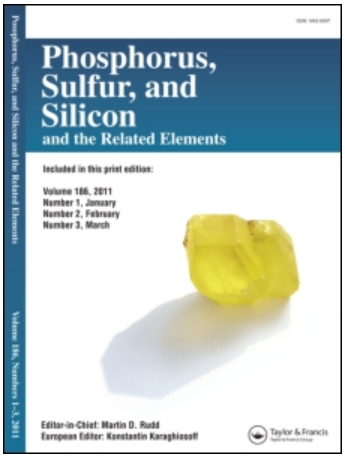

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ON THE SIDE REACTIONS ACCOMPANYING THE TRANS-ESTERIFICATION OF THE ACID DIESTERS OF PHOSPHOROUS ACID

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ON THE SIDE REACTIONS ACCOMPANYING THE TRANS-ESTERIFICATION OF THE ACID DIESTERS OF PHOSPHOROUS ACID

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The side reaction accompanying the trans-esterification of the acid diesters of phosphorous acid is studied, leading to the formation of R—O—R type ethers, where R is the aliphatic group of the acid ester. The products of the side reaction are identified by ^{1}H and ^{13}C-NMR spectroscopy. It is shown that the R—O—R ether is formed as a result of the pyrolysis of dimethyl phosphite.

INTRODUCTION

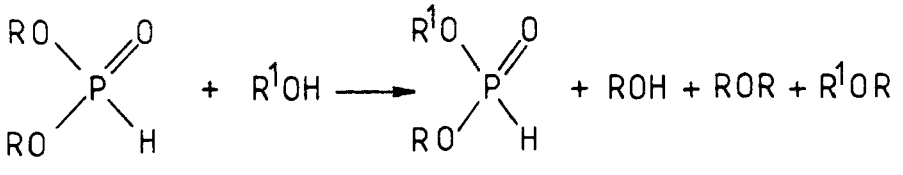
Kirilovich *et al.*[1] have found that the trans-esterification of the dimethylester of phosphorous acid by 2,2-bis(4-hydroxyphenyl)propane is accompanied by a side reaction, leading to the evolution of low boiling products. On the basis of its boiling point (−22.4°C) only, the authors assumed that this product is dimethyl ether.

The gas-chromatographic study of Vogt *et al.*[2] of the transesterification of the diethylester of phosphorous acid by aliphatic diols revealed that the trans-esterification is accompanied by side reactions, as a result of which two types of ethers are obtained: R—O—R^1—OH, where R^1 is the aliphatic part of the diol and R—O—R, where R is the aliphatic part of the phosphorous acid ester.

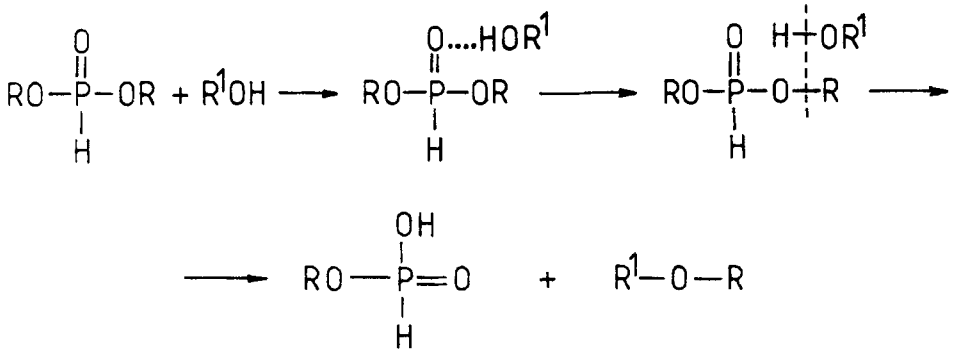
It is the aim of the present paper to study the mechanism of the side reaction, accompanying the trans-esterification of the diester of phosphorous acid by hydroxyl compounds, leading to the formation of ethers of the R—O—R type.

RESULTS AND DISCUSSION

The trans-esterification of the diester of phosphorous acid is accompanied by side reactions, as a result of which the following ether compounds are formed:



According to Vogt *et al.*[2] the formation of ethers of the type R^1—O—R proceeds by the reaction scheme proposed by Runavout *et al.*:[3]

