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Abstract

Full Text

Chemistry

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Phosphorylation with Acyl Phosphites

(Presented by Academician S. I. Vol' fkovich, February 23, 1963)

It was shown earlier that, in the interaction of diethyl acyl phosphites with ethyl alcohol, triethyl phosphite is obtained in small yield, but it was not proved whether triethyl phosphite is formed as a result of phosphorylation of ethanol or of disproportionation of alkyl acyl phosphites [1,2]. The present work is devoted to a detailed study of this reaction with the aim of developing a new method for phosphorylating hydroxyl compounds.

As phosphorylating agents we used tribenzoyl phosphite and butylene-1,3-acetyl phosphite. The use of these products excludes the formation of the target phosphites through disproportionation of the starting substances. The experiments carried out showed that acyl phosphites readily react with alcohols to form neutral phosphites:

$$(C_6H_5COO)_3P + ROH \rightarrow (RO)_3P + C_6H_5COOH$$

$$\text{butylene-1,3-acetyl phosphite} + ROH \rightarrow \text{butylene-1,3-P}{-}OR + CH_3COOH.$$

However, along with neutral phosphites, acid phosphites and esters of carboxylic acids are formed in significant amounts, owing to a side reaction of the former with the carboxylic acid [3]:

$$(RO)_3P + R'COOH \rightarrow (RO)_2P{-}OH + R'COOR.$$

This circumstance devalues the reaction under consideration and makes it unsuitable, in this form, for the phosphorylation of alcohols.

Good results were obtained when the reaction was carried out in the presence of a tertiary amine. In this case, in most experiments only tertiary phosphites are formed in high yield. The course of the reaction is substantially affected by the starting acyl phosphite. Thus, alcoholysis of benzoyl phosphites proceeds at a satisfactory rate only at 35—45°, whereas acetyl phosphites react* already at temperatures below 0°.

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Phosphorylation with acyl phosphites is of a general character. Not only primary, secondary, and tertiary alcohols enter into the reaction, but also acid phosphonates. Thus, upon interaction of butylene-1,3-acetyl phosphite with the monopropyl ester of methylphosphonic acid, a subphosphonate was obtained:

$$\text{butylene-1,3-acetyl phosphite} + CH_3P(=O)(OH)(OC_3H_7) \rightarrow CH_3P(=O)(OC_3H_7)O{-}P(\text{butylene-1,3 fragment})$$

In order to avoid side processes, this reaction was also carried out in the presence of a tertiary amine.

The method of phosphorylating hydroxyl compounds with the aid of acyl phosphites possesses a number of advantages over the method of alcoholysis of chloroanhydr–

* The completion of the reaction was determined by thin-layer chromatography on aluminum oxide.

hydrides ([4]), esters ([5–7]), and amides ([8]) of acids of trivalent phosphorus and can be used for the phosphorylation of carbohydrates and other labile natural substances.

In the present work an attempt was made to use phosphoxanthogenates for phosphorylation; however, in this case no clear-cut results were obtained: the main reaction products proved to be not phosphites, but thiophosphates and other sulfur-containing substances.

The acyl phosphites needed for the study were obtained by interaction of phosphorus trichloride or butylene-1,3-chlorophosphite with metallic salts of the corresponding carboxylic acids ([2]). This reaction is general in character; salts of fatty, aromatic, and heterocyclic acids enter into it. In the interaction of phosphorus trichloride and chlorophosphines with salts of alkylxanthogenic acids, phosphoxanthogenates were obtained.

Thus, on the basis of readily available acyl phosphites, a new convenient method has been developed for the phosphorylation of alcohols and acid esters of phosphorus acids.

Experimental Part

Tribenzoyl phosphite.* To 24 g of sodium benzoate in 100 ml of benzene, in a stream of inert gas, 6.8 g of phosphorus trichloride is added dropwise with vigorous stirring at 5°. Stirring is then continued for 1 h at 20° and 0.5 h at 40°; the precipitate is separated by filtration or centrifugation and washed with benzene, 2 × 30 ml. After removal of the solvent, 18.7 g (95%) of tribenzoyl phosphite is obtained with m.p. 93—94° (from petroleum ether); literature data ([9]): m.p. 93—95°.

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$C_{21}H_{15}O_6P$.	Found, %:	P 7.94; 7.81
	Calculated, %:	P 7.87

Colorless crystals, soluble in alcohol, acetone, benzene, poorly soluble in petroleum ether. The substance changes on storage in air.

Tri-α-furoyl phosphite. Analogously to the above, from 6.8 g of phosphorus trichloride and 21 g of sodium pyromucate in 100 ml of benzene, 16.8 g (92%) of tri-α-furoyl phosphite is obtained with m.p. 123.5—125°.

