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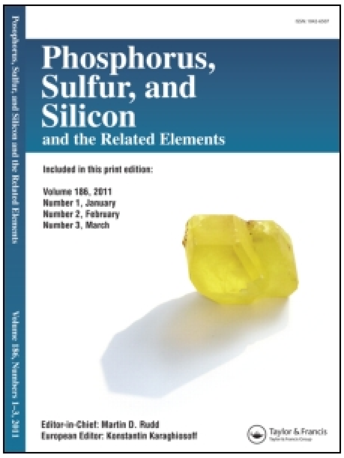

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Syntheses with Hypophosphorous Acid and its Derivatives

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SYNTHESES WITH HYPOPHOSPHOROUS ACID AND ITS DERIVATIVES

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ABSTRACT: The interaction of hypophosphorous acid and its salts with hydroxyl-containing compounds:alkyl halids, isocyanates,formaldehydes and amines was investigated. The new polyfunctional phosphonous acids were obtained.

INTRODUCTION

Hypophosphorous acid (HPA) is an accessible industrial product.It has a high phosphorus content (47%),three reactive groups i.e.an hydroxyl one and two relatively acidic hydrogen atoms directly bonded to phosphorous.

It was known that HPA esters were synthesized [I].The esterification of HPA with polyallylic alcohol or polysacharides as well as with 2-butyne I,4-diol leads to phosphonous acids[2,3].It is assumed that the first step consists in the formation of the HPA esters which then isomerizes into phosphonous acid.The interaction between methil iodide and the sodium salt of HPA has been reported[4].The author assuming the formation not of the corresponding ester but methylphosphonous acid.

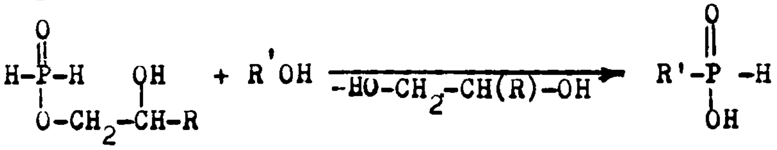
The aim of the present study was to search for synthetyc ways leading to new organophosphorous compounds containing C-P bonds and functional groups.

RESULTS AND DISCUSSION

Interaction between HPA and alcohols.

The interaction between HPA and alcohols was examined[5].We found however that the isolated HPA ester decomposes to dialkyl phosphite (DAP) and phosphine but gives no phosphonous acid.The reaction medium were detected an olefin arising from alcohol dehydration and the corresponding phosphonous acids (in yields above 40%),the latter were determined by IR, NMR spectroscopy and elemental analysis.The mechanism of the reaction is discussed with the view to explaining the products formed.

Experiments were also conducted to obtain HPA esters via interaction with alkylene oxides at room temperature.No hydroxy or phosphonous acids were isolated from the reaction mixture.The addition to the reaction mixture of an equimolar quantity of different hydroxyl-containing compounds gives corresponding phosphonous acid:

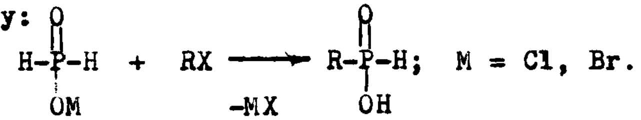


$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O{-}CH_2{-}CH{-}R}{|}}{P}}{-}H}\;\;\overset{\displaystyle OH}{} + R'OH \xrightarrow[]{-HO-CH_2-CH(R)-OH} \mathrm{R'{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}H}$$

When as alcohol 2-butyne-I,4-diol was used I-methylol-I,2-propanedienyl phosphonous acid in yeld 97% was obtained[6].

