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PREPARATION AND REACTIONS OF DIPHENYL PHOSPHITE

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Diphenyl phosphite was prepared by direct esterification of monophenyl phosphite with phenol by using catalysts for esterification of carboxylic acids. Triphenyl phosphite, though could not be obtained by the direct esterification, was obtained from diphenyl phosphite through disproportionation by tertiary amines.

We found that diphenyl and triphenyl phosphites are useful reagents for coupling of carboxylic acids with amines or alcohols and of carbon dioxide or disulfide with amines, and are successfully used for the preparation of peptides,$^{1)}$ polypeptides,$^{2)}$ polyamides,$^{3)}$ and polyureas.$^{4)}$ In these reactions, monophenyl phosphite and phenol are resulted from these phosphites.

$$\begin{array}{lcl} \mathrm{HO\text{-}P(OC_6H_5)_2} + \mathrm{R^1COOH} + \mathrm{R^2NH_2} & \xrightarrow[\text{t-Amine}]{} & \mathrm{R^1CONHR^2} + \mathrm{(HO)_2P\text{-}OC_6H_5} + \mathrm{C_6H_5OH} \\ \mathrm{(1/2\ P(OC_6H_5)_3)} & & \mathrm{(1/2\ (HO)_2P\text{-}OC_6H_5)} \end{array}$$

The reverse reaction of the resulted monophenyl phosphite and phenol into the starting phosphites, that is an esterification, is an important problem for industrial use of these reactions. Although esterifications of phosphorous acid derivatives with alkyl alcohols have been fully studied, no papers of those with phenols have been reported.

We have found also that the disproportionation of diphenyl phosphite is brought about by tertiary amines, resulting in half an equivalent of tri- and monophenyl phosphites, respectively.

We describe here preparative methods for diphenyl phosphite by esterification of monophenyl phosphite with phenol, and for tri- and monophenyl phosphites through the disproportionation of diphenyl phosphite by tertiary amines.

A mixture of monophenyl phosphite (1 equiv, prepared from the ammonium salt$^{5)}$) and phenol (3 equivs) was refluxed in toluene (3 l/mol of the phosphite) containing various catalysts (0.2 equiv) for esterification of carboxylic acids in a modified Soxlet extractor packed with calcium hydride. Distilled toluene was returned into the reaction mixture after dried by passing through the hydride. The reaction mixture after 36 hr was washed with a sodium bicarbonate solution and with water followed by fractional distillation to yield diphenyl phosphite (23% yield), b.p. 135-145/1-2mm.

In another way, a portion of the reaction mixture was diluted with tetrahydrofuran (THF), and subjected to a high speed liquid chromatographic analysis (HLC, UV method) in order to estimate more precise yield of diphenyl phosphite produced.

As shown in Table 1, diphenyl phosphite was obtained in up to about 40% yield, and the yield was improved to 50% by using excess phenol (10 equivs). Further esterification of diphenyl phosphite into triphenyl phosphite did not take place on prolonged heating.

Table 1. Esterification of Monophenyl Phosphite with Phenol

Catalyst	Time(hr)	Yield(%)a) of dipehnyl phosphite
p-$CH_3C_6H_4SO_3H$	12	20(48)b)
	24	31
	36	37
H_2SO_4	12	22
H_3BO_3	12	11
H_3BO_3 + H_2SO_4	12	21
$BF_3.O(C_2H_5)_2$	12	26
CH_3COONa	12	18
$Pb(OOCCH_3)_2.3H_2O$	12	26
$Co(OOCCH_3)_2.4H_2O$	12	22

a) The yield was obtained by menas of the HLC method.

b) A value in the parenthesis is the yield obtained by using 10 equivs of phenol.

