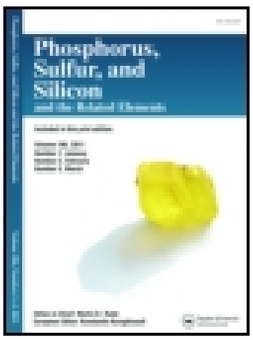

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β-(*N*-ACYLAMINO)VINYLPHOSPHONIUM SALTS—SYNTHESIS AND PROPERTIES

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*A reaction of β-carbonyl phosphorus ylides with imidoyl halides gives hitherto unknown β-(*N*-acylamino)vinylphosphonium salts. The same product can be obtained using the N-monosubtituted amide/Ph_3PBr_2/Et_3N system instead of imidoyl halide. The key step of the reaction probably involves an intramolecular [1,3] O-to-N migration of the vinyl group, converting the primary* O*-imidoylation product into β-(*N*-acylamino)vinylphosphonium salt.*

Keywords: β-Carbonyl ylides; β-(*N*-acylamino)vinylphosphonium salts; imidoylation; imidoyl halides; N-monosubstituted amide/Ph_3PBr_2/Et_3N system; rearrangement

INTRODUCTION

Vinylphosphonium salts **1** have been attracting significant attention of synthetic chemists since 1964, when Schweizer[1] realized that the addition of nucleophiles with a carbonyl function to vinylphosphonium salts results in phosphorus ylides **2**, which can undergo the intramolecular Wittig reaction (Scheme 1). Many carbo- and heterocyclic systems have been synthesized in this way.[2]

Recently, we have preliminarily communicated the synthesis of hitherto unknown β-(*N*-acylamino)vinylphosphonium salts **7** by imidoylation of β-carbonyl phosphorus ylides **4** with imidoyl halides

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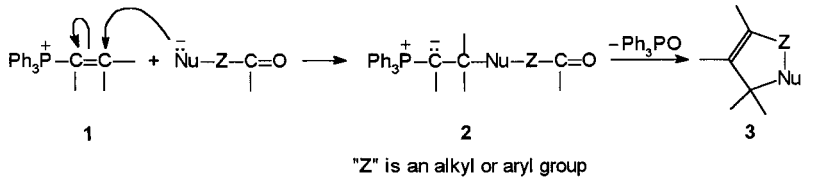
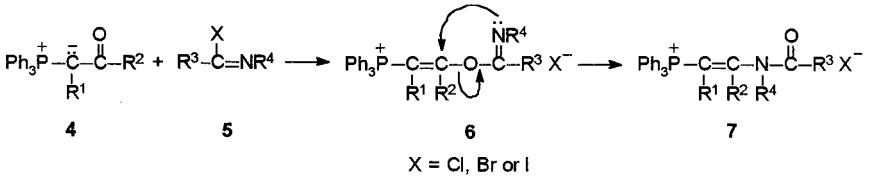


SCHEME 1

5 (Scheme 2).[3] In this article we give a full account concerning this synthesis, including some novel modification of it, which consists in using the N-monosubtituted amide/Ph_3PBr_2/Et_3N system instead of imidoyl halide.

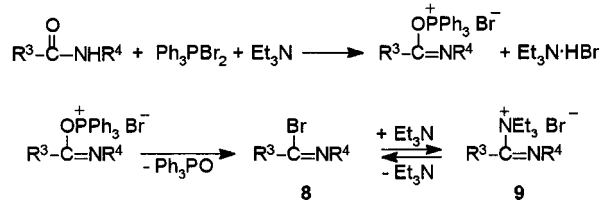
RESULTS AND DISCUSSION

The treatment of the β-corbonyl phosphorus ylide with an imidoyl halide in acetonitrile at room temperature for 24 h results in β-(*N*-acylamino)vinylphosphonium salts **7** as stable, usually crystalline compounds in good yields (procedure A and B, Scheme 2, X = Cl or I). Imidoyl iodides were prepared in situ from imidoyl chlorides by exchange of chlorine with NaI. The obtained vinylphosphonium salts can be precipitated from the reaction mixture with Et_2O and purified further, if necessary, by crystallization from a mixture of MeCN or CH_2Cl_2 with Et_2O or by column chromatography.



