This article was downloaded by: [Florida State University] On: 04 October 2014, At: 23:15 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gpss20</u>

Convenient One Pot Preparation of Acylated Phosphinimines and Aminophosphonium Salts From the Versatile Triphenylphosphonium and Lithium Azayldiide Ph₃P=N-Li

Henri-Jean Cristau, Amer Hammami, Eric Manginot & Eliane Torreilles

^a Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.) , 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

^b Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.) , 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

^c Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.) , 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

^d Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.) , 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France Published online: 17 Mar 2008.

To cite this article: Henri-Jean Cristau , Amer Hammami , Eric Manginot & Eliane Torreilles (1998) Convenient One Pot Preparation of Acylated Phosphinimines and Aminophosphonium Salts From the Versatile Triphenylphosphonium and Lithium Azayldiide Ph₃P=N-Li, Phosphorus, Sulfur, and Silicon and the Related Elements, 134:1, 475-486, DOI: 10.1080/10426509808545488

To link to this article: <u>http://dx.doi.org/10.1080/10426509808545488</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

CONVENIENT ONE POT PREPARATION OF ACYLATED PHOSPHINIMINES AND AMINOPHOSPHONIUM SALTS FROM THE VERSATILE TRIPHENYLPHOSPHONIUM AND LITHIUM AZAYLDIIDE Ph₃P=N-Li

HENRI-JEAN CRISTAU, AMER HAMMAMI, ERIC MANGINOT and ELIANE TORREILLES*

Laboratoire de Chimie Organique E. N. S. C. M. (ESA 5076 du C.N.R.S.), 8, Rue de l'Ecole Normale, 34296 Montpellier, Cedex 5, France

(Received 3 March, 1998; In final form 16 April, 1998)

Starting from gaseous ammonia, through two multisteps reactions, either acylation or alkylation reactions, we have access to different N-substituted aminophosphonium salts, precursors of amines. Preparation and use of the intermediate, the triphenylphosphonium and lithium azayldiide Ph₃P=N-Li 1, were realized in "one pot".

Keywords: azaylide; azayldiide; N-acylated phosphinimine; N-substituted aminophosphonium salts; triphenylphosphonium and lithium azayldiide.

INTRODUCTION

In our earlier works, 1,2 we studied some aspects of the reactivity of the lithiated azayldiide 1, produced *in situ* by double deprotonation of the aminophosphonium salt **8a**, which was synthesized from gazeous ammonia and dibromotriphenyl-phosphorane. On some examples, we have shown that 1 can undergo N-acylation or N-alkylation. We describe a more documented investigation of both reactions.

^{*} Corresponding Author.

ACYLATION OF THE TRIPHENYLPHOSPHONIUM AND LITHIUM AZAYLDIIDE 1: SYNTHESIS OF N-ACYLATED PHOSPHINIMINES

Azayldiid 1 reacts at 60° C with acylating agents (acylchlorides 2, chloroformate 4, anhydride 6) and gives rise to the corresponding N-acylphosphinimines 3 or N-carbalkoxyphosphinimines 5 with good yields (fig. 1; Table I). In these reactions, there is formation of some amount of the phosphinimine 9 as a side product [easily eliminated, after acidification in the final work up, by precipitation as the aminotriphenyl phosphonium chloride 8b], when 1 is in the presence of a substrate with an acidic proton. (We observed that with the esters 10, the transformation of the reactive 1 into its conjugated acid 9 occurs even at 20° C).



Thus we investigated, by ³¹P-NMR spectroscopy in DMSO-d₆ in the presence of N-lithiated aniline, the equilibrium between 9 and 1 and determined the $pK_{a(H_2O)} = 28.1$ for compound 9. This value corroborates the highest basicity of the azayldiide 1 in regard to 9 since the $pK_{a(H_2O)} = 20.6$ for the salt 8a³. Accordingly, the mono and di-deprotonation of the salt 8a, induces an important shielding effect on the phosphorus atom resonance in the ³¹P-NMR spectra. The respective signals of compounds 8a, 9 and 1 appear in DMSO-d₆ at 35.9, 20.4, and -11.0 ppm. But the difference in their ¹³C-NMR spectra is mainly perceptible for their aromatic *ipso* carbon atoms (Table II) as already noted by Ostota – Starzewski,⁴ for the family of compounds $Ph_3P=X(X = CH_2, NH, O, S, Se)$: the chemical shifts of the aromatic carbon atoms, other than ipso, are less affected by the nature of the X groups.

