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Phosphonium bis(glycolates) and phosphinoglycolates: Synthesis, solvolysis, oxidation to (thio)phosphinoylglycolates and use as ligands in Ni-catalyzed ethylene oligomerization

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Dedicated to Prof. P.G. Jones on the occasion of his 60th birthday

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ABSTRACT

Secondary phosphines, glyoxylic acid hydrate and amines react to form organoammonium phosphonium bis(glycolates) **1a**–**d**. In CD_3OD solution, diphenylphosphonium bis(glycolates) undergo reversible solvolysis to phosphinoglycolates **2a**,**b** and acetalic glyoxylic species. The P-dialkyl species **1c** avoids this and maintains the phosphonium bis(glycolate) structure in CD_3OD (*c*Hex_2P) or undergoes further solvolysis with partial formation of R_2PH (R = *t*Bu). Condensation to phosphinoglycines, e.g. **3b**, observed for primary amines, does not take place with *N*-secondary amines at room temperature. Heating leads to condensation but is followed by decarboxylation as shown for the conversion of **2a** to **4a**. Because of the kinetic lability, the phosphonium compounds **1a**–**d** are sensitive to oxidation by air, H_2O_2, or sulfur. The resulting phosphinoyl and thiophosphinoyl glycolates and glycolic acids **5**–**8** are kinetically stable. Precatalyst solutions formed from **1a**, **c**, **d** and Ni(COD)$_2$ in THF developed moderate to good activity in the oligo- or polymerization of ethylene to linear products containing methyl and vinyl end groups. Activity and molecular weights increased with the +I-effect of the P-substitutents. The solution structures of the novel compounds were elucidated by multinuclear NMR spectroscopy. For **7a** a crystal structure analysis is also presented.

1. Introduction

Addition reactions of phosphines or phosphine oxides to aldehydes or ketones have long been studied [1,2] but the behaviour towards α-ketocarboxylic acids has attracted little attention. Concerning phosphines, to our knowledge only the condensation of 1-adamantylphosphine with two equivalents of glyoxylic acid to AdaP(CHOH-COOH)$_2$ has been reported [3]. More important was the reaction of the secondary phosphine oxide Me_2PHO with glyoxylic acid, which afforded the potent herbicide $Me_2P(O)CH(OH)COOH$ (Hoe704) [4,5]. Dimethylthiophosphinoylglycolic acid was synthesized analogously from $Me_2P(S)H$ and glyoxylic acid and structurally characterized by X-ray crystallography [6]. Finally, by reaction of secondary phosphine oxides or sulfides with pyruvic or benzoylformic acid or their esters, other types of 2-phosphinoyl 2-hydroxycarboxylic acids or their esters have also been obtained [7]. The latter also allowed kinetic resolution of enantiomers by lipases [8].

Our studies of the reactions of phosphines with glyoxylic acid are part of broader investigations on the synthesis and reactivity of α-phosphino amino acids [9], in particular phosphinoglycines [10], which extend the research of other groups on synthetic phosphino amino acids with the phosphino group in β- or γ-position or at a phenyl group [11–13]. For our one-pot synthesis of *N*-monosubstituted phosphinoglycines from primary amines, diphenylphosphine and glyoxylic acid hydrate, monitoring by NMR gave evidence of a stepwise condensation via organoammonium phosphinoglycolates. In reactions with secondary amines the second step was not observed. With *N*-methylaniline the corresponding diphenylphosphinoglycolate salt was isolated [10c], whereas in the reaction of diethylamine with dicyclohexylphosphine and glyoxylic acid hydrate (despite a 1:1:1 M ratio) diethylammonium dicyclohexylphosphoniumbis(glycolate) (**1a**) was obtained [10a]. This hints at a more complicated reaction behavior and prompted us to investigate such conversions as well as the properties and selected reactions of organoammonium phosphoniumbis- and phosphino-glycolates in more detail. Because of the close structural relationship of the phosphino glycolates with phosphino acetic acids [14], which are industrially used as catalyst ligands in the first step of the Shell Higher Olefin Process [15], the applicability as ligands in the nickel catalyzed ethylene oligomerization was also investigated.

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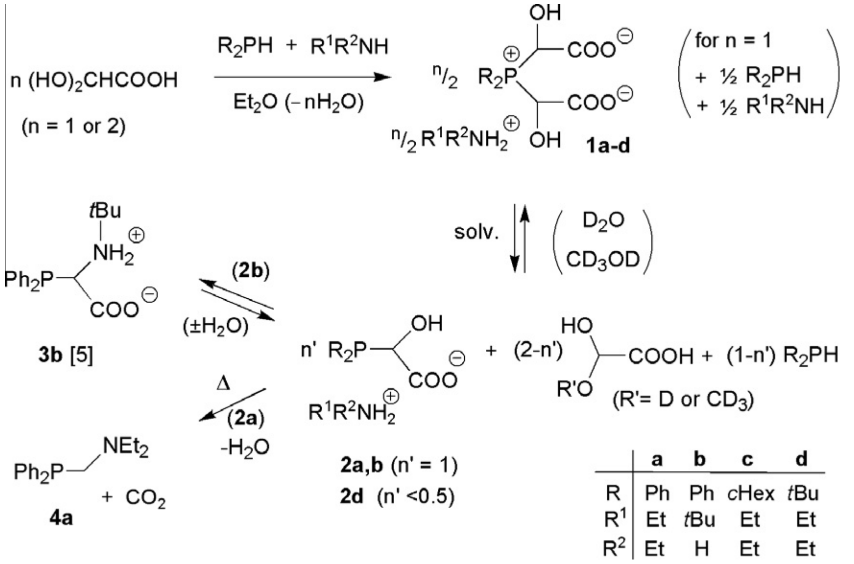

	a	b	c	d
R	Ph	Ph	cHex	tBu
R^1	Et	tBu	Et	Et
R^2	Et	H	Et	Et

Scheme 1. Formation and solvolysis of phosphonium bis(glycolates) and phosphinoglycolates.

