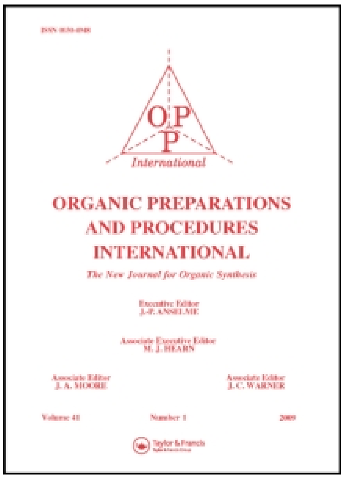

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PREPARATION OF TERTIARY PHOSPHINES USING A CONVENIENT FORM OF LITHIUM DIPHENYLPHOSPHIDE

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PREPARATION OF TERTIARY PHOSPHINES USING A CONVENIENT FORM OF LITHIUM DIPHENYLPHOSPHIDE

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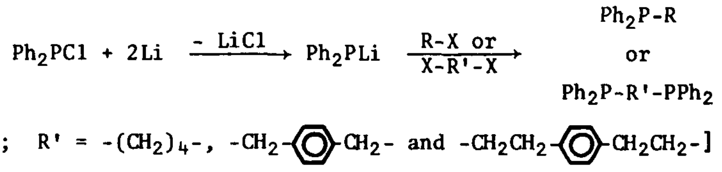
We have utilized, as illustrated in the scheme below, a new and convenient method for the preparation of tertiary diphenylphosphines in excellent yields starting from inexpensive and easily handled chlorodiphenylphosphine.



$$Ph_2PCl + 2Li \xrightarrow{-\ LiCl} Ph_2PLi \xrightarrow[X\text{-}R'\text{-}X]{R\text{-}X\ \text{or}} \begin{matrix} Ph_2P\text{-}R \\ \text{or} \\ Ph_2P\text{-}R'\text{-}PPh_2 \end{matrix}$$

[R = $-CH_3$; R' = $-(CH_2)_4-$, $-CH_2-C_6H_4-CH_2-$ and $-CH_2CH_2-C_6H_4-CH_2CH_2-$]

Since lithium is easily handled compared to the other alkali metals, lithium diphenylphosphide is a convenient source of the diphenylphosphide anion, Ph_2P^-. Lithium diphenylphosphide has been prepared by various methods involving some undesirable routes, e.g. the reaction of diphenylphosphine with phenyllithium[1] (reaction 1). It has also been prepared by the more convenient reaction of triphenylphosphine with lithium metal in tetrahydrofuran[2] (reaction 2).

$$(C_6H_5)_2PH + C_6H_5Li \rightarrow (C_6H_5)_2PLi + C_6H_6 \qquad (1)$$

$$(C_6H_5)_3P + 2Li \rightarrow (C_6H_5)_2PLi + C_6H_5Li \qquad (2)$$

Aguiar *et. al.* have extended the use of lithium diphenylphosphide as prepared by the second reaction by selectively decomposing the phenyllithium with *t*-butyl chloride.[3] They have also extended this reaction to the preparation of lithium diphenylarsenide from triphenylarsine and lithium.[4] In the preparation of tertiary diphenylphosphines using the method of Aguiar *et. al.* by selectively decomposing the phenyllithium, the yields of our products varied quite considerably and were generally less than 50%.[5] By using an excess of the organic halide instead of adding *t*-butyl chloride, good yields were obtained. The present preparation outlined above eliminates the need for the addition of either *t*-butyl chloride or an excess of the organic halide.

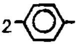
Lithium diphenylphosphide has been used quite extensively in the preparation of diphenyl organophosphorus compounds.[6] Many organophosphorus compounds are used as ligands in transition metal chemistry, and multidentate phosphorus containing ligands often contain the diphenylphosphine group.[7]

EXPERIMENTAL

Chlorodiphenylphosphine was purchased from the Aldrich Chemical Company and the lithium metal from BDH Ltd. Dry analytical grade THF was obtained from Merck and stored over sodium wire. Distillation of the THF from lithium aluminium hydride was found to be unnecessary. Methyl iodide (UNILAB), 1,4-dibromobutane (BDH) and α,α'-dibromo-*p*-xylene (Aldrich Chemical Company) were reagent grade and were used without further purification. β,β'-Dichloro-*p*-diethylbenzene was prepared from the reaction of 1,4-benzenediethanol[8] and thionyl chloride. The compounds were characterized by analyses, infrared, nmr and mass spectra. The infrared spectra were recorded on a JASCO IRA-2 spectrometer, the nmr spectra were obtained using a JEOL MH-100 with TMS as an internal reference, and the mass spectra were recorded on an AEI MS 902S instrument. The analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne. The procedure for the preparation of one of the compounds β,β'-bis(diphenylphosphino)-*p*-diethylbenzene, $Ph_2PCH_2CH_2$$CH_2CH_2PPh_2$, is given. The infrared and nmr spectra of the other products are consistent with the compounds formed. Analytical data are given in the Table.