Acylating Compounds	R	X	T (°C)	t (h)	3 or 5 Yield (%) ^a	Ref
2a	Me	Cl	60	1.5	3a (96)	2
2b	Et	Cl	20	1.5	3b (80)	b
2c	Ph	Cl	20	16	3c (98)	1
4a	OMe	Ci	60	3	5a (93)	2
4 b	OEt	Cl	60	3	5b (95)	2
4c	OCH ₂ Ph	Cl	60	3	5c (90)	2
6	Ph	OC(O)Ph	60	20	3c (48)	b
7	OPh	OPh	60	20	5d (98)	2
10	Et	OEt	60	1	3b (09)	b
10	Et	OEt	20	1	с	b

TABLE I Synthesis of N-substituted phosphinimines 3 or 5 from acylating compounds 2, 4, 6, 7, and 10 (fig. 1)

a) Yields of pure, isolated product based on starting 8a, the complement was the compound 9; b) This work, c) No acylation occurs: the reagent 1 is protonated into 9, and, after acidic work-up into 8.

TABLE II ¹³C-NMR spectra of compounds 1, 8a, and 9 (δ ppm, J (Hz))

Compounds	δ <i>C</i> i	J _{CiP}	δ <i>C</i> _m	J _{CmP}	δ <i>C_{,o}</i>	J _{CoP}	δСр	J _{Cp}
1	134.6	93.5	128.6	11.4	131.7	9.4	131.3	2.7
8a	123.4	102.8	129.9	13.1	132.9	11.4	134.8	2.7
9	134.5	93.8	128.6	11.4	131.7	9.4	131.3	2.8

The results noted in the table I corroborate the advantage of compound 1 compared with its protonated analogue 9, which reacts with acid chlorides 2 to afford the corresponding derivatives 3, but in only 40–50% yields (fig. 2).¹ With the anhydride 6 and the carbonate 7 no reaction occurs when the azaylide 9 is used instead of the lithiated reagent 1. So in spite of its basicity the azayldiide 1, is an efficient nucleophilic reagent.

 $2 \operatorname{Ph_3P=NH} + R \cdot C(O) \cdot C1 \xrightarrow{THF} \operatorname{Ph_3P=N-C(O)-R} + \operatorname{Ph_3P-NH_2} CT$ $9 \quad 2 \qquad \qquad THF \qquad 3 \qquad 8b$ FIGURE 2

ALKYLATION OF THE TRIPHENYLPHOSPHONIUM AND LITHIUM AZAYLDIIDE 1: SYNTHESIS OF SOME NEW AMINOPHOSPHONIUM SALTS

We were also interested by the possible access, from azayldiide 1, to several N-alkylated aminophosphonium salts, which can be considered as effective precursors for poly- or cyclic amines.⁵ Starting from the salt 8a, some cyclizations can be achieved *in situ* (fig. 3), after the initial formation of the lithiated triphenylphosphinimine 1, and subsequent reactions with different diiodoalkanes 11 (n = 4-6). These reactions are performed in THF: the first step at low temperature, the second at 60°C, after slow addition of 1 equivalent of the dihalide. So the corresponding cyclic aminophosphonium salts 12c are obtained and isolated by filtration of the reaction mixture (table III).

Compound 11	p ^a	t (h)	9 % ^b	12c % ^b (%) ^c	16 % ^b	15c %b	17c % ^b	18 % ^b
n = 1	1.1	15	100					
n=2	3	50	100					
n = 3	3	15	35				33	32
n=3	1	40	1				45	20
n = 4	1	15	12	89 (83)				
n = 4	5	26	3	83	10	4		
n = 5	1	24	10	84 (80)		6		
n=5	3	23	5	95 (90)				
n=6	3	65	9	40 (30)	d	d	d	d

TABLE III Phosphorus compounds obtained in the reaction of the azayldiide 1 and diiodoalkanes $I(CH_2)_n I$, 11 (fig. 3)

a) p = number of diiodoalkane equivalents; b) Ratio estimated from the ³¹P-NMR spectra of the reaction mixture; c) Yields of pure, isolated product, based on starting 8a; d) Mixture of unidentified phosphonium salts.