Interaction between alkaline salts of HPA with alkyl halides

The interaction between alkyl halides and hypophosphorous acid salts has been investigated.The interaction of potassium hypophosphite with 3-chloro-I,2-propenediol or with allylbromide in ethanol solution was examined.The compounds were determined by elemental analysis,NMR and IR spectroscopy:



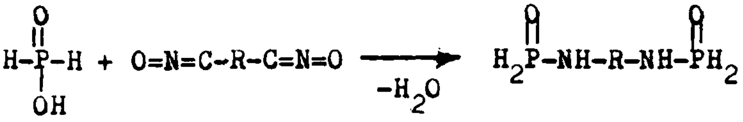
$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OM}{|}}{P}}{-}H} + RX \xrightarrow[-MX]{} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}H};\quad M = Cl,\ Br.$$

In the case of allyl bromide,interestingly,no phosphonous acid containing a double bond was isolated,the product being ethoxyalkylphosphonous acid arising from ethanol addition.It was also attempted to introduce phosphonous group in halogen-containing polymers[7].It was found that potassium hypophosphite reacts with polyvinyl chloride as well as with polychloroprene rubber.The reaction was carried out in ethanol and the polymers obtained have a phosphorous content of 2,5 and 2,2% respectively.They exhibited an improved hydrophilicity and resistance to combustion as well as ion-exchange properties.

Interaction between HPA salts with isocyanates.

The interaction of HPA salts with isocyanates under the conditions of polyurethane formation has been examined[8]. There is an exothermal reaction at about 130°C accompanied by evolution of CO_2. On the grounds of the literature data and the characteristics of the products obtained it can be assumed that several reactions take place i.e. addition of HPA salts over the isocyanate functions, formation of isocyanuric rings and carbodiimide structures. A similar result - an evolution of CO_2, a formation of carbodiimides, and addition over the isocyanate function has been reported for the reaction between isocyanates and dialkyl phosphites[9].

The interaction of aqueous HPA solutions with isocyanates afforded HPA amines according to the scheme:

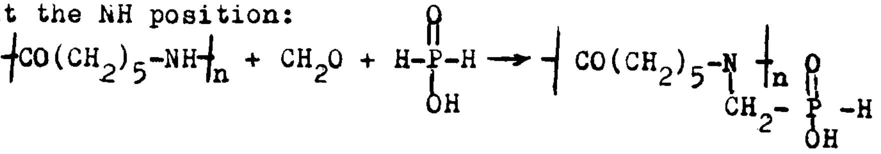


$$H-\underset{OH}{\overset{\overset{O}{\|}}{P}}-H + O=N=C-R-C=N=O \xrightarrow[-H_2O]{} H_2\overset{\overset{O}{\|}}{P}-NH-R-NH-\overset{\overset{O}{\|}}{P}H_2$$

The amines of HPA have been hitherto unknown. They are particularly suitable for preparing phosphorous-containing new compounds, more notably polymers.

Interaction between HPA with formaldehyde and amines.

Hydrogenphosphoryl compounds are known to react with formaldehyde and amines (the Mannich reaction). HPA has been used for similar reactions[10]. The possibilities of phosphorylation of caprolactam and polycaprolactam with HPA and formaldehyde examined. It was found that phosphorylation takes place at the NH position:



$$\left[CO(CH_2)_5-NH\right]_n + CH_2O + H-\underset{OH}{\overset{\overset{O}{\|}}{P}}-H \rightarrow \left[CO(CH_2)_5-\underset{CH_2-\underset{OH}{\overset{\overset{O}{\|}}{P}}-H}{N}\right]_n$$

Phosphorous content in polycaprolactam is 0,9 to 2,6% which means that one methylenephosphonous group corresponds to 12-14 elementary units and the new phosphorylated polycaprolactam show a reduced resistance to combustion.

Some of the newly prepared compounds have been used as polyurethane fire-retardants[8].Almost all of the presently investigated compounds exhibit improved resistance to combustion for polyurethanes in comparison to the commercial fire-retardant Firol-6.Some of the phosphonous acids have been found to act as grouwth regulators or fungicides.

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