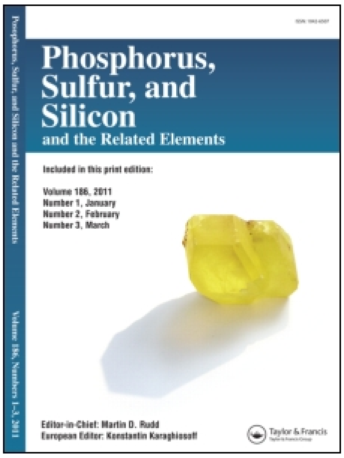

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REACTION BETWEEN 2-HYDROXY ESTERS OF HYPOPHOSPHOROUS ACID AND ALCOHOLS

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REACTION BETWEEN 2-HYDROXY ESTERS OF HYPOPHOSPHOROUS ACID AND ALCOHOLS

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A study of the reaction between esters of hypophosphorous acid and alcohols is carried out. It has been established that the 2-hydroxy esters of hypophosphorous acid react with alcohols as a result of which phosphonous acids are formed. A possible scheme of this reaction is suggested.

Key words: Hypophosphorous acid; esters of hypophosphorous acid; phosphonous acid; esters of phosphonous acid; hypophosphorous–phosphonous rearrangement.

Phosphonous acids (PA) "$R{-}P(=O)(OH)H$" are suggested as complex-formers, antipyrenes, biologically active substances. But they are the least studied of the class of the hydrophosphoryl compounds may be due to the fact that they are comparatively difficult to synthesise. There are some methods known for their preparation from alkyl phosphines[1] or alkyl dichlorophosphines,[2] which are not readily accessible. Hypophosphorous acid (HPA) is also used as a starting raw material. It is known that HPA reacts with olefines according to a radical mechanism.[3] However, in these cases there are some preparatory difficulties in separating the phosphonous and phosphinic acids formed during the reaction. A hydrophosphorolic-acetylene-allene rearrangement is reported to proceed during esterification of hypophosphorous acid with acetylenic alcohols which leads to the formation of phosphonous acids.[4–7] The tautometric equilibrium in the esters of HPA, which is shifted to the three-coordination form, is considered to be the reason for the rearrangement. The high nucleophilicity of the phosphorus atom in this configuration determines the possibility of isomerization, during which compounds with a P—C bond are formed.

In a previous work[8] it was shown that the 2-hydroxy esters of hypophosphorous acid (HEHPA) react with 1,6-butinediol giving 1-methylolallenehypophosphonous acid, which is obtained according to Reference 7 by intramolecular isomerization of the HPA ester with 1,4-butinediol.

The present paper is a further study of the reaction between esters of HPA and alcohols.

RESULTS AND DISCUSSIONS

Experiments on the reaction between esters of HPA and alcohols were carried out. The following materials were used: isobutyl ester of hypophosphorous acid,[9] 2-hydroxypropyl ester- and 3-chlorine-2-hydroxypropyl ester of HPA.[8] The first one was prepared by esterification of HPA with isobutanol under the conditions of azeotropic removal of water with benzene. HEHPA were obtained from propylene oxide or epichlorohydrin and HPA in a solution of benzene, ether, dioxane, or acetone at a temperature up to 35°C. The esters of HPA are known to decompose if they are not in a solution.[10] That is why HEHPA were characterized by ^{31}P-NMR in a solution of ethyl ether. The 2-hydroxypropyl ester of HPA exhibited a triplet signal with a centre at $\delta = 18.79$ ppm and $J_{PH} = 581$ Hz, while the 3-chlorine-2-hydroxypropyl ester showed a signal at $\delta = 20.04$ ppm and $J_{PH} = 575$ Hz. The main signals had a coupling constant of $J_{POCH_2} = 10$ Hz. The tests on the reaction between the esters of HPA and alcohols were performed without isolating the esters from the solution to which the corresponding alcohols were added. The following alcohols were used: isopropanol, isobutanol, pentanol, allyl alcohol, polyethylene glycol-400, polyvinyl alcohol-100 000 and starch.

