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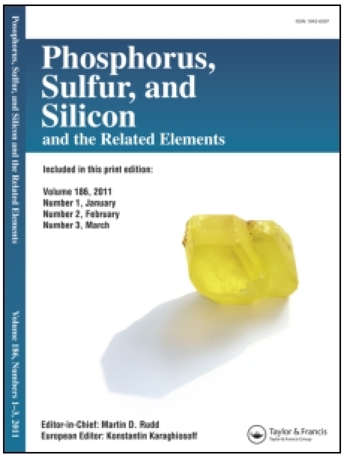

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Synthesis of Organophosphorus Compounds Using Phase Transfer Catalysis

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SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS USING PHASE TRANSFER CATALYSIS

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Abstract α-Hydroxyphosphonates, α-alkoxyphosphonates and mixed alkyl arylalkyl phosphates have been synthetised in phase transfer catalytic reactions. Cyclopropyl phosphates were prepared from vinyl phosphates by the addition of dihalocarbene. Monodealkylation of several phosphates and phosphonates were performed by solubilized halogenide aniones. PTC catalysis was used in the synthesis of unsymmetrically substituted carbodiimides via phosphoramidates.

In general it is not easy to perform any reaction on organophosphorus compounds of the ester type by classical methods without any side reaction such as hydrolysis. The PTC technique has been found useful to avoid side reactions of any type.

The phase transfer catalysis is defined as a two phase reaction between the reagents which are in solid or aqueous form and substrates in organic solvents in the presence of so-called phase transfer catalysts. The reagent can be a salt or an acid or a base; the typical catalysts are onium salts or crown ethers.

Some examples are known from the literature for the use of phase transfer catalysis on organophosphorus compounds as in the Wittig[1] and Wittig-Horner[2] reaction and N-alkylation of phosphoramidate elaborated by Zwierzak[3]. Now we present some reaction on this topic in both solid-liquid and liquid-liquid two phase systems.

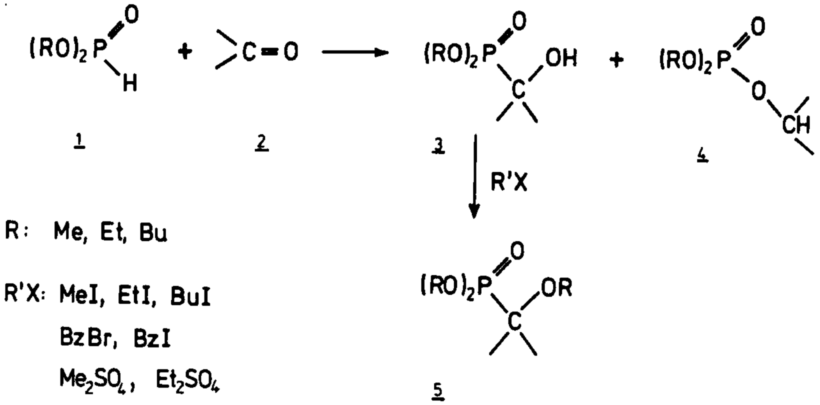
Synthesis and Reactivity of α-Hydroxyphosphonates

α-Hydroxyphosphonates /3/ are carbonyl adducts of dialkyl phosphites

/1/ and several types of oxo compounds. Some of them were synthesised in the literature by base catalysis[4] or on the surface of alumina[5] or cesium fluoride[6] but in many cases the yields are very low.

Reacting the dialkyl phosphite with aliphatic and aromatic aldehydes or ketones we prepared 3 in good yield using solid potassium carbonate or aqueous sodium hydroxide as a base under PTC conditions.

Scheme 1



We studied the reaction of α-hydroxyphosphonates with alkylating agents under phase transfer conditions, Some α-alkoxyphosphonate products /5/ were prepared. These compounds can be synthesised directly from dialkylphosphite, aromatic aldehyde and alkylating agent, too.

The α-hydroxyphosphonates /3/ containing an aromatic ring with an electron withdrawing substituent in the α position transformed into phosphates /4/ with a C→O 1,2-phosphoryl migration. The yields sometimes are better using the liquid-liquid system. This transformation gives a possibility for carrying out a new synthesis of organophosphorus esters from dialkyl phosphite and oxo compounds.

