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A Convenient One-Pot Synthesis of 1,2-Azaphospholanium Salts

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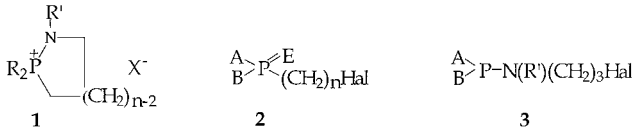
ABSTRACT: *A novel facile one-pot synthesis of the 1,2-azaphospholanes by intramolecular alkylation of 3-halopropyl amides of tricoordinate phosphorus has been suggested. Using this method, a series of the differently N-substituted 1,2-azaphospholanium salts were synthesized. 3-Aminopropylphosphine oxides were obtained by hydrolysis of the salts. A probable mechanism of the 1,2-azaphospholanium salts formation is discussed.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:596–602, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10209

INTRODUCTION

Phosphorus-containing heterocycles are attracting constantly increasing interest owing not only to the special features of their structure and reactivity compared with those of acyclic analogues but to a wide application in organic synthesis and a practical use. From the synthetic standpoint, 1,2-azaphosphacyclanium salts **1** are very promising compounds. Salts **1**, unsubstituted at the nitrogen atom (R′ = H), can enter into the aza-Wittig reaction giving compounds with a C=N bond and a phosphine oxide group, which may be further used in the Horner–Wittig reaction. As a result, a wide variety of acyclic phosphorus-containing organic compounds (imines, ureas, amides, enamines, alkenes, etc.) and nitrogen-containing heterocycles were synthesized [1–4]. Moreover, hydrolysis of the salts **1** might be expected to result in ω-aminoalkylphosphine oxides, which can exhibit complexing properties and biological activity. At the beginning of our investigations, only two 1,2-azaphosphacyclanium salts were obtained by a multistep procedure [1].



1 **2** **3**

Previously we have developed [5–7] a general approach to 1,2-heteraphosphacyclanes by intramolecular alkylation of ω-haloalkyl-substituted compounds of tetracoordinate phosphorus with P=E bond **2** (E = S, NR′). On the basis of this method, a number of N-arylsubstituted 1,2-azaphospholanium and 1,2-azaphosphinanium salts **1** ($n = 3$, 4) were obtained. In this paper, we report a new facile and convenient synthesis of 1,2-azaphospholanes via intramolecular alkylation of 3-halopropyl amides of tricoordinate phosphorus **3**.

RESULTS AND DISCUSSION

By the interaction of diphenyl or dibutylchlorophosphine with 3-halopropylamine hydrohalide in the

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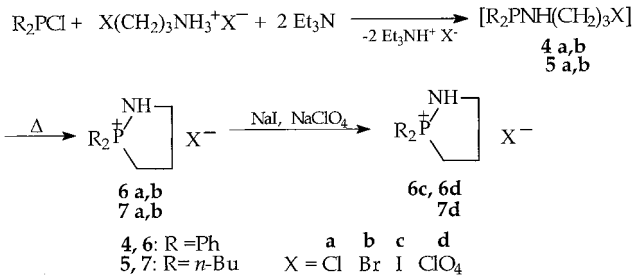
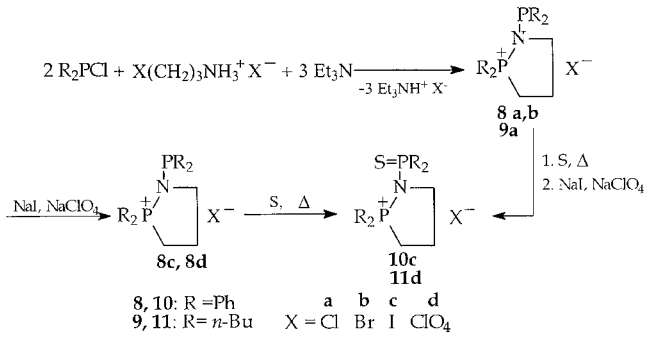


SCHEME 1



SCHEME 2

presence of 2 mol of triethylamine, the corresponding chlorides **6a** and **7a** and bromides **6b** and **7b** were obtained (Scheme 1). They were turned to the more stable iodide **6c** and perchlorates **6d** and **7d** by an anion exchange (Tables 1–3). Perchlorate **6d** was previously prepared via a four-step synthesis [1].