PHOSPHINIMINES

As indicated in Table III, in the cases of diiodobutane or pentane, good yields are obtained of the corresponding salts 12c (n = 4, 5). This means that inside the transient N-(4-iodo-butyl or 5-iodo-pentyl) triphenylphosphinimine 13 (n = 4, 5) the cyclization is promoted by an entropic effect to give the corresponding salts 12c (n = 4, 5). But in the case of the diiodopentane 11 (n = 5), the possible intermolecular reaction between the intermediate salt 13 (n = 5) and the reagent 1 occurs also in a very little extent to give the diphosphinimine 14 (n = 5), that affords the corresponding diaminophosphonium salt 15c (n = 5) (6%), after final work up. Also, as an effect of the concentration of the reagents, when the reaction is run with an excess (5 equivalents) of diiodide 11 (n = 4) with regard to the azayldiide 1 (1 equivalent), the corresponding salt 15c (n = 4) is also obtained together with the salt 16 (n = 4) as by-products.



FIGURE 3

However, with diiodides 11 (n = 1-3), the formation of azaylide 9 becomes important with diiodomethane and 1,2-diiodoethane, the azayldiide 1 acts only as a base. Only in the reaction of 1,3-diiodopropane with azayldiide 1, the N-alkylation is preceded by an elimination process, with formation of three different aminophosphonium salts 8c, 17c, and 18 after work up. With 1,6-diiodohexane the reaction affords a mixture of different salts: the azepane derivative 12c (n = 6), the bisphosphonium 15c (n = 6), and other unidentified salts.

Furthermore some particular dihalogeno compounds such as $Y(CH_2X)_2$ 19, were also considered (fig.4): the α, α' -dibromo-o-xylene 19a ($Y = C_6H_4, X = Br$) reacts with one equivalent of the azayldiide 1 to give good yields of the corresponding triphenyl 2-*iso* indolylphosphonium bromide 20. But the azayldiide 1 in the presence of one equivalent of Z-1,4-dichloro-2-butene 19b (Y = CH=CH, X = Cl), or E-1,4-dichloro-2-butene 19c (Y = CH=CH, X = Cl), or dichloro ether 19d($Y = CH_2$ -O-CH₂, X = Cl) is protonated into 9, owing to an elimination reaction on such dichloro compounds, and consequently, after acidic work up, the phosphonium salt 8b is the only phosphorus compound recovered.



It is noteworthy that, when 1 is caused to react with two equivalents of Z-1,4-dichloro-2-butene 19b, a 1/1 mixture of the salt 8b and the cyclic amino-phosphonium salt 21 is obtained, probably as a result of successive transyluration and alkylation reactions between the *in situ* formed azaylide 9 and a second dichlorobutene molecule 19b. The salt 21 is isolated and characterized by NMR spectroscopy.

The structures of the new compounds 12 - 21, are well established owing to their spectroscopic data, but also by chemical proof: so, we have extended the method of Zimmer^{5b} (fig.5, Table IV) to prepare some phosphonium salts in an independent way.

The salts 12c (n = 4–7), 15c (n = 2–6), or 17c were prepared by reaction of dibromotriphenylphosphorane with the appropriate amount of the corresponding



FIGURE 5

amine (secondary cyclic amine 22, primary diamines NH_2 -(CH_2)_n- NH_2 23 (n = 2-6), or the allyl amine 24 respectively), in the presence of triethylamine, followed by the anion exchange from bromide into iodide

Amines	p ^a	12c (%) ^b	15c (%) ^b	17c (%) ^b
22 (n = 4)	1,1	n = 4 (68)		
22 (n = 5)	1.0	n = 5(65)		
22 (n = 6)	1.0	n = 6(65)		
23 (n = 2)	0.5		n = 2 (62)	
23 (n = 3)	0.5		n = 3 (64)	
23 (n = 4)	0.5		n = 4 (50)	
23 (n = 5)	0.5	· ·	n = 5 (30)	
23 (n = 6)	0.5		n = 6 (30)	
24	1.0			(59)

TABLE IV Phosphorus compounds obtained in the reaction. of Ph3PBr2 with various amines (fig 5)

a) p = number of amines equivalents; b) Yields of pure, isolated product, based on starting amine.

