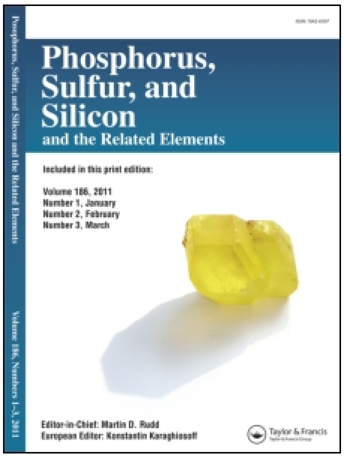

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METHODS FOR SYNTHESIS OF 1-METHYLOLALLENEPHOSPHONOUS ACID AND ITS HYDROXY ESTERS

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From alkylene oxides and hypophosphorous acid 2-hydroxyesters of the hypophosphorous acid are formed. They undergo an exchange reaction with 2-butyne-1,4-diol as a result of which the corresponding glycol and 1-methylolallenephosphonous acid are obtained. The yield of the acid is quantitative. According to this method also 2-hydroxy esters of 1-methylolallenephosphonous acid are formed.

Key words: Hypophosphorous acid esters with acetylenic alcohols; alkylene oxides; 2-hydroxy esters of 1-methylolallenephosphonous acid; allenephosphonous acids; acetylene-allene rearrangement; 2-butine-1,4-diol

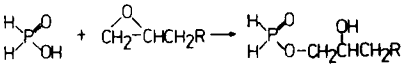
INTRODUCTION

It has been shown[1–4] that during esterification of hypophosphorous acid (HPA) with acetylene alcohols phosphonous acids and not the corresponding esters are obtained. With a yield of 58% 1-methylolallenephosphonous acid is obtained with 2-butyne-1,4-diol. The isomerization is explained[5] as shown in Equation (2). The HPA esters are very unstable[6] and assumed to give transesterification under mild conditions.

We checked the validity of this assumptions by reacting 2-hydroxy esters of HPA and 2-butyne-1,4-diol.

RESULTS AND DISCUSSION

The product from the reaction between HPA and propylene oxide or epichlorohydrin was chosen to be the initial reagent. Data on this reaction are not available in literature. Our studies show that alkylene oxides react exothermally with HPA in an inert medium (benzene, acetone, dioxane). We were not able to isolate and characterize the products obtained, since after the solvent had been eliminated they dissociated forming phosphin, which is characteristic of esters of hypophosphorous acid.[6] The corresponding esters of HPA are thought to be formed in the reaction:



(1)

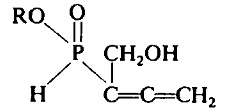
where R = H; Cl.

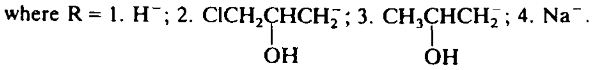
The considerations to choose these esters for transesterification with 2-butyne-1,4-diol are the following: 1) they are readily obtained under normal conditions. It is not necessary to conduct esterification of the acid with alcohols, which takes several hours in inert atmosphere with an azeotropic removal of water, which is connected with a partial decomposition of the esters and contamination of the reaction medium[7] 2) conjugation which can be observed between the esters of HPA and acetylene alcohols, along the chain towards the oxygen at the phosphorus in 2-hydroxy alkyl radical cannot take place.[5]

The products of 2-hydroxy alkyl esters of HPA and 2-butyne-1,4-diol were characterized by their IR- and ^{1}H-NMR spectra (Table I). In a film taken IR-spectrum there were bands of absorption for P=O at 1240 cm^{-1}, for P—H at 2320 cm^{-1}, doublet signal characteristic of C=C=C allene at 1945 and 1975 cm^{-1}, P—C=C=C at 1635 cm^{-1}, C=C=C allene at 1035 cm^{-1}. Bands of absorption of C≡C were missing at 2140–2100 cm^{-1}. As seen from the results of acid number, elementary analysis and IR- and ^{1}H-NMR spectra (see Table I), the product obtained was identical with 1-methylolallenephosphonous acid, described in[4], thus the following reaction proceeded:

TABLE I

^{1}H-NMR data of





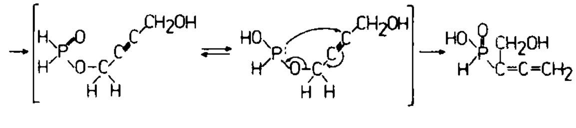
where R = 1. H^-; 2. $ClCH_2\underset{OH}{C}HCH_2^-$; 3. $CH_3\underset{OH}{C}HCH_2^-$; 4. Na^-.