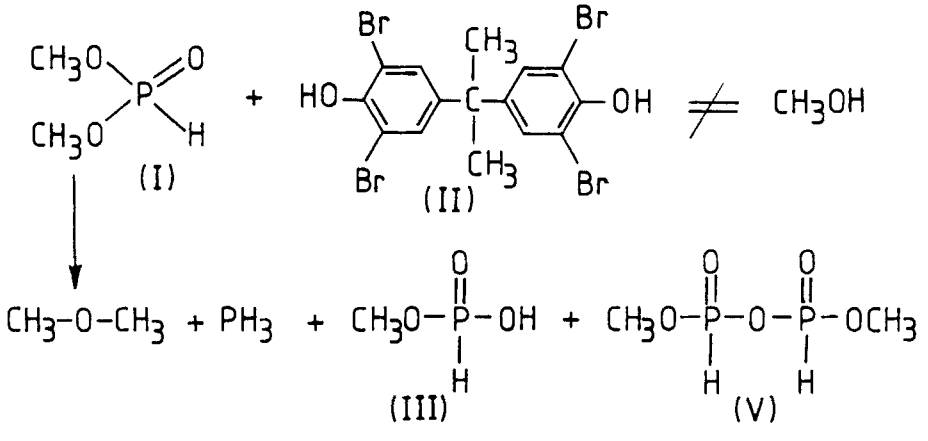


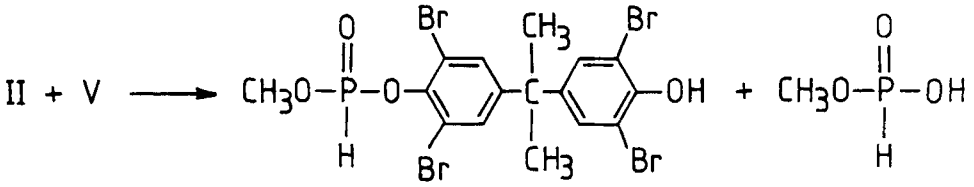
The assumed scheme adequately describes the formation of this type of ether.

According to Kirilovich *et al.*[1] the formation of R—O—R type ether compounds also proceeds by the same reaction scheme. This assumption raises some problems, connected with the finding that the amount of this type of ethers is considerably larger in cases, where the basicity of the hydroxyl compound is very low and the reaction temperature high (155–160°C), and also when the dimethylester of phosphorous acid takes part in the trans-esterification.

In order to elucidate the mechanism of the side reaction, leading to the formation of R—O—R type ethers, we studied the reaction between dibutyl phosphite and *n*-butanol. The gas-chromatographic analysis did not reveal any dibutyl ether among the reaction products. This result implies that the formation of this type of ethers does not follow the reaction scheme proposed by Runavout[3] in as much as in this experiment the conditions were most favorable for its production: high alcoholic concentration and a long reaction time.

We studied also the interaction between the dimethylester of phosphorous acid and 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane:





(IV)

It was established that no trans-esterification occurs in this case and that there is no evolution of CH_3OH. This result was not altogether unexpected, having in mind the very low basicity of the oxygen atom in the hydroxyl group of compound II. The IR spectra revealed that the gas evolved is a mixture of CH_3OCH_3 and phosphine (PH_3).

After the complete removal of dimethyl phosphite by vacuum distillation (checked by NMR spectra), the residue showed the following elemental composition (%): C 32.03; Br 51.20; P 3.38. The constancy in the Br content showed that the latter is not lost during heating, while the presence of phosphorous reveals that the weight increase is due to some phosphorous-containing compounds, which do not evaporate during the distillation of dimethyl phosphite.

The composition of products 1 and 2 (see Experimental Part) was investigated basically by the ^1H and ^{13}C-NMR spectra. It was found that the components of products 1 and 2 have different solubility in $CHCl_3$, HDO and DMSO-d_6. All components are soluble in the last solvent. The analysis of the spectra of product 1 revealed that the starting dimethyl phosphite I is not present. It contains the starting 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane and compound IV. This was corroborated by the ^1H-NMR spectrum of 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane in $CDCl_3$ and DMSO-d_6, as well as by the ^{13}C-NMR spectrum of product 1 in $CDCl_3$. In the ^1H-NMR spectra of the phosphorous containing part of product 1 in DMSO-d_6 signals at 3.94, 3.46 and 3.21 were observed. According to literature the chemical shifts of CH_3 group in monomethyl ester of phosphorous acid III is 3.91 ppm.[4]

The evolution of gas during the heating of dimethyl phosphite in the presence of II and the evolution of dimethyl ether and phosphine, as well as the presence of III in the reaction product, strongly suggests that under these conditions pyrolysis of dimethyl phosphite occurs.

It is known[5] that the pyrolysis of compound I proceeds at 173°C with the formation of the following products: dimethyl ether, phosphine, monomethyl phosphite, and some other condensed phosphorous containing compounds.

The finding of compound IV in the reaction products is rather interesting since trans-esterification has not taken place. The formation of this compound can be explained by the interaction of 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane II with the pyrophosphite V.