Starting from 2 mol of diphenylchlorophosphine and 1 mol of 3-halopropylamine hydrohalide in the presence of 3 mol of triethylamine, 1,2-azaphospholanium salts **8a,b** with Ph_2P group at the nitrogen atom were synthesized (Scheme 2). They were isolated in high yields as iodide **8c** and perchlorate **8d** (Tables 1–3). On heating with sulfur in acetonitrile, iodide **8c** was transformed into sulfide **10c**. By the same procedure, chloride **9a** was obtained from 2 mol of dibutylchlorophosphine and 1 mol of 3-chloropropylamine hydrochloride. Without isolation, it was transformed into sulfide **11d** on heating with sulfur.

We called our attention to the higher yields of diphenylphosphinosubstituted salts **8c,d** as compared with unsubstituted salts **6c,d** (Table 1). To account for this fact, we carried out the ^{31}P NMR monitoring the formation of **6a** by interaction of equivalent amounts of Ph_2PCl and 3-chloropropylamine hydrochloride in the presence of 2 equiv of triethylamine. Unexpected results were obtained. The reaction was found to proceed through *N*-diphenylphosphino-substituted chloride **8a** (Scheme 3, Fig. 1). At first, *N*,*N*-bis(diphenylphosphino)-3-chloropropylamine (**12a**) forms (Eq. 1). It disappears rapidly transforming into **8a** by intramolecular P-alkylation (Eq. 2). As is evident from Fig. 1, **8a** is the prevailing product at the initial stages of the reaction. Its content in the reaction mixture increases to 75% and then gradually falls. Under reaction conditions, **8a** enters into transamidation with the remaining 3-chloropropylamine, giving rise to **6a** and (3-chloropropylamino)diphenylphosphine **4a** (Eq. 3). The content of the latter in the reaction mixture does not exceed 22% during the reaction because it

TABLE 1 Experimental Data of Compounds **6–8, 10**, and **11**

				Found (Calculated)			
	mp (°C)	*Yield (%)*	*Molecular Formula*	*C*	*H*	*N*	*P*
6c	215–218[a] (dec)	58.5	$C_{15}H_{17}INP$	48.77 (48.80)	4.60 (4.64)	3.47 (3.79)	8.29 (8.39)
6d	173.5–175[a,b]	65.5	$C_{15}H_{17}ClNO_4P$	52.73 (52.71)	4.58 (5.02)	4.08 (4.10)	8.97 (9.06)
7d	–[c]	38.5 (82.7)[d]	$C_{11}H_{25}ClNO_4P$[e]	43.55 (43.78)	8.36 (8.29)		10.26 (10.28)
8c	193–196[f] (dec)	80.6	$C_{27}H_{26}INP_2$	58.47 (58.29)	4.40 (4.71)	2.44 (2.52)	11.15 (11.13)
8d	170–172[a]	80.0	$C_{27}H_{26}ClNO_4P_2$	61.73 (61.66)	5.11 (4.98)	2.68 (2.66)	11.47 (11.78)
10c	228–230[g] (dec)	51.6	$C_{27}H_{26}INP_2S$	55.31 (55.38)	4.47 (4.44)	2.36 (2.39)	10.51 (10.60)
11d	180.5–182[h]	49.0	$C_{19}H_{42}ClNO_4P_2S$	47.81 (47.74)	9.05 (8.86)	2.87 (2.93)	12.92 (12.96)

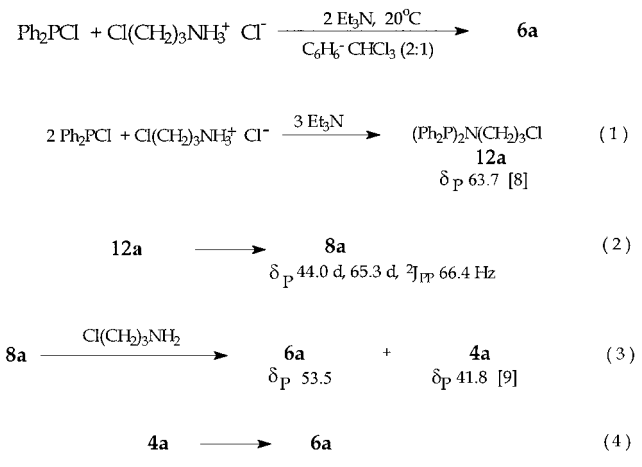
[a] CH_2Cl_2–AcOEt.
[b] Lit. [1]: mp 160–161°C.
[c] Oil, purified by column chromatography on silica gel.
[d] Calculated from ^{31}P NMR spectrum of the crude product.
[e] Found (%): Cl, 11.78. Calculated (%): 11.77.
[f] MeCN–AcOEt.
[g] EtOH–Et_2O–*n*-C_6H_{14}.
[h] MeCN–AcOEt–*n*-C_6H_{14}.