1. OCH_2-δ = 4.1 ppm (m), $J_{CH_2,P}$ = 10.6 Hz; =CH_2-δ = 5.03 ppm (dd), $J_{CH_2,P}$ = 11.2 Hz, J_{CH_2,CH_2} = 2 Hz; P—H-δ = 7.49 ppm (d), $J_{P,H}$ = 568 Hz.

2. OCH_2-δ = 4.1 ppm (m), $J_{CH_2,P}$ = 11.4 Hz; =CH_2-δ = 5.07 ppm (dd), $J_{CH_2,P}$ = 11.6 Hz, J_{CH_2,CH_2} = 2 Hz; P-OCH_2-δ = 3.67 ppm (m), $J_{OCH_2,P}$ = 5.3 Hz; CH—O-δ = 3.83 ppm (m), $J_{CH,CH}$ = 4.5 Hz $ClCH_2$-δ = 3.58 ppm (m), $J_{CH_2,CH}$ = 4.5 Hz; P—H-δ = 7.23 ppm (d), $J_{P,H}$ = 535 Hz.

3. OCH_2-δ = 4.12 ppm (m), $J_{CH_2,P}$ = 11.2 Hz; =CH_2 − δ = 5.12 ppm (dd), $J_{CH_2,P}$ = 11.2 Hz, J_{CH_2,CH_2} = 2 HZ; P—OCH2-δ = 3.66 ppm (m), $J_{OCH_2,P}$ = 5.4 Hz; CH—O-δ = 3.84 ppm (m), $J_{CH,CH}$ = 4.6 Hz; CH_3-δ = 1.06 ppm (d), $J_{CH_3,CH}$ = 4.16 Hz; P—H-δ = 7.25 ppm (d), $J_{P,H}$ = 537 Hz.

4. OCH_2-δ = 4.1 ppm (m), $J_{CH_2,P}$ = 11.2 Hz; =CH_2 δ = 5.04 ppm (dd), $J_{CH_2,P}$ = 11.6 Hz; J_{CH_2,CH_2} = 2 Hz; P—H-δ = 7.21 ppm (d) $J_{P,H}$ = 516 Hz.



(2)

As seen from the scheme, the transesterification of 2-hydroxy esters of HPA with 2-butyne-1,4-diol, with the formation of reactionless glycole, proceeds. The reaction is characterized by low temperature of conductance. There are two isomeric forms of the ester obtained from 2-butyne-1,4-diol—four- and three-coordinated phosphorus atom. The yield of the acid is quantitative.

This method may be applied in the cases of a direct one-stage formation of 2-hydroxy esters of 1-methylolallenephosphonous acid. These esters can be obtained by using 2 (or more) moles of alkylene oxide for one mol HPA. It was established that the excess of alkylene oxide could be removed when the reaction was over by means of distillation, i.e. it interacted neither with some of the products obtained with a hydroxyl group nor with itself. The corresponding glycols—1,2-propanediol or 3-chloro-1,2-propanediol (they are identical with the known ones according to data in the literature) were isolated after the reaction. Most probably the alkylene oxide present in the system joined the P—OH acid group of the forming 1-methylolallenephosphonous acid. This was confirmed by conducting a counter synthesis—propylene oxide or epychlorohydrin joined 1-methylolallenephosphonous acid in a solution of dioxan, during which the corresponding esters were obtained. The esters were determined by elemental analysis (see Experimental). They were bands of absorption in the IR-spectrum, characteristic of the acid cited above. ^{1}H-NMR-data taken in dimethyl sulphoxide are presented in Table I. The esters were readily hydrolized in water. A corresponding sodium salt was obtained from 1-methylolallenephosphonous acid, as well as from esters by titration with sodium hydroxide.

EXPERIMENTAL

On a "Tesla-BS 467"-60 MHz ^{1}H-NMR spectra were taken with an internal standard hexamethyldisiloxan in a solution of dimethyl sulphoxide. The IR spectra were film taken on a UR-20 instrument (Carl Zeiss Jena, GDR).