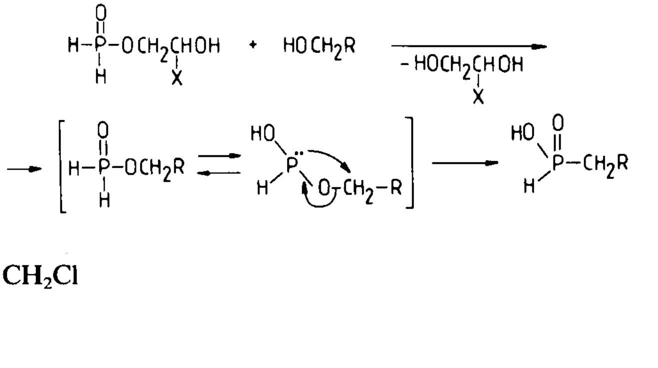
The separation of the reaction products, obtained from the reaction between HEHPA and alcohols, was carried out by extraction with ethyl ether and by distillation of the non-reacted alcohols. Glycols were isolated from the mixture: 1,2-propaniol ($n_D^{20} = 1.4330$) and 3-chloro-1,2-propandiol ($n_D^{20} = 1.4794$). On the remains of this treatment ^{31}P-NMR exhibited signals at $\delta = 32$–36 ppm, which are characteristic of compounds containing P—C bond. From these results it is clear that HEHPA react with alcohols as a result of which glycol is released and compounds with a P—C bond are formed:

$$H_2\overset{O}{\overset{\|}{P}}-OCH_2\overset{X}{\overset{|}{C}}H-OH + HOR \longrightarrow HOCH_2\overset{X}{\overset{|}{C}}H-OH + R-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OH$$

where $x = CH_3$: CH_2Cl.

The results from the analysis of the compounds obtained are presented in Table I while the IR- and ^{1}H-NMR spectra are given in Table II. From the tables it is seen that the absorption maxima of the P═O groups of HPA shift from 1175 to 1210–1230 cm^{-1}, while those of the P—H groups shift from 2370 to 2410–2435 cm^{-1}. Such differences also exist in the constants of the spin–spin interaction in the proton NMR spectra for P—H, recorded under the same conditions in a solution of dimethylsulphoxide.

The preparation of phosphonous acids from the reaction between HEHPA and alcohols may be represented by a scheme which is similar to that for the preparation of allenylphosphonous acid:[8]



where $x = CH_3$; CH_2Cl

TABLE I

Analytical values for alkylphosphinic acids $R_1-P(=O)(H)-OR_2$

R_1	R_2*	Yield	n_D^{20}	Acid number found	Acid number calc.	%P found	%P calc.	%C found	%C calc.	%H found	%H calc.
$(CH_3)_2CH$	1	74	1.4386	496	519.4	27.80	28.70	34.12	33.33	8.47	8.33
	2	81	1.4430	346	338.0	18.82	18.67	—		—	
	3	72	1.4480	266	280.5	15.23	15.50	—		—	
$(CH_3)_2CHCH_2$	1	73	1.4396	441.7	459.8	26.10	25.40	39.80	39.34	9.23	9.02
	2	77	1.4448	302.2	311.7	16.85	17.22	—		—	
	3	69	1.4500	254.2	262.1	14.73	14.49	—		—	
$CH_3(CH_2)_4$	1	82	1.4415	422.3	412.5	23.12	22.79	44.32	44.12	9.38	9.56
	2	84	1.4460	262.0	289.2	15.74	15.98	—		—	
	3	67	1.4525	257.3	246.0	13.84	13.60	—		—	
$CH_2{=}CHCH_2$	1	78	1.4370	534.2	529.3	28.87	29.25	33.82	33.96	6.64	6.60
	2	67	1.4465	327.2	342.1	19.78	18.90	—		—	
	3	65	1.4510	295.4	283.3	15.83	15.66	—		—	
Polyvinyl alcohol			222–228°C	79.7	—	4.40	—				
Starch			260°C destr.	48.0	—	2.80					
Polyethylene glycole			1.4595	98.0	—	5.6	—				

* (R_2 = H for 1; $-CH_2CH(OH)CH_3$ for 2; $-CH_2CH(OH)CH_2Cl$ for 3)

Transesterification followed by isomerization produces phosphonous acids.

