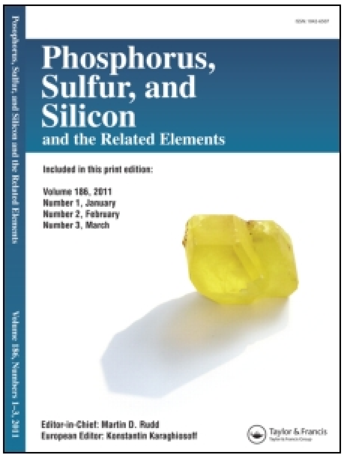

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REACTION OF SALTS OF HYPOPHOSPHOROUS ACID WITH ALKYLHALIDES

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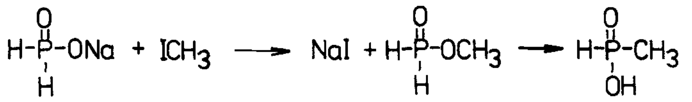
Alkali salts of hypophosphorous acid undergo an exchange reaction with alkyl halides. From the interaction between potassium hypophosphite and allyl bromide or 3-chloro-1,2-propanediol phosphonous acids are formed. A mechanism of the interaction, a variant of the Michaelis–Becker reaction, is proposed.

INTRODUCTION

It is well known that alkyl halides take part in an exchange reaction with alkali salts of phosphoric[1] and phosphorous[2] acids as a result of which the corresponding esters are obtained. Two cases of such an interaction have been recorded for the salts of hypophosphorous acid. In 1940 V. M. Plets[3] reported that he had not obtained the ester of hypophosphorous acid, expected from the reaction of sodium hypophosphite and methyl iodide, but methylphosphonous acid according to the following scheme:



$$\underset{\text{H}}{\overset{\text{O}}{\text{H-}\overset{\|}{\underset{|}{\text{P}}}\text{-ONa}}} + \text{ICH}_3 \longrightarrow \text{NaI} + \text{H-}\overset{\text{O}}{\overset{\|}{\underset{\underset{\text{H}}{|}}{\text{P}}}}\text{-OCH}_3 \longrightarrow \text{H-}\overset{\text{O}}{\overset{\|}{\underset{\underset{\text{OH}}{|}}{\text{P}}}}\text{-CH}_3 \qquad (1)$$

In 1982 it was reported[4] that (cyclic) phospholane had been prepared from epichlorohydrin and sodium hypophosphite.

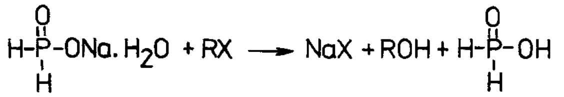
According to some authors[5,6] phosphonous acids are formed during thermal isomerization of esters of hypophosphorous acid. There does not exist a firm opinion on the matter since it has been shown[7] by NMR-spectroscopy that those compounds in a pure state completely disproportionate into phosphite and phosphine in 15 min only at a temperature of 20°C.

Our aim was to check whether a condensation reaction between alkali salts of hypophosphorous acid and alkyl halides could possibly occur. These salts are more readily accessible than the acid itself. Such an interaction could be of interest with respect to the synthesis of esters of the acid which are difficult to prepare by the well-known methods of esterification with alcohols[8] or with diazoalkanes.[9] It is seen from the communication cited[3,4] that phosphonous acids were obtained. These compounds are difficult accessible, because their synthesis is based on precursors which are not readily available. Phosphonous acids could be employed as growth regulators,[10,11] or as bioactive substances.[12]

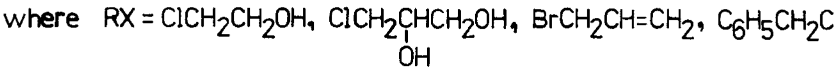
RESULTS AND DISCUSSION

1. *Interaction between sodium hypophosphite monohydrate and alkyl halides*

The reaction was carried out with 2-chloroethanol, 3-chloro-1,2-propanediol, allyl bromide and benzyl chloride. Sodium halides, the corresponding alcohols, and hypophosphorous acid were isolated, in accord with Equation (2),



$$H\text{-}\overset{O}{\underset{H}{P}}\text{-}ONa.H_2O + RX \longrightarrow NaX + ROH + H\text{-}\overset{O}{\underset{H}{P}}\text{-}OH \qquad (2)$$



$$\text{where}\quad RX = ClCH_2CH_2OH,\ ClCH_2\underset{OH}{C}HCH_2OH,\ BrCH_2CH{=}CH_2,\ C_6H_5CH_2Cl$$