β,β'-Bis(diphenylphosphino)-*p*-diethylbenzene. Typical Procedure. - A 250 ml, three-necked, round-bottomed flask, equipped with a water condenser, pressure equalizing dropping funnel and a magnetic stirring bar was flushed with high purity nitrogen. After the flask was flushed with nitrogen, 50 ml of dried THF

TABLE. Analytical Data of Some Tertiary Diphenylphosphines

Compound	Analyses Calcd. (Found)^a				bp./mp.(°C)	Yield(%)
	C	H	P	M.W. (M$^+$)^b		
Ph_2PCH_3	77.99 (78.09)	6.54 (6.78)	15.5 (15.2)	200 (200)^b	148° at 8mm^c	70%
$Ph_2P(CH_2)_4PPh_2$	78.86 (78.56)	6.62 (6.45)	14.5 (14.5)	426 (426)	137-139°^{d}	95%
Ph_2PCH_2--CH_2PPh_2	81.00 (80.34)	5.95 (5.76)	13.0 (13.3)	474 (474)	160-162°	71%
$Ph_2PCH_2CH_2$--$CH_2CH_2PPh_2$	81.26 (80.64)	6.24 (6.43)	12.3 (12.3)	502 (502)	142-144°	87%

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a) Carbon analyses obtained at University of Queensland Microanalytical Service of phosphorus containing compounds have in general been low, although spectral data established the purity of the compounds. *b)* M$^+$ is the Parent Ion found in the Mass Spectrum. *c)* Ref. 9. *d)* Ref. 10.

was admitted. Lithium foil (2 g, 0.29 g.-atoms) was cut into small strips and added to the THF in the flask. The lithium-tetrahydrofuran solution was heated to reflux and the heat source then removed. To this hot solution was added 15.7 g (0.07 mol) of chlorodiphenylphosphine in 40 ml of dried THF in a dropwise manner. After an induction period of approximately 2 min, the solution turned a deep red colour characteristic of the diphenylphosphide anion.[11] The reaction is very exothermic and the dropping rate was adjusted so that the solution continued to reflux moderately. After the addition of the chlorodiphenylphosphine was complete (*ca.* 30min), the solution was refluxed for an additional hour. The solution was then cooled in a salt-ice bath and transferred, through a tube connected by two stopcocks, under nitrogen into another 250 ml three-neck flask. Since lithium is less dense than THF, the excess was easily removed. To the lithium diphenylphosphide solution at 0° was added a solution of 6.0 g (0.03 mol) of β,β'-dichloro-*p*-diethylbenzene in 30 ml of THF in a dropwise manner. After the addition was complete (*ca.* 30 min), the solution was refluxed for one hour. The excess lithium diphenylphosphide was destroyed with a minimum amount (∿ 2 ml) of water at 0°. The β,β'bis(diphenylphosphino)-*p*-diethylbenzene was precipitated out by concentrating the solution and by the addition of approximately 40 ml of a 1:4 water-ethanol solution. The air stable precipitate was collected by filtration and washed with water and ethanol. The white precipitate was recrystallized from methylene chloride-methanol to yield 12.9 g (87%) of β,β'-bis(diphenylphosphino)-*p*-diethylbenzene, mp. 142-144°.

IR (nujol): 1588cm^{-1}(vw), 1510cm^{-1}(vw), 1438cm^{-1}(s), 1330cm^{-1}(vw), 1310cm^{-1}(vw), 1270cm^{-1}(vw), 1204cm^{-1}(vw), 1165cm^{-1}(vw), 1138cm^{-1}(vw), 1095cm^{-1}(w), 1073cm^{-1}(w), 1029cm^{-1}(m), 1005cm^{-1}(m), 938cm^{-1}(w), 864cm^{-1}(m), 778cm^{-1}(m), 755cm^{-1}(s), 734cm^{-1}(s), 711cm^{-1}(w), 698cm^{-1}(s), 549cm^{-1}(m), 505cm^{-1}(m), 488cm^{-1}(m), 455cm^{-1}(m).

NMR (CDCl$_3$): δ ppm 7.56-6.8 (24H, m, aromatic protons), 2.70 (4H, m, CH$_2$), 2.36 (4H, m, CH$_2$) from internal TMS.

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