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**The rearrangement of 1-hydroxy tertiary phosphine oxides  
by the action of alkali**

by

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Ankara, Turquie

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# The rearrangement of 1-hydroxy tertiary phosphine oxides by the action of alkali

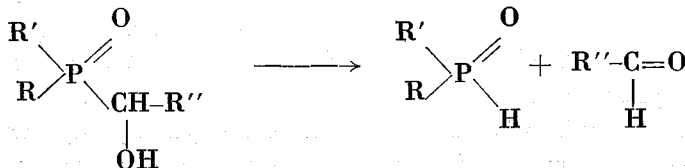
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The rearrangement of 2,2,2-trichloro-1-hydroxyethyl diphenyl phosphine oxide to 2,2-dichlorovinyl diphenylphosphinite by the action of alkali has been investigated. This rearrangement is of considerable theoretical interest as it represents the first reported instance of such transformation of a phosphineoxide to a phosphinic ester.

Unsymmetrical tertiary phosphine oxides have been prepared by the base catalyzed addition of two substituted phosphine oxides to  $\alpha$ - $\beta$  unsaturated nitriles, esters, ketones and and amides by Miller, Bradley and Hamilton.<sup>1</sup> Miller and co-workers<sup>2</sup> also reported the addition of disubstituted phosphine oxides to aldehydes. The adducts were reported as thermally unstable compounds. It is also reported that these adducts are cleaved into dialkyl (or diaryl) phosphine oxide and carbonyl compound by heating with aqueous alcoholic hydrochloric acid and much more susceptible to the action of alkali.

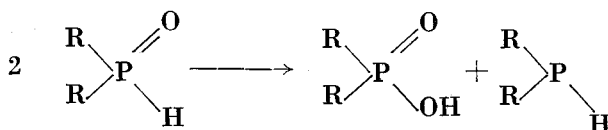
It is believed that the initial step in the basic hydrolysis of these 1-hydroxy tertiary phosphine oxides is cleavage of the oxide to give disubstituted phosphine oxide and carbonyl compound:



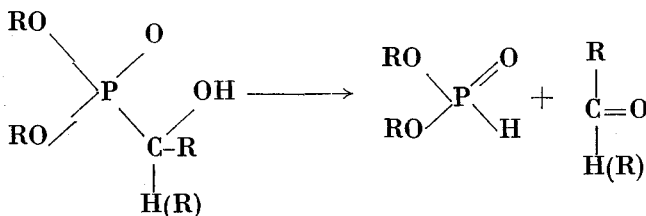
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The second step is believed to be the disproportionation reaction of phosphine oxide to give phosphinic acid and phosphine. The other product of the reaction has not been isolated.



This type of cleavage has been observed by Mosher<sup>3</sup> and by Abramov<sup>4</sup> for the structurally similar dialkyl phosphonates.

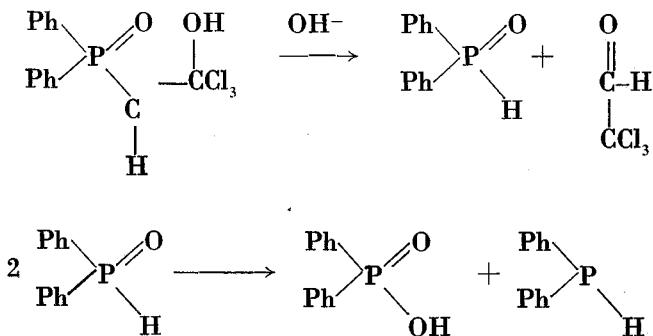


Mosher<sup>3</sup> reported the recovery of 90-100 % of the theoretical amount of aldehyde upon heating dialkyl-1-hydroxyalkyl phosphonates in a 5 % sodium hydroxide solution.

