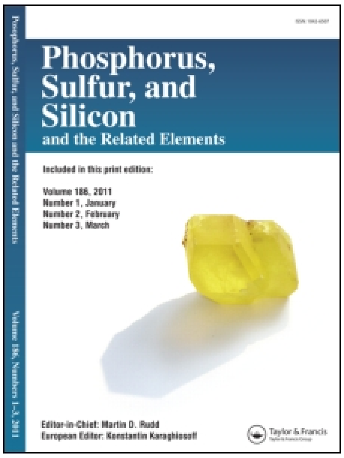

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ORGANOPHOSPHORUS COMPOUNDS WITH TERTIARY ALKYL SUBSTITUENTS. VI[1]: A CONVENIENT METHOD FOR THE PREPARATION OF DI-1-ADAMANTYLPHOSPHINE AND DI-1-ADAMANTYLCHLOROPHOSPHINE

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ORGANOPHOSPHORUS COMPOUNDS WITH TERTIARY ALKYL SUBSTITUENTS. VI[1]: A CONVENIENT METHOD FOR THE PREPARATION OF DI-1-ADAMANTYLPHOSPHINE AND DI-1-ADAMANTYLCHLOROPHOSPHINE

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Di-1-adamantylchlorophosphine **3** is obtained by a three step sequence from commercially available adamantane. Despite the bulky 1-adamantyl groups at the phosphorus atom, it reacts readily with water to give di-1-adamantylphosphine oxide **4**.

Key words: 1-Adamantyl phosphorus compounds, Friedel-Crafts reaction, H/D-exchange, NMR.

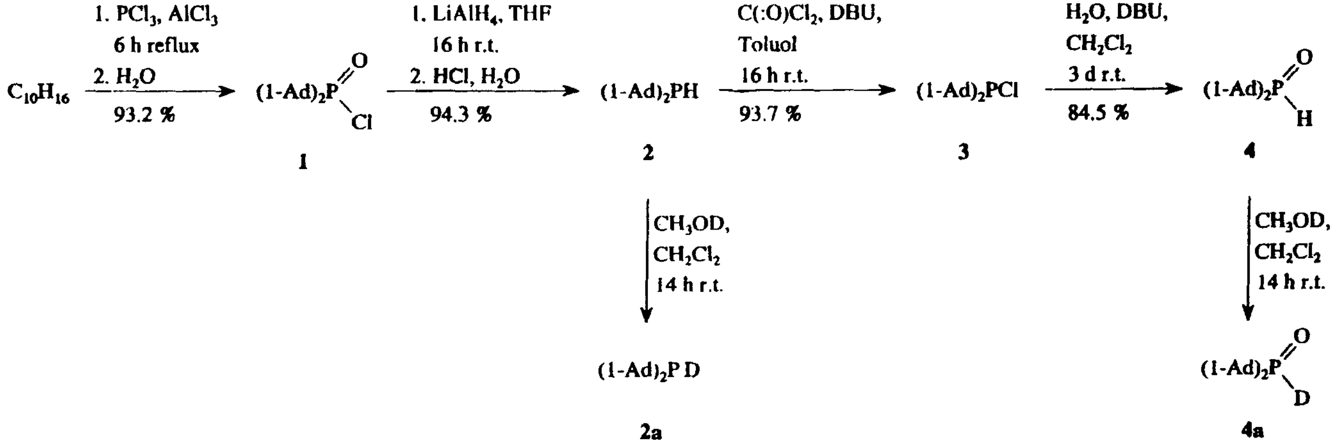
INTRODUCTION

Diorganochlorophosphines are of great utility as starting materials in organo-element- and co-ordination chemistry.[2,3] Steric protection of the phosphorus atom is often used for the kinetic stabilization of thermodynamically unstable molecules.[4] Compared with ^{t}butyl-substituted phosphorus compounds, the analogous 1-adamantyl compounds are of higher stability due to their higher molecular weight and the rigidity of the adamantyl cage.[5-8] While di-^{t}butylphosphine and -chlorophosphine are extensively used in organophosphorus chemistry, the difficulties in preparing and handling 1-adamantyl lithium or 1-adamantyl magnesium reagents[9,10] have hitherto prevented a more widespread application of the analogous 1-adamantyl-substituted compounds.