As indicated in the fig. 6, we carried out with the N,N'-bisaminophosphonium salt 25 a basic hydrolysis,^{5a} which gives quantitatively the corresponding

diamine 26,⁶as verified by GC/MS analysis. The disalt 25 was obtained by a "one pot" deprotonation of the salt 15c (n = 6) followed by a methylation of the transient diphosphinimine 27.



i) 2 n-BuLi, THF, -15°C.; ii) 2 CH₃I, THF, a) -15°C, b) 25°C, c) 65°C, 12h; iii) a) 2% KOH / H₂O, b) HCl as ref 5a.

FIGURE 6

In conclusion, starting from gazeous ammonia conversion to N-acylated phosphinimines or to mono- or polyamino phosphonium salts can be achieved in two reactions, the key step involving the synthesis of the azayldiide 1 which is caused to react with either acylating agents or mono-as well as polyhalogeno alkylating compounds. The P-N bond cleavage under basic conditions allows the access to the corresponding mono- or polyamines from the aminophosphonium salts. This synthetic approach to amines is complimentary to the known methods whose starting materials are azides,⁷ or convertible pre-existent amines.^{8,9}

EXPERIMENTAL SECTION

All experiments were performed under nitrogen using Schlenk techniques. Melting points were determined on a Leitz 350 apparatus. NMR spectra were recorded on a Bruker AC200 instrument (at 200.13 MHz for ¹H-NMR at 50.32 MHz for ¹³C-NMR or 81 MHz for ³¹P-NMR). The chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) for ¹H-NMR and for ¹³C-NMR, and from external H₃PO₄(85%) for ³¹P-NMR. Infrared spectra were obtained on a Perkin-Elmer 377-IR spectrometer, wavelength are given in cm⁻¹. Mass spectra were obtained on a Jeol JMS-DX 300 via direct introduction by positive Electronic Impact (EI+) (70eV). Microanalyses were performed by the Microanalysis Laboratory at E.N.S.C.M. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere over sodium / benzophenone and stored upon sodium.

The phosphonium salts 8a, b, c and N-acyl triphenylphosphinimines 3, and 5 were obtained as described in the literature. ^{1,2,8}

N-(carbaethoxy) triphenylphosphinimine 3b

The acylating reagents were the propionyl chloride 2b, or the ethyl propionate 10b.

mp: 138°C (litt. 139°C);¹⁰ IR (KBr): 3420, 3055, 2960, 2915, 1580, 1560, 1480, 1455, 1430, 1375, 1330, 1295, 1245, 1175, 1155, 1110, 1080, 1028, 995, 845, 775, 720, 690, 530 cm⁻¹; ¹H-NMR: δ (ppm) = 1.19 (t, 3H, ³J_{HH} = 7.50 Hz, CH₂CH₃) 2.50 (q, 2H, ³J_{HH} = 7.49 Hz, CH₂CH₃) 7.35 – 7.78 (m, 15H, aromatics **PPh**); ¹³C-NMR: δ (ppm) = 11.02 (d, ⁴J_{PC}= 2.51 Hz, 1C, CH₃), 33.66 (d, ³J_{PC} = 19.12 Hz, 1C, CH₂), 128.47 (d, ¹J_{PC} = 98.63 Hz, 3C, C_{ipso}), 128.61 (d, ³J_{PC} = 10.06 Hz, 6C, C_{meta}), 132.06 (d, ⁴J_{PC} = 2.51 Hz, 3C, C_{para}), 133.10 (d, ²J_{PC} = 10.06 Hz, 6C, C_{ortho}), 186.25 (d, ²J_{PC} = 10.56 Hz, 1C, CO); ³¹P-NMR: δ (ppm) = 21.52 (s).