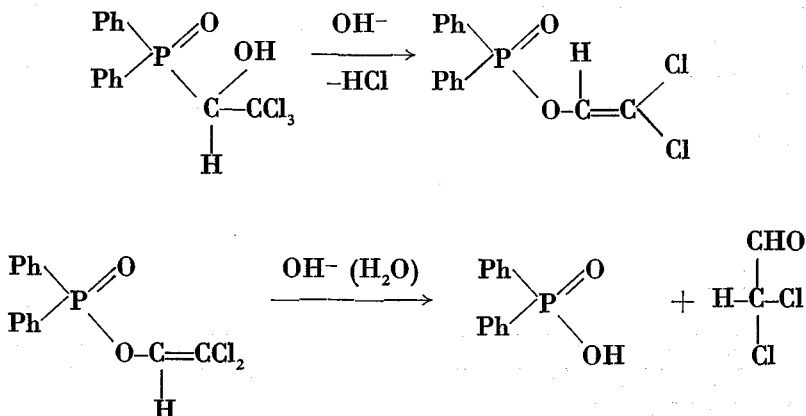
On the other hand Mattson, Spillane and Pearce<sup>5</sup> have reported that 2,2,2-trichloro-1-hydroxyethyl dimethylphosphonate undergoes dehydrochlorination in the presence of alkali to yield a volatile ester. Barthel, Giang and Hall<sup>6</sup> and Lorenz, Henglein and Schrader<sup>6</sup> have independently proved that this new ester is dimethyl -2,2-dichlorovinyl phosphate and 2,2,2-trichloro-1-hydroxyethyl dialkyl phosphonates undergo a rearrangement reaction by the action of alkali.

This paper reports the rearrangement of 2,2,2-trichloro-1-hydroxyethyl diphenylphosphineoxide to 2,2-dichlorovinyl diphenyl phosphinite by the action of alkali. Since 2,2,2-trichloro-1-hydroxyethyl dialkyl phosphonates undergo rearrangement by the action of alkali whereas simple dialkyl-1-hydroxyethyl phosphonates are cleaved under the same condition; a similar rearrangement might be expected for structurally similar tertiary phosphine oxides.

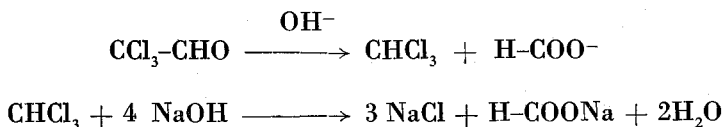
There are two possible paths for the basic hydrolysis of the 2,2,2-trichloro-1-hydroxyethyl diphenyl phosphineoxide. The first step of the path 1 is cleavage of the phosphine oxide to give chloral and diphenylphosphine oxide as Miller reported for the similar compounds. The second step is the disproportionation of diphenylphosphineoxide to diphenyl phosphinic acid and diphenylphosphine:



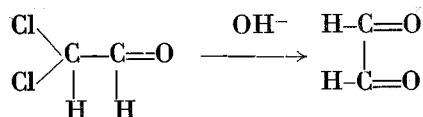
In the path 2 the first step is dehydrochlorination of the 2,2,2-trichloro-1-hydroxyethyl diphenylphosphineoxide by the action of alkali which causes a rearrangement reaction. The second step is the hydrolysis of the product of the rearrangement reaction to give diphenylphosphinic acid and dichloroacetaldehyde.



According to the Path 1 the final product from the carbonyl compound should be chloroform and sodium formate:



According to the second possible path the final product from the carbonyl compound should be glyoxal:



The methanolic solution of 2,2,2-trikloro-1-hydroxyethyl diphenyl phosphine oxide. was refluxed thoroughly with sodium hydroxide. Neither chloroform nor formate anion was found in the reaction mixture The chloroform was investigated by Fujiwara<sup>6</sup> and Feigle and Jungreis methods, and formate anion by Eeegrive<sup>11</sup> and Hoptpn<sup>11</sup> methods. Glyoxal was identified by the condensation reaction with o-aminophenol and then the formation an inner complex salt with calcium ions.<sup>12</sup>

The expected product from the rearrangement reaction has been prepared by Kharashova and Kamai method<sup>13</sup> and its physical and chemical properties were found to be identical. The comparison of the infrared spectra of the known phosphinic ester and the first product isolated from the rearrangement reaction mixture also showed that they were identical.