After a convenient synthesis of 1-adamantyldichlorophosphine is known since 1987,[11] the recently observed di-substitution of PCl_3 with adamantane under Friedel-Crafts conditions[12,13] enables the high yield synthesis of di-1-adamantylphosphine and -chlorophosphine in a simple and efficient way (Scheme I).

RESULTS AND DISCUSSION

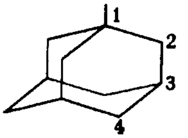
Light yellow di-1-adamantylphosphinic chloride **1** was obtained as an amorphous solid in 93.2% yield by refluxing a mixture of adamantane and aluminium trichloride in phosphorus(III) chloride, followed by hydrolysis.[12,13] Reduction of **1** with lithium aluminium hydride in tetrahydrofuran led to di-1-adamantylphosphine **2** in nearly quantitative yield.[12,14] By treatment of **2** with phosgene (as a 20% solution in



SCHEME I Synthesis of compounds **1**–**4**, **2a** and **4a**.

TABLE I

^{1}H-, ^{13}C- and ^{31}P-NMR data of compounds **1–4**



No.	δ(P)	δ(H)	δ(C^1) ^{1}J(PC)	δ(C^2) ^{2}J(PC)	δ(C^3) ^{3}J(PC)	δ(C^4) ^{4}J(PC)
1	86.51	1.75 - 2.17 ($C_{10}\underline{H}_{15}$)	45.61	36.83	27.79	36.32
			60.01	2.20	10.86	1.55
2	18.23	1.56 - 1.93 ($C_{10}\underline{H}_{15}$)	34.05	43.32	28.75	36.70
	^{1}J(PH) 209.1	2.70 (P$\underline{H}$)	15.29	9.84	7.97	
3	138.45	1.66 - 2.05 ($C_{10}\underline{H}_{15}$)	40.06	36.07	27.14	36.30
			42.31	1.10	10.33	
4	60.40	1.53 - 1.93 ($C_{10}\underline{H}_{15}$)	37.68	36.60	27.45	36.54
	^{1}J(PH) 427.0	5.52 (P(:O)$\underline{H}$)	60.62		9.60	

The NMR investigations were carried out at room temperature with $CDCl_3$ as solvent.

toluene) in the presence of 1,8-diaza[5.4.0]undec-7-en (DBU) di-1-adamantylchlorophosphine **3** was obtained as a pale yellow solid which was found pure by ^{1}H- and ^{31}P-NMR-spectroscopy. Further purification of **3** is possible by recrystallization from PCl_3/n-hexane (1:1). In contrast to this, the same reaction using triethylamine as a base gave the desired product **3** only in poor yield.[7] (The base strength of DBU is also high enough to liberate $(1\text{-Ad})_2PI$ from the highly stable phosphonium salt $[(1\text{-Ad})_2P(H)I]^+I^-$[7,15]).

When a solution of **3** in dichloromethane was stirred with water in the presence of catalytic amounts of DBU, quantitative hydrolysis with formation of di-1-adamantylphosphine oxide **4**[13] as the only product was observed.

When solutions of **2** or **4** in a mixture of CH_2Cl_2/CH_3OD were kept for 14 hours at room temperature quantitative exchange of the P-H protons for deuterium with formation of **2a** and **4a** was found to occur.

^{1}H-, ^{13}C- and ^{31}P-NMR data of **1–4** are presented in Table I.

EXPERIMENTAL

Adamantane and DBU were purchased from Janssen Chimica, phosgene (20% solution in toluene) from Fluka. Tetrahydrofuran was dried over KOH, toluene over sodium. Melting points are uncorrected. NMR: Bruker AC 200. MS: Finnigan MAT 8430. Further experimental details: Lit.[5].

Di-1-adamantylphosphinic chloride 1

A mixture of 200 g (1.47 mol) of adamantane, 210 g (1.57 mol) of aluminium(III) chloride and 650 ml of phosphorus(III) chloride was refluxed for 6 h. Then the excess of phosphorus(III) chloride was distilled off until a viscous substance remained. After addition of 1.5 l of chloroform the resulting suspension was cautiously hydrolyzed with 1 l of an ice/water mixture. After separation of the layers, the organic layer was dried over sodium sulfate and evaporated to give **1** as a faintly yellow solid. Yield: 259.4 g (93.2%); mp.: 195°C (Lit.[12]: 95%; mp.: 197–199°C).

