A Convenient Synthesis of Triphenylphosphine Acylimides Using *N*-Lithiated Triphenylphosphine Imide

H.J. Cristau,* E. Manginot, E. Torreilles

Laboratoire de Chimie Organique, Unité Associée au C.N.R.S N° 458, E.N.S.C.M., 8, rue de l'Ecole Normale, F-34053 Montpellier Cedex, France

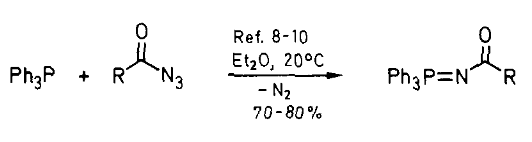
A series of triphenylphosphine acylimides and *N*-(triphenylphosphoranylidene)carbamates have been readily prepared by direct acylation of the *N*-lithiated triphenylphosphine imide.

In continuation of our synthetic studies in the field of metalated phosphonium ylides (diylides,[1-3] or yldiide[4,5]), we have developed the reactivity of a powerful reagent,[6] the *N*-lithiated triphenylphosphine imide **2** as a synthetic equivalent of NH_2^- and NH_2^{2-} anions.

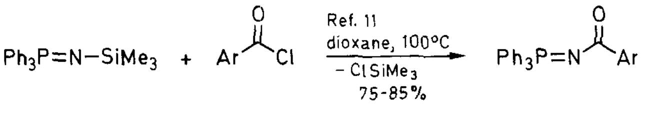
Here we describe its one-pot reactivity toward acylating agents. By this procedure, a high yielding synthesis of varied phosphine acylimides **4** and *N*-(triphenylphosphoranylidene)carbamates **6** was realized.

Some synthetic routes to these compounds have already been reported:[7]

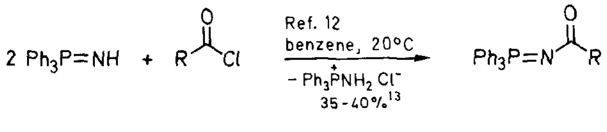
– The first compound of this type, the triphenylphosphine benzoylimide (**4e**), was reported by Staudinger[8] and was obtained in high yield using a mixture of benzoyl azide and triphenylphosphine. The reaction has been widely applied to other systems.[9,10] However, this method is potentially hazardous owing to the explosive nature of organic azides.



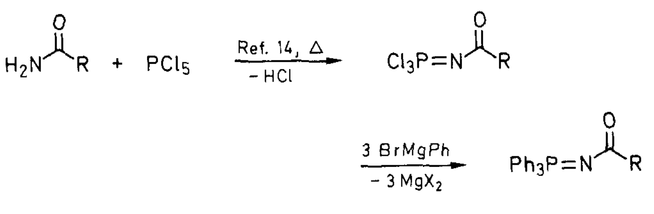
– *N*-Silylated phosphinimimes[11] may be acylated, but they are difficult to prepare and considerably less reactive than their lithiated analogs.



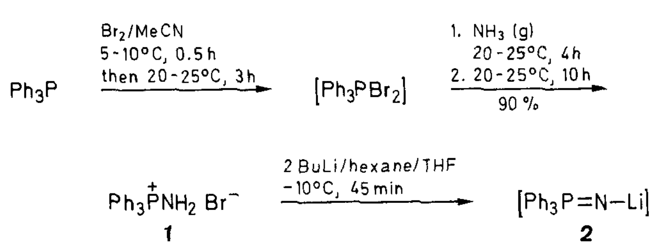
– Stepanek[12] used triphenylphosphine imide, but it must be used in twofold excess and it is also less reactive than its lithiated derivative.



– Another possibility is given by the Kirsanov reaction followed by a Grignard reaction.[14]



Now, the *N*-lithiated triphenylphosphine imide $Ph_3P{=}N{-}Li$ (**2**), easily prepared by a one-pot reaction from the phosphonium bromide (**1**), appears more reactive than other analogs: only one mole of reagent per mole of acylating agent is necessary in such reaction (Scheme 1).