Experiments on the reaction between isobutyl ester of hypophosphorous acid and alcohols were performed. When trying to eliminate the solvent (benzol) by distillation, decomposition of the products occurred which was accompanied by a release of phosphin and formation of yellow phosphorus. During the distillation the alcohol, added to the system, also was removed (e.g. pentanol). These results show that the isobutyl ester of HPA does not react with alcohols. The formation of phosphin and yellow phosphorus resulted from the decomposition of the isobutyl ester with HPA after elimination of the solvent.[10]

The following mechanism is also possible:

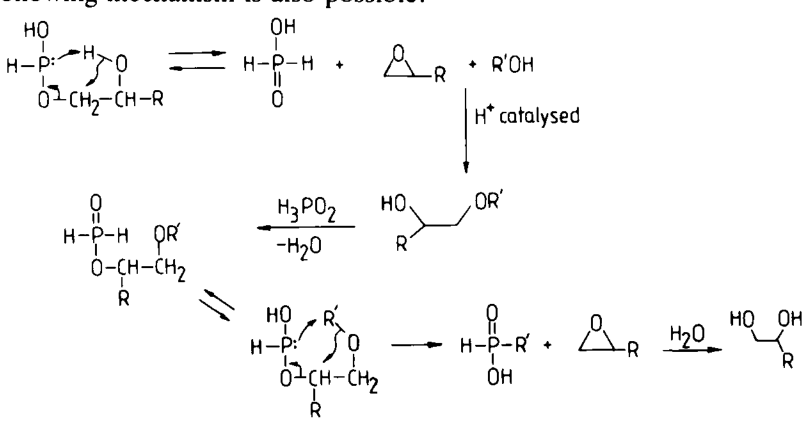
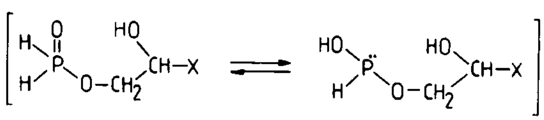


TABLE II

Spectroscopic data for R_1—P(=O)(H)—OR_2 (R_2 = H for 1; —$CH_2CH(OH)CH_3$ for 2; —$CH_2CH(OH)CH_2Cl$ for 3)

