Synthesis of Diaminodiphenylphosphonium Salts

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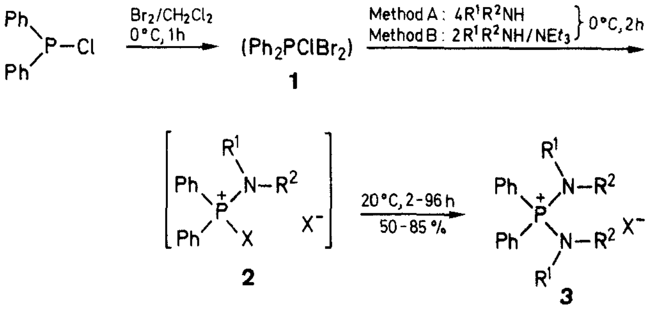
A new general synthesis of diaminodiphenylphosphonium salts consists of the successive reactions of chlorodiphenylphosphine with bromine and then with primary or secondary amines. The method can be applied to various types of amines.

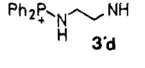
Our interest in diylide chemistry[1-2] led us to elaborate a simple, efficient, and general synthesis of diaminodiphenylphosphonium salts **3** ($R^2 = H$) which are used as precursors for diazadiylides.[3] Several syntheses of salts **3** are known, using for example the reactions between dichlorophosphine, amine, and halogenated compounds[4-6] or the reactions between tetraphenyldiphosphine and amines.[7,8]

We describe here a new synthesis of salts **3** in which Horner's preparation[9-12] of monoaminophosphonium salts has been adjusted to the *in situ* preformed trihalophosphorane **1**. Thus, the diaminophosphonium salts **3a–j** can be prepared by reaction of bromine with chlorodiphenylphosphine and subsequent disubstitution of halogen on phosphorus by primary or secondary amines. This preparation is performed as a one-pot procedure (without isolation of the intermediates **2**). It is quite general with regard to the nature of the groups R^1 and R^2 (alkyl, aryl, and functionally substituted alkyl) and it can also be performed with hydrazines ($R^1 = NHPh$, $R^2 = H$) in place of amines (preparation of salt **3k**).



	R^1	R^2	X
3a	Bu	H	Br
3b	*i*-Pr	H	Br
3c	*t*-Bu	H	Br
3'd[a]	CH_2CH_2	H	Br
3e	CH_2Ph	H	Br
3f	Ph	H	Br
3g	$CH_2CH{=}CH_2$	H	Br
3h	CH_2CO_2Et	H	BPh_4
3i	Bu	Bu	BPh_4
3j	CH_2Ph	Bu	OTs
3k	NHPh	H	Br

[a] 1,2-Ethanediamine is used as the amine, the product being 2,2,7,7-tetraphenyldecahydro-1,3,6,8,2,7-tetraazadiphosphecine-2,7-diium dibromide:



3'd

Table 1. Diaminophosphonium Salts **3** Prepared

Product	Reaction Conditions		Method	Yield (%)	mp (°C)[a] (Solvent)	Molecular[b] Formula
	Temperature (°C)	Time (h)				
3a[c]	20	20	A	82	71 (MeOAc)	$C_{20}H_{30}BrN_2P$ (409.4)
3b	20	18	A	75	220 ($MeOH/H_2O$)	$C_{18}H_{26}BrN_2P$ (381.3)
3c	46	96	A	55	241 ($CH_2Cl_2/EtOAc$)	$C_{20}H_{30}BrN_2P$ (409.4)
3'd[d]	20	48	B	50	270 ($CHCl_3/EtOAc$)	$C_{28}H_{32}Br_2N_4P_2 + H_2O$ (664.4)
3e[e]	20	2	A	85	114 ($CH_2Cl_2/EtOAc$)	$C_{26}H_{24}BrN_2P$ (477.4)
3f[f]	20	20	A	60	243 (EtOH)	$C_{24}H_{22}BrN_2P$ (449.3)
3g	20	18	A	55	92 ($CH_2Cl_2/EtOAc$)	$C_{18}H_{22}BrN_2P$ (377.3)
3h	20	88	B	65	110 ($C_5H_{11}OH$)	$C_{44}H_{46}BN_2O_4P$ (708.6)
3i	20	96	A	30	178 ($CH_2Cl_2/EtOAc$)	$C_{52}H_{66}BN_2P$ (760.9)
3j	82[g]	72	B	60	108 ($EtOAc/C_6H_{14}$)	$C_{41}H_{29}N_2O_3PS$ (680.9)
3k	20	72	A	65	282 (h)	$C_{24}H_{24}BrN_4P$ (479.4)

