total of 18.75 mmoles of ozone had been delivered to the reaction mixture. Titration of the iodine liberated in the off-gas trap showed that in this period, 3.75 mmoles had gone through unreacted and thus exactly 15.0 mmoles of ozone had been absorbed by the 15.0 mmoles of phosphite. An infrared spectrum of the tributyl phosphate produced showed it to be identical with that obtained by standard methods.

In a companion experiment, 25.0 g. (100 mmoles) of tributyl phosphite was oxidized at $-60°$ using no solvent. Ozone flow was stopped when 24 mmoles of ozone had been added. An aliquot of the reaction mixture was titrated with standard methanol–iodine solution and, from this, the total unreacted phosphite was determined to be 51.6 mmoles. Thus, the 24 mmoles of ozone had oxidized essentially 48.4 mmoles of phosphite. Repetition of this experiment using oxygen-free ozone prepared *via* the silica gel procedure of Cook, *et al.*,[13] gave exactly the same stoichiometric results.

Ozone Oxidation of Triaryl Phosphites. (a) Tris-(p-tolyl) Phosphite.—A standardized ozone–oxygen stream was added to a solution of 17.6 g. (50 mmoles) of tris-(p-tolyl) phosphite in 100 ml. of dry methylene chloride at 5–10° until oxidation of phosphite was complete. A total of 26 mmoles of ozone was absorbed. Removal of solvent gave 18.4 g. of sticky crystals. These were dissolved in 100 ml. of ether and extracted with 15 ml. of 3 M sodium hydroxide solution. After washing and drying, the solvent was removed giving 17.5 g. (95.5%) of colorless crystals, m.p. 72–75°. One recrystallization from petroleum ether gave good quality tris-(p-tolyl) phosphate, m.p. 75–77°, lit.[29] m.p. 76–78°.

(b) Tris-(p-t-butylphenyl) Phosphite.—Ozone was added to 23.9 g. (50 mmoles) of freshly distilled phosphite in 100 ml. of methylene chloride exactly as described in (a). Approximately 25 mmoles was required to complete the oxidation. Workup as in the previous case gave 22.8 g. (92.3%) of colorless solid, m.p. 95–98°. One recrystallization from ethanol gave pure tris-(p-t-butylphenyl) phosphate, m.p. 99–100°, lit.[29] m.p. 101°.

(c) Triphenyl Phosphite.—Repetition of experiments a and b using 15.5 g. (50 mmoles) of freshly distilled triphenyl phosphite but only 50 ml. of methylene chloride solvent resulted in the consumption of 22.0 mmoles of ozone and formation of 16.4 g. of crude phosphate. crystallizing point 45.5°, as brown colored crystals. Treatment with alkali as in previous cases gave 15.5 g. (95%) of colorless triphenyl phosphate, c.p. 48.7°,[30] lit.[29] m.p. 49°. The above experiment was repeated under dilute conditions with 160 ml. of solvent. The total ozone consumption amounted to 25.2 mmoles. The apparent more efficient

(28) (a) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 198; (b) H. Tsubomura and J. M. Kliegman, *J. Am. Chem. Soc.*, **82**, 1314 (1960).

(29) See ref. 28a, pp. 258–263.

(30) The crystallizing point of high quality commercial triphenyl phosphate was 49.0°.

utilization of ozone at high phosphite concentration was confirmed by addition of exactly 25 mmoles of ozone to 31 g. (100 mmoles) of triphenyl phosphite at 25° using no solvent. The resulting mixture of triphenyl phosphate and unreacted phosphite was treated with 100 ml. of dry methanol and allowed to stand 4 hr. to effect methanolysis of triphenyl phosphite. Excess methanol and trimethyl phosphite were stripped from the reaction mixture under reduced pressure. The residue was taken up in 75 ml. of ether and extracted thoroughly with three 50-ml. portions of 3 M sodium hydroxide solution. The ether solution of triphenyl phosphate was then washed, dried with Drierite, and the solvent removed. The resulting triphenyl phosphate amounted to 20.0 g. (61.4 mmoles), c.p. 46.5°.

