Synthesis of Diphenyldialkylphosphonium Salts

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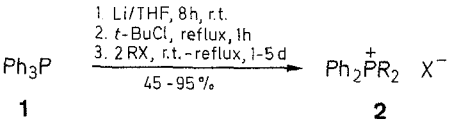
A general method for the synthesis of the title compounds by a one-pot reaction is described. It consists in the double alkylation of lithium diphenylphosphide, obtained by the reaction of triphenylphosphine, lithium and *tert*-butyl chloride. This procedure can also be used for α-functional alkylating agents.

Our studies on diylide chemistry[1] led us to investigate a simple, efficient and general synthesis of dialkyldiphenylphosphonium salts **2**. Among the various synthetic preparation of phosphonium salts, alkylation of phosphine predominates.[2] Furthermore, it is well documented that lithium diphenylphosphide, conveniently accessible by reaction of lithium with triphenylphosphine,[3] can be easily alkylated to the corresponding phosphine. Accordingly, dialkyldiphenylphosphonium salts **2** can be simply obtained by an additional second alkylation of this phosphine. In spite of the synthetic potential of this approach, the synthesis of dialkylphosphonium salts starting from lithium diphenylphosphide has been reported only occasionally.[4]

We now report a general one-pot procedure that can be extended to several phosphonium salts **2** including salts with α-functional alkyl groups.



1 **2**

Pure lithium diphenylphosphide solution is obtained by the reaction of two equivalents of lithium with triphenylphosphine in tetrahydrofuran followed by addition of one equivalent of *tert*-butyl chloride[4] (thus phenyllithium is eliminated and secondary deprotonations or alkylations are avoided).

In the reaction of lithium diphenylphosphide with RX, the nature of the halogen depends on the structure of R. Thus when R is an alkyl group, best results are obtained with an alkyl iodide; when R is benzylic or allylic, X can be either iodine or bromine; but when R is a α-functional group, X must be chlorine. Accordingly, the first alkylation takes place very easily at room temperature, leading to the intermediate phosphine; the second alkylation requires in some cases higher temperature (see Table).

Table. Synthesis of Diphenyldialkylphosphonium Salts **2**

Product	RX	Conditions of Step 3		Yield (%)	mp (°C)[a] (solvent)	Molecular[b] Formula or Lit. mp (°C)	IR (KBr)[c] ν (cm^{-1})	^{31}P-NMR[d] ($CHCl_3$/H_3PO_4 ext.) δ	^{1}H-NMR ($CDCl_3$/TMS)[e] of group R: δ, J (Hz)
		Time (d)	Temp. (°C)						
2a	CH_3I	1	r.t.	95	255 (EtOH)	256[5]	1435, 742	20.4	2.80 (d, 6H, $J_{(PH)}$ = 14)
2b	CH_3CH_2I	1	reflux	90	209 (EtOH)	209[6]	1430, 775, 742	31.8	1.27 (dt, 6H, $J_{(PH)}$ = 20, $J_{(HH)}$ = 7.6); 3.30 (dq, 4H, $J_{(PH)}$ = 13.2, $J_{(HH)}$ = 7.6)
2c	$CH_3(CH_2)_2I$	4	reflux	80	165 ($EtOH$/Et_2O)	164[7]	1435, 760–752 (d)	27.2	1.0–1.95 (m, 10H); 3.20 (br, 4H)
2d	$(CH_3)_2CHI$	5	reflux	60	126 ($CHCl_3$/EtOAc)	$C_{18}H_{24}IP$ (398.1)	1438–1432 (d), 747, 730–722 (d)	42.8	1.32 (dd, 12H, $J_{(PH)}$ = 18, $J_{(HH)}$ = 7,5); 4.13 (br, 2H)
2e	$CH_3(CH_2)_3I$	2	reflux	80	156 ($EtOH$/Et_2O)	154[8]	1448, 795–786 (d)	27.8	0.98 (br, 6H); 1.30–1.90 (m, 8H); 3.15 (br, 4H)
2f	$I(CH_2)_5I$	1	r.t.	45	271 (EtOH)	261–262[9]	1448–1437 (d), 775, 739, 728	16.6	1.65–2.50 (m, 6H); 3.30 (br, 4H)
2g	CH_2=$CHCH_2Br$	2	r.t.	80	167 ($CHCl_3$/EtOAc)	170[10]	1439–1431 (d), 750	22.5	4.40 (dd, 4H, $J_{(PH)}$ = 14, $J_{(HH)}$ = 5.0); 5.50 (br, 6H)
2h	$(CH_3)_2C$=$CHCH_2Br$	2	r.t.	75	200 ($CHCl_3$/EtOAc)	$C_{22}H_{28}BrP$ (403.1)	1440–1430 (d), 754, 747	24.7	1.48 (dd, 12H, $J_{(PH)}$ = 18, $J_{(HH)}$ = 4.5); 4.18 (dd, 4H, $J_{(PH)}$ = 14, $J_{(HH)}$ = 8); 5.05 (br, 2H)
2i	$C_6H_5CH_2Br$	2	r.t.	85	260 ($CHCl_3$/EtOAc)	252–254[4]	1438–1432 (d), 798, 750	26.8	5.02 (d, 4H, $J_{(PH)}$ = 15.0); 7.13 (s, 10H)
2j	$C_6H_5COCH_2Cl$	3	r.t.	80	219 ($CHCl_3$/EtOAc)	$C_{28}H_{26}ClO_3P$[f] (476.7)	1673–1661 (d), 1450–1438 (d), 760	21.5	3.35 (s, 2H (H_2O)); 6.18 (d, 4H, $J_{(PH)}$ = 14); 7.2–8.6 (m, 10H)

[a] Uncorrected, measured with a Mettler FP 5 apparatus.
[b] Satisfactory microanalyses obtained: C ±0.26; H ±0.11; P ±0.18; X ±0.18.
[c] Recorded on a Perkin-Elmer 377 Infrared spectrophotometer.
[d] Obtained on a Bruker WP-80 spectrometer.
[e] Obtained on a Varian EM 360 spectrometer.
[f] Isolated as monohydrated salt.

Alkylation of Lithium Diphenylphosphide; General Procedure:
To a solution of triphenylphosphine (26.23 g, 0.1 mol) in anhydrous THF (200 mL), lithium (1.39 g, 0.2 at.g) is added at room temperature under nitrogen. The red solution is stirred for 8 hours at room temperature, and then *tert*-butyl chloride (9.25 g, 0.1 mol), diluted in THF (50 mL), is added. After gentle reflux for one hour, the reaction mixture is cooled to room temperature, and the halogenated compound RX (0.2 mol), diluted in THF (50 mL), is added. After efficient stirring for 1 to 5d (Table) the phosphonium salt **2** is obtained either by filtration or by evaporation of the solvent and then recrystallized.

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