### Experimental

#### Reagents:

*2,2,2-trichloro-1-hydroxyethyl diphenylphosphineoxide* : was prepared by adding chloral to diphenyl phosphine oxide as previously described by Quin and Montgomery.<sup>14</sup> The crude product recryst-

tallized from methanol. m.p. 172-173° yield 81 %. Reported values: m.p. 122-23<sup>15</sup> 157.5-158<sup>16</sup> and 171.5-172.5<sup>14</sup>

*Diphenylphosphine oxide*: was prepared by the action of phenyl magnesium bromide on diethylhydrogene phosphite according to the original work of Haunt and Saunders<sup>16</sup> But only 100 ml of 10 % hydrochloric acid solution was used during the hydrolysis of Grignard complex. So yield increased up to 54 %. m.p. 54.5-56. °C Reported values: m.p. 53-56° yield-%. 48.

*Chloral*: obtained by heating (Fluka) chloralhydrate over concentrated sulphuric acid.

*Dichlorovinyl diphenyl phosphinite* (diphenylphosphinic acid dichlorovinyl ester) was prepared by action of butyldiphenyl phosphinite on chloral according to the original method reported by Kharashova and Kamai<sup>13</sup> Recrystallized from petroleum ether. m.p. 45° Reported values: b<sub>6.5</sub> 205-6.5° m.p. 44. 5-45°

*Butyldiphenyl phosphinite*: was prepared by the action of diphenyl chlorophosphine (diphenylphosphinous chloride) on butanol in the presence of pyridine of dry ether as a variation of Arburov and Nikonorov's method<sup>16</sup>.

27 ml (0.5 moles) diphenyl chlorophosphine was added while continuously stirring to a solution of 14 ml (0.15 moles) butanol and 12 ml pyridine in 150 ml dry ether. Colling in a carbon dioxide atmosphere. After stirring 40 minutes more, the mixture was filtered of from salt (pyridinium chloride) and the solvent ether was removed by the distillation.

The crude product was distilled at 133-135°/0.3 mm Hg.  $n_D^{20}=1.5745$  Reported values: b<sub>2</sub> 142-3  $n_D^{20}=1.5750$ <sup>19</sup> b<sub>6.5</sub> 157.5 - 158.5°  $n_D^{20}=1.5728$ <sup>21</sup>

*Diphenylchlorophosphine*- obtained from Fluka. Redistilled and used- b.p 178-180° /18 mm.

2,2-dichlorovinyl diphenyl phosphinite from 2,2,2-trichloro-1-hydroxyethyl diphenyl phosphineoxide:

A mixture of 4.50 g. of 2,2,2-trichloro-1-hydroxyethyl diphenyl phosphine oxide 8 g of sodium hydroxide, 20 ml of water and 80

ml of alcohol was allowed to stand at room temperature for 12 hours. The mixture was extracted with petroleum ether boiling 60-70°C. The extract washed twice with water and then dried over magnesium sulphate for 40 min. Removal of petroleum ether by the suction under reduced pressure left an oil. The impurities removed by vacuum distillation. at 60-62°C/9mm. Then main product distilled at 179-181/3 mm. its melting point was found 45°C and identified as 2,2-dichlorovinyl diphenylphosphinite.

### ÖZET

Bu çalışmada 2,2,2-trikloro-1-hidroksietil difenil fosfin oksidin bazı ortamda 2,2-diklorovinil difenilfosfinitine çevrilmesi incelenmiştir. Bu çevrilme teorik yönden oldukça ilginçtir, çünkü daha önce yapı benzerliği olan fosfonatların bazı ortamda fosfat esterlerine çevrildiği bulunduğu halde fosfinoksitlerin fosfinitlere çevrilmesi olasılığı üzerinde durulmamıştır.

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