$C_{20}H_{30}ClOP$ (352.88)
MS (70 eV): m/z (%) = 352 (3) $[M]^+$, 135 (100) $[C_{10}H_{15}]^+$.

Di-1-adamantylphosphine **2**

To a solution of 40 g (0.11 mol) of di-1-adamantylphosphinic chloride **1** in 400 ml of THF, cooled to −14°C by an ice/sodium chloride mixture, was added 10 g (0.26 mol) of lithium aluminium hydride in 1 g portions over a period of 60 min. After warming to room temperature, the reaction mixture was stirred for 16 h, again cooled to −14°C, and hydrolyzed with 200 ml of 1 M hydrochloric acid. After separation of the layers, the organic layer was dried over sodium sulfate and evaporated to give pure di-1-adamantylphosphine **2** as a colourless, amorphous solid. Yield: 31.4 g (94.3%); mp.: 132°C (Lit.[14]: 86.0%; mp.: 134°C).

$C_{20}H_{31}P$ (302.44)
MS (70 eV): m/z (%) = 302 (4) $[M]^+$, 135 (100) $[C_{10}H_{15}]^+$.

Di-1-adamantylchlorophosphine **3**

At −14°C to a solution of 4.04 g (13.4 mmol) of di-1-adamantylphosphine **2** and 2.41 g (15.8 mmol) of DBU in 100 ml of toluene were added 10 g of a 20% solution of phosgene in toluene (corresponding to 2 g/20.2 mmol phosgene) over a period of 20 min. The colour of the solution changed to pale yellow and the evolution of gas (carbon monoxide) and the formation of a solid (DBU·HCl) were observed, when the reaction mixture was stirred for 16 h at room temperature. After filtration and removal of the solvent in vacuo (0.1 mm Hg), di-1-adamantylchlorophosphine **3** was isolated as a pale yellow solid, which was washed twice with 10 ml of n-hexane and dried in vacuo (0.1 mm Hg). The ^1H- and ^{31}P-NMR spectra showed that the remaining solid was pure **3**. Yield: 4.23 g (93.7%); mp.: 148°C (Lit.[13]: 27.9 %; mp.: 148–150°C). Recrystallization of **3** from n-hexane/PCl_3 (1:1) led to a product with a slightly increased melting point (150°C).

$C_{20}H_{30}ClP$ (336.88)
MS (70 eV): m/z (%) = 336 (5) $[M]^+$, 135 (100) $[C_{10}H_{15}]^+$.

Di-1-adamantylphosphine oxide **4**

A solution of 3.82 g (11.3 mmol) of di-1-adamantylchlorophosphine **3**, 1.0 g (55.5 mmol) of water, and 0.1 ml of DBU in 40 ml of dichloromethane was stirred for 3 d at room temperature. After removal of the solvent in vacuo (0.1 mm Hg) di-1-adamantylphosphine oxide **4** was isolated as a colourless solid, which was purified by recrystallization from n-hexane. Yield: 3.04 g (84.5%); mp.: 257°C (Lit.[12]: 255–258°C).

$C_{20}H_{31}OP$ (318.44)
MS (70 ev): m/z (%) = 318 (18) $[M]^+$, 135 (100) $[C_{10}H_{15}]^+$.

H/D Exchange in **2** *and* **4** *with formation of* **2a** *and* **4a**

Solutions of 0.30 g (1 mmol) of di-1-adamantylphosphine **2** and 0.32 g (1 mmol) of di-1-adamantylphosphine oxide in 5 ml of dichloromethane/3 ml of CH_3OD were stirred for 14 h at room temperature. Subsequently the solutions were investigated by ^{31}P-NMR-spectroscopy.

2a: ^{31}P-NMR (CH_2Cl_2/CH_3OD): $\delta = 18.27$ [t, $^1J(PD)$ 32.1].
4a: ^{31}P-NMR (CH_2Cl_2/CH_3OD): $\delta = 60.54$ [t, $^1J(PD)$ 66.1].

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