A Convenient and Facile Synthesis of Dialkylphosphines

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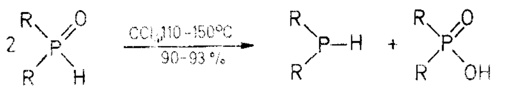
A series of simple dialkylphosphines **2** has been prepared by the thermal disproportionation of dialkylphosphine oxides **1** induced by the $R_2P(O)Cl/R_2PCl$ system, generated *in situ* from **1** with a catalytic amount of carbon tetrachloride.

Simple dialkylphosphines **2** can be prepared by means of various methods.[1] The most convenient in laboratory practice, however, is a thermal disproportionation of dialkylphosphine oxides **1**.[2,3]



1a-e **2a-e**

Such disproportion usually proceeds efficiently at high temperatures (**1a**; 180–200 °C; Ref.[2]) and requires relatively long time (**1e**; 24 h; Ref.[3]). It has been recently shown that the disproportionation of **1** is efficiently accelerated by the dialkylphosphinic chloride/dialkylchlorophosphine ($R_2P(O)Cl/R_2PCl$) system, which can be generated „in situ" when **1** is subjected to chlorination with a catalytic amount of carbon tetrachloride.[4]

Herein we wish to report the application of this system for the synthesis of simple dialkylphosphines. It has been found that the most efficient synthetic procedure for dialkylphosphines of low molecular weight (**2a, b, c**) involves heating of the appropriate dialkylphosphine oxide **1** in the presence of 1–2 mol % of carbon tetrachloride with continuous removal of the phosphine **2** by distillation.

For secondary phosphines of higher molecular weight (**2e**), the best result is obtained when the respective mixture of **1** with ~ 2 mol % of carbon tetrachloride is heated in a sealed tube at 150 °C for 2 h and than distilled. A slightly modified procedure can be applied for the preparation of diallylphosphine (**2d**), which easily undergoes polymerization even at room temperature. This modification involves preliminary heating of the starting diallylphosphine oxide (**1d**) with a small quantity of carbon tetrachloride under normal pressure to produce a small amount of diallylchlorophosphine, which is essential to induce the subsequent thermal disproportionation under reduced pressure. The structure of **2d** was confirmed by elemental analysis and spectral data.[5]

All boiling points are uncorrected. Starting materials, diethylphosphine oxide,[2] di-*n*-propylphosphine oxide,[9] di-*n*-butylphosphine oxide,[10] diallylphosphine oxide,[4] di-*n*-octylphosphine oxide,[11] diethylchlorophosphine,[12] diethylphosphinic chloride,[13] di-*n*-octylphosphinic chloride[14] are prepared according to literature procedures. Carbon tetrachloride is purified by standard methods before use. ^{1}H-NMR spectra were recorded at 80 MHz using a Tesla BS 487 C spectrometer with TMS as an internal standard. The simulated spectra were obtained using the NMRCAL program with an 8K NIC-1082 computer. The NMR parameters for the vinyl protons of **2d**, obtained according with ABX procedure, were approximated by interpolation to obtain better correspondence between the frequency lines of the simulated (80 MHz) and the observed spectra.

Diethylphosphine 2a; Typical Procedure for the Synthesis of 2 of Low Molecular Weight:

To solid diethylphosphine oxide (8.5 g, 80 mmol), placed in a flask equipped with a distilling head, is added carbon tetrachloride [0.154 g, 1 mmol; or diethylchlorophosphine (1 mmol) or diethylphosphinic chloride (1 mmol)]. The resulting mixture is gradually heated in an atmosphere of dry argon until spontaneous disportionation occurs (~ 130 °C). Then the mixture is carefully heated to distill off the product at 85–90 °C. Redistillation gives analytically pure **2a**; yield: 3.34 g (93 %); b.p. 85 °C.

