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CLEAVAGE OF PHOSPHORUS–CARBON BONDS WITH SODIUM/NAPHTHALENE. FACILE PREPARATION OF UNSYMMETRICAL DIPHOSPHINES

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Summary

Sodium/naphthalene was found to be a homogeneous, mild and selective reagent for the reductive cleavage of aryl–phosphorus bonds. Such cleavage reactions are very useful in the convenient synthesis of unsymmetrical diphosphines from commercially available and air-stable diphosphines.

The reactions of metal phosphides with alkyl halides constitute the most important method for the preparation of phosphines [1]. The generation of metal phosphides can be achieved by the reactions of alkali metals either with air-sensitive secondary phosphines, halo-phosphines and biphosphines or, less frequently, with air-stable tertiary aryl phosphines owing to the slow reaction rates. Recently, ultrasound irradiation was found to accelerate the rate as well as to improve the product purity of the reactions of the alkali metal-induced reductive cleavage of P–Ph bonds [2,3]. Thus, phosphides and symmetrical diphosphides could be easily prepared from the readily available aryl phosphines and diphosphines, respectively. However, such a method failed to give monophosphides from symmetrical diphosphines [3]. Only the dianions $^{-}PhP(CH_2)_nPPh^{-}$ (**2a–2e**) and the unreacted starting materials $Ph_2P(CH_2)_nPPh_2$ (**1a–1e**) could be obtained even when the diphosphines were used in large excess. The failure of the reactions to stop at the monoanion stage might be due to the heterogeneity of the reactions and the high reactivity of the alkali metals.

Later we found that monophosphides could be generated from the corresponding aryl diphosphines **1a–1e** by reaction with sodium/naphthalene [4] and thus unsymmetrical diphosphines $HPhP(CH_2)_nPPh_2$ (**4a–4e**) and $MePhP(CH_2)_nPPh_2$ (**5a–5e**) could be prepared accordingly. When symmetrical diphosphines **1a–1e** (1 equiv) were treated with sodium/naphthalene (0.95 equiv) followed by quenching with saturated NH_4Cl, unsymmetrical diphosphines **4a–4e** were selectively produced in

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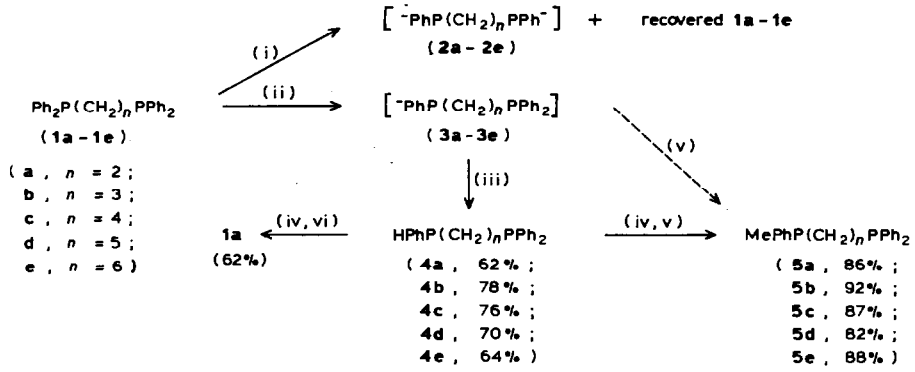
TABLE 1