SCHEME 2

The preparation of imidoyl halides is rather labor consuming. Apart from that, imidoyl halides, being highly reactive substances, must often be prepared as required, some of them tending to undergo self-condensation.[4] Taking into account these disadvantages, we tried to use the N-monosubtituted amide/Ph_3PBr_2/Et_3N system as a source of an imidoylating agent generated in situ. In 1990 we provided some spectral evidence, that the new imidoylating agent generated from N-monosubtituted amides and Ph_3PBr_2 in the presence of Et_3N had the structure of N,N,N,N′-tetrasubstituted amidinium salts **9**, and could be detected based on a characteristic strong $\nu_{C=N}$ absorption band at about



SCHEME 3

1700 cm^{-1} (Scheme 3).[5] N,N,N,N′-Tetrasubstituted amidinium salts **9** can remain in equilibrium with imidoyl bromide **8**; both of these compounds can act as an effective imidoylating agent.

As had been expected, the treatment of β-carbonyl phosphorus ylides with the N-monosubtituted amide/Ph_3PBr_2/Et_3N system in CH_2Cl_2 at room temperature for 24 h gives β-(*N*-acylamino)vinylphosphonium bromides **7**, usually in good yields (procedure C) (Table I). Before adding an ylide, in all the cases we detected in the reaction mixture a strong absorption band of the imidoylating agent at about 1700 cm^{-1}, as well as the characteristic set of absorption bands of triphenylphosphine oxide at 1439, 1191, and 1120 cm^{-1}, the intensity of which approximately corresponds to the total conversion of Ph_3PBr_2 into Ph_3PO.

The structures of the β-(*N*-acylamino)vinylphosphonium salts were confirmed by their spectroscopic properties (IR, ^1H-, and ^{13}C-NMR) and satisfactory elemental analyses (Table II), as well as, in the case of the compound **7e**, by a single crystal X-ray structure determination, which revealed its Z-configuration (Figure 1). The crystallographic data (excluding structure factors) for the structure **7e** have been deposited with the Cambridge Crystallographic Data Center as a supplementary publication number CCDC 166899. In the case of compounds **7a** and **7d**, the magnitude of the J_{H-H} coupling constants at the double bond (14.7–15.3 Hz) suggests rather an *E*-configuration of the salts. In the case of compound **7g** we have obtained evidently a mixture of two possible stereoisomers.

It is obvious, that the final reaction product **7** cannot be formed in a simple, direct way from ylide **4** and imidoyl halide **5**. In order to explain our results we assume this reaction to involve the *O*-imidoylated intermediate **6** and the [1,3] O-to-N sigmatropic migration of its vinyl group. A similar kind of [1,3] sigmatropic migrations is well-known in the literature;[6] e.g., *O*-imidoylated carboxamides undergo a similar rearrangement.[5,7] An analogous rearrangement probably also takes place in the case of the similar, well-known acylation of β-carbonyl

TABLE I Synthesis of β-(*N*-Acyloamino)vinylphosphonium Salts **7**

Ylide **4**		Imidoylating agent			β-(*N*-Acyloamino)vinylphosphonium salt **7**				IR	Elemental analyses (calcd./found) [%]			
R^1	R^2	R^3	R^4	X	No.	Procedure	Yield [%]	m.p. [°C]	[cm^{-1}]	C	H	N	P
H	H	Me	Ph	I	**7a**	B	91	133–134	1690	61.21/61.12	4.59/4.66	2.55/2.41	5.64/5.77
H	H	Ph	Me	Cl	**7b**	A	71	238–239	1688	73.44/73.51	5.50/5.74	3.06/3.00	6.76/6.63
H	H	Ph	Me	Br	**7c**	C	71	242–243	1695	66.94/67.00	5.02/5.09	2.79/2.92	6.17/6.18
H	H	Ph	$PhCH_2$	Cl	**7d**	A	64	273–275	1687	76.47/76.70	5.47/5.30	2.62/2.78	5.80/6.00
H	Me	Ph	Me	Cl	**7e**	A	66	140–141	1661	73.80/73.54	5.77/5.92	2.97/2.91	6.56/6.42
H	Me	Ph	Me	I	**7f**	B	85	182–183	1663	61.71/62.09	4.83/4.59	2.49/2.74	5.50/5.42
H	Me	Ph	Me	Br	**7g**[a]	C	80	196–198	1664	67.45/67.19	5.27/5.30	2.71/2.85	6.00/5.97
H	Me	Ph	Ph	Cl	**7h**	A	72	192–193	1674	76.47/76.21	5.47/5.22	2.62/2.32	5.80/5.61
H	Me	Ph	$PhCH_2$	Cl	**7i**	A	87	175–177	1668	76.70/76.48	5.70/5.91	2.56/2.62	5.65/5.48
H	Me	$(CH_2)_5$		Br	**7j**	C	79	205.5–206	1663	65.59/65.31	5.91/5.88	2.83/3.00	6.26/6.24
Me	H	Ph	Me	Cl	**7k**	A	99	Resin	1698	73.80/73.51	5.77/6.01	2.97/3.04	6.56/6.36
Me	H	$(CH_2)_4$		Br	**7l**	C	62	Resin	1692	65.01/65.33	5.67/5.44	2.92/2.80	6.45/6.15

[a] A mixture of two stereoisomers in the ratio of 68:32.