Scheme 1

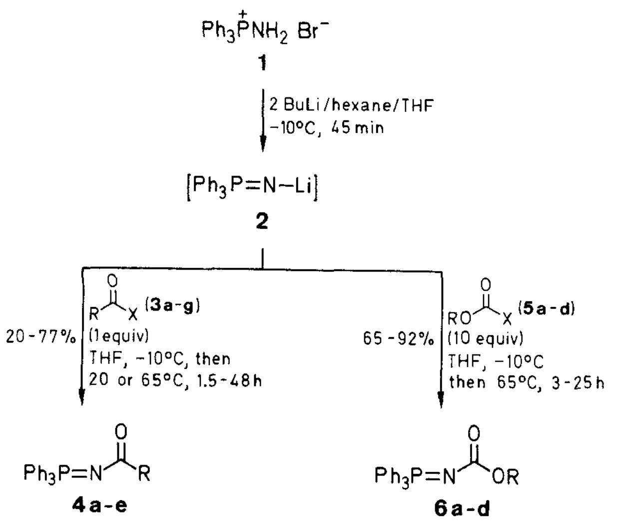
The phosphonium bromide **1** is stable to hydrolysis and can be prepared in large quantity from triphenylphosphine, bromine and ammonia.

Depending on the reactivity of the various carbonyl derivatives, the acylations are carried out in tetrahydrofuran at 65 °C or at room temperature within a few hours (Scheme 2). Generally, the final product is obtained with a good yield by recrystallization in an appropriate solvent (Table).

The reactivity of the aza-yldiide **2** is nearly the same towards anhydrides and acyl chlorides (Table), and its affinity toward different carbonyl compounds is very important. We also point that the phosphonium aza-yldiide **2** reacts only with activated esters, and that the P=N bond is, in the resulting phosphine acylimides, particularly stable toward hydrolysis.

In conclusion, the phosphonium aza-yldiide is a simple and efficient reagent for the general synthesis of phosphine acylimides, compounds which offer plenty of possibilities for further transformations: a) one-pot asymmetric alkylation of the nitrogen atom in the compounds **4** and **6** with chiral acyl groups;[15] b) one-pot substitution of alkoxy groups in carbamates **6** by different nucleophiles;[16] c) application of this reaction to polyfunctional compound preparation.[17]

These possibilities are now under investigation by considering other electrophilic entities.



3	R	X	4	R	5	R	X	6	R
a	Me	Cl	a	Me	a	Me	Cl	a	Me
b	Me	OAc	b	CCl_3	b	Et	Cl	b	Et
c	Me	OEt	c	$CClF_2$	c	Bn	Cl	c	Bn
d	CCl_3	OEt	d	CF_3	d	Ph	OPh	d	Ph
e	$CClF_2$	OEt	e	Ph					
f	CF_3	OEt							
g	Ph	OEt							

Scheme 2

All reactions were carried out under a purified N_2 atmosphere. All glassware was dried and flushed with N_2 before use. All reagents were of commercialy quality from freshly opened containers, and were purchased from Prolabo, Fluka and Aldrich Chemical Co. THF was freshly distilled from Na and stored on Na. MeCN, distilled from P_2O_5 was stored on molecular sieve type 3 Å. Melting points were measured on a Mettler PF5 apparatus. IR spectra were recorded on a Perkin-Elmer 377 infrared spectrophotometer. ^1H-NMR were recorded on a Varian EM 360 or Bruker AC 250 MHz spectrometer, and ^{31}P-NMR were obtained using a Bruker WP 80 MHz spectrometer.

Aminotriphenylphosphonium Bromide (1):

In a round-bottomed flask fitted with a magnetic stirrer, a gas inlet and addition funnel, to a suspension of Ph_3P (105 g, 0.4 mol) in MeCN (700 mL), Br_2 (20.5 mL, 0.4 mol) in MeCN (300 mL) is added dropwise at 5–10 °C over 30 min and stirring is still maintained 3 h at 20–25 °C. Then a NH_3 bubbling is carried out over 4 h, and stirring is continued at 20–25 °C for 10 h. The solvent is evaporated at 20 Torr. The mixture is diluted with H_2O (1 L), and extracted with $CH_2Cl_2/CHCl_3$ (7:3) (4 × 1 L) until we obtain a clear aqueous solution. The combined organic layers are washed with a 10% aq NaBr (1 L), dried (Na_2SO_4) and the solvent is removed *in vacuo*. The residue is dissolved in a mixture of CH_2Cl_2 and MeOH (7:3) (400 mL) and precipitated in Et_2O (4 L). A white precipitate is isolated by filtration, dried at 3 Torr at 60 °C on P_2O_5 over 10 h to afford the pure product; yield: 124 g (0.34 mol, 87%); mp 249 °C.