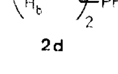
Di-*n*-octylphosphine (2e); Typical Procedure for the Synthesis of 2 of Higher Molecular Weight:

Di-*n*-octylphosphine oxide (3.02 g, 11 mmol) and carbon tetrachloride (0.031 g, 0.2 mmol), sealed in a glass tube, are heated for 2 h at 150 °C. The resulting mixture is distilled in an atmosphere of dry argon to give analytically pure **2e**; yield: 1.31 g (92 %); b.p. 139–140 °C/1 torr.

Diallylphosphine 2d:

Diallylphosphine oxide (2.0 g, 15.4 mmol) and carbon tetrachloride (0.0237 g, 0.154 mmol), placed in a flask equipped with a distilling head, are heated in an atmosphere of dry argon for 15 minutes at 110 °C (normal pressure) and then at 115–117 °C under reduced pressure (0.5 torr) until an exothermic reaction occurred. Diallylphosphine is collected in a condensing tube cooled with dry ice. Redistillation gives analytically pure **2d**; yield: 0.71 g (91 %); b.p. 134–136 °C.

$C_6H_{11}P$	calc.	C 63.15	H 9.70	P 27.15
(114.1)	found	63.00	9.65	26.91



2d

Table. Preparation of Dialkylphosphines **2**

2	R	Yield[a] (%)	b.p. (°C)		^{31}P-NMR	δ (ppm)
			found	reported	found[b]	reported[c]
a	C_2H_5	93	85	83–86[7]	–56.0	–55.5
b	n-C_3H_7	90	134–135	136[8]	–74.0	–73
c	n-C_4H_9	91	178–180	178[8]	–70.5	–69.5
d	$H_2C{=}CHCH_2$	91	134–136		–69.8	
e	n-C_8H_{17}	92	139–140/ 1.1 Torr	140–142[3]/ 1.1 Torr	–69.7	–71.5

[a] After redistillation.

[b] Measured at 36.43 MHz with a Bruker HFX90 spectrometer in benzene solution using 85% H_3PO_4 as an external standard.

[c] The reported literature value (Ref. 6) are given with the opposite sign.

^{31}P-NMR (Et_2O): $\delta = -70.3$ ppm (dm, $J_{PH} = 196$ Hz).

^{1}H-NMR ($CDCl_3$): $\delta = 2.33$ (m, 4H, $^2J_{PH} = 2.35$, $^3J_{HPH}$ – not observed due to rapid intermolecular exchange of P-H hydrogen), $^3J_{HH} = 7.34$, $^4J_{HH}a = -0.88$, $^4J_{HH}b = -1.17$, CH_2P); 3.11 (s, 1H, PH); 4.98 (m, 2H, $^2J_{HH} = 2.06$, $^3J_{HH} = 9.39$, $^4J_{HP} = 2.4$, H^a); 5.01 (m, 2H, $^3J_{HH} = -17.31$, $^4J_{HP} = 2.8$, H^b); 5.78 (m, 2H, $^3J_{HP} = 4.1$, H^c).

^{1}H-NMR (C_6D_6): $\delta = 2.14$ (m, 4H, $^3J_{HPH} = 6.5$ Hz, other J values as above, CH_2P); 3.02 (dm, 1H, $^1J_{PH} = 196$, $^3J_{HPH} = 6.5$ Hz); 4.7–5.0 (4H, overlapped: m, 2H^a; m, H^b); 5.45–5.85 (m, 2H, H^c).

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(5) A unique feature of the ^{1}H-NMR spectrum of **2d** is a different appearance of the two lateral portions of the PH proton signal split by the phosphorus atom ($J_{PH} = 196$ Hz) an by the methylene protons ($J_{CH_2PH} = 6.5$ Hz), respectively. While the left portion is a regular quintet the right one shows a multiplet structure that is strongly dependent on the spectrometer frequency (60 MHz, 80 and 90 MHz). The experimental (80 MHz) and the calculated spectra of the P$\underline{H}$ (80 MHz) have an excellent fit. The spectral parameters used for calculation are given in the experimental part, coupling of the P$\underline{H}$ to the vinyl protons being neglected.
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