Wasserlösliche Phosphane, XIV [1]
Hydrophile Derivate des Triphenylphosphans mit NH₂-, COOH- und P(O)(OR)₂-funktionalisierten Seitenketten
Water Soluble Phosphanes, XIV [1],
Hydrophilic Derivatives of Triphenylphosphane with NH₂, COOH and P(O)(OR)₂ Functionalized Side Chains
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Aminomethyl, Carboxymethyl, Phosphanomethyl Derivatives, α-Amino- and α-Hydroxy-
methyl Phosphonic Acid and Phosphane Oxide Derivatives, 2-Diphenylphosphano Cinnamic Acid

Nucleophilic phosphanylation of ortho-fluorophenylacetic acid or ortho-fluorobenzylamine
with PhPH₂ using KOtBu as the base affords the hydrophilic tertiary phosphanes 3 and 4a with
terminal CH₂-COOH and CH₂-NH₂ substituents. The corresponding secondary phosphane ligands 2 or 5 may be obtained by Pd-catalyzed P-C coupling of ortho-iodophenylacetic acid
with PhPH₂ or selective nucleophilic phosphanylation of ortho-fluorophenylacetic acid. Novel
phosphonatomethyl derivatives 7a, 7b of triphenylphosphate have been obtained in a two sta-
gge synthesis using ortho-iodobenzylchloride or meta-iodobenzylbromide as starting materials.
Arbusov reaction with P(OEt)₃ and Pd-catalyzed P-C coupling reactions with Ph₃PH gave the
esters 7a, 7b. Purification of 7a was achieved via its BH₃ adduct 8a. Deprotection,
hydrolysis and neutralisation with NaOH affords the water soluble sodium salts 9a, 9b. α-Hydroxy and
α-benzylamino derivatives 12 and 14 of ortho-diphenylphosphonobenzyl phosphonate (e.g. 7a)
and the corresponding Me₂P(O) analogs 13 and 16 are accessible in a straightforward manner
by addition of (MeO)₂P(O)H or Me₂P(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 Ph₃P=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.