The sodium halides and alcohols thus prepared were identical to the corresponding substances described in the literature. Hypophosphorous acid was determined by phosphorus analysis, acid number and IR-analysis (see Experimental). Signals of protons bonded to P-atom at $\delta = 7.14$ ppm, $^1J = 566$ Hz were observed in the ^{1}H-NMR-spectrum (in D_2O).

The exchange reaction proceeds quantitatively with respect to the sodium halides formed. The alcohols were separated from the hypophosphorous acid by distillation under vacuum. In the case of the 3-chloro-1,2-propanediol reaction formation of hypophosphorous acid was proved only by ^{1}H-NMR-data. When attempting to distill the glycerol formed during the reaction, due to the high boiling temperature, part of the hypophosphorous acid was found to disproportionate into phosphine and phosphorous acid (^{1}H NMR-signals, $\delta_{P\text{-}H} = 4.45$ ppm, $^1J_{P\text{-}H} = 684$ Hz), in accord with Equation (3),[13]

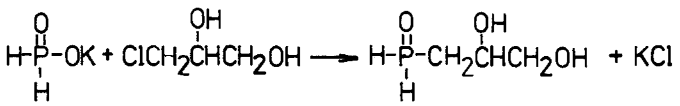
$$3\,H_3PO_2 \xrightarrow{120^\circ C} PH_3 + 2\,H_3PO_3 \qquad (3)$$

Organophosphorus compounds were not found in the reaction of sodium hypophosphite monohydrate with the above alkyl halides. During the formation of sodium halides conditions for the synthesis of the corresponding hypophosphorous acid esters were created. However, these esters are hydrolyzed by the water present in the reaction mixture in an equimolar amount.

2. *Reaction between potassium or ammonium hypophosphite and 3-chloro-1,2-propanediol or allyl bromide*

The reactions between the salts of hypophosphorous acid and 3-chloro-1,2-propanediol or allyl bromide were studied in more detail. The reactions were conducted in the absence of water. Potassium and ammonium hypophosphites were used.

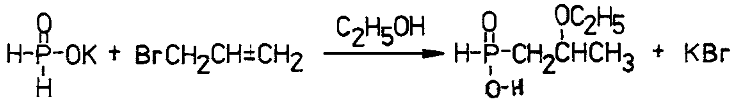
2,3-dihydroxypropylphosphonous acid was isolated as a result of the reaction of the salts with excess 3-chloro-1,2-propanediol:



$$\mathrm{H{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}OK + ClCH_2\overset{OH}{\overset{|}{C}}HCH_2OH \longrightarrow H{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}CH_2\overset{OH}{\overset{|}{C}}HCH_2OH + KCl} \tag{4}$$

That was established by elemental analysis, acid number, and IR-spectrum (see Experimental). In the ^1H n.m.r. spectrum a resonance at $\delta = 7.08$ ppm, $^1J = 531.44$ Hz, and multiplets for the carbon-bonded hydrogen atoms – $\delta_{PC\underline{H}_2} = 3.79$ ppm, $^2J = 11.52$ Hz; $\delta_{C\underline{H}} = 3.59$ ppm, $^3J_{H\text{-}H} = 5.37$ Hz; $\delta_{C\underline{H}_2} = 3.67$ ppm (in $CDCl_3$ apparatus "Bruker WM-250" (250 MHz)) were observed.

