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PHOSPHITE ADDITION TO CARBONYL GROUP AND PHOSPHORYL MIGRATION UNDER PHASE TRANSFER CATALYTIC CIRCUMSTANCES

IMRE PETNEHÁZY, ZSUZSA M. JÁSZAY, LÁSZLÓ TŐKE

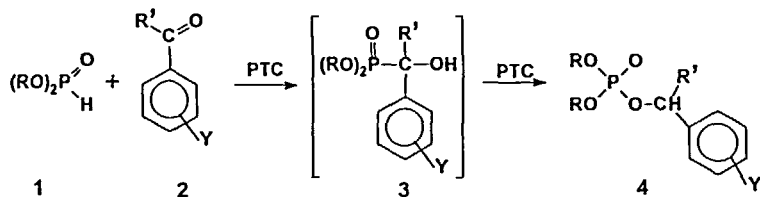
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Abstract The rearrangement of α -hydroxyphosphonates to phosphates under PTC conditions usually run in a different way and gives better yield as that found in homogenous system.

The phase transfer catalysis is defined as a two phase reaction between the reagents which are in solid or aqueous phase and substrates in organic solvents in the presence of so called phase transfer catalyst. α -Hydroxyphosphonates can rearrange by a C→O phosphoryl migration resulting in the formation of phosphates.

Synthesis of phosphoric acid esters from aldehydes and ketones

According to the literature α -hydroxyphosphonates (3) can be prepared by the addition reaction of dialkyl phosphites (1) to aldehydes or ketones (2). In homogenous phase the reaction needs sodium alcoholate catalyst¹ and the yield are generally low because of the side reactions. These side reactions can be eliminated by performing the addition reaction on the surface of alumina². This system gives good yield only in the case of aldehydes. Improving the surface by caesium fluoride³ ketones also provide α -hydroxyphosphonates.



PTC: solid/liquid K_2CO_3 / aprotic solvent, QX or crown ether, 50–70°C

liquid/liquid aprotic solvent / 50% NaOH, QX, 20°C

R: Me, Et, iPr

Y: Cl, diCl, H, NO_2

R': H, Me

Using potassium carbonate as a base in solid-liquid PTC circumstances at room temperature we succeeded in isolating α -hydroxyphosphonates which couldn't be prepared by any of the known methods, but at higher temperature the rearrangement of α -hydroxyphosphonate to mixed phosphate ester (4) was observed.

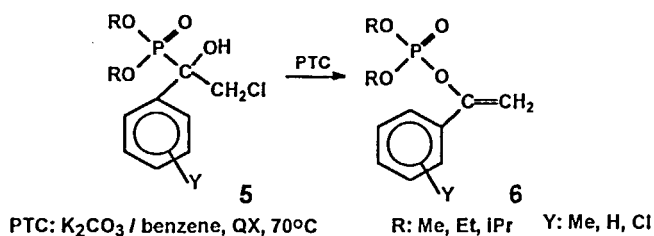
There is a relationship between the yield of the phosphate and the substituent of the aromatic ring; reaction with more electron withdrawing substituent gives higher yield in solid-liquid PTC circumstances. Though in some cases the liquid-liquid PTC reaction provides the product in excellent yield.

This procedure of ours is a new one pot method for the preparation of the mixed phosphate esters from dialkyl phosphites and oxo compounds. Numerous mixed esters have been prepared in this way. The procedure seems to be superior to those described in the literature since they acylate an alcohol by phosphorus diester chloride, and mixed ester so obtained is strongly contaminated because of the side reactions.

Synthesis of vinyl phosphates from α -chloromethyl- α -hydroxyphosphonic acid esters

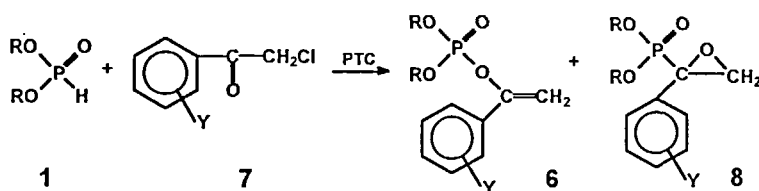
The reaction is known from the literature in homogenous phase in the presence of sodium alcoholate producing two types of products⁴, vinyl phosphate (6) and phosphonooxirane (8).

In a two phase reaction the rearrangement of the α -chloromethyl- α -hydroxyphosphonate (5) was formed selectively; the only product is the vinyl phosphate which can be prepared in good yield.



The relative values of yields show that the increasing bulkiness of the phosphoryl group retards the rearrangement. Namely, in case of isopropyl group the yield is lower than in case of the smaller ethyl or methyl group.

Using the same one pot method which was used for the preparation of mixed esters in the reaction of the chloroacetophenone (7) with dialkyl phosphite both vinyl phosphate (6) and phosphonooxirane (8) were formed in comparable ratio.