Triphenyl phosphite was obtained in another way from diphenyl phosphite through disproportionation as shown below.

$$2\ HO\text{-}P(OC_6H_5)_2 \xrightarrow[\text{t-Amine}]{} (HO)_2P\text{-}OC_6H_5 \ + \ P(OC_6H_5)_3$$

The reaction was carried out at room temperature by mixing diphenyl phosphite (1 equiv) and tertiary amines (2 equivs) for 1 or 20 hr in the absence of solvents. The reactions with imidazole and triethylamine were conducted in THF in a similar manner. Similarly to that for the esterification, the yield of triphenyl phosphite produced was calculated by means of the HLC analysis after dilution of the resulted reaction mixture with THF (Table 2). Triphenyl phosphite was also obtained as precipitate in 41% yield, when the reaction mixture after 20 hr in the presence of pyridine was treated with water containing alcohol and cooled.

The disproportionation was significantly affected by the presence of tertiary amines. Conversion after 1 hr was increased with increasing basicity of the amines. Lower conversion with α-picoline and 2,6-lutidine of relatively higher basicity

Table 2. Tertiary Amine Promoted Disproportionation of Diphenyl Phosphite into Tri- and Monophenyl Phosphites[a)]

Tertiary amine	mol	pKa	Triphenyl phosphite[b)] Conversion(%)
None	-	-	0
Pyridine	0.02	5.23	30(80)
α-Picoline	0.02	5.97	24(74)
β-Picoline	0.02	5.52	46(70)
γ-Picoline	0.02	6.02	58(76)
2,6-Lutidine	0.02	6.99	10(80)
Imidazole	0.02	7.12	88(88)
Triethylamine	0.001	10.87	10
	0.003		54
	0.005		88
	0.01		88
	0.02		90
	0.04		88

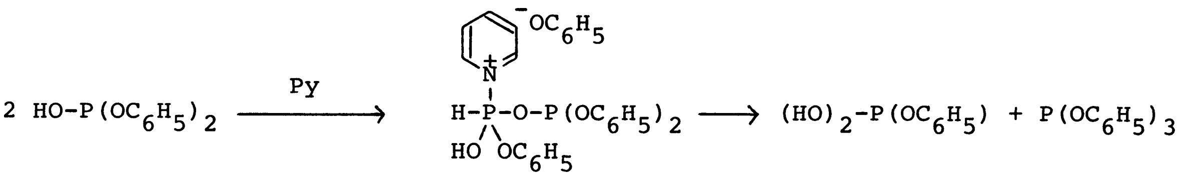
a) The reaction was carried out at room temperature for 1 hr by using diphenyl phosphite (0.01 mol).

b) Values in the parentheses were obtained after 20 hr.

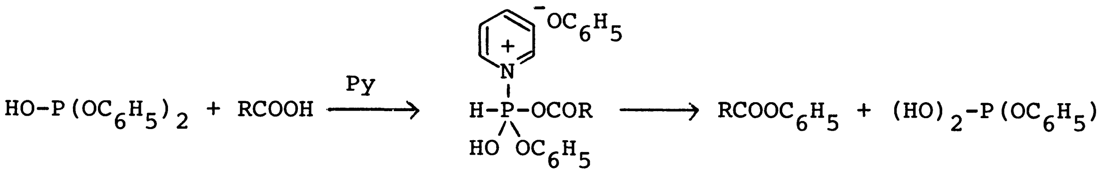
suggested that the steric hindrance around the nitrogen atom also influenced the reaction. The reaction was also affected by the amount of the amines, indicating that the amine stoichiometrically participated in the reaction. However, no marked differences in conversion among the tertiary amines were seen on prolonged reaction time, and diphenyl phosphite unreacted was not practically observed in the reaction mixture. These results show that diphenyl phosphite could be throughly consumed to yield maximally half an equivalent of triphenyl phosphite. Therefore, two mol of diphenyl phosphite might be transformed into one mol of tri- and monophenyl phosphites, respectively, although monophenyl phosphite could not be separated and characterized by the column employed for the HLC analysis because of overlapping with diphenyl phosphite unchanged and pyridines.

The disproportionation seemed to be limited to diaryl phosphites, since dialkyl phosphites such as diethyl phosphite showed no changes under the conditions.

The reaction was assumed to be an esterification of enolized diphenyl phosphite (an acid component) with the phosphite through the N-phosphonium salt (I) as observed in that (II) of carboxylic acids with the phosphite.$^{6)}$



(I)



(II)

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