



## Synthesis and properties of zwitterionic phosphonioglycolates



Kaleswara Rao Basvani<sup>a</sup>, Olga S. Fomina<sup>a,b</sup>, Dmitry G. Yakhvarov<sup>b,c</sup>, Joachim Heinicke<sup>a,\*</sup>

<sup>a</sup> Institut für Biochemie, Ernst-Moritz-Armdt-Universität Greifswald, Felix-Hausdorff-Str. 4, 17487 Greifswald, Germany

<sup>b</sup> A.E. Arbuzov Institute of Organic and Physical Chemistry, Arbuzov str. 8, 420088 Kazan, Russian Federation

<sup>c</sup> A.M. Butlerov Institute of Chemistry, Kazan (Volga Region) Federal University, Kremlevskaya str. 18, 420008 Kazan, Russian Federation

### ARTICLE INFO

#### Article history:

Received 29 April 2013

Accepted 14 September 2013

Available online 26 September 2013

#### Keywords:

P compounds

Phosphonium

Glycolates

Zwitterionic compounds

### 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 ethereal 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<sub>2</sub>O. 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.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Hydroxyalkylations of primary and secondary phosphanes with aldehydes and ketones to  $\alpha$ -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  $\alpha$ -hydroxyalkyl-triphenylphosphoniumsulfonates [5]. In the course of investigations on phosphanyl glycines and heterocyclic  $\alpha$ -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  $\omega$ -phosphoniocarboxylates, available by reaction of tertiary phosphanes with  $\omega$ -haloalkancarboxylates [9], *N*-acyl bromoglycine derivatives [10], activated  $\alpha,\beta$ -unsaturated carboxylic acids [11] or by addition of CO<sub>2</sub> 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<sub>2</sub>PH 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<sub>2</sub>O 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  $\alpha$ -CH protons are

\* Corresponding author. Fax: +49 3834 864377.

E-mail address: [heinicke@uni-greifswald.de](mailto:heinicke@uni-greifswald.de) (J. Heinicke).