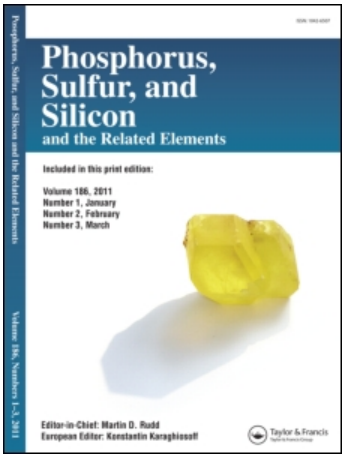

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Henri-Jean Cristau; Amer Hammami; Eric Manginot; Eliane Torreilles

To cite this Article Cristau, Henri-Jean , Hammami, Amer , Manginot, Eric and Torreilles, Eliane(1998) 'Convenient One Pot Preparation of Acylated Phosphinimines and Aminophosphonium Salts From the Versatile Triphenylphosphonium and Lithium Azayldiide $Ph_3P=N-Li$', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 475 — 486
To link to this Article: DOI: 10.1080/10426509808545488
URL: http://dx.doi.org/10.1080/10426509808545488

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 475-486
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CONVENIENT ONE POT PREPARATION OF ACYLATED PHOSPHINIMINES AND AMINOPHOSPHONIUM SALTS FROM THE VERSATILE TRIPHENYLPHOSPHONIUM AND LITHIUM AZAYLDIIDE Ph_3P=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 Ph_3P=N-Li **1**, were realized in "one pot".

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

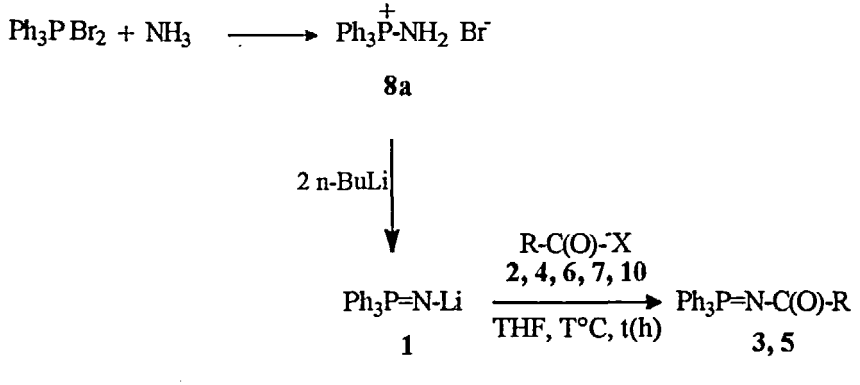
INTRODUCTION

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 dibromotriphenylphosphorane. 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).



2 R = Alkyl, Aryl; X = Cl
3 R = Alkyl, Aryl
4 R = O-alkyl; X = Cl
5 R = O-alkyl, O-Ph
6 R = Ph; X = O-C(O)-Ph
7 R = O-Ph; X = O-Ph
10 R = Et; X = O-Et

FIGURE 1

Thus we investigated, by ^{31}P-NMR spectroscopy in DMSO-d_6 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 **8a**[3]. Accordingly, the mono and di-deprotonation of the salt **8a,** induces an important shielding effect on the phosphorus atom resonance in the ^{31}P-NMR spectra. The

respective signals of compounds **8a, 9** and **1** appear in DMSO-d_6 at 35.9, 20.4, and −11.0 ppm. But the difference in their ^{13}C-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.

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

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	Cl	60	3	**5a** (93)	2
4b	OEt	Cl	60	3	**5b** (95)	2
4c	OCH_2Ph	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	c	b

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 ^{13}C-NMR spectra of compounds **1, 8a,** and **9** (δ ppm, J (Hz))

Compounds	δ C_i	J_{CiP}	δ C_m	J_{CmP}	δ C_o	J_{CoP}	δ Cp	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.

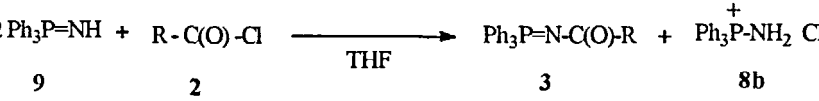


FIGURE 2

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).

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

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

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

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.