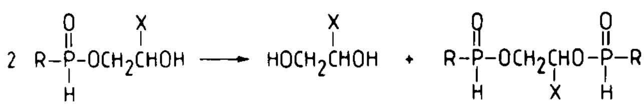
R_1	R_2	^{1}H-NMR	IR (cm^{-1}) P=O	IR (cm^{-1}) P—H
$H_2P(O)OH$		PCH_2—7.025 ppm (t), J_{P,H_2} 550.1 Hz	1175	2370
$(CH)_2CH$	1	PH—7.06 ppm (d), $J_{P,H}$ 543 Hz;		
		CH—3.42-3.76 ppm (m);		
		CH_3—1.01 ppm (d), $J = 6$	1220	2415
	2	PH—7.12 ppm (d), $J_{P,H}$ 553 Hz	1223	2415
		PH—7.10 ppm (d), $J_{P,H}$ 548 Hz;		
	3	CH—O—3.83 ppm (m), J_{CH_2,CH_2} 4.5 Hz	1210	1410
$(CH_3)_2CHCH_2$	1	PH—7.04 ppm (d), $J_{P,H}$ 536 Hz;		
		PCH_2—3.21 ppm (d.d.), J_{P,CH_2} 16.3 Hz;		
		$CHCH_2$—3.42 ppm (m), J_{CH,CH_2} 4.5 Hz;		
		CH_3—1.04 ppm (d), J_{CH_3CH} 6 Hz	1220	2418
	2	PH—7.16 (d), $J_{P,H}$ 560 Hz;		
		$POCH_2$—3.67 ppm (m), J 5 Hz;		
		OCH—3.84 ppm, $J = 4.5$ Hz	1225	2420
	3	PH—7.07 ppm (d), $J_{P,H}$ 555 Hz	1218	2420
$CH_3(CH_2)_4$	1	PH—6.96 ppm (d), $J_{P,H}$ 531 Hz;		
		PCH_2—3.44 ppm (m), J_{P,CH_2} 14 Hz	1230	2425
	2	PH—7.06 ppm (d), $J_{P,H}$ 560 Hz	1235	2425
	3	PH—7.08 ppm (d), $J_{P,H}$ 552 Hz	1232	2427
CH_2=$CHCH_2$	1	PH—6.02 ppm (d), $J_{P,H}$ 535 Hz;		
		PCH_2—3.52 ppm (d.d.), J_{P,CH_2} 13.5 Hz;		
		CH_2=CH—5.33 ppm (m), J_{CH,CH_2} 7.4 Hz	1218	2410
	2	PH—7.04 ppm (d), $J_{P,H}$ 542 Hz	1220	2410
	3	PH—7.01 ppm (d), $J_{P,H}$ 545 Hz	1220	2410
Polyvinyl alcohol		PH—6.98 ppm (d), $J_{P,H}$ 520 Hz	1225	2415
Starch		PH—7.04 ppm (d), $J_{P,H}$ 562 Hz	1220	2420
Polyethylene glycol		PH—6.97 ppm (d), $J_{P,H}$ 538 Hz	1225	2418

This difference in the reaction capacity of HEHPA, on the one hand, and on the other of the isobutyl ester, no doubt is a result of the presence of hydroxide group in HPHPA. The direct participation of this group in the activation of the phosphorus component seems to be quite likely. This group may be assumed to form an internal complex which helps to shift the equilibrium towards the tricoordinated form of the ester of HPA:



where x = CH_3; CH_2Cl.

It has been established that the reaction between HEHPA and aliphatic alcohols, which are liquids at normal temperature, may proceed as a one-stage reaction without a solvent. For the purpose of solubilizing HPA in the corresponding alcohol, alkylene oxide was added. The reaction proceeded at about 50°C. It was established that one mol of alcohol and one or two mols of alkylene oxide react with one mol of HPA. The excesses of alkylene oxide and alcohol used may be eliminated from the reaction medium, after the reaction is finished, by distillation. When two or more mols of alkylene oxide were used, the corresponding 2-hydroxy ester of phosphonous acid ($R-\overset{\overset{O}{\parallel}}{\underset{\underset{H}{|}}{P}}-OCH_2\overset{\overset{OH}{|}}{C}HX$) was formed in a single stage. The structures of these esters were proved by acid number, element analysis for phosphorus, IR- and ^1H-NMR spectra. When trying to distill the 2-hydroxy ester of PA, at a temperature of about 100°C, the corresponding glycol was released as a result of condensation:



where $x = CH_3$; CH_2Cl.

EXPERIMENTAL

Methods of analysis: The proton spectra were taken on Bruker WM (250 MHz), inner standard—TMS, in a solution of dimethylsulphoxide, while the phosphorylized polyvinyl alcohol and starch were recorded in a solution of D_2O. ^{31}P-NMR were taken on the same apparatus with a frequency of 10 1.27 MHz with an external standard of 85% H_3PO_4. The IR spectra were takn on film using a UR-20 instrument (Carl Zeiss-Jena).

