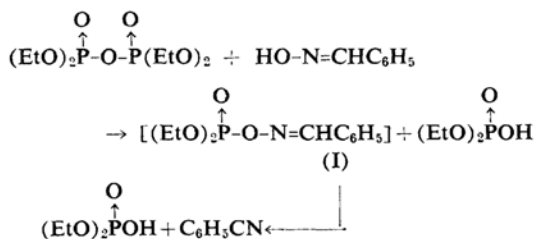


The Preparation of Diethyl Phosphate

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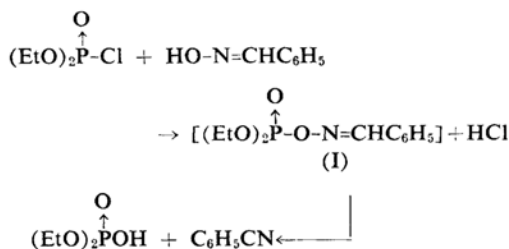
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Intramolecular dehydration reactions of primary nitroparaffins^{1,2)}, aldoximes^{3,4)} and hydroxamic acids⁵⁾ into nitrile oxides, nitriles and isocyanates, respectively, by means of organic reagents have been described in preceding papers. It was shown in them⁴⁾ that benzaldoxime is dehydrated by means of esters of phosphoric acid and it was demonstrated that the dehydration proceeds through an intermediate, diethyl benzaldimino phosphate (I), formed by the bond fission of pyrophosphate linkage by an attack of benzaldoxime.



This type of reaction was extended to the preparation of diethyl phosphate from diethyl chlorophosphonate by means of compounds containing a hydroxyl group which are readily dehydrated to give unsaturated compounds, such as benzaldoxime and *tert*-butyl alcohol.

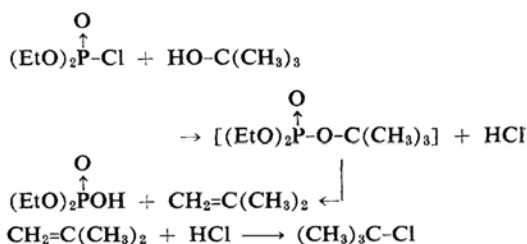
The reaction of benzaldoxime with diethyl chlorophosphonate initially yields diethyl benzaldimino phosphate (I), which in turn decomposes to give diethyl phosphate and benzonitrile in good yields.



When diethyl chlorophosphonate and benzaldoxime are allowed to react in dry benzene

at room temperature, a violent reaction takes place and a large amount of benzaldoxime hydrochloride, which retards the formation of I, precipitates. Since the hydrochloride decomposes into benzaldoxime and hydrogen chloride on gentle heating, the reaction is best effected when two reactants are mixed at one time and heated at about 70°C.

On the other hand, the reaction of *tert*-butyl alcohol with diethyl chlorophosphonate does not take place at room temperature, but it is effected well by refluxing them in carbon tetrachloride for 3 hr. Isobutylene, hydrogen chloride and *tert*-butyl chloride formed by the addition of hydrogen chloride to isobutylene are obtained along with diethyl phosphate.



As described in the experimental part, *tert*-butyl alcohol is dehydrated in a nearly quantitative yield; however, the yield of diethyl phosphate is comparatively low. This may be attributed to a useless dehydration of *tert*-butyl alcohol catalyzed by the phosphate formed. The use of 2 mol. of *tert*-butyl alcohol did not lead to a good result though the yields of isobutylene and *tert*-butyl chloride were increased.

These methods for the preparation of diethyl phosphate from diethyl chlorophosphonate are a simpler procedure than that reported by Toy⁶⁾ which involves 2 steps of hydrolysis.

Moreover, an attempt to prepare diethyl chlorophosphonate in a better yield by the reaction of phosphorus oxychloride with 2 mol. of ethyl alcohol gave a successful result. Several methods⁷⁻¹⁰⁾ are reported in the literature for this reaction; however, the yield is less than 25% even when a basic medium

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such as pyridine is used. In the present experiment, in order to avoid unnecessary heating, the reaction was carried out in petroleum ether under 0°C over a period of 4.5 hr. After the completion of the reaction, the solvent was removed at room temperature under reduced pressure and distilled. By this method, a 76% yield of diethyl chlorophosphate was obtained.

As shown in Table II, the yield of diethyl chlorophosphate became higher when the amount of reactants was smaller, and also it can be noted that the elevation of reaction temperature over 0°C resulted in a decrease of the yield.

Experimental

Diethyl Phosphate.—*By Means of Benzaldoxime.*—To 17.2 g. (1/10 mol.) of diethyl chlorophosphate dissolved in 10 ml. of carbon tetrachloride was added at one time with vigorous stirring a solution of 12.1 g. (1/10 mol.) of benzaldoxime in 10 ml. of carbon tetrachloride. Then the reaction mixture was refluxed on a water bath for an hour. After the evolution of hydrogen chloride, the carbon tetrachloride was removed and 9 g. (87% yield) of benzonitrile (b. p. 78°C/16 mmHg) and 11 g. (71% yield) of diethyl phosphate (b. p. 112~127°C/0.02 mmHg) were obtained.

If a solution of the aldoxime was added more slowly at room temperature, a white precipitate melting at about 80°C was obtained. This substance generated hydrogen chloride on heating and gave benzaldoxime by means of distillation. Besides that, from the filtrate were obtained benzonitrile and diethyl phosphate in 51% and 35% yields, respectively.

By Means of tert-Butyl Alcohol.—A mixture of 17.2 g. (1/10 mol.) of diethyl chlorophosphate and 7.5 g. (1/10 mol.) of *tert*-butyl alcohol dissolved in 10 ml. of carbon tetrachloride was refluxed on a water bath for 3 hr. During this period, isobutylene and hydrogen chloride were generated from the mixture. Distillation gave *tert*-butyl chloride and diethyl phosphate. The yields and boiling points are listed in Table I.

TABLE I

Product	Yield	B. p.
Isobutylene	1.5 l. 67%	
<i>tert</i> -Butyl chloride	3.5 g. 38%	49~50°C/760 mmHg
Diethyl phosphate	7.5 g. 48%	111~114°C/0.005 mmHg

Diethyl Chlorophosphate.—The preparation of diethyl chlorophosphate from phosphorus oxychloride was tried under several conditions as listed in Table II. In the case of 1 mol. of phosphorus oxychloride, the best procedure was found to be as follows: To 153.5 g. (1 mol.) of phosphorus oxychloride dissolved in 80 ml. of petroleum ether cooled by an ice-salt bath was added with vigorous stirring a solution of 105 g. (2.28 mol.) of 99% ethyl alcohol in 50 ml. of petroleum ether at a rate such that the addition was completed in about 3.5 hr. The stirring was continued for an hour after all the solution of ethyl alcohol had been added. During this period, the temperature was maintained under 0°C and then the stirring was further continued without the ice-salt bath until the mixture was warmed to room temperature. After the hydrogen chloride dissolved in the reaction mixture and the petroleum ether were removed under reduced pressure at room temperature, diethyl chlorophosphate was obtained by distillation, b. p. 72°C/6 mmHg, yield 130 g. (76%).

TABLE II

Solvent	Rate of addition hr.	Reacn. time hr.	Moles of POCl ₃	Yield %	Reacn. temp. °C
CCl ₄	1	1.5	0.2	80	0
CCl ₄	1	1.5	0.2	43	room temp.
PE	1	2	0.2	85	0
PE	3.5	5	1	76	0
CCl ₄	2	4.5	1.65	50	0

PE=petroleum ether

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