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Synthesis and properties of zwitterionic phosphonioglycolates

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ABSTRACT

Reaction of diphenylphosphane with glyoxylic acid hydrate in diethyl ether furnished diphenylphosphanylglycolic acid **1** and in a 1:2 molar ratio almost quantitatively the zwitterionic phosphonioglycolic acid glycolate **2**. Tertiary phosphanes with aryl or alkyl groups (phenyl, *m*/*p*-tolyl, *p*-anisyl, *n*-butyl, *tert*-butyl) react similarly to triorganylphosphonioglycolates **3a**–**h**, which like **2** precipitate from the etheral solutions of the reactants. Tri-*n*-butylphosphonioglycolate (**3e**) forms an ionic liquid and tri-*tert*-butylphosphonioglycolate (**3f**) a viscous product whereas the other phosphonioglycolates are solids. Yields and stabilities of **3a**–**e** increase with the P-basicity of the starting phosphane whereas bulky groups like *tert*-butyl cause destabilization. Compound **2** is the most stable phosphonioglycolate with only minor amounts of **1** in the solvolysis equilibrium in D_2O. The triaryl and tributylphosphonioglycolates **3a**–**f** decompose in protic solvents with recovery of tertiary phosphanes. On heating at 100 °C the compounds decompose to the corresponding phosphine oxides, minor amounts of glycolic acid and unidentified products.

1. Introduction

Hydroxyalkylations of primary and secondary phosphanes with aldehydes and ketones to α-hydroxyalkyl derivatives have long been known [1]. Whereas hydroxymethylphosphanes, obtained with formaldehyde, have found widespread use as reagents in phosphanylmethylations of amines or syntheses of P–C–N heterocycles [2] and in particular as ligands for improved water solubility of transition metal complexes for medicinal and catalytic applications [3], the addition products of tertiary phosphanes with aldehydes are more labile and have received much less attention. Their formation usually requires suitable electrophilic trapping agents and strictly anhydrous conditions [4]. Exceptions are zwitterionic α-hydroxyalkyl-triphenylphosphoniumsulfonates [5]. In the course of investigations on phosphanylglycines and heterocyclic α-phosphanyl amino acids [6,7], formed by condensation of glyoxylic acid with phosphanes and primary amines or 2-phosphanylalkylamines, respectively, we observed the reaction of the P–H moiety with glyoxylic acid as the initial step. In addition, the three-component reaction with N-secondary amines led to organoammonium phosphanylbis(glycolates) even in a 1:1:1 molar ratio [8]. To find out if the condensation of phosphanes with glyoxylic acid hydrate depends on the presence of a P–H function and amine or is attributed only to the Lewis basicity of the phosphane, the reactivity of glyoxylic acid hydrate toward diphenylphosphane and some tertiary phosphanes was studied. A condensation reaction with the latter should also open a facile way to the still unknown phosphonioglycolates and extend the variety of ω-phosphoniocarboxylates, available by reaction of tertiary phosphanes with ω-haloalkancarboxylates [9], *N*-acyl bromoglycine derivatives [10], activated α,β-unsaturated carboxylic acids [11] or by addition of CO_2 to phosphorus ylides [12].

2. Result and discussion

In contrast to the formation of a diphenylphosphonium-bis(glycolate) from an equimolar mixture of diphenylphosphane, glyoxylic acid hydrate and diethylamine in diethyl ether [8], the reaction of equimolar amounts of diphenylphosphane with glyoxylic acid hydrate furnished good yields of the monocondensation product **1**. Only with a second equivalent of glyoxylic acid hydrate the bis-condensation product **2** precipitated in excellent yields from the ethereal solution of the reactants (Scheme 1). If **2** was formed only after complete reaction of Ph_2PH to **1** or also parallel with **1** is not clear, but **1** is more stable than **2** in diethyl ether and thus the main product in this solvent for a 1:1 molar ratio. In D_2O solution of **2** small equilibrium amounts of **1** (ca. 10 mol%) are observed. This may be the reason of the air sensitivity of the solution of **2** whereas solid **2** and usual phosphonium compounds are air stable. It should further be mentioned that the acidic α-CH protons are

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