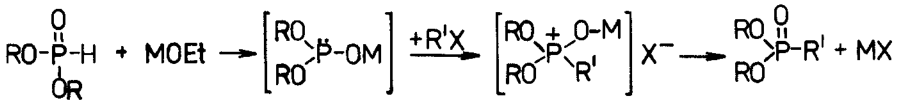
The reaction with allyl bromide was conducted in a solution of ethanol. Instead of the expected allyl derivative propyl-2-oxethylphosphonous acid was isolated:



$$\mathrm{H{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}OK + BrCH_2CH{=}CH_2 \xrightarrow{C_2H_5OH} H{-}\underset{O\text{-}H}{\overset{O}{\overset{\|}{P}}}{-}CH_2\overset{OC_2H_5}{\overset{|}{C}}HCH_3 + KBr} \tag{5}$$

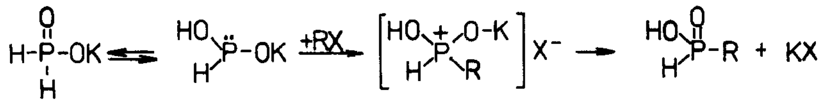
The structure of the product was determined by elemental analysis, acid number, and IR-spectrum (see Experimental). Signals from the presence of 6 types of protons were found in the ^1H NMR-spectrum (in D_2O). There were no signals from protons bonded to allylic carbon (δ 5.2–6.05 ppm). Signals in the ^1H resonance were observed at $\delta_{P\underline{H}}$ 6.75 ppm, (d), $^1J = 547$ Hz (PH); $\delta_{C\underline{H}_3}$ 0.92 ppm (t), and 1.23 ppm (t), $\delta_{C\underline{H}_2}$ 2.68 ppm (m), $\delta_{C\underline{H}}$ 3.62 ppm (m). Signals of a complex multiplet with a large spin–spin coupling constant were assigned to the $PC\underline{H}_2$ protons.[14]

The mechanism of formation of the phosphonous acid may be visualized as a variant of the Michaelis–Becker reaction.[15] It involves the reaction of alkali salts formed from organic hydrophosphoryl compounds and alkyl halides, as a result of which compounds with a phosphorus-carbon bond are formed, according to Equation (6),



$$\mathrm{RO{-}\underset{OR}{\overset{O}{\overset{\|}{P}}}{-}H + MOEt \longrightarrow \left[\begin{matrix}RO\\RO\end{matrix}\!\!>\ddot{P}{-}OM\right] \xrightarrow{+R'X} \left[\begin{matrix}RO\\RO\end{matrix}\!\!>\overset{+}{P}\!<\!\begin{matrix}O\text{-}M\\R'\end{matrix}\right]X^- \longrightarrow \begin{matrix}RO\\RO\end{matrix}\!\!>\overset{O}{\overset{\|}{P}}{-}R' + MX} \tag{6}$$

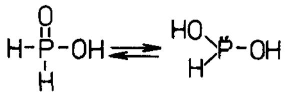
This reaction is regarded as one in which the reaction centre is a three-coordinated phosphorus atom. The preparation of phosphonous acids from alkali salts of hypophosphorous acid and alkyl halides may be presented, according to a similar scheme (Equation 7),



$$\mathrm{H{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}OK \rightleftharpoons \begin{matrix}HO\\H\end{matrix}\!\!>\ddot{P}{-}OK \xrightarrow{+RX} \left[\begin{matrix}HO\\H\end{matrix}\!\!>\overset{+}{P}\!<\!\begin{matrix}O\text{-}K\\R\end{matrix}\right]X^- \longrightarrow \begin{matrix}HO\\H\end{matrix}\!\!>\overset{O}{\overset{\|}{P}}{-}R + KX} \tag{7}$$

The presence of a three-coordinated phosphorus atom will account for the nucleophilic attack of the carbon cation formed during the reaction.