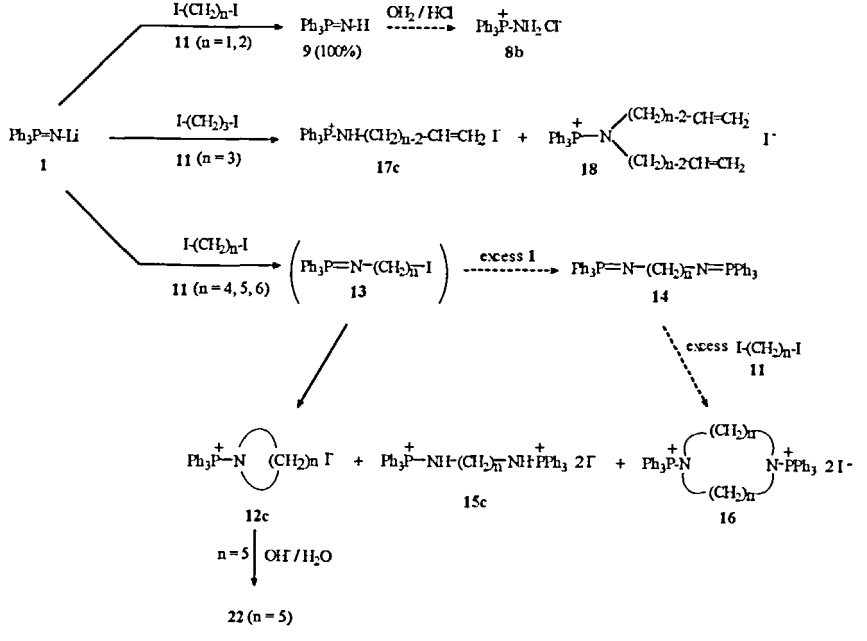


FIGURE 3

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**($Y = CH_2\text{-}O\text{-}CH_2$, 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.

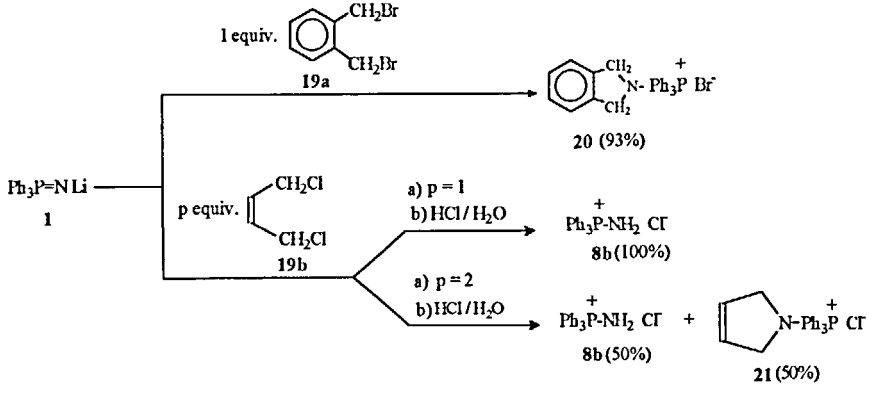


FIGURE 4

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 aminophosphonium 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

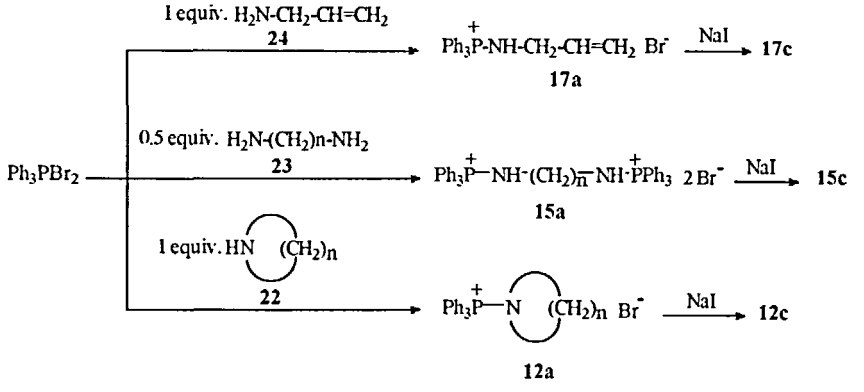


FIGURE 5

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

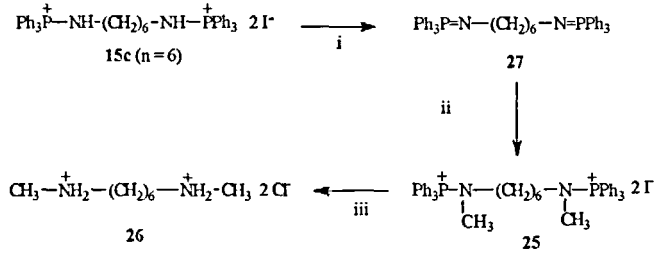
TABLE IV Phosphorus compounds obtained in the reaction. of Ph_3PBr_2 with various amines (fig 5)

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)

