A Convenient Method for the Synthesis of 1-Adamantyldichlorophosphine

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1-Adamantyldichlorophosphine is obtained in good yield by reduction of 1-adamantyldichlorophosphine sulfide with triphenylphosphine in toluene. It can be quantitatively reduced to 1-adamantylphosphine with lithium alanate in ether.

Adamantane derivatives are excellent model compounds due to their unique skeletal geometry and rigidity. Although oxygen-, nitrogen-, sulfur-, halogen-, and silicon-containing adamantane derivatives are being extensively investigated only few reports on the synthesis of phosphorus-containing adamantanes have hitherto appeared.[1-4]

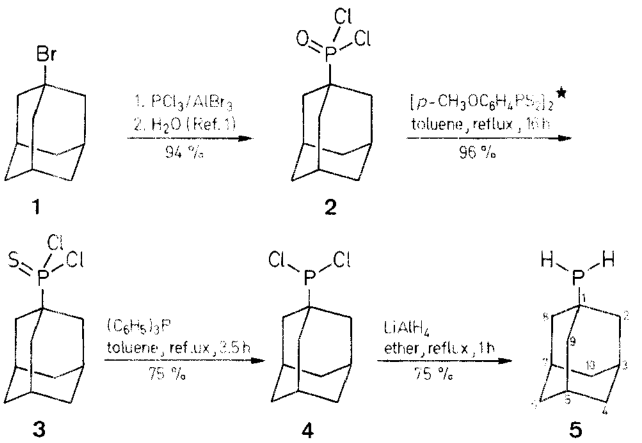
Dihalophosphines are attractive ligands in coordination chemistry and starting materials in organophosphorus chemistry. Today, there still is no efficient method for the direct synthesis of dihalogenophosphines. The most suitable method for their synthesis is the Friedel-Crafts alkylation of phosphorus(III) chloride.[1] However this method[1,3] requires the reduction of 1-adamantyldichlorophosphine oxide with lithium aluminium hydride and affords only low yields.

Here, we report the synthesis of 1-adamantyldichlorophosphine (**4**) by an efficient reduction method which avoids formation of 1-adamantylphosphine and leads to 1-adamantyldichlorophosphine by a three-step sequence in an overall yield of 68% (Scheme).

Yellow crystalline 1-adamantyldichlorophosphine oxide (**2**) is prepared in nearly quantitative yield according to Lit.[1] Reaction of compound **2** with Lawesson reagent[5] in boiling toluene for 16 hours affords 1-adamantyldichlorophosphine sulfide (**3**) in nearly quantitative yield. Heating of this product with triphenyl-

Table. ^{13}C-NMR and ^{31}P-NMR Data of Compounds 1–5

Compound	^{13}C-NMR (C_6D_6/TMS$_{int}$)								^{31}P-NMR (C_6D_6/85% H_3PO_{4ext}) δ (ppm)
	C-1		C-2, C-8, C-9		C-3, C-5, C-7		C-4, C-6, C-10		
	δ(ppm)	$^1J_{CP}$(Hz)	δ(ppm)	$^2J_{CP}$(Hz)	δ(ppm)	$^3J_{CP}$(Hz)	δ(ppm)	$^4J_{CP}$(Hz)	
1	65.5		35.8		32.9		49.65		
2	49.05	88.09	35.2	4	27.83	15.3	35.9	2.8	61.3
3	52.8	59.1	35.4	3.53	28.2	15.1	35.7	2.9	113
4	41.6	48.1	34.9	16.1	28.2	9.2	36.6	1	190.9
5	47	43.9	45.1	8.6	29.4	7.7	36.6	0.9	−83.6 ($^1J_{PH}$ = 189 Hz)



★Lawesson's Reagent

phosphine in boiling toluene for 3.5 hours leads to 1-adamantyldichlorophosphine (**4**) which is isolated as a colorless solid in 75% yield. Compound **4** can be quantitatively reduced to 1-adamantylphosphine (**5**) with lithium aluminium hydride in ether.

