

Wasserlösliche Phosphane, XIV [1]

## Hydrophile Derivate des Triphenylphosphans mit NH<sub>2</sub>-, COOH- und P(O)(OR)<sub>2</sub>-funktionalisierten Seitenketten

Water Soluble Phosphanes, XIV [1].

Hydrophilic Derivatives of Triphenylphosphane with NH<sub>2</sub>, COOH and P(O)(OR)<sub>2</sub> Functionalized Side Chains

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Aminomethyl, Carboxymethyl, Phosphanomethyl Derivatives,  $\alpha$ -Amino- and  $\alpha$ -Hydroxymethyl Phosphonic Acid and Phosphane Oxide Derivatives, 2-Diphenylphosphano Cinnamic Acid

Nucleophilic phosphanylation of *ortho*-fluorophenylacetic acid or *ortho*-fluorobenzylamine with PhPH<sub>2</sub> using KO<sup>t</sup>Bu as the base affords the hydrophilic tertiary phosphanes **3** and **4a** with terminal CH<sub>2</sub>-COOH and CH<sub>2</sub>-NH<sub>2</sub> substituents. The corresponding secondary phosphane ligands **2** or **5** may be obtained by Pd-catalyzed P-C coupling of *ortho*-iodophenylacetic acid with PhPH<sub>2</sub> or selective nucleophilic phosphanylation of *ortho*-fluorophenylacetic acid. Novel phosphonomethyl derivatives **7a**, **7b** of triphenylphosphane have been obtained in a two stage synthesis using *ortho*-iodobenzylchloride or *meta*-iodobenzylbromide as starting materials. Arbusov reaction with P(OEt)<sub>3</sub> and Pd-catalyzed P-C coupling reactions with Ph<sub>2</sub>PH gave the esters **7a**, **7b**. Purification of **7a** was achieved via its BH<sub>3</sub> adduct **8a**. Deprotection, hydrolysis and neutralisation with NaOH affords the water soluble sodium salts **9a,9b**.  $\alpha$ -Hydroxy and  $\alpha$ -benzylamino derivatives **12** and **14** of *ortho*-diphenylphosphanobenzyl phosphonate (e.g. **7a**) and the corresponding Me<sub>2</sub>P(O) analogs **13** and **16** are accessible in a straightforward manner by addition of (MeO)<sub>2</sub>P(O)H or Me<sub>2</sub>P(O)H to *ortho*-phosphanobenzaldehyde **11a** or its benzaldimino derivative **15**, respectively. An improved synthesis for **11a-11c** has been developed. Reaction of **11a** with the Wittig reagent Ph<sub>3</sub>P=C(H)COOEt and subsequent hydrolysis of the intermediate ester **17a** affords *ortho*-diphenylphosphano cinnamic acid **17**. The catalytical activity of **1**, **9a**, **9b** and related ligands in Suzuki-type coupling reactions has been investigated.