New Method for Synthesis of Methylenebis(diarylphosphine) Monoxides

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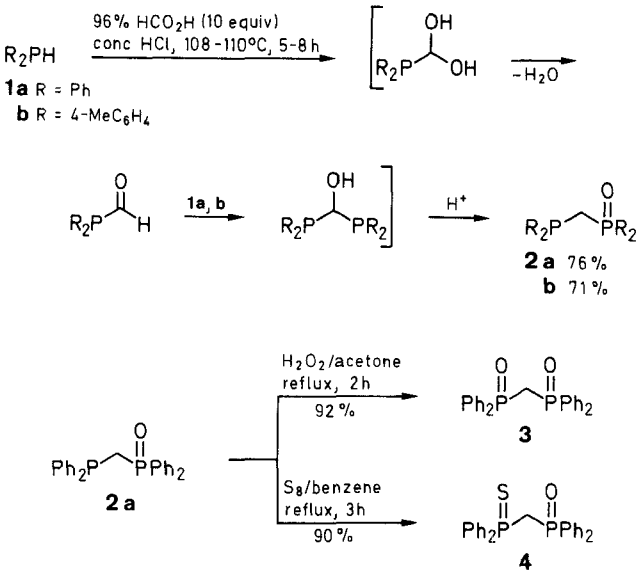
Synthesis of methylenebis(diphenyl- and methylenebis(di-*p*-tolylphosphine) monoxides, via the reaction of diarylphosphines with formic acid in presence of concentrated hydrochloric acid is described. Methylenebis(diphenylphosphine) monoxide is oxidized with hydrogen peroxide and sulfur into the corresponding methylenebis(diphenylphosphine) dioxide and methylenebis(diphenylphosphine) monoxide monosulfide. Attempts to carry out this reaction with butylphenyl- and dibutylphosphines failed.

Methylenebis(diphenylphosphine) monoxide **(2a)** is used as a ligand in complexes of chromium, molybdenum, vanadium,[1] platinum and palladium[2,3] as well as rhodium.[4,6] In latter case the complexes are used as catalysts in olefin hydroformylation[4] and carboxylic acid anhydride carbonylation.[5] Moreover, monoxide **2a** is a starting compound for the synthesis of β-substituted *trans*-(diphenylphosphino)ethylenes and their derivatives[7] via the reaction with aromatic aldehydes which occurs regio- and stereospecifically.

Monoxide **2a**, first described in 1975,[1] was produced by the reaction of diphenylchlorophosphine with diphenylphosphinomethyllithium[1,3] as well as by alkylation of methylenebis(diphenylphosphine) with benzyl bromide followed by the alkaline decomposition of the resulting (phosphinomethyl)diphenylbenzylphosphonium bromide.[8]

A convenient synthesis of monoxides **2a,b** from diarylphosphines **1a,b** and formic acid in presence of concentrated hydrochloric acid is described.

A tenfold excess of formic acid is used as solvent and the reaction is completed in 5–8 h by refluxing a mixture of starting reagents. By oxidation with hydrogen peroxide and sulfur, monoxide **2a** is converted to methylene bis(diphenylphosphine) dioxide **(3)** and methylenebis(diphenylphosphine) monoxide monosulfide **(4)**, respectively.



Attempts to carry out the same reaction with butylphenyl- and dibutylphosphines failed. After prolonged refluxing, the reaction mixture contained, as indicated by ^{31}P-NMR spectroscopy, the starting phosphines.

Diphenylphosphine (**1a**) was obtained by thermal disproportionation of diphenylphosphinous acid in presence of the catalytic amounts of diphenylphosphinic acid.[9]

All operation with P(III) compounds were conducted under argon. Melting points were measured with Anschütz thermometers. ^{31}P-{^{1}H} NMR spectra were recorded on Bruker AC-200 spectrometer, using 85% H_3PO_4 as external standard.

Diphenylphosphine (1a):
A mixture of diphenylphosphinous acid (101.0 g, 500 mmol) and diphenyl phosphinic acid (5.5 g, 25 mmol) is heated in Claisen flask at 165–175 °C (in a bath) for 15 min and then diphenylphosphine is distilled off (41.3 g, 94%, bp 141–143 °C/6 Torr).[12] The residue is dissolved at 80–90 °C in 20% NaOH (10.0 g, 250 mmol). Then the solution is washed with $CHCl_3$ and filtered. The filtrate is acidified with HCl and the resulting precipitate is filtered off and dried in air; yield: 54.5 g (100%); mp 191–193 °C.

Methylenebis(diphenylphosphine) Monoxide (2a); Typical Procedure:
A stirred mixture of diphenylphosphine (**1a**; 5.3 g, 28 mmol), 96% HCO_2H (10 mL, 280 mmol) and conc HCl (5 mL) is refluxed at 108–110 °C for 5 h. Then it is extracted with $CHCl_3$ (30 mL). The extract is washed with aq $NaHCO_3$, dried (Na_2SO_4) and evaporated *in vacuo*. The residue is recrystallized from DMF; yield: 4.2 g (76%); mp 187.5–188.5 °C (DMF) (Lit.[1] mp 191–192 °C).

^{31}P-NMR (DMF/85% H_3PO_{4ext}: $\delta = -26.4$ (P), 27.9 (PO), $J_{pp} = 50.5$ Hz.

Methylenebis(di-*p*-tolylphosphine) Monoxide (2b):
Obtained in a similar manner to monoxide **2a** from di(*p*-tolyl)phosphine (**1b**)[13] (2.3 g, 10.7 mmol), 96% formic acid (4 mL, 107 mmol) and conc. HCl (3 mL) by refluxing for 8 h; yield: 1.7 g (71%); mp 166–167 °C (EtOAc/EtOH).

$C_{29}H_{30}OP_2$ (456.5) calc. C 76.30 H 6.62 P 13.57
found 76.02 6.73 13.19

^{31}P-NMR (DMF/85% $H_3PO_{4ext} = -28.5$ (P), 28.0 (PO), $J_{pp} = 47.8$ Hz.

Methylenebis(diphenylphosphine) Dioxide (3):
Monoxide **2a** (8.0 g, 20.8 mmol) is refluxed with 30% H_2O_2 (8.5 mL, 83.2 mmol) in acetone (60 mL) for 2 h. Then it is evaporated *in vacuo* at 50 °C, the residue is dissolved in $CHCl_3$ (40 mL). The solution is washed with acidified aq. $FeSO_4$ (30 mL), H_2O (30 mL) and aq. $NaHO_3$ (30 mL), dried (Na_2SO_4) and evaporated *in vacuo*. The residue is recrystallized from EtOAc; yield: 7.9 g (92%); mp 186–186.5 (EtOAc) (Lit.[10] mp 181–182 °C).

^{31}P-NMR (EtOH/85% H_3PO_{4ext}: $\delta = 28.4$ (PO).

Methylenebis(diphenylphosphine) Monoxide Monosulfide (4):
Monoxide **2a** (5.0 g, 12.5 mmol) is refluxed with sulfur (0.4 g, 12.5 mmol) in benzene (50 mL) for 3 h. The resulting solution is evaporated *in vacuo*, the residue is recrystallized from benzene/EtOAc; yield: 4.9 g (90%); mp 216.5–217 °C (benzene/EtOAc) (Lit.[11] mp 212–214 °C).

^{31}P-NMR ($CHCl_3$/85% H_3PO_{4ext}): $\delta = 24.5$ (PO), 36.6 (PS).

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