The position of the P-atom at C-1 of the adamantane skeleton was confirmed by ^{13}C-NMR spectrometry. Thus, for compounds **2**–**5** only four doublets appear in the spectrum due to the four types of C-atoms with respect to the P-atom: C-1; C-2, C-8, C-9; C-3, C-5, C-7; C-4, C-6, C-10.

All reactions are carried out under an inert gas (argon).

1-Adamantyldichlorophosphine Oxide (2):[1]
To a solid mixture of 1-bromoadamantane (**1**; 14.6 g, 68 mmol) and aluminium bromide (26.4 g, 99 mmol), phosphorus(III) chloride (135 ml, 1.55 mol) is added dropwise at room temperature. The mixture is refluxed for 5 h, then allowed to gradually cool to room temperature. The mixture is filtered and washed with benzene (60 ml). The addition of carbon tetrachloride (450 ml) gives a suspension, which is hydrolyzed by ice/water (200 ml). The organic layer is separated, dried with anhydrous sodium sulfate and evaporated to give product **2** as yellow crystals; yield: 18.3 g (94%); m.p. 101–102 °C.

$C_{10}H_{15}Cl_2OP$ calc. C 47.45 H 5.95 P 12.24
(253.1) found 47.48 5.91 12.29

IR (KBr): ν = 1265 (PO); 540 (P-Cl) cm^{-1}.

1-Adamantyldichlorophosphine Sulfide (3):
To a stirred suspension of Lawesson reagent (13.1 g, 32 mmol) in toluene (80 ml) is added under stirring a solution of 1 adamantyldichlorophosphine oxide[1] (**2**; 8.1 g, 32 mmol) in toluene (60 ml). The mixture is refluxed during 16 h, then cooled, and filtered. The filtrate is evaporated and the residual matter is dissolved in ether (150 ml). Unreacted Lawesson reagent is precipitated by addition of hexane. The mixture is filtered and the solvent removed to give compound **3** as colorless crystals; yield: 8.3 g (96%); m.p. 128–130 °C.

$C_{10}H_{15}Cl_2PS$ calc. C 44.62 H 5.62 P 11.91 S 11.50
(269.2) found 45.42 5.79 11.68 11.74

MS (FD): m/e = 268 (^{35}Cl-M$^+$).

IR (KBr): ν = 720 (PS); 510 (P-Cl) cm^{-1}.

1-Adamantyldichlorophosphine (4):
A solution of 1-adamantyldichlorophosphine sulfide (**3**; 8.8 g, 33 mmol) in degassed toluene (50 ml) is added dropwise to a stirred solution of triphenylphosphine (8.6 g, 33 mmol) in degassed toluene (50 ml). The mixture is refluxed in the dark for 3.5 h. After cooling, the solvent is removed and the residual oil distilled under reduced pressure (50 °C/0.01 torr) to give product **4** as colorless crystals; yield: 5.9 g (75%); m.p. 54–55 °C.

$C_{10}H_{15}Cl_2P$ calc. C 50.66 H 6.37 P 13.06
(237.1) found 51.50 6.27 11.47

MS (FD): m/e = 236 (^{35}Cl-M$^+$).

IR (KBr): ν = 490 (P-Cl) cm^{-1}.

1-Adamantylphosphine (5):
A solution of 1-adamantyldichlorophosphine (**4**; 0.5 g, 2.11 mmol) in dry ether (4 ml) is added dropwise to a stirred suspension of lithium aluminium hydride (0.29 g, 7.6 mmol) in anhydrous ether (3 ml). The mixture is heated to reflux for 1 h, then allowed to gradually cool to room temperature. It is hydrolyzed with 35% hydrochloric acid. The aqueous layer is extracted with ether (3 × 10 ml). The organic layers are combined, dried with anhydrous sodium sulfate, and evaporated. The residue is purified by distillation to afford **5** as an oil; yield: 0.27 g (75%); b.p. 75 °C/0.01 torr).

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