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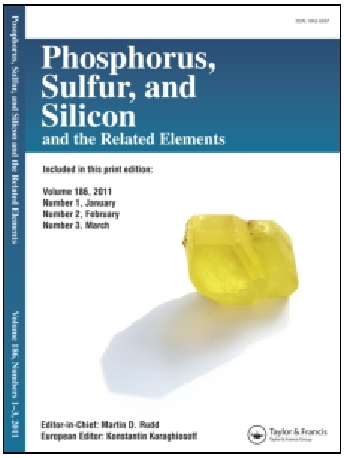

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ACYLATION OF PHOSPHORUS SUBSTITUTED CH-ACIDS UNDER PHASE TRANSFER CATALYSIS CONDITIONS

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Abstract. Acylation of phosphoryl- and thiophosphoryl acetonitriles under phase transfer catalysis (PTC) conditions leads in high yields to C-acylated products existing as Z-isomers of the corresponding enol forms. They are stabilized by strong intramolecular H-bonds. On the contrary, acylation of phosphorylacetone proceeds mainly at the oxygene atom and gives Z and E enolacetate. Phosphorus trichloride was used as an acylating agent under PTC conditions. S-Alkyldichlorophosphites were obtained by the reaction with mercaptanes. Alcohols react with PCl_3 in the presence of sodium carbonate to result in dialkylphosphites.

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INTRODUCTION

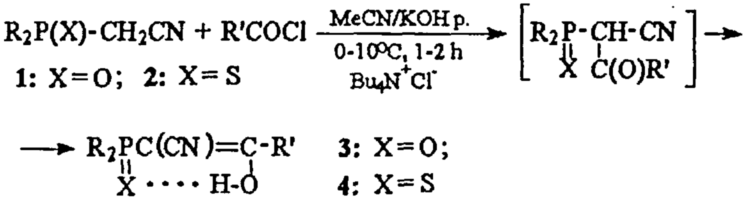
PTC is known to be widely used in such reactions as the Wittig, Horner, Todd-Atherton, Michaelis-Becker, Pudovik reactions and others. However, acylation reactions of carbanions generated from phosphoryl substituted CH-acids, in particular, phosphorylacetonitriles, phosphorylacetones and some others appeared to be outside investigation.

ACYLATION OF PHOSPHORYLACETONITRILES

Acylation of potassium salts of dialkoxyphosphorylacetonitriles is known. Kirilov and Petrov[1,2] carried it out under classic conditions carefully avoiding moisture traces. They have got acylation products in low yields, no more than 15-30%. The authors established that the C-acylated derivatives existing in equlibrium with their Z-enol forms were obtained.

The application of PTC called for the investigation of substrate CH-acidity. We have measured CH-acidity of phosphoryl- 1 and thiophosphorylacetonitriles 2 by the indicator transmetallation method in DMSO[3]. They proved to be CH-acids of a medium power with pKs equal to 15-20. Thus they are assigned to the CH-acids easily reacting under PTC conditions. Thiophosphoryl compounds were on the average 0.9 pK unit stronger than phosphoryl analogues.

The action of acylchlorides on **1** under PTC conditions resulted in C-acylation with the complete transformation of acyl derivatives to Z-enols **3** [4]. Acyl derivatives were obtained in high yields, which were in direct relation with the CH-acidity of the initial phosphoryl compounds. So at pK about 17, the yields approached the quantitative ones, at pK about 19, they were 72-75%, and at pK near 20, they were about 30%. Steric hindrances to the intermediate generation also influenced the reaction.



$$R_2P(X)\text{-}CH_2CN + R'COCl \xrightarrow[0\text{-}10^{\circ}C,\ 1\text{-}2\,h;\ Bu_4N^+Cl^-]{MeCN/KOH\,p.} \left[R_2\underset{X}{\overset{}{\underset{\|}{P}}}\text{-}\underset{C(O)R'}{\underset{|}{CH}}\text{-}CN \right] \rightarrow$$

1: X=O; **2**: X=S

$$\rightarrow R_2\underset{X\cdots\cdots H\text{-}O}{\underbrace{\underset{\|}{P}C(CN)=\underset{|}{C}}}\text{-}R'$$

3: X=O; **4**: X=S

As for thioanalogues **2**, the yields of the acylation products were about 20% lower. In the presence of typical interphase catalyst, Bu_4NCl the yields increased by about 10-15%. It is no need in catalysts in the case of **1**. Probably the initial compounds **1** or the product of their acylation may play the role of the interphase catalysts.

Our acyl derivatives belong to triacylmethanes, the class of the extremely easy-to-enolize substances. As a rule they are completely enolized to give cis-enols stabilized by strong intramolecular hydrogen bonds. However, for dibenzoylmethane and tribenzoylmethane the existence of the triketo form in solutions or in the crystal state is typical.