TABLE II ^{1}H and ^{13}C-NMR Spectra of β-(*N*-Acyloamino)vinylphosphonium Salts **7**

No.	^{1}H-NMR ($CDCl_3$/TMS, δ (ppm))	^{13}C NMR [$CDCl_3$/TMS, δ (ppm)/J_{C-P}(Hz)]							
					Ph_3P^+				
		>C=O	P^+–C=	C–N	C^1	C^2	C^3	C^4	Other carbons
7a	7.75–7.21 (m, 20H, Ph), 7.10 (dd, 1H, J_{P-H} = 13.8 Hz, J_{H-H} = 14.7 Hz, CH), 6.92 (dd, 1H, J_{P-H} = 17.0 Hz, J_{H-H} = 14.9 Hz, CH), 2.05 (s, 3H, Me)	176.6	86.1/99.5	151.1/17.6	119.2/91.1	133.7/10.7	130.2/13.1	134.5/3.0	135.6, 128.7, 125.2, 122.5 (Ph); 25.5 (Me)
7b	7.8–7.2 (m, 22H, Ph and CH), 3.78 (s, 3H, Me)	170.9	83.5/100.5	150.8/17.8	119.4/91.4	133.8/10.6	130.2/12.9	134.7/3.0	132.8, 131.3, 128.6, 127.8 (Ph); 34.5 (Me)
7c	7.8–7.6 (m, 15H, Ph), 7.48–7.13 (m, 7H, Ph and CH), 3.78 (s, 3H, Me)	170.9	83.3/100.6	150.9/17.8	119.2/91.6	133.8/10.6	130.2/13.0	134.8/3.0	132.6, 131.3, 128.6, 127.9 (Ph); 34.8 Me)
7d	7.82–7.26 (m, 25H, Ph), 7.05 (dd, 1H, J_{P-H} = 14.1 Hz, J_{H-H} = 15.0 Hz, CH), 6.84 (dd, 1H, J_{P-H} = 17.4 Hz, J_{H-H} = 15.3 Hz, CH), 5.87 (s, 2H, CH_2)	171.6	85.1/100.5	149.7/17.8	119.1/91.8	133.8/11.0	130.2/12.9	134.7/3.0	136.2, 133.0, 131.5, 128.9, 128.8, 128.6, 128.1, 127.5 (Ph); 47.9 (CH_2)
7e	7.90–7.18 (m, 18H, Ph), 6.98 (d, 1H, J_{P-H} = 16.5 Hz, CH), 6.77 (d, 2H, J = 7.2 Hz, *o*-Ph), 2.98 (s, 3H, Me), 2.75 (s, 3H, Me)	170.4	99.4/97.6	161.6/8.6	120.6/92.5	133.8/10.3	130.0/12.8	134.3/3.1	133.2, 131.0, 128.4, 127.0 (Ph); 37.8 (NMe); 26.1/ 15.4 (CMe)

(Continued on next page)

TABLE II ^{1}H and ^{13}C-NMR Spectra of β-(*N*-Acyloamino)vinylphosphonium salts **7** *(Continued)*

