Oxidation of Trialkyl Phosphites by Epoxides

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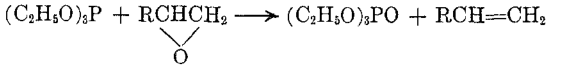
Received February 18, 1957

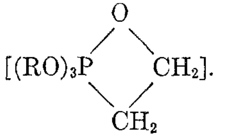
Much interest has been focused recently upon the oxidation reactions of trivalent phosphorus compounds. Particularly prominent have been the reactions of trialkyl phosphites with carbonyl compounds,[1] and of trisubstituted phosphines with oxidizing agents.[2,3] This note reports some preliminary data on another new reaction[4,5] of phosphites.

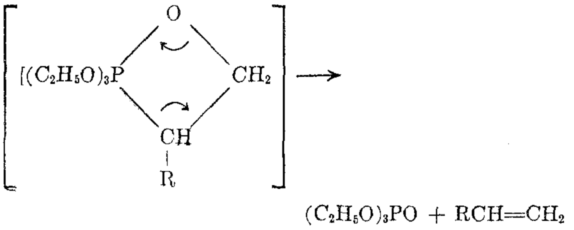
Triethyl phosphite was oxidized very smoothly to triethyl phosphate by ethylene oxide and propylene oxide at 150–175°. The epoxides were reduced to the corresponding olefins.



$$(C_2H_5O)_3P + RCHCH_2 \longrightarrow (C_2H_5O)_3PO + RCH{=}CH_2$$

There are indications that the reaction is applicable to other phosphites and epoxides. It is hoped that this additional work will be published in more detail at a later date.

Although the phosphite might attack the epoxide oxygen directly, recent mechanism discussions[1,6–8] suggest a nucleophilic attack on carbon to produce intermediates like $[(RO)_3\overset{+}{P}\text{–}CH_2CH_2\text{–}\overset{-}{O}]$ or  Should such an attack occur, then the following rearrangement could account for the observed products.



EXPERIMENTAL

Reaction of triethyl phosphite with ethylene oxide. A mixture of 133 g. (0.8 mole) triethyl phosphite and 35.2 g. (0.8 mole) ethylene oxide was placed under 50 p.s.i.g. of dry nitrogen in a 300-ml. stainless steel bomb. The bomb was rocked and heated slowly to 174° over a period of 3 hr. The pressure rose steadily to 275 p.s.i.g. at 154°, then rapidly to 400 p.s.i.g. at 174°. These conditions were held for 1 hr., then heat was removed and the bomb allowed to cool overnight. The gas which formed consisted of 92.3 mole per cent ethylene, 3.5% ethylene oxide, 2.1% nitrogen, and minor quantities of other contaminants.

Distillation of the liquid product gave three fractions:

(1) 22 g., b.p. 62–80° C. (24 mm.), was mostly triethyl phosphite with some triethyl phosphate.

Anal. Calcd. for $C_6H_{15}PO_3$: P, 18.7. Found: P, 18.1.

(2) 87 g., (60%) b.p. 80–113° (mostly 110°) (24 mm.), was triethyl phosphate.

Anal. Calcd. for $C_6H_{15}PO_4$: P, 17.0. Found: P, 16.7.

(3) 16 g., residue, was essentially all phosphate.

Anal. Found: P, 16.4.

Reaction of triethyl phosphite with propylene oxide. A mixture of 133 g. (0.8 mole) triethyl phosphite and 46 g. (0.8 mole) propylene oxide was rocked in a bomb for 23 hr. The temperature was 150° and the pressure rose to 350 p.s.i.g. The gas was 95.9 mole per cent propylene.

Distillation of the 155.5 g. of liquid product gave four fractions:

(1) 3.1 g., b.p. 33–34°, was mostly propylene oxide.

(2) 30.4 g., b.p. 54–58° (20 mm.), was essentially all triethyl phosphite.

Anal. Found: P, 18.2.

(3) 86 g. (59.5%), b.p. 58–108° (mostly 97–108°) (20 mm.), was nearly all phosphate.

Anal. Found: P, 17.2.

(4) 14.7 g., residue, was mostly phosphate with some unidentified higher boiling material.

Anal. Found: P, 14.9.

Identification of products. The gas samples were analyzed by mass spectrometry. The phosphorus compounds were identified by boiling point differences, elemental analyses, and infrared spectra. The spectra were particularly helpful because the elemental analyses occasionally were erratic due to the formation of solid masses that resisted combustion.

Triethyl phosphate has a very characteristic, strong absorption peak at 7.86–7.95 μ which is attributed to the P=O stretching motion.[9] In addition, there is a very strong absorption at 10.30 μ. This latter absorption is subject to some discussion,[9–11] but apparently it is due to the P—O stretching in the P—O—C structure of trialkyl phosphates.

The phosphites, of course, do not have the P=O absorption at 7.86–7.95μ. In triethyl phosphite the peak at 10.30μ is absent also, but there is a comparable, very strong absorption at 10.84μ. Although little is known about this peak, it seems reasonable to believe that it is caused by the P—O stretching in P—O—C structures of phosphites.