That is why we thoroughly investigated the enolization of our compounds using NMR, IR and mass-spectra, bromometric titration and X-ray analysis. All the acylderivatives obtained were found to represent the pure enol forms. In none of the cases the presence of the keto forms were obsereved. In liquid or in the crystal state, enols have the Z configuration which is stabilized by strong intramolecular hydrogen bonds. In solutions of non-hydroxylic solvents, only one Z form is present. In hydroxylcontaining media it exists in equilibrium with the E-form. But the Z form with its own intramolecular hydrogen bond is still retained. The content of the Z and E forms in the equlibrium state depends on the nature of the substituents at the carbone atom.

We were interested in the problem of transformation of stereoisomers. Does it proceed through a keto form or via the mesomeric anion?

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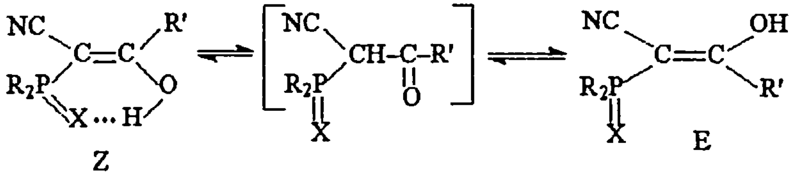

We studied the acidities of the substances obtained by the potentiometric method in 75% alkohol. They proved to be very strong acids with pK_s of 4.40-4.83. Thus in solutions of enol forms, mesomeric anions are always present at an appreciable concentration. That is why the Z=E transformation is rather likely to go without the keto form involvement.

We have also investigated the sterioisomer ratio of $[(EtO)_2P(O)C(CN)=C(R')O]^-M^+$, (M = K and Bu_4N) salts in MeCN and CD_3OD solutions by the NMR technique. The results obtained confirmed of Z=E transformation proceeding through the mesomeric anion. Acyl derivatives of thiophosphorylacetonitriles proved also to be completely enolized. They form Z enols 4 with the intramolecular hydrogen bond P=S...H-O. It is known that the thiophosphoryl group is less capable of hydrogen bonding although H-bonds still occur and can be rather strong. In our case, all the data, namely PMR, IR and especially X-ray analysis, confirm the formation of the intramolecular H-bond with the P=S group. At the same time, its less strength endows some peculiarities to the enolized thioderivatives. Particularly it tells upon the ability of these derivatives to benzoylation of enol hydroxyle under PTC conditions.

$$\mathbf{2} + PhCOCl \longrightarrow \mathbf{4} + R_2P(S)C(CN)=C(Ph)OCOPh \quad (Z)$$

For phosphoryl derivatives we in no case observed benzoylation of the enol hydroxyl even if there was a great excess of benzoyl chloride.

ACYLATION OF PHOSPHORYLACETONES.

It is known from V.G.Sakhibullina's, N.A.Polezhaeva's and B.A.Arbuzov's works[5,6] that under classic conditions, the alkaline enolates of phosphorylacetone were acylated at the oxygen atom resulting in Z-acylenols. On acylation of the phosphorylacetone in the presence of triethylamine, a mixture of the Z and E isomers in the ratio of 2:1 was formed.

We have found that phosphorylacetone is readily acylated under PTC conditions in the system "diethyl ether or TGF/solid alkali" in the presence of tetrabutylammonium salts.

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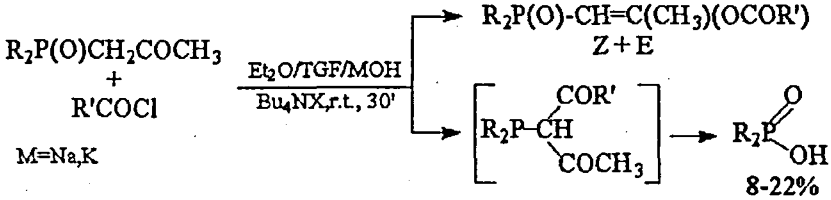
In this case too, the reaction occures mainly at the oxygen atom leading to the final product as a mixture of the Z and E isomers. The ratio of isomers is in close agreement with that obtained in performing this reaction in the presence of triethylamine.[6]



The corresponding phosphorus acids are formed as side products under PTC conditions in the yields from 8% to 22%. This suggests that C-acylation might take place simultaneously with O-acylation, but triacylmethanes obtained are easily cleaved at the P-C bond.

PHOSPHORUS TRICHLORIDE AS ACYLATING AGENT.

We undertook an effort to use PCl_3 under PTC conditions, in spite of it is hydrolyzed very easy. We hoped that PCl_3 being in the organc phase in the two phase system liquid/dry potassium carbonate may phosphorylate a substrate, which is also located in the organic phase, faster than it undergoes hydrolysis. We have used mercaptanes as substrates in this reaction and obtained thiodichlorophosphites in 75-85% yields. There were no need in catalysts.

$$RSH + PCl_3 \xrightarrow[TBA]{CH_2Cl_2/K_2CO_3} RSPCl_2 \qquad 75\text{-}85\%$$

Then we have carried out the reaction of alcohols with PCl_3 in the two phase system using dry Na_2CO_3 at room temperature and obtained $(RO)_2PHO$ in high yields and in the entirely pure state. This method is quite technological.

CONCLUSION

Our results show that PTC method harbours a lot of new and interesting things for organophosphorus chemistry especially with the use of easily hydrolized reagents.

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