No.	^{1}H-NMR ($CDCl_3$/TMS, δ (ppm))	^{13}C NMR [$CDCl_3$/TMS, δ (ppm)/J_{C-P}(Hz)]							
					Ph_3P^+				
		>C=O	P^+–C=	C–N	C^1	C^2	C^3	C^4	Other carbons
7f[a]	7.87–7.67 (m, 15H, Ph_3P), 7.45–7.38, (m, 1H, Ph), 7.32–7.25 (m, 2H, Ph), 6.93 (d, 1H, J_{P-H} = 16.2 Hz, CH), 6.90–6.85 (m, 2H, Ph), 2.84 (s, 3H, Me), 2.56 (s, 3H, Me)	169.2	98.2/94.9	160.9/8.0	120.6/92.5	133.5/10.7	129.7/12.8	134.1/3.0	133.3, 130.7, 128.0, 127.1 (Ph); 36.7 (NMe); 24.8/15.5 (CMe)
7g[b]	7.85–7.20 (m, 18H, Ph), 6.89 (d, 1H, J_{P-H} = 16.8 Hz, CH), 6.77 (d, 2H, J = 7.2 Hz, *o*-Ph), 2.99 (s, 3H, Me), 2.75 (s, 3H, Me)	170.2	99.14/99.5	161.6/8.6	120.4/92.8	133.6/10.3	139.7/13.1	134.0/3.1	133.0, 130.7, 128.2, 126.8 (Ph); 37.8 (NMe); 26.0/15.5 (CMe)
7g[c]	7.85–7.20 (m, 20H, Ph), 5.85 (d, 1H, J_{P-H} = 14.4 Hz, CH), 3.62 (s, 3H, Me), 2.06 (d, 3H, J = 1.8 Hz, Me)	172.5	90.3/102.2	165.0/11.5	119.6/90.7	133.2/10.6	130.5/13.1	134.7/3.1	131.7, 128.7, 128.5 (Ph); 38.4 (NMe); 23.3/5.7 (CMe)
7h	7.9–6.5 (m, 26H, Ph and CH), 2.45 (s, 3H, Me)	170.3	98.2/94.4	161.0/5.2	120.1/91.8	134.1/10.3	130.0/13.0	134.0/3.0	133.0, 130.8, 127.8, 127.3 (PhCO); 137.5, 128.5, 124.1, 122.2 (PhN); 27.4 (CMe)

7i	7.85–7.22 (m, 25H, Ph), 6.25 (d, 1H, CH, J_{P-H} = 14.4 Hz, CH), 5.52 (s, 2H, CH_2), 1.66 (s, 3H, Me)	172.1	98.8/95.9	164.4/10.6	119.0/90.6	133.2/10.9	130.6/13.3	135.1/3.1	136.8, 135.7, 131.9, 129.00, 128.98, 128.6, 128.5, 127.8 (Ph); 52.3 (CH_2); 24.3/5.3 (Me)
7j	7.89–7.62 (m, 15H, Ph), 6.86 (dd, 1H, J_{P-H} = 16.8 Hz, J_{H-H} = 0.9 Hz, CH), 3.34–3.27 (m, 2H, CH_2), 2.60 (s, 3H, Me), 1.72–1.32 (m, 8H, $(CH_2)_4$)	175.8	99.7/96.1	161.7/4.9	119.9/92.2	134.1/10.4	129.7/13.1	134.2/3.1	49.1, 36.5, 28.8, 28.5, 22.4 (CH_2); 26.0/15.5 (Me)
7k	7.88–7.18 (m, 20H, Ph), 6.91 (d, 1H, J_{P-H} = 20.4 Hz, CH), 3.75 (s, 3H, Me), 2.42 (d, 3H, J_{P-H} = 15.6 Hz, Me)	171.8	95.0/91.9	149.5/25.8	117.5/89.3	133.7/10.2	130.5/12.6	135.1/2.6	132.0, 131.1, 128.7, 127.9 (Ph); 36.0 (NMe); 16.6/8.3 (CMe)
7l	7.92–6.85 (m, 16H, Ph and CH), 3.19–3.11 (m, 2H, CH_2), 1.81–1.40 (m, 6H, $(CH_2)_3$), 2.45 (d, 2H, J_{P-H} = 14.9 Hz, Me)	170.8	97.2/94.4	151.1/19.2	118.3/91.1	133.9/10.5	130.1/12.9	134.8/3.0	47.2, 37.9, 23.6, 23.8, 17.1 (Me)

[a] In DMSO-d_6.
[b] Minor stereoisomer.
[c] Major stereoisomer.