PREPARATION OF **4a–4e** FROM **1a–1e**

Starting material	Reaction time for reductive cleavage (d)	Product	B.p. (0.05 Torr) oven temp. (°C)	IR (cm^{-1})	NMR (δ (ppm))	MS (m/z)	Elemental analysis (Found (calcd.) (%))	
							C	H
1a	1	**4a**	180–200	3080, 2950, 2300, 1190	7.2 (br s, 15H), 1.6–2.5 (m, 4H), 4.2 (dt, *J* 210, 6 Hz, 1H)	322 (M^+), 213, 183, 109, 108 (base)	74.3 (74.5)	6.1 (6.2)
1b	2	**4b**	150–190	3080, 2950, 2350, 1190	7.2 (br s, 15H), 1.4–2.3 (m, 6H), 4.0 (dt, *J* 2100 6 Hz, 1H)	336 (M^+), 259, 227 (base), 150, 109, 108	75.4 (75.0)	6.7 (6.55)
1c	3	**4c**	150–190	3080, 2950, 2350, 1190	7.2 (br s, 15H), 1.3–2.1 (m, 8H), 4.1 (dt, *J* 210, 6 Hz, 1H)	350 (M^+), 273, 241 (base), 164, 109, 108	75.0 (75.4)	6.5 (6.8)
1d	3	**4d**	150–200	3080, 2950, 2350, 1190	7.2 (br s, 15H), 1.2–1.9 (m, 10H), 4.1 (dt, *J* 210, 6 Hz, 1H)	364 (M^+), 288, 255 (base), 179, 109, 108	75.8 (75.8)	7.0 (7.1)
1e	4	**4e**	170–200	3080, 2950, 2350, 1190	7.2 (br s, 15H), 1.0–1.6 (m, 12H), 4.1 (dt, *J* 210, 6 Hz, 1H)	378 (M^+), 302, 269 (base), 193, 109, 108	76.2 (76.2)	7.5 (7.4)



SCHEME 1. (i) Li, ultrasound; (ii) sodium/naphthalene; (iii) NH_4Cl; (iv) n-BuLi; (v) MeI; (vi) PhBr.

high yields (Table 1). A small amount of the unreacted starting material **1a–1e** could be separated from the products easily by vacuum distillation because of the large difference in their boiling points. The purified compounds **4a–4e** were then deprotonated with n-BuLi followed by alkylation with electrophiles, e.g. MeI, to give the unsymmetrical ditertiary phosphines **5a–5e** easily (Table 2). Bromobenzene could also be used in place of MeI to react with **4a** to produce **1a** in 62% yield. The monophosphides **3a–3e** generated from the reductive cleavage reaction step were quenched directly with MeI to give the products **5a–5e** as well. However, this route was not preferred because a trace of the unreacted starting materials left in the product mixtures could be removed only with extreme difficulty at this stage because the boiling points and R_f values of **1a–1e** and **5a–5e** are very close. Only repetitive distillation could produce pure products, with severe loss of material. Attempted double cleavage of the diphosphines **1** with 2 equiv of sodium/naphthalene failed. For example, treatment of **1e** with an excess of sodium/naphthalene for 6 d produced mainly the monophosphide **3e** and only less than 20% of the diphosphide anion **2e**. The diphosphides **2a–2e** are prepared more conveniently by the procedure developed earlier [3].

The preparation of some of the unsymmetrical diphosphines related to **4a–4e** and **5a–5e** has been achieved by indirect and multistep reaction sequences [5–7]. Our method apparently provides the most straightforward, efficient and general way towards the synthesis of this class of compounds. It should also be noted that the monophosphide anion **3e** could be prepared in 64% yield even when the two phosphine groups of the starting material **1e** were six carbons apart.

Although it has been known as an electron-transfer agent for years [4], sodium/naphthalene has rarely been used to cleave a phosphorus–aryl bond [8] probably because of its low reactivity for this purpose in comparison with that of an alkali metal. However, it has several advantages over alkali metals when used in the reductive cleavage of P–Ph bonds. It presents no problems in cases where stoichiometry is essential since an accurate quantity of naphthalene is easier to measure than alkali metals. The reaction medium is homogeneous and thus the manipulations are very simple. The completeness of the reductive cleavage reaction can easily be detected by observing the disappearance of the dark-green colour of the naphthalene radical anion. Most importantly, the reaction is mild and thus