The large peaks in the 10.00- to 10.84-μ range are particularly helpful in analyzing mixtures of phosphites and phosphates. They are of essentially equal intensity, so the relative sizes shown in the spectrum of a mixture are a good indication of the composition of that mixture.

Known, redistilled samples of phosphite and phosphate were used as standards in the spectral work.

Acknowledgment. The author is grateful to the Union Oil Co. of California for permission to publish this work, to Messrs. D. O. Alford and A. Menefee for the spectral studies, and to Mr. S. V. Vande-

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grift for capable assistance with the experimental sections.

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Preparation and Properties of Tetrachloroethylene Oxide

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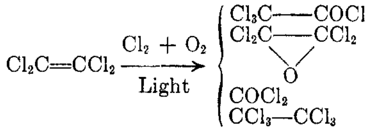
Received February 18, 1957

The photochemical oxidation of tetrachloroethylene has been studied by several previous investigators.[1-8] The primary object of these workers was the preparation of trichloroacetyl chloride, with only one making reference to tetrachloroethylene oxide as a byproduct.[5,6]

In the present study, tetrachloroethylene, kept saturated with oxygen and with an excess of chlorine added, was exposed to sunlight at 36–40°. Under these conditions the following products were obtained: trichloroacetyl chloride, tetrachloroethylene oxide, phosgene, and hexachloroethane.

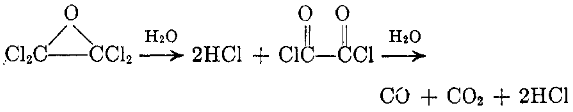


After most of the phosgene was removed, under vacuum, at room temperature, analysis of the liquor was 40 mole per cent trichloroacetyl chloride, 9 mole per cent tetrachloroethylene oxide, 8 mole per cent hexachloroethane, and 43 mole per cent tetrachloroethylene.

Vacuum distillation through a helices-packed, five-foot, distillation column gave a solution whose analysis showed it to contain 40 mole per cent trichloroacetyl chloride, 54 mole per cent tetrachloroethylene oxide, and 6 mole per cent tetrachloroethylene. Trichloroacetyl chloride was removed from this solution by washing with dilute alkali. The tetrachloroethylene was converted, by addition of chlorine, to hexachloroethane, then the solution vacuum distilled through a short, center rod column. A trace of trichloroacetyl chloride was removed with a dilute alkali wash, then the purified tetrachloroethylene oxide dried with calcium chloride. The infrared spectrum (Fig. 1) shows that the material is free from trichloroacetyl chloride, tetrachloroethylene, and hexachloroethane. The photochemical oxidation was repeated at −3–0°, 60–75°, and at 80°. The highest yield of tetrachloroethylene oxide was obtained at 60–75°.

Tetrachloroethylene oxide rearranges to trichloroacetyl chloride upon heating. The specific reaction rates for this conversion at 65°, 80°, and 100° are 6×10^{-7}, 8.9×10^{-6}, and 1.2×10^{-4} sec.$^{-1}$, respectively. The energy of activation is approximately 31.4 kcal./mole.

Tetrachloroethylene oxide reacts readily with methanol in the presence of mercuric chloride, evolving hydrogen chloride and forming methyl trichloroacetate. It reacts rapidly with *N* potassium hydroxide in methanol to give potassium oxalate as the major product. When stirred with either dilute basic or acidic aqueous solutions, the epoxide very slowly partially rearranges to its isomer and partially decomposes to give carbon monoxide, carbon dioxide, and hydrogen chloride. The latter reaction probably forms oxalyl chloride as an intermediate, which then hydrolyses to carbon monoxide, carbon dioxide, and hydrogen chloride.[9] In concentrated sulfuric acid, however, tetrachloroethylene oxide undergoes rapid and exothermic rearrangement to trichloroacetyl chloride.



EXPERIMENTAL[10]

Photochemical oxidation of tetrachloroethylene. The reactor was made from two sections of borosilicate glass pipe, 2 ft. long by 3 in. diameter, joined together at both ends by 3 in. pipe. The lower section contained a cold finger, while a plane-parabolic mirror of 8 sq. ft. was focused on the upper section. The reactor was charged with 3 gal. of commercial grade (Stauffer) tetrachloroethylene, excess oxygen and chlorine were added, and the solution was agitated and exposed to sunlight for 12 hr. The temperature was controlled at 36–40°. Phosgene was removed by aspiration. Infrared analysis of the solution showed: 40% CCl_3COCl, 9% $(CCl_2)_2O$, 43% C_2Cl_4, 8% C_2Cl_6 (mole %).

Separation of tetrachloroethylene oxide. The solution was distilled through a 5-ft., vacuum-jacketed distilling column of 1-in. diameter, packed with $^1/_8$ inch borosilicate glass helices. Using a reflux/take-off ratio of 30/1, 310 ml., boiling 32–36.3° (45 mm.–38 mm.), was collected in 23 hr. Infrared analysis of the distillate showed: 40% CCl_3COCl, 54% $(CCl_2)_2O$, 6% C_2Cl_4 (mole %).

Trichloroacetyl chloride was removed by washing with dilute aqueous alkali. Tetrachloroethylene was chlorinated

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