Preparation and Reactions of Ozone Adducts with Triaryl Phosphites. (a) Tris-(p-tolyl) Phosphite.—A solution of 8.81 g. (25 mmoles) of tris-(p-tolyl) phosphite in 30 ml. of dry methylene chloride was added slowly to a hell of 100 ml. of methylene chloride at −70° along with a standardized ozone-oxygen stream. The rate of addition of the phosphite was kept slightly slower than the addition of ozone so that a blue color of excess ozone was maintained in solution. Ozone flow was stopped immediately after addition of phosphite was complete. The cold solution was sparged for 5 min. with dry nitrogen to sweep excess ozone into the off-gas trap. The total amount of ozone delivered during the reaction period was 30.8 mmoles of which 6.3 passed through into the potassium iodide traps in the off-gas line. Thus the 25 mmoles of phosphite had reacted with 24.5 mmoles of ozone. The presence of the phosphite-ozone compound was demonstrated by addition of 16.2 g. (65 mmoles) of tributyl phosphite dissolved in 20 ml. of dry methylene chloride. Addition was completed in about 5 min. A vigorous reaction occurred and strong cooling was necessary to keep the temperature below −40°. After 30 min. at −50 to −70°, the reaction was allowed to warm to room temperature. An aliquot of solution was then removed and unreacted tributyl phosphite was determined by iodine titration. The presence of 21 mmoles of unreacted phosphite[31] was indicated; thus, 44 mmoles of tributyl phosphite had been oxidized.

(b) Tris-(p-t-butylphenyl) Phosphite.—Ten grams (20.9 mmoles) of the pure redistilled phosphite in 30 ml. of dry methylene chloride was treated with ozone exactly as in a. A total of 20.1 mmoles of ozone was absorbed. Addition of excess (50 mmoles) tributyl phosphite resulted in oxidation of 36 mmoles of the latter.

(c) Triphenyl Phosphite.—The procedure of a was again repeated using 7.75 g. (25 mmoles) of triphenyl phosphite. Exactly 25 mmoles of ozone was absorbed during the concurrent addition period. The cold solution was treated with 15.0 g. (60 mmoles) of tributyl phosphite. Back titration of unreacted phosphite indicated oxidation of 45 mmoles of the tributyl phosphite by the intermediate triphenyl phosphite-ozone compound.

In a companion experiment involving 15.5 g. (50 mmoles) of triphenyl phosphite with roughly the same amount of methylene chloride as solvent the final products were isolated as a check on the analytical method. Thus 25 g. (100 mmoles) of tributyl phosphite was added to the triphenyl phosphite-ozone compound at low temperature. After the oxidation was complete, solvent was removed and the residual mixture of triphenyl phosphate and tributyl phosphate was subjected to vacuum distillation. A small fore-run of tributyl phosphite and presumably some dibutyl phosphite was obtained along with the main fraction of tributyl phosphate, 22.0 g. (84 mmoles), b.p. 144–148° (7 mm.), n^{25}D 1.4230. The infrared spectrum of this material showed no serious deviations from that of authentic tributyl phosphate. The non-volatile triphenyl phosphate was obtained from the pot residue by dissolving in 100 ml. of ether and extracting thoroughly with three 50-ml. portions of 3 M sodium hydroxide solution. The ether layer was washed, dried and the solvent removed, giving 15.9 g. (49 mmoles) of almost colorless triphenyl phosphate, c.p. 47.2°.

An identical experiment was carried out where trimethyl phosphite (12.4 g. or 100 mmoles) was added to the phosphite-ozone adduct. The reaction was essentially identical. Distillation of the trimethyl phosphate produced gave 11.6

g. (83 mmoles), b.p. 68–71° (7 mm.), n^{25}D 1.3944. Approximately 15.8 g. (48.5 mmoles) of triphenyl phosphate, c.p. 48.2°, was recovered from the still residue.

These experiments provide conclusive evidence that a 1:1 adduct of triaryl phosphite and ozone can be formed and that these intermediates are capable of oxidizing nearly two additional moles of a trialkyl phosphite which is subsequently added.

Additional Reactions of Triphenylphosphate-Ozone Adduct. (a) Reaction with Triphenyl Phosphite.—The ozone adduct of triphenyl phosphite (25 mmoles) in about 120 ml. of methylene chloride was prepared as previously described. To this solution at −70° was added 17 g. (55 mmoles) of triphenyl phosphite. No apparent reaction occurred until the temperature was raised to about −40°. A moderately exothermic reaction then took place which subsided within 10 minutes. The reaction was held at −50° for 30 min. and then allowed to warm to room temperature. The solvent was removed and the phosphate-phosphite residue was dissolved in 50 ml. of dry methanol and allowed to stand for 4 hr. The characteristic odor of trimethyl phosphite was detectable within minutes. In early experiments the amount of unreacted phosphite at this stage was estimated by iodine titration.[32] When this result was found to be unreliable, the actual triphenyl phosphate present was determined by isolation. Methanol and the bulk of the alkyl phosphite produced by alcoholysis were removed in vacuo. The residue was taken up in 100 ml. of ether and extracted three times with 50-ml. portions of 3 M sodium hydroxide solution. After washing thoroughly and drying, the ether was removed leaving a residue of good quality triphenyl phosphate, c.p. 47.5° amounting to 16.5 g. (50.6 mmoles).