		C	H	N
$C_{18}H_{17}BrNP$	calc.	60.35	4.77	3.91
(359.7)	found	60.03	4.80	3.79

(Microanalysis obtained without recrystallization)

^1H-NMR ($CDCl_3$/TMS): δ = 6.80–7.10 (m, 2H, NH_2), 7.55–8.05 (m, 15H, Ph).

^{31}P-NMR ($CHCl_3$/MeOH): δ = 35.98 (s).

Table. Triphenylphosphine Acylimides **4a–e** and *N*-(Triphenylphosphoranylidene)carbamates **6a–d** Prepared

Substrate	Time (h)	Temp. (°C)	Product	Yield[a] (%)	mp (°C)[b] (solvent)	Molecular[c] Formula or Lit. mp (°C)	IR (KBr) (cm^{-1}) $\nu_{P=N}$, $\nu_{C=O}$	^1H-NMR ($CDCl_3$/TMS) δ, J(Hz)	^{31}P-NMR ($CHCl_3$/D_2O) δ, J(Hz)
3a	1.5	65	**4a**	70	169.2 (CH_2Cl_2/PE)	164[14]	1360, 1590	2.25 (d, 3H, $^3J_{HP}$ = 3), 7.35–8.00 (m, 15H)	20.55
3b	5	20	**4a**	75					
3c	48	65	**4a**	0					
3d	3	65	**4b**	20[d]	188.2 (MeOH)	183–184[12]	1300, 1640	7.45–8.05 (m, 15H)	22.80
3e	4	65	**4c**	75	159.6 (MeOH)	$C_{20}H_{15}ClF_2NOP$ (389.8)	1365, 1635	7.35–7.95 (m, 15H)	23.35 (t, $^4J_{PF}$ = 5)
3f	2.5	65	**4d**	77	165.8 (MeOH)	161–162[12]	1400, 1635	7.40–8.00 (m, 15H)	23.40 (q, $^4J_{PF}$ = 5)
3g	22	65	**4e**	71	190.7 (CH_2Cl_2/PE)	192[18]	1335, 1590	7.30–8.15 (m, 18H), 8.30–8.55 (m, 2H)	20.65
5a	3	65	**6a**	92	137.0 (EtOAc/PE)	134–136[11]	1290, 1630	3.65 (s, 3H), 7.35–8.00 (m, 15H)	20.90
5b	3	65	**6b**	87	135.8 (EtOAc/PE)	136[11]	1275, 1630	1.20 (t, 3H, CH_3, $^3J_{HH}$ = 7), 4.10 (q, 2H, CH_2, $^3J_{HH}$ = 7), 7.30–8.00 (m, 15H)	20.80
5c	25	65	**6c**	87	107.3 (EtOAc/PE)	$C_{26}H_{22}NO_2P$ (411.5)	1265, 1610	5.05 (s, 2H), 7.00–7.90 (m, 20H)	20.76
5d	22	65	**6d**	65	114.0 (Et_2O/PE)	114–116[11]	1300, 1660	7.00–8.10 (m, 20H)	22.30

[a] Yield of pure product after recrystallization

[b] Uncorrected, measured on a Mettler FP 5 apparatus. PE = Petroleum Ether.

[c] Satisfactory microanalyses obtained: C ±0.25, H ±0.20, N ±0.30.

[d] $Ph_3P{=}NLi$ apparently reacts with chlorine atom.

Triphenylphosphine Acylimides 4a–e and *N*-(Triphenylphosphoranylidene)carbamates 6a–d; General Procedure:
In a dried N_2 filled, round-bottomed flask fitted with magnetic stirrer, graduate addition funnel and thermometer, to a suspension of compound **1** (1.5 g, 4.2 mmol) in anhydrous THF (50 mL), a solution of BuLi (2.15 N) in hexane (3.9 mL, 8.4 mmol) is added dropwise at $-10\,^\circ$C. Stirring is continued at $-10\,^\circ$C over 45 min (clear yellow solution). To this solution, a carbonyl reagent (4.2 mmol, 1 equiv) is added at $-10\,^\circ$C, and then the mixture is stirred at 20 or 65 °C for a few hours (Table). The mixture is neutralized by the addition of 10% aq HCl (3 mL, 8.4 mmol, 2 equiv) at 0 °C. CH_2Cl_2 (20 mL) and H_2O (30 mL) are then added. Aqueous phase is extracted by CH_2Cl_2 (2×20 mL). The organic layers are washed by sat. NaCl, dried (Na_2SO_4), and filtered. The solvent is evaporated. The resulting solid product is then purified by recrystallization in an appropriate solvent (Table).

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