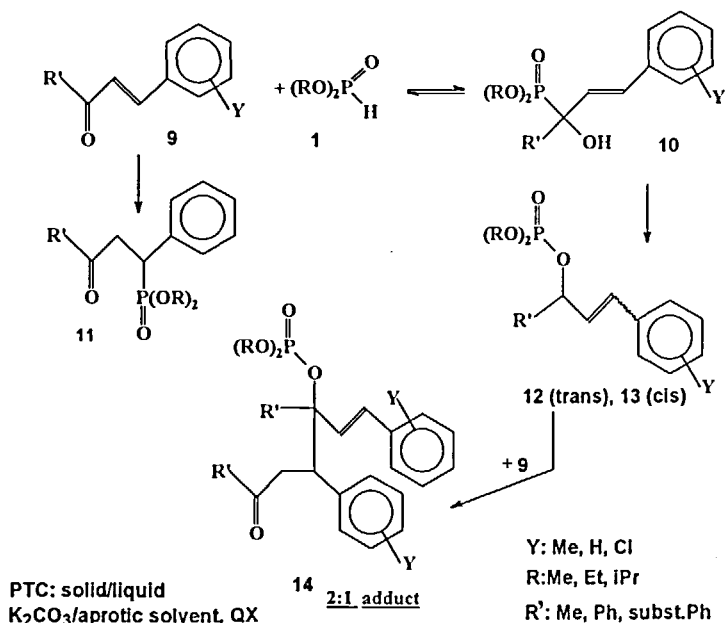
The ratio of the products shows again that the migration of the bulky phosphoryl group is hindered. In case of isopropyl group the yield of phosphonooxirane (8) is more than three times as high as that of vinyl phosphate (6).

This phenomenon may be due to the difference in binding strength of the substrates 1 and 5 to the surface of the potassium carbonate.

Reactions of enones with dialkyl phosphites

In the reaction of dialkyl phosphites (1) with α,β -unsaturated oxo compounds (9) in the presence of a base in protic solvent the products are α -hydroxy-allyl-phosphonate (10), γ -ketophosphonate (11) and several diphosphonates (1:2 adduct), the letters can be formed in the reaction of γ -ketophosphonate (11) with an other molecule of dialkyl phosphite^{5,6}.

We have investigated the reaction of a series of dialkyl phosphites with α,β -unsaturated oxo compounds under solid-liquid PTC conditions.



Here, beside the three types of products, namely α -hydroxy-allyl-phosphonate (10), γ -ketophosphonate (11) and phosphoric acid allylic esters (12 and 13) a further product (14) was also isolated in crystalline form from the reaction mixture, and identified as 14.

The ratio of the phosphates (12+13+14) to γ -ketophosphonate (11) was unchanged during the reaction, which may be explained by supposing the parallel formation of the γ -ketophosphonate and the phosphates as shown in the Scheme.

The ratio of the products depends on the substituent on the phenyl ring and on the alkyl moiety of the phosphite. In the case of electron withdrawing substituent the ratio of phosphates to γ -ketophosphonate is higher while in case of electron donating substituent it is lower than that of the unsubstituted compound. With increase of the bulkiness of phosphite moiety the ratio of the phosphate becomes lower, namely the rearrangement is restricted similarly to the rearrangement mentioned in the previous chapter. Temperature also influences the ratio of the products, high temperature favours the formation of γ -ketophosphonate.

We assume that the allylic esters (12 and 13) are formed on the surface of the potassium carbonate by a phosphoryl migration from the deprotonated form of α -hydroxy-allyl-phosphonate (10). For the formation of 14 we assumed an addition of the anion from 12 to the β -position of enone and subsequent protonation of the adduct so formed.

The differences observed in the structure of the final products in homogenous phase and in PTC conditions may be due to the solid surface of the potassium carbonate, which serves not only as a base but decreases the probability of the attack of a second phosphite to the anion of α -hydroxyphosphonate formed and kept on the surface.

REFERENCES

1. V. S. ABRAMOV, *Zh. Obshch. Khim.*, **22**, 643 (1952).
2. F. TEXIER-BOULLET and A. FOUCAUD, *Synthesis*, **1982**, 916.
3. F. TEXIER-BOULLET and A. FOUCAUD, *Synthesis*, **1982**, 165.
4. G. STUTZ, *Bull. Soc. Chim. France*, **1964**, 2333.
5. R. A. CHERKASOV, V. I. GALKIN, A. B. KHABIBULLINA, and K. AL'KURDI, *Phosphorus, Sulfur, and Silicon*, **49/50**, 61 (1990).
6. E. ÖHLER and E. ZBIRAL, *Chem. Ber.*, **124**, 175 (1991).