The present results demonstrate that the formation of ethers of the R—O—R type during the trans-esterification of dimethyl phosphite by hydroxyl-containing compounds having a low basicity of the oxygen atom in the hydroxyl group, e.g. as in

compound II and 1,3-dichloropropanol-2, is to be attributed to the pyrolysis of the dimethyl ester of the phosphorous acid under the conditions of transesterification.

EXPERIMENTAL

Starting chemicals: dimethylester of phosphorous acid (I), Fluka, vacuum distilled under Ar, $n_D^{20} = 1.4022$; dibutylester of phosphorous acid, Fluka, vacuum distilled under Ar, $n_D^{20} = 1.4240$; *n*-butyl alcohol, $n_D^{20} = 1.4009$; 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (II).

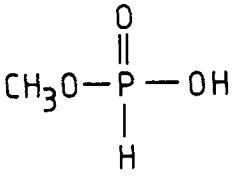
A. Interaction between dibutyl phosphite and n-butanol. The reaction is carried out at 138°C in three-neck flask, provided with a capillary for Ar introduction, a thermometer, and a reflux condenser. 0.109 moles (21.17 g) of dibutyl phosphite are mixed with 0.176 moles (13.08 g) of *n*-butanol in the flask. After 12 hours of heating the mixture is cooled to 70°C and subjected to vacuum distillation.

B. Interaction between dimethyl phosphite (I) and 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (II). 50 g (0.092 moles) of II are mixed with 30 g (0.25 moles) of I in a three-necked flask, provided with a capillary for Ar introduction, a thermometer, and a reflux condenser. The reaction proceeds for 6 hours at 160°C. The gas evolved is collected in a liquid nitrogen trap. The reaction mixture is then cooled to 90–95°C and the unreacted dimethyl phosphite is removed by vacuum distillation at 1 torr. The weight of the products after the removal of the dimethyl phosphite is 57.6 g. After the vacuum distillation the reaction mixture is treated with dry tetrahydrofurane. Thereby two layers are formed: the upper layer contains the dissolved compound II, while the lower consists of products insoluble in tetrahydrofurane. In the following the upper layer will be denoted as product 1, while the lower as product 2.

C. Identification of the reaction products. The ^1H and ^{13}C-NMR spectra were recorded with a Bruker WM (FT) apparatus at 250 MHz for ^1H and 63.93 MHz for ^{13}C in solutions of $CDCl_3$ and DMSO-d_6. The chemical shifts of the signals, δ in ppm are referred to an internal standard TMS or DSS.

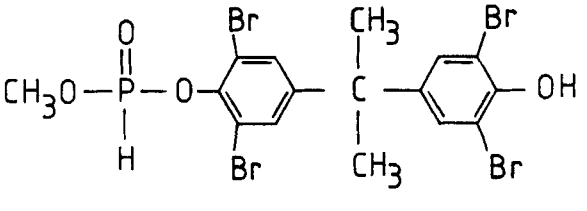
Product 1: consists of compound II, ^1H chemical shifts δ (ppm) in $CDCl_3$: 1.57 (6 H, $C\underline{H}_3$—C—$C\underline{H}_3$); 7.35 (4 H, aromatic protons); 5.50 (1 H, O$\underline{H}$); in DMSO-d_6: 1.59, 7.35 and 7.99 accordingly.

^{13}C chemical shifts δ (ppm) in $CDCl_3$: 30.61 ($\underline{C}H_3$–C—$\underline{C}H_3$); 60.52 (CH_3—$\underline{C}$—CH_3); 109.78 (C-3); 130 (C-2); 144.18 (C-1); 147.71 (C-4); compound III, ^1H chemical shifts δ (ppm) in DMSO-d_6: 3.94 (broad singlet, 3 H, $C\underline{H}_3O$—P); 7.99 (broad singlet, 1H, P—O$\underline{H}$); 6.72 (1 H, P$\underline{H}$, $^1J_{P-H} = 630$ Hz);



and compound IV: ^1H chemical shifts δ (ppm) in $CDCl_3$: 3.91 doublet, 3 H, $C\underline{H}_3O$—P); 1.57 (singlet, 6 H, $C\underline{H}_3$—C—$C\underline{H}_3$); 7.25 (singlet, 4 H, aromatic protons); in DMSO-d_3: 3.80, 1.61 and 7.40, 7.48 accordingly.

^{13}C chemical shifts δ (ppm) in $CDCl_3$: 30.61 ($\underline{C}H_3$—C—$\underline{C}H_3$); 57.2 (CH_3—$\underline{C}$—CH_3); 117.96 (C-3); 130.81 (C-2); 148.06 (C-6); 41.84 ($\underline{C}H_3O$—P)



Product 2: The ^1H-NMR spectrum showed the presence of compound III and dimethyl phosphite.[4] The chemical shifts at 3.45 and 3.21 are probably due to pyrostructures—such as V. The IR data confirm the structures of the above compounds.

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