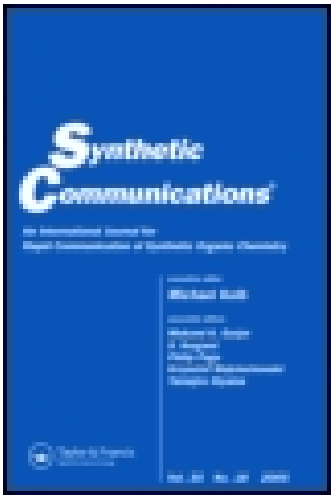

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Efficient One-Pot Procedures for the Preparation of Secondary Phosphines

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EFFICIENT ONE-POT PROCEDURES FOR THE PREPARATION OF SECONDARY PHOSPHINES

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Abstract:

Secondary phosphines R_2PH or RR'PH (R and R' = alkyl, cycloalkyl) have been obtained in good yields by preparing lithium phosphide from lithium, red phosphorus and *t*-butylalcohol in liquid ammonia and subsequent alkylation in the presence of alkali amide, prepared in the same flask.

Recently[1], we developed an efficient method for the cleavage of P–P bonds in red phosphorus, consisting of dropwise addition of *t*-butylalcohol to a mixture of red phosphorus, lithium and liquid ammonia. Subsequent addition of alkyl halides gave primary alkylphosphines RPH_2 in good to excellent yields.

$$P + 3\,Li + 2\,t\text{-}C_4H_9OH \xrightarrow[-33^\circ C]{\text{liq. } NH_3} 2\,t\text{-}C_4H_9OLi + LiPH_2 \xrightarrow{RHal} RPH_2$$

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In our present communication it is shown how this *in situ* generation of phosphide anion can be exploited to prepare, in the same flask, secondary phosphines.

Depending on the nature of the desired secondary phosphine and of the alkylating agent one (or both) of the procedures a and b may be applied:

a. Generation of $LiPH_2$ as mentioned above, followed by conversion of an additional amount of alkalimetal into alkali amide (under the influence of iron nitrate), and subsequent addition of two equivalents of the alkylating agent. Good results are obtained if the alkyl halide and alkali amide are well compatible. In this respect the slightly soluble sodamide is preferred over the completely soluble potassium amide.

$$P \xrightarrow[\text{liq. } NH_3]{3\ Li + 2\ t\text{-}C_4H_9OH} LiPH_2 \xrightarrow{MNH_2 + 2\ RHal} R_2PH$$

b. Carrying out a sequence of generating $LiPH_2$, addition of alkyl halide (RHal), conversion of alkali metal into the amide and introduction of the second portion of alkyl halide: this may be the same (RHal) as that used for the alkylation of $LiPH_2$, giving rise to the formation of a symetrical secondary phosphine R_2PH, or a different R'Hal, affording a non-symmetrical phosphine.

$$P \xrightarrow[\text{liq. } NH_3]{3\ Li + 2\ t\text{-}C_4H_9OH} LiPH_2 \xrightarrow{RHal} R_2PH$$

$$R_2PH \xrightarrow[2.\ RHal \text{ or } R'Hal]{1.\ M \rightarrow MNH_2} R_2PH \text{ or } RR'PH$$

Procedures a and b, ilustrated below by the experimental procedures give an easy access to a variety of secondary phosphines.

Experimental

General

All operations were carried out under nitrogen.

t-Butylalcohol was distilled from (5 % by weight) commercial *t*-BuOK. Red phosphorus was purified by treatment with a dilute aqueous solution of potassium carbonate, rinsing three times with hot (70 °C) water and subsequent suction filtration (G-2 sintered glass) and washing with acetone (four times) and dry ether (three times). The ether was removed by evacuation. For a smooth dissolution of lithium in liquid ammonia it is essential to introduce the pieces (~0.1 - 0.2 g) with a fresh cutting surface into the ammonia. This can be done by cutting the metal above a powder funnel placed on one of the necks of the flask. The metal must be clean, i.e. not be covered by a crust of oxide (only the usual thin black coating may be present). Oxide crusts present on the surface of sodium are removed before weighing.

The products showed purities of at least 96 % (GLC, ^{1}H NMR).