TABLE 2 IR, ^{1}H NMR, and ^{31}P NMR Data for Compounds **6–8, 10**, and **11**

		NMR in $CDCl_3$: Multiplicity, J (Hz)	
	IR (KBr) (cm^{-1})	*^1H*	*^{31}P*
6c	2400–3300 (NH)	2.38 (m, 2H, $\underline{CH_2}CH_2P$); 2.92 (dt, $^3J_{PH} = 8.4$, $^3J_{HH} = 7.2$, 2H, CH_2N); 3.69 (dt, $^2J_{PH} = 11.2$, $^3J_{HH} = 6.4$, 2H, CH_2P); 6.61 (d, $^2J_{PH} = 16.8$, 1H, NH); 7.41–8.07 (m, 10H, $2C_6H_5$)	53.8 s
6d	3200–3500 (NH)	2.36 (m, 2H, $\underline{CH_2}CH_2P$); 2.90 (dt, $^3J_{PH} = 8.4$, $^3J_{HH} = 7.2$, 2H, CH_2N); 3.66 (dt, $^2J_{PH} = 10.8$, $^3J_{HH} = 6.0$, 2H, CH_2P); 5.33 (d, $^2J_{PH} = 16.8$, 1H, NH); 7.57–7.80 (m, 10H, $2C_6H_5$)	54.3 s
7d	3200–3500[a] (NH)	0.91 (t, $^3J_{HH} = 6.8$, 6H, $2CH_3$); 1.39–1.60 (m, 8H, $2\underline{CH_2}\underline{CH_2}CH_3$); 2.11–2.21 (m, 4H, $2CH_2P$); 2.26–2.37 (m, 2H, $\underline{CH_2}CH_2P$); 2.43 (dt, $^3J_{PH} = {}^3J_{HH} = 7.6$, 2H, CH_2N); 3.36 (dt, $^2J_{PH} = 10.8$, $^3J_{HH} = 6.4$, 2H, CH_2P); 4.12 (d, $^2J_{PH} = 16.0$, 1H, NH)	74.0 s
8c	–	2.51–2.62 (m, 2H, $\underline{CH_2}CH_2P$); 3.61–3.70 (m, 4H, $CH_2P + CH_2N$); 7.19–7.94 (m, 20H, $4C_6H_5$)	44.7 d, 64.2 d; $^2J_{PP} = 66.6$
8d	–	2.45–2.56 (m, 2H, $\underline{CH_2}CH_2P$); 3.32 (dt, $^3J_{PH} = {}^3J_{HH} = 7.2$, 2H, CH_2N); 3.58 (dt, $^2J_{PH} = 9.6$, $^3J_{HH} = 6.4$, 2H, CH_2P); 7.17–7.83 (m, 20H, $4C_6H_5$)	44.8 d, 64.1 d; $^2J_{PP} = 66.6$
10c	612, 622[b] (P=S)	2.47 (m, 2H, $\underline{CH_2}CH_2P$); 3.62 (m, 2H, CH_2N); 3.99 (m, 2H, CH_2P); 7.37–8.13 (m, $4C_6H_5$)	62.9 d, 63.0 d; $^2J_{PP} = 6.6$
11d	586[b] (P=S)	0.94 (t, $^3J_{HH} = 7.2$, 6H, $2CH_3$); 0.95 (t, $^3J_{HH} = 7.2$, 6H, $2CH_3$); 1.41–1.66 (m, 16H, $4\underline{CH_2}\underline{CH_2}CH_3$); 2.06 (m, 4H, $2CH_2P$=S); 2.31 (m, $^3J_{PH} = 13.2$, $^3J_{HH} = 6.8$, 2H, $\underline{CH_2}CH_2P$); 2.60 (m, 2H, CH_2N); 2.74 (m, 4H, $2CH_2P$); 3.56 (m, 2H, CH_2P^+)	78.7 d, 85.6 d; $^2J_{PP} = 6.0$

[a] In $CHCl_3$ solution.
[b] Raman spectroscopy.