TABLE 2

PREPARATION OF **5a–5e** FROM **4a–4e**

Starting material	Product	IR (cm^{-1})	NMR (δ (ppm))	MS (m/z)	Elemental analysis (Found (calcd.) (%))	
					C	H
4a	**5a**	3080, 2950, 1500, 1460, 1440	7.2 (br s, 15H), 1.4–2.3 (m, 4H) 1.25 (d, 3H, *J* 2 Hz)	336 (M^+), 321 (base), 259, 245, 185, 183, 109, 108	75.1 (75.0)	6.5 (6.5)
4b	**5b**	3080, 2950, 1500, 1460, 1400	7.2 (br s, 15H), 1.4–2.3 (m, 6H), 1.25 (d, 3H, *J* 2 Hz)	350(M^+), 335 (base), 273, 259, 185, 183, 109, 108	75.5 (75.4)	6.8 (6.9)
4c	**5c**	3080, 2950, 1500, 1460, 1440	7.2 (br s, 15H), 1.3–2.2 (m, 8H), 1.25 (d, 3H, *J* 2 Hz)	364 (M^+), 349 (base), 287, 241, 185, 183, 109, 108	75.7 (75.8)	7.1 (7.1)
4d	**5d**	3080, 2950, 1500, 1460, 1440	7.2 (br s, 15H) 1.3–2.0 (m, 10H), 1.25 (d, 3H, *J* 2 Hz)	378 (M^+), 363 (base), 301, 255, 185, 183, 109, 108	76.15 (76.2)	7.5 (7.4)
4e	**5e**	3080, 2950, 1500, 1460, 1440	7.2 (br s, 15H), 1.25–1.9 (m, 12H), 1.25 (d, 3H, *J* 2 Hz)	392 (M^+), 377 (base), 315, 269, 185, 183, 109, 108	76.4 (76.5)	7.7 (7.65)

highly selective for the generation of the monophosphide anion from a symmetrical diphosphine, and produces unsymmetrical diphosphines, which are otherwise difficult to prepare.

Experimental

All reactions and work-up procedures were manipulated under an anhydrous nitrogen atmosphere. All solvents were dried and deoxygenated before use. Melting points were determined on a Yanado MP-21 melting point apparatus and were uncorrected. NMR spectra were recorded on a JEOL FX-100 NMR spectrometer as solutions in C_6D_6. IR spectra were recorded on a Perkin–Elmer 297 Infrared spectrophotometer as solutions in C_6H_6. Mass spectra were taken on a JEOL JMS-D-100 mass spectrometer. Elemental analyses were done at the National Taiwan University, Taipei.

*Preparation of the diphosphines $HPhP(CH_2)_nPPh_2$ **4a–4e** from $Ph_2P(CH_2)_nPPh_2$*

To a solution of naphthalene (327 mg, 1.95 mmol) in THF (10 ml) was added finely cut sodium metal (60 mg, 2.5 mmol). The mixture was sonicated (Bransonic 220 cleaner) at room temperature during which a dark-green colour developed indicating the formation of the naphthalene radical anion. After 30 min of stirring, excess sodium metal was removed and the resulting solution was added to a solution of a bis(diphenylphosphino)alkane **1a–1e** (1 mmol) in THF (20 ml) at 0°C. The reaction mixture was then stirred at room temperature for 2–4 d during which time a dark red colour developed gradually as the green colour faded. The reaction mixture was cooled to −10°C and saturated NH_4Cl (5 ml) was added dropwise. The stirring was continued for another 30 min and then THF was removed under reduced pressure. Brine (10 ml) was added, the mixture was extracted with benzene (5 × 10 ml), and the combined organic layers were dried (Na_2CO_3). The organic solvent was removed under reduced pressure and the resulting product was distilled first at 120°C/1 Torr to remove naphthalene and other low boiling components and then redistilled with Kugelrohr at 0.05 Torr to give the pure product **4a–4e** (Table 1).

*Preparation of the diphosphines $MePhP(CH_2)_nPPh_2$ **5a–5e** from **4a–4e***

To a solution of **4a–4e** (1 mmol) in THF (10 ml) at −78°C, n-BuLi (1.2 mmol) was added dropwise over a period of 30 min during which time a dark red colour gradually developed. After another 30 min of stirring, MeI (1 mmol) in THF (5 ml) was added slowly and stirring was continued at −78°C for 10 min and at room temperature for 30 min. THF was then removed under reduced pressure and brine (10 ml) was added. The mixture was extracted with benzene (5 × 10 ml) and the combined organic layers were dried (Na_2CO_3). After the removal of the organic solvent under reduced pressure, the crude mixture was eluted through a column of neutral aluminium oxide with benzene to give the pure product **5a–5e** (Table 2).

*Reaction of diphosphine monoanion **3a** with bromobenzene to give **1a***

The same reaction conditions and purification procedure as those described for the preparation of **5a–5e** were used for the reaction of **4a** with bromobenzene in place of MeI to give the diphosphine **1a** in 62% yield.

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