General procedure for the synthesis of N-cycloamino-triphenylphosphonium salt 12c from the reagent 1

To a suspension of compound **8a** (1.5 g, 4.2 mmol) in anhydrous THF (50 ml), in a dried nitrogen filled, round-bottomed flask fitted with magnetic stirrer, graduated addition funnel and thermometer an hexane solution of *n*-BuLi (2.15 N, 3.9 ml, 8.4 mmol) is added dropwise at -10° C. Stirring is continued at this temperature over 45 min. To this solution, the diiodoalkylane **11** (p × 4.2 mmol = p equiv.) is added at -10° C, and the mixture is stirred at 65°C for t hours (table III). The heating is removed and the reaction mixture is allowed to reach room temperature. The crude precipitated salt **12c** is isolated by filtration and purified by recrystallization (ethyl acetate / dichloromethane).

1-pyrrolidino-triphenylphosphonium iodide 12c (n = 4)

The alkylating reagent is the 1,4-diiodobutane **11** (**n** = 4) (4.2 mmol, 0.56 ml) mp: 216°C; IR (KBr): 2940, 1580, 1475, 1430, 1375, 1310, 1195, 1155, 1110, 1065–1055,1000, 950, 860–840, 760, 730, 690, 550; 540, 520 cm⁻¹; ¹H-NMR: δ (ppm) = 2.45–2.60 (m, 4H, C-CH₂-CH₂-C), 3.65–3.80 (m, 4H, N-CH₂), 8.05–8.30 (m, 15H aromatics); ¹³C-NMR : δ (ppm) = 27.3 (d, ³J_{PC} = 7.9 Hz, 2C, C β), 50.7 (d, 2C,C $_{\alpha}$, ²J_{PC}= 3.1Hz), 120.0 (d, 1C_{ipso}, ¹J_{PC} = 102.7 Hz), 130.9 (d,

 ${}^{2}C_{\text{meta}}$, ${}^{3}J_{\text{PC}}$ = 13.1 Hz), 134.0 (d, ${}^{2}C_{\text{ortho}}$, ${}^{2}J_{\text{PC}}$ = 10.8 Hz), 135.8 (d, ${}^{2}C_{\text{para}}$, ${}^{4}J_{\text{PC}}$ = 2.8 Hz); ${}^{31}P$ -NMR: δ (ppm) = 38.53 (s). Anal. calcd. for $C_{22}H_{23}$ INP: C, 57.53; H, 5.05; N, 3.11; Found: C, 57.22; H, 4.97; N, 3.11. [M-H⁻]⁺= 332.

1-piperidino-triphenylphosphonium iodide 12c (n = 5)

The alkylating reagent is the 1,5-diiodopentane 11 (n = 5) (4.2 mmol, 0.63 ml).

mp: 241°C; IR (KBr): 2940, 1580, 1475, 1430, 1375, 1310, 1195, 1155, 1110, 1065–1055, 1000, 950, 860–840, 760, 730, 690, 550, 540, 520 cm⁻¹; ¹H-NMR: δ (ppm) = 1.60–1.70 (m, 2H, CCH₂CH₂CH₂C), 1.70–1.85 (m, 4H, CCH₂CH₂CH₂C), 3.5–3.25 (m, 4H, NCH₂), 7.70–7.90 (m, 15H, aromatics), ¹³C-NMR : δ (ppm) = 23.6 (s, 1C, C_{γ}), 26.3 (d, ³J_{PC} = 5.3 Hz, 2C, C_{β}), 48,3 (s, 2C, C_{α}), 119 (d, ¹J_{PC} = 102.4 Hz, 1C, C_{ipso}), 131.0 (d, ³J_{PC} = 13.0 Hz, 2C, C_{meta}), 134.1 (d, ²J_{PC} = 10.6 Hz, 2C, C_{ortho}), 135.9 (d, ⁴J_{PC} = 2.9Hz, 2C, C_{para}); ³¹P-NMR: δ (ppm) = 44.45 (s). Anal. calcd. for $C_{23}H_{25}$ INP: C, 58.36; H, 5.32; N, 2.95. Found: C, 58.38; H, 5.36; N, 2.79. [M-H⁻]⁺ = 346.