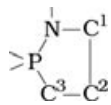
undergoes intramolecular cyclization into chloride **6a** (Eq. 4). The quantity of the ultimate product **6a** increases constantly in the reaction mixture and amounts up to 85% within 80 h (Fig. 1).



SCHEME 3

The possibility of the transamidation (Eq. 3) was confirmed by an independent experiment (Scheme 4). When 1 mmol of iodide **8c** and 1.3 mmol of 3-bromopropylamine hydrobromide were refluxed for 2 h in C_6H_6–$CHCl_3$ solution in the presence of 1.5 mmol of triethylamine, 74% of a iodide **6c** and bromide **6b** mixture was obtained (^{31}P NMR

TABLE 3 ^{13}C NMR Chemical Shifts and Multiplicities for the Ring Carbon Atoms of Compounds **6, 8**, and **10**[a]



	C-3 ($^1J_{CP}$)	*C-2 ($^2J_{CP}$)*	*C-1 ($^2J_{CP}$)*
6c	25.9 d (64.7)	23.1 s	46.0 d (11.1)
6d	25.4 d (65.6)	23.5 s	46.9 d (11.0)
8c	26.9 d (61.6)	24.4 s	50.0 dd (15.9; 5.0)
8d	25.5 d (62.6)	24.0 s	49.9 dd (15.5; 5.0)
10c	29.6 d (64.4)	23.0 d (5.8)	55.4 d (13.7)

[a] δ (ppm) and J (Hz) (in parentheses) in $CDCl_3$ solution.

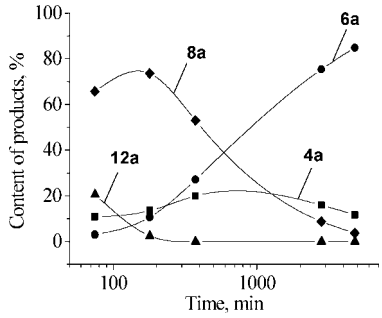


FIGURE 1 The time dependence of the reaction mixture composition for Ph_2PCl and 3-chloropropylamine hydrochloride (1:1) interaction in benzene–chloroform solution at 20°C in the presence of 2 mol of Et_3N (^{31}P NMR monitoring data).

spectroscopy data). By the subsequent treatment of the mixture with sodium iodide, 1.22 mmol (61%) of iodide **6c** was isolated.

Contrary to diphenylchlorophosphine, by reaction of dibutylchlorophosphine with 3-chloropropylamine hydrochloride, the amide **5a** is formed as intermediate product (δ_P 39.7 ppm [10]).

The structures of all compounds obtained were confirmed by ^1H, ^{31}P, ^{13}C NMR, and IR (Raman) spectroscopy. The crystal structure of **8d** was determined by X-ray analysis (Fig. 2).

The geometry of **8d** is similar to that of previously investigated 1,2,2-triphenyl-1,2λ^4-azaphospholanium iodide [7]. For example, the lengths of P(1)—N(1) bonds are equal to 1.636(4) and 1.644(4) Å, respectively. The five-membered ring is characterized by the envelope conformation, with the deviation of the C(2) atom by 0.56 Å. It is noteworthy that the nitrogen atom in **8d** is planar, and the sum of the bond angles at the nitrogen atom is 359.9° as in all known 1,2-azaphospholanium cycles (see Refs. [1,7]). Thus, the presence of the positively charged phosphorus atom results in the stabilization of the planar configuration of the nitrogen. The P(2)—N(1) bond in **8d** (1.736(3) Å) is equal to the corresponding value in *N*-(diphenylphosphino)-*N*-(diphenylthiophosphoryl)-alanine methyl ester (1.737(3) Å) [11]. The conformation of the PPh_2 group in respect to azaphospholanium cycle is such that the lone electron pair (Lp) of the P(2) atom is antiperiplanar to the N(1)—C(1) bond (the pseudotorsion angle LpP(2)N(1)C(1) is 174°). It might be supposed that some elongation of the N(1)—C(1) bond (1.522(5) Å) in **8d** in comparison to 1,2,2-triphenyl-1,2λ^4-azaphospholanium iodide (1.492(6) Å) is probably due to the Lp(P)—σ(N(1)—C(1)) interaction.