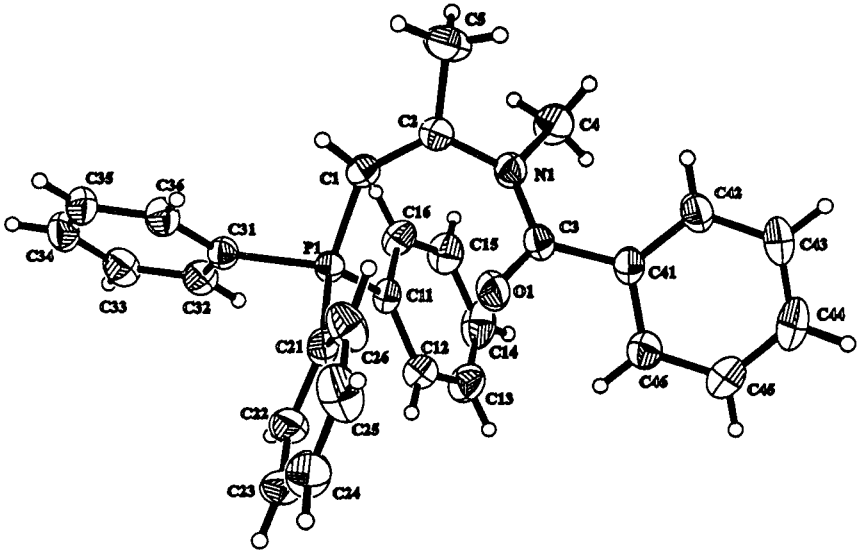


FIGURE 1 ORTEP-Plot of the β-(N-benzoylamino)-β-methylvinyltriphenyphosphonium chloride **7e**.

ylides; however, being a degenerate rearrangement, it cannot be directly observed.

CONCLUDING REMARKS

The reported reactions offer a convenient way for the synthesis of β-(*N*-acyloamino)vinylphosphonium salts. The phosphonium salts **7** can be considered to be prospective precursors for the synthesis of amino derivatives of carbo- and heterocyclic systems (see Scheme 1), and some important reagents for organic synthesis like *N*-acylynamines[8] (by β-elimination of Ph_3P and HX if $R^2 = H$) or *N*-vinylamides (by hydro-dephosphoniation of phosphonium salts **7**).

EXPERIMENTAL

General

M.p.s, determined in capillary tubes, are uncorrected. IR spectra were recorded on a Zeiss Specord M 80 spectrophotometer; the measurements were carried out in $CHCl_3$ (0.2 *M*) using cells of 0.105 mm. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian UNITY

INOVA-300 spectrometer at operating frequencies of 300 and 75.5 MHz, respectively, in the FT mode using *TMS* as an internal standard.

Starting Materials

Commercial grade acetonitrile and CH_2Cl_2 were distilled and dried over molecular sieves 4A. The following reagents were of commercial quality (Aldrich): (triphenylphosphoranylidene)acetaldehyde, 1-(triphenylphosphoranylidene)-2-propanone and 2-(triphenylphosphoranylidene)propionaldehyde. The synthesis and properties of the following compounds have been reported in the literature: N-phenylacetimidoyl chloride,[9] N-methylbenzimidoyl chloride,[10] N-benzylbenzimidoyl chloride,[11] and N-phenylbenzimidoyl chloride.[12]

Synthesis of β-(N-Acyloamino)vinylphosphonium Chlorides 7 Using Imidoyl Chlorides (General Procedure A)

To a solution of imidoyl halide **5** (2.4 mmol) in MeCN (3.6 ml) ylide **4** (2 mmol) was added and the mixture was left at room temperature for 24 h. The phosphonium salt was precipitated from the reaction mixture with Et_2O (5–8 ml). The product can be purified further, if necessary, by column chromatography on silica gel eluting with a mixture of CH_2Cl_2 and MeOH (97:3 or 99:1, v/v). Crude **7** can usually be recrystallized by dissolving in acetonitrile or CH_2Cl_2 and precipitating with diethyl ether (1:1–1:2; v/v).

Synthesis of β-(N-Acyloamino)vinylphosphonium Iodides 7 Using Imidoyl Chlorides (General Procedure B)

To a solution of imidoyl halide **5** (2.4 mmol) in MeCN (3.6 ml) NaI (0.30 g, 2 mmol) and ylide **4** (2 mmol) was added and the mixture was left at room temperature for 24 h. The precipitated NaCl was filtered off and the phosphonium salt was isolated from the reaction mixture as described above (procedure A).

Synthesis of β-(N-Acyloamino)vinylphosphonium Bromides 7 Using the N-monosubstituted Amide/Ph_3PBr_2/Et_3N System (General Procedure C)

To a solution of triphenylphosphine (0.63 g, 2.4 mmol) in CH_2Cl_2 (8 ml) a solution of bromine (0.38 g, 2.4 mmol) in CH_2Cl_2 (1 ml) was added at room temperature under argon atmosphere. After 30 min Et_3N (0.85 ml, 6 mmol) and amide (2.2 mmol) was added. After next 30 min ylide (2 mmol) was added and the mixture was left at room temperature

for 24 h. The solvent was evaporated and the phosphonium salt was isolated from the reaction mixture by column chromatography as described above (procedure A).

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