[a] Uncorrected, measured with a Mettler FP 5 apparatus.

[b] Satisfactory microanalyses obtained: C ±0.28, H ±0.24, N ±0.33, P ±0.21.

[c] The corresponding iodide, **3a'**, was obtained by ion exchange with NaI in H_2O (25°C, 15 min); mp 114°C. The microanalysis (Footnote b) was performed with this compound: $C_{20}H_{20}IN_2P$ (456.3).

[d] This cyclic bis-phosphonium salt (formula, see under formula scheme) was isolated and characterized as the monohydrate. MS (FAB): $m/z = 565$ $(M - {}^{81}Br)^+$, 485 $(M - 2\,Br)^{2+}$, 185.17.

[e] The corresponding iodide, **3e'** (mp 159°C), and the corresponding tetraphenylborate, **3e''** (mp 153°C), were obtained by ion exchange with NaI in H_2O and with $NaBPh_4$ in MeOH, respectively. These products were analyzed (Footnote b): **3e'**, $C_{26}H_{26}IN_2P$ (524.4); **3e''**, $C_{50}H_{46}BN_2P$ (716.7).

[f] The corresponding tetraphenylborate, **3f'**, was obtained by ion exchange with $NaBPh_4$ in MeOH; mp 189°C. This product was analyzed (Footnote b).

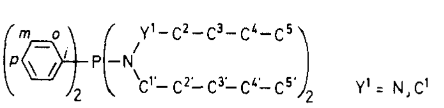
[g] The reaction was carried out in MeCN.

[h] The salt **3k** was extracted with MeOH (Soxhlet apparatus) and recrystallized.

Table 2. IR-, ^{1}H-NMR-, ^{13}C-NMR and ^{31}P-NMR-Spectral Data of Compounds **3**