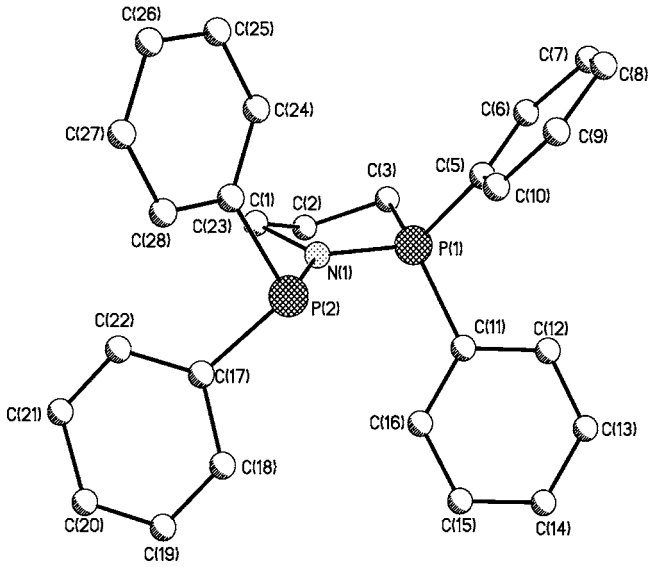
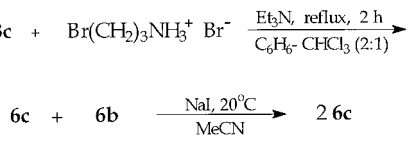


FIGURE 2 The general view of the cation of perchlorate **8d**. The selected bond lengths (Å): P(1)–N(1) 1.636(4), P(1)–C(3) 1.792(5), P(1)–C(5) 1.790(4), P(1)–C(11) 1.791(4), P(2)–N(1) 1.736(3), P(2)–C(17) 1.820(5), P(2)–C(23) 1.830(5), N(1)–C(1) 1.522(5); bond angles (°): N(1)–P(1)–C(5) 115.8(2), N(1)–P(1)–C(11) 111.7(2), C(5)–P(1)–C(11) 107.1(2), N(1)–P(1)–C(3) 96.5(2), C(5)–P(1)–C(3) 112.0(2), C(11)–P(1)–C(3) 113.7(2), N(1)–P(2)–C(17) 103.7(2), N(1)–P(2)–C(23) 102.7(2), C(17)–P(2)–C(23) 103.2(2), C(1)–N(1)–P(1) 112.6(3), C(1)–N(1)–P(2) 123.8(3), P(1)–N(1)–P(2) 123.5(2).

It should be mentioned also that the unsubstituted at the nitrogen atom 1,2-azaphospholanium salts **6a,b** and **7a,b** readily undergo the P—N bond hydrolysis with the formation of ammonium salts $R_2P(O)(CH_2)_3NH_3^+X^-$ (**13a,b** and **14a,b**). Thus, in an attempt to isolate 1,2-azaphospholanium chloride **6a** by the crystallization of the reaction mixture from C_2H_5OH–CH_3CN–AcOEt, ammonium chloride **13a** was obtained. The iodide **6c** and perchlorate **6d** are stable to storage in crystalline state at 20°C. However, iodide **6c** is completely transformed into **13c** on keeping at 20°C for several hours in H_2O–C_2H_5OH solution or over a long period of time in CH_2Cl_2–AcOEt solution. By the alkaline hydrolysis of **6d**, (3-aminopropyl)diphenylphosphine oxide $Ph_2P(O)(CH_2)_3NH_2$ (**15**) was isolated.

In summary, a novel facile and convenient method of the 1,2-azaphospholanium salts synthesis has been developed. It may be expected that this method would be appropriate for the preparation



SCHEME 4

both of the other types of 1,2-azaphospholanes and of 1,2-azaphosphacyclanes with the various ring size.