1-perhydroazepinyl-triphenylphosphonium iodide 12c (n = 6)

The alkylating reagent is the 1,6-diiodohexane 11 (n = 6) (4.2 mmol, 0.70 ml).

mp: 219°C; IR (KBr): 2940, 1580, 1475, 1430, 1375, 1310, 1195, 1155, 1110, 1065–1055, 1000, 950, 860–840, 760, 730, 690, 550, 540, 520 cm⁻¹; ¹H-NMR: δ (ppm) = 1.50–1.65 (m, 4H, CCH₂CH₂CH₂CH₂C), 1.65 (m, 4H, CCH₂CH₂CH₂CH₂CH₂CH₂CH₂C, 3.40–3.50 (m, 4H, NCH₂), 7.70–7.90 (m, 15H, aromatics). ¹³C-NMR: δ (ppm) = 26.7 (s, 2C, C_γ), 30.0 (d, ³J_{PC} = 5.5 Hz, 2C, C_β), 51.4 (d, ²J_{PC} = 2.1 Hz, 2C, C_α), 119.6 (d, ¹J_{PC} = 102.1 Hz, 1C, C_{ipso}, 131.0 (d, ³J_{PC} = 12.9 Hz, 2C, C_{meta}), 134.2 (d, ²J_{PC} = 10.5 Hz, 2C, C_{ortho}), 135.9 (d, ⁴J_{PC} = 2.8H z, 2C, C_{para}). ³¹P-NMR: δ (ppm) = 44.45 (s). Anal. calcd. for C₂₃H₂₅INP: C, 59.15; H, 5.58; N 2.87. Found: C, 59.34; H, 5.46; N, 3.21. [M-H⁻]⁺ = 360.

2-isoindolyl-triphenylphosphonium bromide 20

The alkylating reagent is the α, α' -dibromo-o-xylene **19a.** (4.2 mmol, 0.60 ml).

mp: 210°C; IR (KBr): 2980, 1570, 1430, 1335, 1280, 1170, 1110, 1025, 990, 830, 750, 730, 610, 530, 490 cm⁻¹; δ (ppm) = 4.80 (d, 4H, ${}^{3}J_{PH} = 4.0$ Hz, NCH₂), 7.30 (s, 4H, aromatics C₆H₄), 7.50 – 8.20 (m, 15H, aromatics PPh); ${}^{31}P$ -NMR: δ (ppm) = 40.62 (s). Anal. calcd. for C₂₆H₂₃BrNP: C, 65.28; H, 5.27, N 2.93. Found: C, 65.30; H, 5.26; N, 2.67.

PHOSPHINIMINES

1,5-dihydro-1-azolyl-triphenylphosphonium iodide 21

The alkylating reagent is the cis-1,4-dichloro-2-butene **19a** (2.1 mmol, 0.25 ml). The iodide salt is obtained by anion exchange, using an aqueous solution of NaI.

¹H-NMR: δ (ppm) = 5.25 (d, 2H, PhCH₂), 7.30 (s, 5H, aromatics PhCH₂), 7.55 – 8.05 (m, 15H, aromatics PPh). ³¹P-NMR: δ (ppm) = 22. 94 (s). Anal. calcd. for C₂₂H₂₁INP: C; 57.78; H, 4.59; N, 3.06. Found: C, 57.62; H, 4.58; N, 2.99.