Compound	IR (KBr) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) of the Amino Groups δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS)[a, b] $\delta_{PhP,\ amino\ group}$, J (Hz)	^{31}P-NMR ($CHCl_3$/ 85% $H_3PO_{4\,ext}$) δ
3a	3400, 1660, 1120, 1090, 730, 690	0.57–1.93 (m, 14H, $2C_3H_7$), 2.70–3.33 (ddt, 4H, $J = 7$, $J_{HP} = 7$, $2NCH_2$), 6.57 (dt, 2H, $J = 7$, $J_{HP} = 14$, 2NH)	14.1 (C^4), 20.4 (C^3), 33.6 (6.3, C^2), 41.1 (1.8, Y^1), 123.9 (124.9, *i*), 129.8 (13.6, *m*), 133.1 (11.3, *o*), 134.3 (2.9, *p*)	+37.5[c]
3b	3430, 1160, 1050, 920, 750, 690	1.2 (d, 6H, $J = 7$, $2CH_3$), 3.0–3.83 (m, 2H, 2NCH), 6.47 (dd, 2H, $J = 11$, $J_{HP} = 15$)	25.1 (4.8, C^2), 44.0 (Y^1)[e], 124.7 (125.4, *i*), 129.5 (13.8, *m*), 133.4 (11.4, *o*), 134.2 (*p*)[e]	+33.7
3c	3430, 1620, 1100, 1065, 1020, 1000, 700, 750	1.35 (s, 18H, $6CH_3$), 6.33 (d, 2H, $J_{HP} = 15$, 2NH)	31.9 (4.3, C^2), 55.6 (3.1, Y^1), 126.8 (123.3, *i*), 129.7 (13.7, *n*), 133.5 (11.6, *o*), 134.3 (3.0, *p*)	+25.9
3′d	3400, 1120, 1090, 730, 690	3.2 (m, 8H, $4NCH_2$), 7.28 (m, 4H, $J_{HP} = 12.7$, 4NH)	42.8 (Y^1)[e], 123.3 (126.4, *i*), 131.1 (13.6, *m*), 134.2 (11.3, *o*), 136.0 (*p*)[e]	+36.3 ($CHCl_3$/MeOH)
3e	3450, 1585, 1120, 1060, 1030, 730, 690	4.13 (dd, 4H, $J = 7$, $J_{HP} = 12$), $2NCH_2$), 6.28–6.8 (dt, 2H, $J = 7$, $J_{HP} = 14$, 2NH)	44.3 (Y^1)[e], 123.3 (126.4, *i*), 129.6 (13.8, *m*), 133.2 (11.4, *o*), 134.4 (*p*)[e], 138.7 (4.6,C^2)[f]	+38.1[d]
3f	3400, 1120, 1040, 730, 690	7.09 (m, 2H, 2NH), 7.25–8.20 (m, 10H, $2NC_6H_5$)	122.0 (7.5, C^2), 123.3 (128.3, *i*), 125.2 (C^4), 130.7 (C^3), 131.1 (14.0, *m*), 133.8 (11.6, *o*), 136.2 (*p*)[e], 139.3 (Y^1)	+27.4 ($CHCl_3$/MeOH)
3g	3450, 1640, 1125, 1050, 750, 690	3.4–3.93 (ddd, 4H, $J = 6, 7$, $J_{HP} = 11$, $2NCH_2$), 4.97 (dd, 2H, $J = 10.2, 1.3$, $2CH_2CH{=}CH\underline{H}_{trans}$), 5.13 (dd, 2H, $J = 17, 1.3$, $2CH_2CH{=}CH\underline{H}_{cis}$), 5.63–6.33 (ddt, 2H, $J = 17, 10.2, 6$, $2C\underline{H}{=}CH_2$), 6.53–7.13 (dt, 2H, $J = 7$, $J_{HP} = 14.5$, 2NH)	43.4 (Y^1)[e], 117.5 (C^3), 123.7 (126.3, *i*), 129.7 (13.7, *m*), 133.1 (11.4, *o*), 134.4 (2.8, *p*), 135.1 (5.9, C^2)	+38.4
3h	1740, 1160	1.3 (t, 6H, $J = 7.15$, $2CH_3$), 3.83 (dd, 4H, $J = 6.9$, $J_{HP} = 13.3$, $2NCH_2$), 4.20 (q, 4H, $J = 7.15$, $2OCH_2$), 6.75 (dt, 2H, $J = 6.9$, $J_{HP} = 13.4$, 2NH)	14.4 (C^4), 42.8 (Y^1)[e], 62.1 (C^3), 122.5 (128.8, *i*), 130.2 (14.0, *m*), 133.3 (11.5, *o*), 135.1 (*p*)[e], 170.6 (5.7, C^2)	+40.3
3i	1120, 1035, 925, 750, 700	0.7–1.8 (m, 28H, $4C_3H_7$), 2.7–3.4 (m, 8H, $4NCH_2$)	14.0 (C^4), 20.4 (C^3), 31.2 (C^2)[e], 48.2 (2.9, Y^1), 121.4 (123.8, *i*), 130.7 (13.4, *m*), 133.4 (10.6, *o*), 136.1 (2.8, *p*)	+53.5
3j	3060, 1600, 1115, 1215, 740, 680	0.45–1.80 (m, 14H, $2C_3H_7$), 2.85–3.40 (m, 4H, $2NC\underline{H}_2{-}C_3H_7$), 4.6 (d, 4H, $2NC\underline{H}_2{-}C_6H_5$)	13.8 (C^4), 20.2 (C^3), 30.3 (C^2)[e], 49.2 (Y^1)[e], 51.5 ($C^{1'}$)[e], 121.4 (123.5, *i*), 130.7 (13.5, *m*), 134.2 (10.8, *o*), 135.8 (*p*)[e], 138 ($C^{2'}$)[e,f]	+53.8
3k	3450, 1600, 1120, 685, 740	6.6–8.35 (m, 10H, NC_6H_5), 8.50 (s, 2H, $2N\underline{H}{-}NHPh$), 9.30 (d, 2H, $J = 31$, $2NH{-}N\underline{H}Ph$)	114.7 (C^3), 121.4 (C^5), 121.9 (129.8, *i*), 130.2 (C^4), 130.8 (13.2, *m*), 134.0 (10.3, *o*), 136.1 (*p*)[e], 149.6 (8.7, C^2)	+37.8 (DMSO)