EXPERIMENTAL

All reactions were carried out in argon atmosphere using anhydrous solvents. NMR ^{1}H (400.13 MHz), ^{31}P (161.98), and ^{13}C (100.61) spectra were recorded on Bruker AMX-400 spectrometer with TMS as an internal standard (^{1}H, ^{13}C) and 85% H_3PO_4 as an external standard (^{31}P). IR spectra were determined on UR-20 spectrometer and "Magna IR 750" (Nicolet) Furie spectrometer (KBr pellets), and Raman spectra on Joben Yvon U-1000 ($\lambda = 514.5$ nm) spectrometer.

*2,2-Diphenyl-1,2λ⁴-azaphospholanium Iodide (**6c**) and Perchlorate (**6d**) and 2,2-Dibutyl-1,2-λ⁴-azaphospholanium Perchlorate (**7d**)*

To a suspension of 3.8 mmol of 3-halopropylamine hydrohalide in 15 ml of benzene–chloroform (2:1) mixture, a solution of 8.3 mmol of triethylamine in 5 ml of benzene-chloroform mixture was added dropwise with stirring. After 20 min, 3.8 mmol of diphenylchlorophosphine (or dibutylchlorophosphine) in 10 ml of the same solvent mixture was added dropwise at 2–4°C. The mixture was stirred for an hour at 2–4°C and was then refluxed for 1 h. After cooling, triethylamine hydrohalide was filtered off, the solvents were removed in vacuo, the residue was dissolved in 10 ml of acetonitrile, and 7.6 mmol of sodium iodide (or sodium perchlorate) in acetonitrile was added. The precipitate of sodium chloride (bromide) was filtered off, the solvent was evaporated in vacuo, and the residue was dissolved in methylene chloride. The excess of sodium iodide (perchlorate) was filtered off, the solvent was removed, and the residue was crystallized or purified by column chromatography (Tables 1–3).

*1-Diphenylphosphino-2,2-diphenyl-1,2λ⁴-azaphospholanium Iodide (**8c**) and Perchlorate (**8d**)*

The compounds were prepared from 7.6 mmol of diphenylchlorophosphine, 3.8 mmol of 3-halopropylamine hydrohalide, and 12.5 mmol of triethylamine in a mixture of benzene–chloroform (2:1) by the procedure for the synthesis of **6c,d** (Tables 1–3).

*1-Diphenylthiophosphoryl-2,2-diphenyl-1,2λ⁴-azaphospholanium Iodide (**10c**)*

To a solution of 0.44 g (0.79 mmol) of **8c** in 10 ml of acetonitrile, 0.031 g (0.97 mg atom) of sulfur in 3 ml of benzene was added, and the mixture was refluxed for 1.5 h. The excess of sulfur was filtered off, the solvent was evaporated in vacuo, and the residue was triturated with ether to give 0.45 g of the solid product containing 85.4% of **10c** (^{31}P NMR spectroscopy data). After recrystallization, 0.24 g of iodide **10c** was obtained (Tables 1–3).

*1-Dibutylthiophosphoryl-2,2-dibutyl-1,2λ⁴-azaphospholanium Perchlorate (**11d**)*

To a solution of **9a** obtained from 1.64 g (9.1 mmol) of dibutylchlorophosphine, 0.50 g (3.8 mmol) of 3-chloropropylamine hydrochloride, and 1.15 g (11.4 mmol) of triethylamine in a benzene–chloroform (2:1) mixture, 0.12 g (3.8 mg atom) of sulfur was added. The reaction mixture was refluxed for 1 h, and the precipitate formed was filtered off. The solvents were removed in vacuo, the residue was dissolved in 10 ml of acetonitrile, and 0.90 g (7.4 mmol) of sodium perchlorate in 10 ml of acetonitrile was added. The reaction mixture was worked up as previously mentioned, and 0.89 g of **11d** was isolated after crystallization (Tables 1 and 2).

^{13}C NMR ($CDCl_3$): 13.2, 13.4 (CH_3); 20.3 (d, $^{3}J_{CP} = 1.9$ Hz), 20.9 (d, $^{3}J_{CP} = 1.9$ Hz) ($\underline{CH_2}CH_3$); 23.3 (d, $^{2}J_{CP} = 4.6$ Hz), 23.5 (d, $^{2}J_{CP} = 5.1$ Hz), 23.6 (d, $^{2}J_{CP} = 4.4$ Hz) ($\underline{CH_2}CH_2P$); 23.9 (d, $^{1}J_{CP} = 3.2$ Hz, $CH_2P{=}S$); 27.9 (d, $^{1}J_{CP} = 51.5$ Hz), 32.3(d, $^{1}J_{CP} = 60.5$ Hz) (CH_2P^{+}); 51.4 (d, $^{2}J_{CP} = 11.6$ Hz, CH_2N).