2. Result and discussion

2.1. Phosphoniumbis(glycolates) and phosphinoglycolates

Our investigations began with the three component reaction of diphenylphosphine and diethylamine with glyoxylic acid hydrate in diethyl ether in a 1:1:1 M ratio. A few minutes after combining the solutions a white precipitate was formed. Elemental analyses and NMR spectra provided evidence that the product is the phosphoniumbis(glycolate) **1a** (yield 47%). When the synthesis was repeated in a 1:1:2 M ratio the yield of **1a** was improved to 70%. NMR spectra measured in D_2O confirmed the phosphoniumbis(glycolate) structure by two phosphorus resonances in the range of phosphonium signals (δ 27.7, 27.5 ppm) and two PCH doublets in the proton and ^{13}C NMR spectra. This was evidence of formation of both of the two diastereoisomer pairs, *rac* and *meso*, caused by the two asymmetric P-CH(OH) carbon centers. NMR spectra in CD_3OD, however, indicated solvolysis with formation of phosphinoglycolate **2a** and glyoxylic acid semiacetale (Scheme 1). Because crystallization of **1a** from a concentrated methanol solution still lead to the isolation of **1a**, the solvolysis must be an equilibrium reaction. This indicates that **2a** reacts with glyoxylic acid methanol semiacetale back to **1a** when the latter precipitates after exceeding its solubility. The phosphinoglycolate **2a** was obtained in high yield and with satisfying elemental analyses by reaction of the oil formed from glyoxylic acid and diethylamine in diethyl ether[2] with diphenylphosphine in THF. X-ray diffraction of crystals of **2a** confirmed the diethylammonium phosphino glycolate nature but poor crystallinity prevented sufficient refinement (R1 ca. 14%) to afford detailed data. In solution the structure was confirmed by ^{31}P, ^{13}C and ^{1}H NMR spectra. In contrast to **1a**, which decomposed in attempts to prepare $CDCl_3$ solutions by warming, **2a** was sufficiently soluble in this solvent to allow for measuring without interference by solvolysis reactions. Compound **2a** displayed the phosphorus resonance at δ 6.2 ppm and conclusive proton and ^{13}C doublets for P*CH*OH in the OCH signal range. In D_2O and CD_3OD solutions, however, signals due to solvolysis equilibria were observed. Attempts to achieve conversion of **2a** to the *N*,*N*-disubstituted diphenylphosphinoglycin **3a** by thermally induced condensation failed due to facile decarboxylation, leading to the formation of the known [16] diethylaminomethylphosphine **4a**.

To evaluate if primary alkylamines, which form *N*-monosubstituted phosphinoglycines in the 1:1:1 three-component reaction with diphenylphosphine and glyoxylic acid hydrate in diethyl ether [10a–c], are able to provide phosphoniumbis(glycolates), the behavior of *N*-*tert*-butyl-diphenylphosphinoglycine (**3b**) towards glyoxylic acid hydrate was studied. On dissolution of **3b** in D_2O, solvolysis to **2b** (δ 6.7 ppm) was observed. Stronger dilution with water or aqueous NaOH(D) caused further decomposition with formation of Ph_2PH and Ph_2PD. The addition of small amounts of acetic acid, which binds the *tert*-butylammonium cations as acetate, led to the appearance of the signals of **1b**, i.e. phosphorus signals for two pairs of diastereoisomers and two P*CH*O proton and carbon doublets, which is indicative for the phosphoniumbis(glycolate). A quantitative conversion of **3b** to **1b** was observed in D_2O solution by addition of an equimolar amount of glyoxylic acid hydrate. The NMR spectra of the white precipitate, measured in D_2O solution, indicated pure **1b**. In analogy to **1a**, in CD_3OD, a solvolysis equilibrium of **1b** with formation of monoglycolate **2b**, glyoxylic acid CD_3OH-semiacetale and smaller amounts of **3b** along with partial decarboxylation to **4b** were observed (δ ^{31}P 27.2, 26.1; 7.4, 3.1, −19.9 ppm; rel. int. 8:6:60:14:12%).

In addition to diphenylphosphine, dicyclohexyl- and di-*tert*-butylphosphine were also used in this study to evaluate the behavior of the more P-basic dialkylphosphines to this condensation. The reactions with diethylamine and glyoxylic acid hydrate (molar ratios ca. 1:1:1) proceeded analogous to the above conversions, and instead of monoglycolates, they furnished phosphinobis(glycolates) **1c** and **1d**; these were identified by elemental analysis and solution NMR spectra. The solution of **1c** in D_2O and also in CD_3OD displayed the signals characteristic for the *rac*/*meso* bis(glycolates). Only a trace of the solvolysis product **2c** was observed in CD_3OD. The bulky di-*tert*-butylphosphine derivative **1d** was sufficiently soluble in $CDCl_3$ to allow for characterization by solution NMR spectra but suffered from partial decomposition to tBu_2PH and glyoxylic acid derivatives and was labile in D_2O or CD_3OD solution. In these solvents mixtures were formed including large amounts of tBu_2PH. The monoglycolate **2d** was prepared in an inverse procedure with addition of tBu_2PH to a THF solution of diethylammonium glyoxylate (molar ratio ca. 1:1:1, 10% excess of Et_2NH). Product separation with extraction by diethyl ether lead to a product that could be conclusively characterized by NMR in $CDCl_3$

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[2] Proton and carbon NMR spectra indicate formation of diethylammonium glyoxylate hydrate along with small signals of a labile hemiaminal (see supplementary data).