It is well known that hypophosphorous acid exists in two tautomeric forms, with the equilibrium strongly shifted to the left at 20°C:

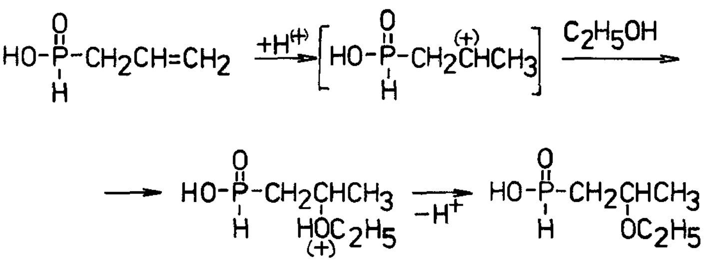


(8)

The active form (of oxidation) of the acid is the one with a three-coordinated phosphorus atom.[16] Its concentration determines the rate of isotropic exchange of the hydrogen atoms[17] or of the oxygen atoms.[18] Stable derivatives corresponding to the three-coordinated form of hypophosphorous acid have been prepared and isolated (dialkyloxyphosphines).[19,20]

The results from the interaction between potassium or ammonium hypophosphite and 3-chloro-1,2-propanediol, or allyl bromide, as well as the above consideration lead us to assume that the reaction proceeds according to a mechanism whereby the main part is played by the three-coordinated form of the salts of hypophosphorous acid.

The formation of 2-oxethyl-propylphosphonous acid, instead of the expected allyl phosphonous acid, may be explained by the well-known alkoxylation reaction of olefins by alcohols in acidic medium, according to Equation (9),



(9)

EXPERIMENTAL

1. *Interaction between $NaOP(O)H_2 \cdot H_2O$ and allyl bromide.* Sodium hypophosphite (5.3 g; 0.05 mol) monohydrate were dissolved in 40 ml of ethanol and 9.1 g (0.075 mol) of allyl bromide were added. The solution was heated to 68–70°C when a salt started to precipitate. The reaction continued for about one hour and a half. The salt was filtered off. The volatile products were separated by distillation. The filtration was carried out again. A total of 5.15 g of salt (NaBr) and 2.9 g of allyl alcohol, $n_D^{20} = 1.4130$, were formed. A yellow liquid 3.3 g, $n_D^{20} = 1.4574$, was left, which is suggested to be H_3PO_2, found P, 46.84%, calc. P, 49.96%, acid number, found 837; calc. 850 mg KOH/g; IR-spectrum $\nu_{P=O}$ 1220 cm^{-1}, ν_{P-H} 2410–2395 cm^{-1} (film between KBr plates).

2. *Preparation of 2,3-dihydroxypropylphosphonous acid.* A mixture of potassium hypophosphite (5.2 g (0.05 mol)) and 30 ml of 3-chloro-1,2-propanediol was heated to about 110°C. After 1 h a salt started to precipitate. The salt was filtered off. Excess 3-chloro-1,2-propanediol was distilled under vacuum (ca. 3 mm Hg) at 70°C. A salt was formed, and was again filtered off 6.8 g of a product, a viscous oil with $n_D^{20} = 1.4570$, was left; acid number, found 388 mg KOH/g, calc. 400.7 mg KOH/g; found P, 22.02, calc. P, 22.14; IR-spectrum, 1175–1220 cm^{-1} (P=O), 2420–2385 cm^{-1} (P—H), 2960–2880 cm^{-1} (CH and CH_2) 3600–3300 cm^{-1} (OH) (film between KBr plates).

3. *Preparation of 2-oxethylpropylphosphonous acid.* To a solution of 5.2 g (0.05 mol) of potassium hypophosphite in 40 ml of dry ethanol 10 g (0.083 mole) of allyl bromide were added. The reaction mixture was heated with stirring to 70°C. After 1 h a salt was formed which, after cooling, was filtered off. Subsequently, the solvent and excess allyl bromide were distilled off. A total of 5.9 g of KBr was

formed. 7.59 g of a viscous oil was left, with $n_D^{20} = 1.4512$. Found, P, 20.21, calc. P, 20.39, IR-spectrum: 1215–1195 cm^{-1} (P=O), 2420–2385 cm^{-1} (P—H), 2975–2880 cm^{-1} (CH, CH_2, CH_3), 1080 cm^{-1} (CH—O—CH_2) (in layer).

METHODS OF ANALYSIS

^{1}H NMR spectra were recorded on Tesla BS 487 C (80 MHz) and Bruker WM (250 MHz) spectrometers, as solutions in $CDCl_3$ and D_2O, with TMS as an internal standard. The IR spectra were run on a UR-20 instrument (Carl Zeiss Jena, GDR).

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