Transamidation of 1-Diphenylphosphino-2,2-diphenyl-1,2λ⁴-azaphospholanium Iodide **8c** *with 3-Bromopropylamine Hydrobromide*

To a suspension of 0.28 g (1.3 mmol) of 3-bromopropylamine hydrobromide in 15 ml of benzene–chloroform (2:1) mixture, 0.15 g (1.5 mmol) of triethylamine was added under stirring. The mixture was held at 20°C for 1 h and then 0.56 g (1.0 mmol) of iodide **8c** was added. The mixture was stirred for 30 min at 20°C and refluxed for 2 h. According to ^{31}P NMR spectroscopy, the reaction mixture involving 74% of iodide **6c** and bromide **6b** was obtained. The precipitate formed was filtered off, the solvents were removed in vacuo, the residue was dissolved in 5 ml of acetonitrile, and a solution of 0.30 g (2.0 mmol) of sodium iodide in 5 ml of acetonitrile was added. The mixture was worked out by the procedure adopting for the synthesis of compounds **6**. After recrystallization of the residue from the ethyl acetate–methylene chloride mixture, 0.45 g (61%) of iodide **6a** was isolated. mp 215–217°C (dec); ^{31}P NMR ($CDCl_3$): δ 53.6 ppm.

*3-(Diphenylphosphoryl)propylammonium Chloride (***13a***)*

From 0.85 g (3.8 mmol) of diphenylchlorophosphine, 0.50 g (3.8 mmol) of 3-chloropropylamine hydrochloride, and 0.84 g (8.3 mmol) of triethylamine in 30 ml of the benzene–chloroform solution, under conditions previously described for the synthesis of **6c**, the reaction mixture containing 86.3% of chloride **6a** was obtained (^{31}P NMR spectroscopy data). The solvents were evaporated in vacuo, and 0.62 g of **13a** was isolated by crystallization of residue from ethanol–acetonitrile–ethyl acetate. Yield 55.4%, mp 183–184°C. IR (KBr) ν(cm^{-1}): 1180 (P=O), 2400–3200 (NH_3^+). ^{31}P NMR (CD_3OD): δ 38.0. ^{1}H NMR (CD_3OD): δ 2.07–2.17 (m, 2H, $\underline{CH_2}CH_2P$); 2.75–2.82 (m, 2H, CH_2P); 3.27 (m, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2N); 7.74–8.02 (m, 10H, $2C_6H_5$). ^{13}C NMR (CD_3OD): δ 20.4 (s, $\underline{C}H_2CH_2P$); 26.4 (d, $^1J_{CP}$ = 70.1 Hz, CH_2P); 40.3 (d, $^3J_{CP}$ = 15.4 Hz, CH_2N); 129.4 (d, $^3J_{CP}$ = 12.0 Hz, C_{meta}), 131.1 (d, $^2J_{CP}$ = 9.8 Hz, C_{ortho}), 131.9 (d, $^1J_{CP}$ = 99.1 Hz, C_{ipso}), 132.8 (s, C_{para}) (C_6H_5). Anal. Calcd for $C_{15}H_{19}ClNOP$: C, 60.92; H, 6.48; N, 4.74; P, 10.47%. Found: C, 60.98; H, 6.43; N, 4.65; P, 10.47%.