In an identical experiment the reaction mixture was held at −40 to −50° for an additional 16 hr. before allowing the temperature to rise, the total amount of triphenyl phosphate isolated was 20.6 g. (63 mmoles), c.p. 47.1°.

Samples of adduct for low temperature n.m.r. measurements[17] were prepared in the manner described previously except that methyl chloride was used as the solvent to which both ozone and phosphite were concurrently added. Triphenyl phosphite was added as usual in methylene chloride. On completion of addition, the solution was concentrated by boiling out methyl chloride under slightly reduced pressure keeping the temperature around −40°. This solution, concentrated to around 30 ml., was used for the n.m.r. measurement at −60°. In a companion experiment 25 mmoles of triphenyl phosphite was added prior to concentrating. After oxidation of this was complete, concentration was effected and the n.m.r. spectrum determined.[17] In the first determination, a single peak $\delta_{H_3PO_4}$ = + 63 ± 1 p.p.m. was observed while in the second solution a peak at +18.5 p.p.m. corresponding to triphenyl phosphate[18] appeared along with a second signal at +62 ± 1 p.p.m. corresponding to the adduct or a second structurally similar intermediate.

(b) Thermal Decomposition.—Twenty-five mmoles of triphenyl phosphite-ozone adduct was prepared in about 120 ml. of methylene chloride. The cold solution was warmed to 30° over about 0.5 hr. Evolution of oxygen proceeded smoothly beginning at about −15°. The off-gas was passed through a −75° methylene chloride trap, a water trap and then into a wet test meter. The uncorrected column of gas amounted to 710 ml. When corrected for heat expansion in the system, vapor pressure of water and reduced to standard conditions, it amounted to about 515 ml. (theor. about 560 ml.). Isolation of triphenyl phosphate from the residue gave 8.1 g. (99%), c.p. 48.4°, of pure material after an alkaline wash to remove a trace of colored acidic impurity.

(c) Oxidation of Other Substrates.—The ability of triphenyl phosphite-ozone adduct to oxidize other materials was demonstrated. In the first experiment, 17.3 mmoles of triphenyl phosphite was added at −70° to 70 ml. of methylene chloride concurrently with a standardized ozone stream. Exactly 17.3 mmoles of ozone was absorbed; after removal of excess ozone with a nitrogen stream, 40 mmoles of tributylphosphine was added. Vigorous oxidation occurred exactly as in the case of trialkyl phosphites. Back titration of unreacted phosphine with standard iodine solution indicated that 29.3 mmoles of

(31) The maintenance of anhydrous conditions is extremely important during these steps.

(32) Cf. Analytical Procedure and footnote 15.

the latter had been oxidized. In a second experiment, 50 mmoles of adduct in a solvent mixture of methyl chloride (70 ml.) and methylene chloride (30 ml.) was treated with 6.5 g. of freshly distilled dimethyl sulfide. Oxidation was rapid. After 1 hr. at −50° the solvent was carefully removed. The amount of sulfoxide (66 mmoles) and sulfone (3.6 mmoles) in the residue was determined by gas phase chromatography.[33] This represented a total of 73 milliatoms of oxygen placed upon the sulfide substrate.

When excess dimethyl sulfoxide was added to 50 mmoles of adduct in a separate experiment, little reaction appeared to occur at −40°. The mixture was held at −30 to −40° for 24 hr. Workup and determination of sulfone as in the previous case indicated that only 59 mmoles of sulfoxide had been oxidized. Isolation of the sulfone by quenching the residue mixture in ether yielded 5.3 g. (55 mmoles) of fairly good quality dimethyl sulfone, m.p. 103–106°, lit.[34] m.p. 109.5°.