1. Di(*n*-pentyl)phosphine:

A 2-l, three-necked (vertical necks!), round-bottomed flask was equipped with a combination of a gas inlet and a dropping funnel, an efficient mechanical stirrer and a gas outlet. In the flask was placed ~900 mL of anhydrous liquid ammonia and in the dropping funnel a mixture of 0.40 mol of *t*-butylalcohol and 50 ml of diethyl ether. Nitrogen was introduced and very small pieces of sodium (~0.1 g each) were introduced with intervals, until the blue colour persisted (in the case of a good quality of the ammonia <0.5 g is needed). The flask was then surrounded by cotton wool and placed in a pan. A slurry of red phosphorus (6.7 g, 0.22 mol) in ~ 10 mL of diethyl ether was then rinsed into the flask, using the minimal amount of ether (< 30 mL) (the flow of N_2 was temporarily stopped). Subsequently 4.65 g (0.66 mol) of lithium was introduced over 10 min in pieces of ~ 0.1 - 0.2 g. The mixture of *t*-C_4H_9OH and ether was added dropwise over 1.5 h, while N_2 (~ 300 mL/ min) was passed through the flask. The blue (or, toward the end blue-green) colour disappeared as a rule at the moment of completion of the addition. In order to rinse adhering metal from the upper part of the wall, stirring was temporarily stopped and the flask swirled manually. Introduction of a very small additional amount of *t*-C_4H_9OH may be necessary to effect complete discharge of the blue

colour. The inlet, dropping funnel and outlet were temporarily removed and ~ 1 g of the required amount of 4.6 g (0.20 mol) of sodium was introduced. After the solution had become uniformly blue, ~ 300 mg of powdered $Fe(NO_3)_3$ (nonahydrate) was introduced. After the blue colour had disappeared (a brown solution was formed) the remaining amount of sodium was added and the flask was equipped again as before (this temporary absence of the equipment seems to be necessary in order to admit traces of oxygen, which assist in the catalytic conversion of Na into $NaNH_2$). *n*-Pentyl bromide (60.0 g, 0.40 mol) was added dropwise over 45 min, while introducing N_2 (~ 300 mL/ min) (If the volume of the ammoniacal solution has decreased to less than ~ 0.5 L due to evaporation, an additional amount of ~ 200 mL has to be introduced prior to addition of the alkyl bromide) After an additional period of 45 min the outlet was removed and the flask placed in a water bath at 40°C, the flow of N_2 being continued: towards the end of the evaporatation procedure the flow was increased to about ~ 1 L/ min and a solution of 50 g of ammonium chloride in 500 mL of water (previously perfused with nitrogen) was cautiously added with vigorous stirring. After separation of the layers (some practical skill is required because some black amorphous material usually is present between the layers), three extractions with pentane were carried out (the black slurry was repeatedly rinsed with pentane). After drying the organic solution over potassium carbonate, it was concentrated in a water pump vacuum. The remaining liquid was distilled through a 25 - 30 cm Vigreux column affording the product, bp 110°C/ 15 mm Hg, n^{20}_D 1.459, in 72 % yield. (In connection with strong foaming during the distillation a 500-mL flask should be used).

2. Di(cyclopentyl)phosphine:

The apparatus of exp 1 was used, and a solution of 0.22 mol of $LiPH_2$ was made as described above. Cyclopentyl bromide (0.20 mol, 30.0 g) was added dropwise over 1 h with efficient stirring and introduction of N_2, the flask being insulated in cotton wool. After an additional period of 45 min 200 mL of liquid ammonia were introduced and the dropping funnel-inlet combination and outlet were removed. The introduction of N_2 was stopped temporarily and 1 g of the required amount of a 0.20 mol (4.6 g) of sodium was introduced (the flow of N_2 was stopped). When the solution had become uniformly blue, 250 mg of powdered $Fe(NO_3)_3.9H_2O$ was introduced. After disappearance of the blue colour (a brown solution was

formed) the remaining Na was introduced in 0.5 g pieces. The equipment was again placed on the flask. After ~ 30 min the blue colour had been replaced by brown, indicating complete conversion of the sodium. In the dropping funnel was placed 0.22 mol of cyclopentyl bromiode. This was added dropwise over 45 min. After an additional 1 h the ammonia was removed as described above. The product, $(c\text{-}C_5H_9)_2PH$, bp 115°C/ 15 mm Hg, n^{20}_D 1.511, was isolated as described for $(n\text{-}C_5H_{11})_2PH$, yield 65 %.

3. Ethyl *n*-heptyl phosphine:

This procedure was closely similar to exp 2. The outlet was combined with a thermometer. First ethyl bromide (0.22 mol, 24.0 g) was added dropwise over 15 min, while keeping the temperature of the reaction mixture between –35 and –40°C by occassional cooling in a bath with liquid nitrogen. After an additional period of 45 min (at ~ –35°C) sodamide was prepared in the flask (from 0.20 mol, 4.6 g of sodium) while keeping the temperature at ~ –35°C (just below the bp of ammonia). Subsequently, *n*-heptyl bromide (0.20 mol, 36.0 g) was added dropwise over 20 min with vigorous stirring and cooling between –40 and –45°C. After the addition the cooling bath was removed and stirring was continued for 45 min. The work up was carried out as described in exp 2. Ethyl *n*-heptyl phosphine, bp 100°C/ 15 mm Hg, n^{20}_D 1.458, was obtained in 55 % yield. The residue consisted mainly of ethyl diheptyl phosphine.

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