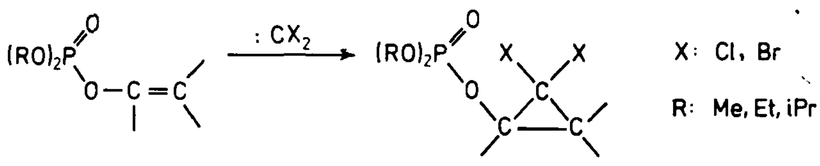
The α-hydroxyphosphonates /3/ and the other products /4/,/5/ can also be produced in parallel. We assume according to our kinetic measurements that the first step of the reaction in solid-liquid circumstances is the deprotonation of the dialkyl phosphite on the surface of potassium carbonate by the effect of the catalyst. The main reaction is the attack of the oxo compound on the phosphite anion bound on the surface. The intermediate can be protonated to α-hydroxyphosphonate /3/ or can react with an alkylating agent resulting in α-alkoxyphosphonate /5/ or can transform to a phosphate /4/ by migration in a parallel reaction (Scheme 1).

Synthesis of Cyclopropyl Phosphates

One of the most famous phase transfer catalytic reactions is the addition of dihalocarbene on olefins[7]. We carried out this reaction on the double bound of vinyl phosphates /6/ without the decomposition of the ester groups (Scheme 2).

The reaction was performed in a liquid-liquid system in concentrated sodium hydroxide and chloroform at room temperature. The conversion was almost quantitative. Most of the products are crystalline and the thermal stability of dibromocarbene adducts is less then the chloro ones.

Scheme 2



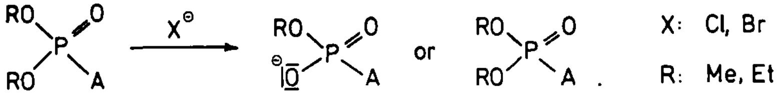
6 7

All of these dihalocyclopropyl phosphates /7/ have insecticidal activity.

Monodealkylation of Several Phosphorus Esters

However the selective monodealkylation of organophosphorus esters is an important reaction in the nucleotide chemistry there has not been reported a really good method in the literature.

Scheme 3



8 9 10

A: CH_2–CO–Ph (a), COPh (b), CH(OH)Ph (c), C(CH_2Cl)(OH)Ph (d)

OCH_3 (e), OC(Ph) = CHCl (f), OCH_2Ph (g)

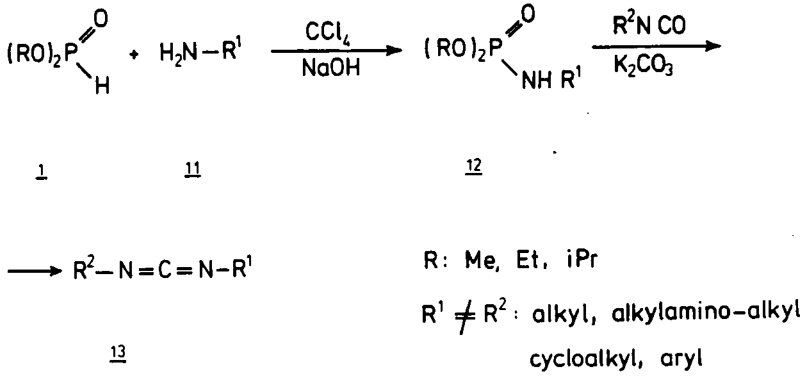
Recently we published[8] the monodealkylation of β-ketophosphonate /8a/ and vinyl phosphate /8f/ by refluxing 8 in an apolar solvent with alkali halide in the presence of PTC catalyst. Now we present the synthesis of mono acids /10b-e,g/ or mono salts /9b-e,g/. The compounds 9 and 10 are useful intemediates for the preparation of mixed esters (Scheme 3).

Synthesis and Reaction of Phosphoramidates

Phosphorylation of amines results in phosphoramidates which can be applied as protected derivatives or intermediates for further nitrogen compounds.

Some phosphoramidates /12/ were synthesised from dialkyl phosphite /1/ and amine /11/ in liquid-liquid PTC by Zwierzak's method[3]. Reacting these types of amides with isocyanates in the presence of solid potassium carbonate we prepared unsymmetrically substituted carbodiimides /13/ in good yield. The reaction takes place without any catalyst; we assume that the reaction goes on the surface of potassium carbonate and one of the intermediates containing phosphorus plays the role of phase transfer catalyst (Scheme 4).

Scheme 4



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