Hydrolysis of **6c** *and Preparation of 3-(Diphenylphosphoryl)propylammonium Iodide (***13c***)*

A solution of 0.30 g (0.81 mmol) of **6c** in 24 ml of ethanol–water (1:1) solution was allowed to stand for several hours at 20°C, and the solvents were evaporated in vacuo. After crystallization of residue from the mixture of ethanol–acetonitrile–ethyl acetate, 0.18 g of **13c** was obtained. Yield 58.1%, mp 190–192°C. IR (KBr), ν(cm^{-1}): 1162 (P=O), 1610, 2300–3300 (NH_3^+). ^{31}P NMR (CD_3OD): δ 37.8. ^{1}H NMR (CD_3OD): δ 1.91–2.01 (m, 2H, $\underline{CH_2}CH_2P$); 2.62–2.70 (m, 2H, CH_2P); 3.12–3.17 (m, 2H, CH_2N); 7.61–7.89 (m, 10H, C_6H_5). ^{13}C NMR (CD_3OD): δ 20.4 (s, $\underline{CH_2}CH_2P$); 26.5 (d, $^1J_{CP}$ = 72.0 Hz, CH_2P); 40.3 (d, $^3J_{CP}$ = 14.8 Hz, CH_2N); 129.4 (d, $^3J_{CP}$ = 12.0 Hz, C_{meta}), 131.1 (d, $^2J_{CP}$ = 9.8 Hz, C_{ortho}), 131.8 (d, $^1J_{CP}$ = 100.9 Hz, C_{ipso}), 132.9 (d, $^4J_{CP}$ < 3.6 Hz, C_{para}) (C_6H_5). Anal. Calcd for $C_{15}H_{19}INOP$: C, 46.53; H, 4.94; N, 3.66; P, 8.00%. Found: C, 46.39; H, 4.87; N, 3.77; P, 8.00%.

Alkaline Hydrolysis of **6d** *and Preparation of (3-Aminopropyl)diphenylphosphine Oxide (***15***)*

To a solution of 0.4 g (1.17 mmol) of perchlorate **6d** in 35 ml of H_2O, 7.3 ml of 0.2 N aqueous NaOH was added. The reaction mixture was evaporated up to 8–10 ml and extracted with chloroform (3 × 10 ml). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated to solid, which was triturated with ether, filtered off, and dried in vacuo to give 0.23 g of **15**. Yield 77%, mp 78–81°C. IR (KBr) ν(cm^{-1}): 1172 (P=O), 1628, 3309, 3372 (NH_2). ^{31}P NMR ($CDCl_3$): δ 33.1. ^{1}H NMR ($CDCl_3$): δ 1.29 (br. s, 2H, NH_2); 1.68–1.77 (m, 2H, $\underline{CH_2}CH_2P$); 2.27–2.34 (m, 2H, CH_2P); 2.76 (t, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2N); 7.42–7.75 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 21.6 (s, $\underline{CH_2}CH_2P$); 26.6 (d, $^1J_{CP}$ = 71.5 Hz, CH_2P); 40.5 (d, $^3J_{CP}$ = 14.2 Hz, CH_2N); 128.6 (d, $^3J_{CP}$ = 11.8 Hz, C_{meta}), 130.6 (d, $^2J_{CP}$ = 9.5 Hz, C_{ortho}), 131.8 (d, $^4J_{CP}$ = 1.7 Hz, C_{para}), 132.0 (d, $^1J_{CP}$ = 99.2 Hz, C_{ipso}) (C_6H_5). Anal. Calcd for $C_{15}H_{18}NOP$: C, 69.48; H, 7.00; N, 5.40; P, 11.95%. Found: C, 69.28; H, 7.01; N, 5.16; P, 11.95%.

X-Ray Crystal Structure Determination of **8d**

At 298 K, crystals of $C_{27}H_{26}ClNO_4P_2$ (M = 525.88) are orthorhombic. Space group $P2_12_12_1$, a = 8.271(4) Å, b = 13.602(7) Å, c = 22.968(9) Å, V = 2584(2) Å^3, Z = 4, d_{calc} = 1.352 g cm^{-3}, μ(Mo Kα) = 3.06 m^{-1}, F(000) = 1096. Intensities of 13,338 reflections were measured with a SMART 1000 CCD diffractometer at 110 K (λ(Mo Kα) = 0.71072 Å, ω-scans with 0.3 step in ω and 20 s per frame exposure, $2\theta < 52°$), and 5044 independent reflections (R_{int} = 0.0386) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to wR_2 = 0.1454 and GOF = 1.084 for all independent reflections (R_1 = 0.0590 was calculated against F for 2983 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0 on IBM PC/AT. Crystallographic data (excluding structure factors) for the reported in this paper structure have been deposited to the Cambridge Crystallographic Data Centre as supplementary no. CCDC-209266. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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