1. Preparation of phosphonous acids. An amount of 0.1 mol of dry, crystalline hypophosphorous acid, prepared by low-temperature vacuum-evaporization of a water solution, was dissolved in 0.1 mol of the corresponding alcohol. An amount of 0.1 mol of alkylene oxide (propylene oxide or epichlorhydrin) was added to the solution in parts at constant stirring. The reaction proceeded for about one hour at a temperature of 45–50°C. The mixture was cooled and repeatedly extracted with ethyl ether, which extracted either propylene glycol or 3-chloro-1,2 propandiol. The ethyl ether and non-reacted alcohol were removed from the remains by distillation under reduced pressure. The corresponding phosphonous acid was obtained—a colourless liquid, soluble in ethyl alcohol, water, dimethylsulphoxide, dimethylformamide.

2. Preparation of 2-hydroxypropyl ester of phosphonous acids. An amount of 0.1 mol of crystalline hypophosphorous acid was dissolved in 0.1 mol of the corresponding alcohol. To the solution, at constant stirring, 0.2–0.3 mol of propylene oxide were added. The reaction was conducted at about 50°C for one hour and a half. After cooling the reaction mixture was repeatedly extracted with ethyl ether, which extracted the propylene glycol. The ethyl ether and volatile products were eliminated by distillation under reduced pressure. What remained was the respective 2-hydroxy ester of phosphonous acid—colourless liquid, soluble in alcohol, dimethylformamide, dimethylsulphoxide.

3. Preparation of 3-chlorine-2-hydroxypropyl ester of phosphonous acids. An amount of 0.1 mol of crystalline hypophosphorous acid was dissolved in 0.1 mol of the corresponding alcohol. 0.2–0.3 mol of epichlorohydrin were added to the solution at constant stirring. The reaction was conducted at a temperature of about 50°C for about one hour and a half. After cooling the reaction mixture was extracted several times with ethyl ether which extracted 3-chloro-1,2-propanediol. Low-boiling substances were removed from the remains by distillation under reduced pressure at a temperature up to 80°C. The respective 3-chloro-2-hydroxy ester of phosphonous acid remained—a colourless liquid, soluble in ethyl alcohol, dimethylformamide, dimethylsulphoxide.

4. Phosphorylation of polyvinyl alcohol. In 20 ml of dimethylformamide 1 g (0.02 mol) of crystalline hypophosphorous acid was dissolved. An amount of 4.4 g of polyvinyl alcohol, molecular weight—100 000, was added. A part of the polymer dissolved while the other swelled in the solvent. To the mixture, at constant stirring, 5.8 g (0.1 mol) of propylene oxide were added in parts. The mixture was heated at 50–55°C for about one hour and a half. 20 ml of water were added to the mixture. Then the solution was reprecipitated in 200 ml of ethyl alcohol. The precipitate obtained was filtered and washed with ethyl alcohol up to a neutral pH of the filtrate. The product was dried at 60°C under reduced pressure up to a constant weight. The product obtained was 4.9 g with a softening point of 222–228°C.

5. Phosphorylation of starch. An amount of 4.5 g of starch was added to 20 ml of dimethylsulphoxide and was heated at a temperature of about 60°C up to the formation of a gel. 1.5 g of crystalline hypophosphorous acid were added to it. An amount of 3 g of propylene oxide was added in parts at constant stirring. The reaction proceeded for about one hour and a half at a temperature of 50–55°C. 20 ml of water were added and the solution was reprecipitated in about 150 ml of ethyl alcohol. The precipitate obtained was filtered and washed with ethyl alcohol up to a neutral pH of the filtrate. The product obtained was dried under reduced pressure at 60°C up to a constant weight. 4.9 g of phosphorylized starch were obtained.

6. Phosphorylation of polyethyleneglycol. To 4 g of polyethyleneglycol, molecular weight—400, 1.5 g of crystalline hypophosphorous acid were added. After dissolution of the acid, 1.32 g of propylene oxide were added to the mixture in parts at constant stirring. The reaction proceeded for about one hour and a half at 50°C. The reaction mixture was extracted several times with ester which extracted the propyleneglycol. The remains were dried under reduced pressure at 60°C up to constant weight. The product obtained was 5.1 g, soluble in ethyl alcohol, dimethylsulphoxide and dimethylfosfamide.

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