1. Preparation of 1-methylolallenephosphonous acid

A. With epichlorohydrin

To a solution of 6.6 g (0.1 mol) hypophosphorous acid in 50 ml of dioxane 9.2 g (0.1 mol) of epichlorohydrin, dissolved in 20 ml of dioxane were added dropwise. Mixing was performed at constant stirring so that the temperature of the reaction mixture could not rise above 35°C. After the whole amount of epichlorohydrin had been added, 8.6 g (0.1 mol) of 2-butyne-1,4-diol were added to the mixture. The reaction mixture was heated up to 50°C and at that temperature it was stirred for one hour. Dioxane was distilled off under 12 mm Hg. The residue was treated several times with diethyl ether. The ether was distilled after which 11 g of 3-chloro-1,2-propanediol with $n_D^{20} = 1.4794$ remained. The residue after the extraction was dried under reduced pressure at 50°C. A yield of 12.86 g (96%) of 1-methylolallenephosphonous acid was obtained, $n_D^{20} = 1.5422$. The acid number found 415.2, calc. 418.6. The content of P, % found 23.04, calc. 23.13.

B. With propylene oxide

To a solution of 6.6 g (0.1 mol) hypophosphorous acid in 50 ml of dioxane 5.8 g (0.1 mol) of propylene oxide, dissolved in 20 ml of dioxane, were added dropwise. The mixing was performed by a constant intensive stirring so that temperature of the reaction mixture could not exceed 27°C. After the whole amount of propylene oxide had been added, 8.6 g (0.1 mol) of 2-butyne-1,4-diol were added. The reaction mixture was heated up to 50°C and then it was stirred for about one hour. Dioxane was distilled off under a pressure of about 12 mm Hg. The residue was treated several times with diethyl ether. The ether was distilled after which 7.6 g of 1,2-propanediol, $n_D^{20} = 1.4328$, were left. The remains from the extraction with ether were dried under decreased pressure at 50°C. 12.94 g (a yield of 97%) of 1-methylolallenephosphonous acid, $n_D^{20} = 1.5418$, were obtained. The content of P, % found 23.11, calc 23.13.

2. Preparation of sodium salt of 1-methylolallenephosphonous acid. In 20 ml of ethyl alcohol 1.34 g of 1-methylolallenephosphonous acid were dissolved and then titrated with alcoholic sodium hydroxide up to $pH = 7$. The precipitate formed was filtered, washed with diethyl ether and dried. 1.5 g of sodium salt were obtained. It neither melted nor decomposed up to 300°C. The content of P, %, found 19.83, calc. 19.87.

3. Preparation of 2-hydroxypropyl ester of 1-methylolallenephosphonous acid. To a solution of 6.6 g (0.1 mol) hypophosphorous acid in 50 ml of dioxane 15 g of propylene oxide, dissolved in 20 ml of dioxane, were added dropwise. The mixture was obtained by constant intensive stirring so that the temperature of the reaction mixture could not exceed 27°C. After the whole amount of propylene oxide had been added, 8.6 g (0.1 mol) of 2-butyne-1,4-diol were added. The temperature was increased up to 50°C and then the mixture was stirred for one hour at this temperature. Dioxane and unreacted propylene oxide were distilled under reduced pressure of about 12 mm hg. The residue was treated several times with portions of diethyl ether. The ether was distilled during which 5.8 g of 1,2-propanediol, $n_D^{20} = 1.4328$ were formed. The remains from the extraction with ether was dried under reduced pressure. An amount of 17.9 g 2-hydroxypropyl ester of 1-methylolallenephosphonous acid, $n_D^{20} = 1.5000$, was obtained. The yield was 94%. The content of P, %, found 17.11, 16.18, calc. 16.14 Acid number, found 288.6, calc. 292.18.

4. Preparation of 3-chloro-2-hydroxypropyl ester of 1-methylolallenephosphonous acid. To a solution of 6.6 g (0.1 mol) hypophosphorous acid, dissolved in 50 ml of dioxane, 18.4 g (0.2 mol) of epichlorohydrin, dissolved in 20 ml of dioxane, were added dropwise. Mixing was performed at constant intensive stirring so that the temperature of the reaction mixture should not exceed 32°C. After adding the whole amount of epichlorohydrin, 8.6 g (0.1 mol) of 2-butyne-1,4-diol were added. The reaction mixture was heated up to 50°C and then stirred for one hour at that temperature. Dioxane was distilled under reduced pressure of about 12 mm Hg. The remains were repeatedly treated with diethyl ether. The ether was distilled and 11 g of 3-chloro-1,2-propanediol, $n_D^{20} = 1.4794$, were formed. The remains from the extraction with ether were dried under decreased pressure. A product of 20.7 g, $n_D^{20} = 1.5474$, was formed. The content of P, % found 13.83, 13.58, calc. 13.72.

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