General procedure for the synthesis of N-cycloamino-triphenylphosphonium 12a,c, 15a,c, or 17a,c from the dibromophosphorane PPh₃Br₂

To a solution of triphenylphosphine (1.5 g, 5.7 mmol, 1 equiv.) in anhydrous benzene (50 ml), in a dried nitrogen filled, round-bottomed flask fitted with magnetic stirrer, graduated addition funnel and thermometer a solution of anhydrous Br₂ (0.33 ml, 5.7 mmol) in benzene is added dropwise over 20 min at 5°C. Stirring is continued at this temperature during 2 hours. To this suspension, the mixture of amine 22, 23, or 24 ($p \times 5.7$ mmol, p equiv., Table V) and triethylamine (10 ml, 5.7 mmol) in toluene is added at room temperature. The mixture is stirred at 25°C for 15 hours, and then hydrolyzed by addition of H₂O (70 ml), at 0°C. At room temperature, CH₂Cl₂ (20 ml) and H₂O (30 ml) are then added. The aqueous phase is extracted by CH_2Cl_2 (3 × 30 ml) and then by a saturated aqueous NaCl solution, dried (Na₂SO₄), and filtered. The filtrate is concentrated to 10-15 ml and precipitated into diethylether (200 ml). The precipitate is the corresponding aminotriphenylphosphonium salt 12a, 15a, or 17a, which is isolated by filtration and after classical anion exchange (CHCl₂/3 equiv. NaI aqueous solution) the salts 12c, 15c, or 17c (Table V were isolated and purified by recrystallization (ethyl acetate / dichloromethane).

- Compounds	δppm	Compounds	δppm
15c (m = 2)	39.2	15c (n = 6)	37.9
15c (n = 3)	39.1	17c (n = 3)	39.9
15c (n = 4)	38.0	18 (n = 3)	44.9
15c (n = 5)	37.7		

TABLE V ³¹P-NMR spectra of some phosphonium salts: 15c, 17c and 18

Synthesis of the bis (N,N'-dimethyl NN'-1,6-hexylidene) aminotriphenylphosphonium diiodide 25

To a suspension of (N,N'-1,6-hexylidene) bisaminotriphenylphosphonium diiodide 15c (n = 6) (2.5 mmol, 2.0 g) in anhydrous THF (50ml), a solution of *n*-BuLi (2.15N, 5 mmol, 2.3 ml) in hexane is added at -15° C. After 1h of stirring, CH₃I (25 mmol, 1.5 ml) is added dropwise at - 15°C. The mixture is then maintained 1h at 20°C, and 12h at 65°C. After hydrolysis the organic compounds are extracted with CH₂Cl₂ (3 × 20 ml) and washed with a solution of 10% NaI (20ml), dried over Na₂SO₄, concentrated, and precipitated by dropwise addition to diethyl ether (200ml). The salt 25 is isolated by filtration with 81 % yield.

¹H-NMR: δ (ppm) = 0.80 – 1.10 (m, 4H, CCH₂CH₂C) 1.40 – 1.80 (m, 4H, NCH₂CH₂) 3.05 (d, 6H, CH₃, ³J_{HP} = 11.0 Hz) 2.90 – 3.25 (m, 4H, NCH₂); ³¹P-NMR: δ (ppm) = 47.0 (s). The ammonium salt 26,⁹ was obtained with 68 % yield from the salt 25 after basic hydrolysis by (2%) KOH as indicated in the reference 5b, followed by acidic treatment by (10%) HCl of the formed intermediate amine.

References

- [1] H.J. Cristau, J. Kadoura, E. Torreilles, Bull. Soc. Chim. Fr; 515 (1989).
- [2] H.J. Cristau, E. Manginot, E. Torreilles, Synthesis, 382 (1991).
- [3] M.I. Kabatschnik, Phosphorus 117, 1 (1971).
- [4] K.A Ostota Starzewski, H.T. Dieck, Inorg. Chem., 18, 1507 (1979).
- [5] a) H. Zimmer, M. Jayawant, P. Gutsh, J. Org. Chem., 35, 2826 (1970).
 b) H. Zimmer, G. Singh, J. Org. chem., 28, 483 (1963).
- [6] S. Tschesche, Chem.Ber., 62,105 (1929).
- [7] B. Carboni, M. Vaultier, R. Carrié, Tetrahedron Lett., 29, 1279 (1988).
- [8] B. Ganem, Acc. Chem. Res., 15, 290 (1982).
- [9] R.J. Bergeron, Acc. Chem. Res., 19, 105 (1986).
- [10] P. Frøyen, Phosphorus, Sulfur, and Silicon, 78, 161 (1993).