$C_{15}H_9O_9P$.	Found, %:	P 8.41; 8.33;	C 49.64; 49.57;	H 2.69; 2.72
	Calculated, %:	P 8.52;	C 49.45;	H 2.47

Colorless crystals that darken on storage, soluble in acetone, alcohol, benzene, poorly soluble in petroleum ether.

1,3-Butylene acetyl phosphite. To 12 g of potassium acetate, in a stream of inert gas, 15.45 g of 1,3-butylene chlorophosphite ([10]) is added over 30 min at 30—35°; stirring is then continued for 1.5-2 h under reflux of ether and the precipitate is separated. After removal of the ether and distillation of the remaining oil, 10.1 g (56.6%) of 1,3-butylene acetyl phosphite is obtained with b.p. 114—115°/12 mm, n_D^{20} 1.4560, d_4^{20} 1.1836.

$C_6H_{11}O_4P$.	Found, %:	P 16.96; 16.94
	Calculated, %:	P 17.42

A colorless mobile liquid with a faint phosphite odor, soluble in most organic solvents. On storage the substance decomposes.

Tributyl phosphite. 5 g of tribenzoyl phosphite, 4 g of triethylamine, and 7 g of butyl alcohol are heated for 7 h in an atmosphere of inert gas at 50°. Then, at a residual pressure of 7-10 mm Hg and the minimum temperature, the excess butyl alcohol is distilled off, and the remaining mass is treated with 10 ml of benzene and 10 ml of water. The organic part is separated,** and the aqueous part is extracted twice with benzene, 3 ml each time. The benzene solution is dried for 1 h over

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* V. G. Terekhov took part in carrying out this and the following experiment.
** Attention should be paid to the completeness of phase separation on standing.

with sodium sulfate, the solvent is distilled off, and 4 ml of benzene is added to the residue, which is likewise removed in vacuo (if the solvent distilled off is cloudy, this operation is repeated). After distillation of the remaining oil, 1.1 g (39%) of tributyl phosphite was obtained, b.p. 132-133° (20 mm), n_D^{20} 1.4341. Literature data: b.p. 120°/10 mm [11], n_D^{16} 1.4339 [12].

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1,3-Butylene butyl phosphite. Analogously to the above, from 4.3 g of 1,3-butylene ethyl phosphite, 2.7 g of triethylamine, and 1.9 g of butyl alcohol, upon keeping the reagents in an inert-gas atmosphere for 12 h at 20-25°, 1.95 g (42%) of 1,3-butylene butyl phosphite was obtained, b.p. 94-95°/9 mm, n_D^{20} 1.4474. Literature data: b.p. 75-76°/4 mm, n_D^{20} 1.4472 [10].

1,3-Butylene isopropyl phosphite. Analogously to the above, from 1.8 g of 1,3-butylene ethyl phosphite, 1.1 g of triethylamine, and 0.7 g of isopropyl alcohol, 1.1 g (60%) of 1,3-butylene isopropyl phosphite was obtained, b.p. 62-64°/6 mm, n_D^{20} 1.4431.

Found, %:	P 17.21; 17.18
$C_7H_{15}O_3P$. Calculated, %:	P 17.41

A colorless mobile liquid with a faint phosphite odor; the substance is miscible with most organic solvents and moderately soluble in water.

1,3-Butylene tert-butyl phosphite. Analogously to the above, from 4.3 g of 1,3-butylene ethyl phosphite, 2.7 g of triethylamine, and 1.9 g of tert-butyl alcohol, 1.1 g (25%) of 1,3-butylene tert-butyl phosphite was obtained, b.p. 68-70°/6 mm, n_D^{20} 1.4458.

Found, %:	P 16.27; 15.84
$C_8H_{17}O_3P$. Calculated, %:	P 16.15

A colorless mobile liquid with a faint phosphite odor; the substance is miscible with most organic solvents and poorly soluble in water.

O,O-1,3-Butylene O-propyl methylsubphosphonate. Analogously to the above*, from 1.8 g of 1,3-butylene ethyl phosphite, 1.1 g of triethylamine, and 1.5 g of monopropyl methylphosphonate, 0.5 g (19.4%) of subphosphonate was obtained, b.p. 100-110° (bath)/10^{-4} mm, n_D^{20} 1.4530.

Found, %:	P 23.86; 23.79
$C_8H_{18}O_5P_2$. Calculated, %:	P 24.22

A viscous liquid, soluble in most organic solvents and appreciably soluble in water.

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* In this case the substance was distilled without washing with water.

Note: Figure translations are in progress. See original paper for figures.

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