[a] Assignments:



[b] **3c** in $CDCl_3$/MeOH; **3′d**, **3f** and **3k** in DMSO-d_6.

[c] Corresponding iodide **2a′**: +37.9.

[d] Corresponding iodide **2e′**: +38.4

[e] J is not detected using a 250 MHz spectrometer.

[f] Other chemical shifts of **3e**: 127.7 (1), 128.7 (4); and of compound **3j**: 126.7 (1), 128.5 (4).

Chlorodiphenylphosphine and the amines were purchased from Prolabo or Aldrich Chemical Co. and were used after distillation under N_2. Bromine was purchased from Prolabo Chemical Co. and was dried before use by shaking with conc. H_2SO_4. Dichloromethane and acetonitrile were freshly dried and distilled. IR spectra were recorded on a Perkin-Elmer 377 Infrared spectrophotometer. ^{1}H-NMR spectra were obtained using a Varian EM360 spectrometer, with the exception of the spectra of compounds **3e**, **3f** and **3h** obtained on a Bruker AC250 MHz spectrometer. ^{31}P-NMR were obtained using a Bruker WP80 MHz spectrometer.

Diaminophosphonium Salts 3a–j; General Procedure:

To a solution of chlorodiphenylphosphine (27 mL, 0.15 mol) in anhydrous CH_2Cl_2 (150 mL), under N_2, a solution of Br_2 (7.6 mL, 0.15 mol) in CH_2Cl_2 (50 mL) is added dropwise over 60 min. Then, either a solution of the amine (0.6 mol) (Procedure A) or a mixture of the amine (0.3 mol) and NEt_3 (30.36 g, 0.3 mol) (Procedure B) in CH_2Cl_2 (100 mL) is added at 0 °C over 2 h, and efficient stirring is continued at 20 °C for 2 to 96 h (Table 1). The phosphonium salt **3** is isolated either by filtration or by evaporation of the solvent, and then recrystallized (Table 1, 2).

Diaminophosphonium Salt 3k:

To a solution of chlorodiphenylphosphine (10.76 mL, 580 mmol) in anhydrous CH_2Cl_2 (100 mL) under N_2, a solution of Br_2 (2.95 mL, 580 mmol) in CH_2Cl_2 (30 mL) is added dropwise over 60 min at 20 °C. A solution of phenylhydrazine (25 mL, 250 mmol) in CH_2Cl_2 (150 mL) is then added over 2 h at 0 °C and stirring is continued at r.t. for 3 d. The mixture is filtered to give a pinkish solid which is suspended and stirred in water (300 mL), dried, and then extracted with MeOH in a soxhlet apparatus. (Table 1, 2).

We acknowledge the technical assistance of M. Eric Manginot and the financial support of Anvar Agency to this work.

Received: 15 February 1989; revised: 11 September 1989

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