



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 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 D₂O. 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.

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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 phosphanyl glycines 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

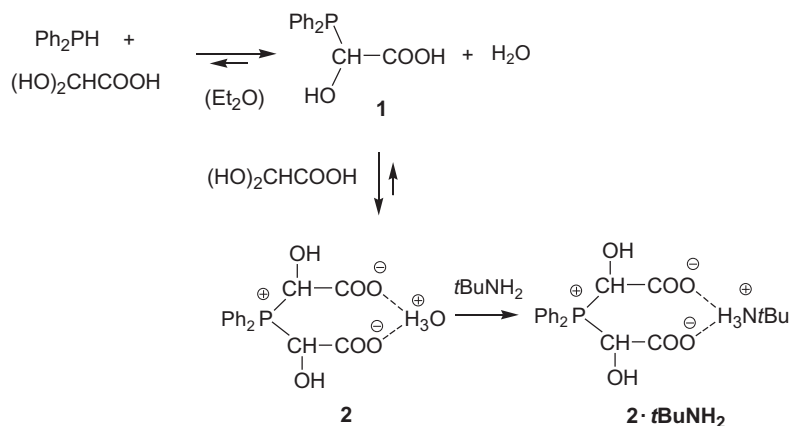
phosphane, the reactivity of glyoxylic acid hydrate toward diphenylphosphane and some tertiary phosphanes was studied. A condensation reaction with the latter should also open a facile way to the still unknown phosphonioglycolates and extend the variety of ω -phosphoniocarboxylates, available by reaction of tertiary phosphanes with ω -haloalkancarboxylates [9], *N*-acyl bromoglycine derivatives [10], activated α,β -unsaturated carboxylic acids [11] or by addition of CO₂ 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 Ph₂PH 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 D₂O 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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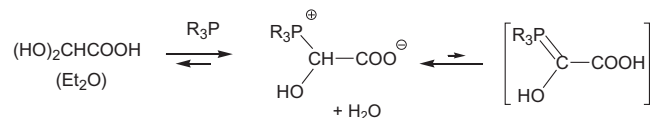
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Scheme 1. Formation of diphenylphosphanyl glycolic acids **1** and **2**.

rapidly exchanged against deuterium ions (see below). In the less acidic *tert*-butylammonium salt **2**·**tBuNH₂**, prepared for comparison of NMR data by addition of one equivalent of *t*BuNH₂ to freshly formed **2**, this H–D exchange is much slower.

Triorganyl phosphonioglycolates. The formation of **2** shows, that the reaction of phosphanes with aldehydes does not depend on the presence of a P–H function but only on the Lewis-base properties and the stability of the product, at least in the case of reactive aldehydes like glyoxylic acid. This inspired us to study also reactions with tertiary phosphanes, particularly triaryl phosphanes, since structurally related arylphosphonio keto compounds of the type $RPh_2P^+CH_2C(O)R' X^-$ are able to form ethylene oligomerization catalysts with Ni(COD)₂ in the presence of a further tertiary phosphane [13]. Triarylphosphanes were found to react in ethereal solution with glyoxylic acid monohydrate at room temperature with immediate formation of white precipitates of insoluble zwitterionic α -phosphonioglycolates **3a–d** (Scheme 2). However, these proved to be much less stable than **2**, particularly in the case of **3a**, and must be separated after 10–20 min to avoid consecutive reactions. To remove unconverted reactants and water they were washed with dry diethyl ether. The yields were moderate to good and increased in the order $R = Ph < m\text{-Tol} < p\text{-Tol} < p\text{-Anis}$. The more bulky tris-*o*-tolylphosphane, however, did not undergo a visible reaction, which hints at a marked steric impact on this reaction or the stability of the product. Similarly, pyruvic acid or phenylglyoxylic acid did not form precipitates with tris-*p*-tolylphosphane. The more P-basic trialkylphosphanes also form phosphoniumglycolates. *n*Bu₃P is distinguished from the arylphosphanes by formation of an oily condensation product **3e**, which separated in good yield from the ethereal phase but did not crystallize within four weeks at room temperature. The bulky tri-*tert*-butylphosphane also forms a viscous oily precipitate **3f**, but the yield was lower. Whereas unconverted diphenylphosphane was completely removed by repeated washing of the oil with ether, considerable amounts of unconverted glyoxylic acid or condensation products thereof [14] could not be separated from the product in this case.



R	Ph	<i>m</i> Tol	<i>p</i> Tol	<i>p</i> Anis	<i>n</i> Bu	<i>t</i> Bu
3	a	b	c	d	e	f

Scheme 2. Synthesis of phosphonioglycolates **3a–f**.

Diphosphanes, represented by the P-alkyldiphenyl-type 1,2-*bis*(diphenylphosphanyl) ethane (DPPE), reacted instantaneously with two equivalents of glyoxylic acid hydrate to give a white precipitate **3g** (Scheme 3). Due to the low solubility, the yield of **3g** was nearly quantitative. Reaction of excess glyoxylic acid hydrate with 2-diphenylphosphanylphenol furnished the phosphonioglycolate **3h**. The hydroxy-group in *ortho*-position suggests the possibility of further cyclocondensation reactions but neither a heterocyclic zwitterionic benzoxaphospholium-2-carboxylate nor a lactole structure could be detected. However, the elemental analysis and occurrence of a weak O–¹³CH–O carbon resonance ($\delta = 93.9$ ppm) in the carbon NMR spectrum account for addition of the excessive glyoxylic acid by the OH group as labile hemiacetale.

Usually, condensations of tertiary phosphanes with aldehydes require acid catalysts or reagents and trapping of the water to avoid the back or side reactions [4,5]. The intrinsic acidity of glyoxylic acid hydrate and the electron withdrawing effect of the COOH group at the acetalic reaction site act synergistically and enhance the reactivity, allowing rapid reaction under mild conditions. It is assumed that the proton either induces cleavage of water from the CH(OH)₂ moiety or adds to the oxygen of the free aldehyde carbonyl group, followed by addition of the nucleophilic phosphane at carbon. Diethyl ether seems particularly suitable for this reaction because of the solubility of the reactants and of the small amounts of water, formed in the condensation, but separation of the zwitterionic phosphonioglycolates by low solubility. The Lewis basicity of ether and ability to transfer protons in addition to the reactants may also play a role.

Properties. Isolated dry triarylphosphonioglycolates are much more stable than the crude products before separation but still decompose slowly under inert conditions at room temperature. A sample of **3a**, measured 4 months after the synthesis by ³¹P MAS NMR, displayed about 85% **3a**, 13% of triphenylphosphine oxide (**4a**) and traces of Ph₃P. A sample of **3g** with diarylalkyl substitution pattern, measured after 2 years, consisted still mainly of **3g**, but minor amounts of DPPE monoxide and dioxide were detected by ³¹P MAS NMR on the basis of their typical ³¹P NMR data [15]. Solution spectra repeated after prolonged storage of isolated **3a** and **c** also confirmed slow decomposition, much slower for **3c** (after 2 years only traces of **4c**) with the more P-basic starting phosphane than for **3a** (complete decomposition after one year). Fast decomposition takes place also for **3c** on heating. At 100 °C (1 h) it converted to a slightly brownish solid that dissolved only partly in CDCl₃, leaving a brown viscous residue. **4c**, *p*-Tol₃P and a small amount of an unidentified phosphine oxide or phosphonium compound (*p*-Me integral ratio ca. 60:30:10) as well as a

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