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**,[6]as 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 CH_3I, THF, a) -15°C, b) 25°C, c) 65°C, 12h; iii) a) 2% KOH / H_2O, 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 ^{1}H-NMR at 50.32 MHz for ^{13}C-NMR or 81 MHz for ^{31}P-NMR). The chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) for ^{1}H-NMR and for ^{13}C-NMR, and from external H_3PO_4(85%) for ^{31}P-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}; ^{1}H-NMR: δ (ppm) = 1.19 (t, 3H, $^3J_{HH}$ = 7.50 Hz, $CH_2\mathbf{CH_3}$) 2.50 (q, 2H, $^3J_{HH}$ = 7.49 Hz, $\mathbf{CH_2}CH_3$) 7.35 – 7.78 (m, 15H, aromatics **PPh**); ^{13}C-NMR: δ (ppm) = 11.02 (d, $^4J_{PC}$= 2.51 Hz, 1C, CH_3), 33.66 (d, $^3J_{PC}$ = 19.12 Hz, 1C, CH_2), 128.47 (d, $^1J_{PC}$ = 98.63 Hz, 3C, C_{ipso}), 128.61 (d, $^3J_{PC}$ = 12.07 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); ^{31}P-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}; ^{1}H-NMR: δ (ppm) = 2.45–2.60 (m, 4H, C-$\mathbf{CH_2}$-$\mathbf{CH_2}$-C), 3.65–3.80 (m, 4H, N-$\mathbf{CH_2}$), 8.05–8.30 (m, 15H aromatics); ^{13}C-NMR : δ (ppm) = 27.3 (d, $^3J_{PC}$ = 7.9 Hz, 2C, Cβ), 50.7 (d, 2C,C_α, $^2J_{PC}$= 3.1Hz), 120.0 (d, 1C_{ipso}, $^1J_{PC}$ = 102.7 Hz), 130.9 (d,

$2C_{meta}$, $^3J_{PC}$ = 13.1 Hz), 134.0 (d, $2C_{ortho}$, $^2J_{PC}$ = 10.8 Hz), 135.8 (d, $2C_{para}$, $^4J_{PC}$ = 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. $[M\text{-}H^{\cdot}]^+$= 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}; ^{1}H-NMR: δ (ppm) = 1.60–1.70 (m, 2H, $CCH_2\mathbf{CH_2}CH_2C$), 1.70–1.85 (m, 4H, $\mathbf{CCH_2}CH_2CH_2C$), 3.5–3.25 (m, 4H, $\mathbf{NCH_2}$), 7.70–7.90 (m, 15H, aromatics), ^{13}C-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}) ; ^{31}P-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. $[M\text{-}H^{\cdot}]^+$ = 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}; ^{1}H-NMR: δ (ppm) = 1.50–1.65 (m, 4H, $CCH_2\mathbf{CH_2}\mathbf{CH_2}CH_2C$), 1.65 (m, 4H, $\mathbf{CCH_2}CH_2CH_2\mathbf{CH_2}C$), 3.40–3.50 (m, 4H, $\mathbf{NCH_2}$), 7.70–7.90 (m, 15H, aromatics). ^{13}C-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}). ^{31}P-NMR: δ (ppm) = 44.45 (s). Anal. calcd. for $C_{23}H_{25}INP$: C, 59.15; H, 5.58; N 2.87. Found: C, 59.34; H, 5.46; N, 3.21. $[M\text{-}H^{\cdot}]^+$= 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, $^3J_{PH}$ = 4.0 Hz, $\mathbf{NCH_2}$), 7.30 (s, 4H, aromatics C_6H_4), 7.50 – 8.20 (m, 15H, aromatics **PPh**); ^{31}P-NMR: δ (ppm) = 40.62 (s). Anal. calcd. for $C_{26}H_{23}BrNP$: C, 65.28; H, 5.27, N 2.93. Found: C, 65.30; H, 5.26; N, 2.67.

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.

^{1}H-NMR: δ (ppm) = 5.25 (d, 2H, Ph**CH$_2$**), 7.30 (s, 5H, aromatics **PhCH$_2$**), 7.55 – 8.05 (m, 15H, aromatics **PPh**). ^{31}P-NMR: δ (ppm) = 22. 94 (s). Anal. calcd. for $C_{22}H_{21}INP$: 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 PPh_3Br_2

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 Br_2 (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 × 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 H_2O (70 ml), at 0°C. At room temperature, CH_2Cl_2 (20 ml) and H_2O (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 (Na_2SO_4), 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 ($CHCl_3$/3 equiv. NaI aqueous solution) the salts **12c, 15c,** or **17c** (Table V were isolated and purified by recrystallization (ethyl acetate / dichloromethane).

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

Compounds	δ *ppm*	*Compounds*	δ *ppm*
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		

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, CH_3I (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 CH_2Cl_2 (3 × 20 ml) and washed with a solution of 10% NaI (20ml), dried over Na_2SO_4, concentrated, and precipitated by dropwise addition to diethyl ether (200ml). The salt **25** is isolated by filtration with 81 % yield.

^{1}H-NMR: δ (ppm) = 0.80 − 1.10 (m, 4H, CCH_2CH_2C) 1.40 − 1.80 (m, 4H, NCH_2CH_2) 3.05 (d, 6H, CH_3, $^3J_{HP}$ = 11.0 Hz) 2.90 − 3.25 (m, 4H, NCH_2); ^{31}P-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.

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