Ozone Oxidation of Phosphines. (a) Tributylphosphine.—Ozone (69 mmoles) was absorbed from a standardized ozone–oxygen stream on a cold −70° column of silica gel.[13] The column was then swept with dry nitrogen and slowly warmed over about 4 hr. The gas stream was added to a solution of 20.2 g. (100 mmoles) of tributylphosphine in 100 ml. of dry methylene chloride. Reaction was complete before the column was swept free of ozone. Sweeping was continued with the off-gas going into potassium iodide traps. Of the 69 mmoles of ozone delivered 55.2 were consumed in oxidation of the phosphine. Tributylphosphine oxide, 20.0 g. (92%), b.p. 123–125° (1 m.m.), m.p. 61–63°, lit.[29] b.p. 300°, was isolated by removal of solvent and distillation of residue.

(b) Triphenylphosphine.—Oxygen-free ozone[13] (42 mmoles) was swept by a nitrogen stream into a solution of

13.1 g. (50 mmoles) of triphenylphosphine in 90 ml. of methylene chloride at −65°. When oxidation was complete, excess ozone in the solution and on the silica gel column was swept into potassium iodide traps. The total ozone consumed oxidizing the phosphine was 32.3 mmoles. Removal of solvent gave 13.8 g. (99%) of good quality triphenylphosphine oxide, m.p. 153–155°, lit.[29] m.p. 153°.

Ozone Oxidation of Dialkyl Sulfides.—The following experiments, though lacking in precise quantitative detail, illustrate clearly the pronounced effect of high substrate concentration upon ozone proportion.

(a) Diethyl Sulfide.—To 18 g. (200 mmoles) of diethyl sulfide in 50 ml. of methylene chloride at −60° was added a standardized ozone–oxygen mixture until 72.8 mmoles of ozone had been absorbed. Solvent was removed from the mixture and the residue carefully fractionated. In all, a total of approximately 11.2 g. (105 mmoles), b.p. 66–75° (4 mm.), lit.[35] b.p. 83–85° (12 mm.), of diethyl sulfoxide along with 6.0 g. (49 mmoles) of diethyl sulfone, m.p. 67–72°, lit.[36] m.p. 72°, was obtained. This represents a total of roughly 203 milliatoms of oxygen placed upon sulfur by approximately 73 mmoles of ozone.

(b) Dibutyl Sulfide.—Ozone (74.3 mmoles) was added to 29.3 g. (200 mmoles) of dibutyl sulfide at 0–5° without solvent. Toward the end of the addition some solid began to separate. No ozone passed through the reaction vessel into the potassium iodide traps. Without isolation of products (presumably sulfoxide and sulfone as in the case of diethyl sulfide) the crude mixture was subjected to elemental analysis. The values obtained were C, 59.25; H, 11.35; S, 19.18. By difference the oxygen content was determined as approximately 10.0%. From this and the weight of sample (32.6 g.) it was calculated that approximately 202 milliatoms of oxygen had been introduced into the substrate under these conditions.

(33) We thank Dr. E. M. Emery and Mr. A. Bybell for these measurements.

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Organomercury Chemistry. A Novel Synthesis of Vinyl Esters, Vinyl Ethers and Vinyl Thioethers[1]

By Donald J. Foster and Erich Tobler

Organomercury compounds containing vinyl or substituted vinyl groups adjacent to a mercury atom undergo reactions that are not observed in the absence of the unsaturation. Divinylmercury reacts with organic acids to form the corresponding vinyl ester and metallic mercury. The reaction goes through a vinylmercuric ester intermediate that can be isolated if desired. Phenols and thiophenols react with divinylmercury to form aryl vinyl ethers or thioethers rather than nuclear mercurated products. Even alkyl thiols react with unsaturated organomercury compounds to yield the corresponding alkyl thioethers.

Introduction

The reaction of organomercury compounds of the general formula R_2Hg, where R is alkyl, aryl or aralkyl, with a variety of reagents has been studied quite extensively. Thus inorganic[2−4] and organic[5−9] acids cleave organomercury compounds to

(1) Presented at the 138th Meeting of The American Chemical Society, New York, N. Y., Sept., 1960.

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form a hydrocarbon, RH, and an organomercuric ester, RHgX or $R'CO_2HgR$, according to eq. 1 and 2.

$$R_2Hg + HX \longrightarrow RH + RHgX \qquad (1)$$

$$R_2Hg + R'CO_2H \longrightarrow RH + R'CO_2HgR \qquad (2)$$

While the rate of cleavage varies considerably with the substituent R, the product is always a hydrocarbon and a mercuric ester. The reaction of organomercury compounds with phenols is described in a series of papers by Koton.[10−14] Dialkyl- and diarylmercury compounds react with phenols to

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