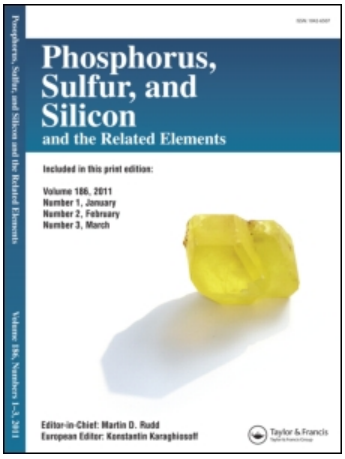

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β-Aminovinylphosphonium Salts—A Novel Synthesis, Properties, and Structure

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The deacylation of easily accessible β-(N-acylamino)vinylphosphonium salts with methanol or some other nucleophiles gives β-aminovinylphosphonium salts in good yields. As indicated by the spectroscopic properties and by the results of single crystal X-ray diffraction studies the N-alkyl derivatives of the investigated compounds should be considered as strongly resonance stabilized β-iminium ylides rather than β-aminovinylphosphonium salts. In the case of N-aryl derivatives, the β-iminium ylide resonance structures are probably less pronounced.

Keywords β-aminovinylphosphonium salts; β-iminium ylides; β-(*N*-acylamino)-vinylphosphonium salts; deacylation; imine-enamine tautomerism

INTRODUCTION

β-Aminovinylphosphonium salts **1** were obtained first by Schweizer et al. in 1977, by the nucleophilic addition of primary aromatic amines or hydrazine derivatives to propargyltriphenylphosphonium bromide in boiling acetonitrile (Scheme 1).[1] A very similar method for the synthesis of these phosphonium salts was extensively used later by Palacios et al.[2,3]

As follows from Scheme 1, Schweizer's method, which starts from the commercially available propargyltriphenylphosphonium bromide, allows to obtain only 2-amino-1-propenylphosphonium salts.[1–3]

Despite the fact that β-aminovinylphosphonium salts have been known for only about 30 years, they have found many important applications in organic synthesis. They were used for the synthesis of

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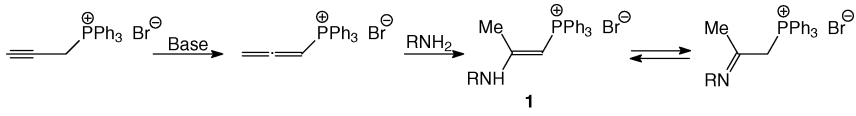
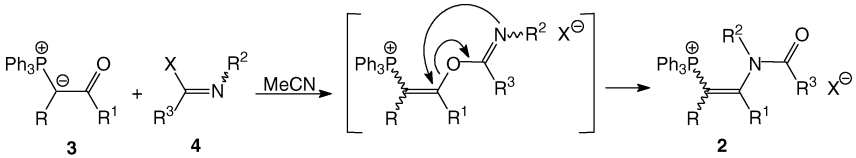


SCHEME 1

quinoline derivatives,[1] as well as of secondary E-allylamines and optically active γ-amino acid derivatives via 1-aza-1,3-dienes.[2] Both allylamines and γ-amino acids represent two important classes of compounds due to their occurrence in natural products and application in medical chemistry as chemotherapeutic agents2$^-$allylamines and 1-aza-1,3-dienes are useful building blocks in organic synthesis, as well.[2]

Recently, we have communicated the simple synthesis of β-(*N*-acyl-*N*-alkylamino)vinylphosphonium salts **2** by imidoylation of β-carbonyl phosphorus ylides **3** with imidoyl halides **4** or similar imidoylating agents (Scheme 2).[4] Two other very complicated multi-step syntheses of β-(*N*-acylamino)vinylphosphonium salts were described earlier by Brovarets et al.[5] In this paper, we describe a simple and effective method for the synthesis of β-aminovinylphosphonium salts **1** by deacylation of β-(*N*-acyl-*N*-alkylamino)vinylphosphonium salts **2** with methanol or other nucleophiles, as well as the results of our studies on their structure.

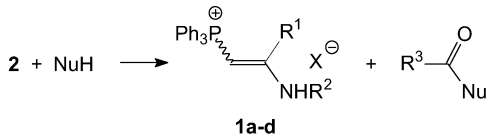


R = H or Me; R^1= H or Me; R^2 = Me, Ph or $PhCH_2$; R^3 = Me or Ph; X = Cl, Br or I

SCHEME 2

RESULTS AND DISCUSSION

Treatment of β-(*N*-acyl-*N*-alkylamino)vinylphosphonium salts in methanol with DBU at room temperature for 24 h results in the formation of β-(*N*-alkylamino)vinylphosphonium salts **1** as stable, crystalline compounds, which are obtained in good to very good yields (Scheme 3, Table I). The starting β-(*N*-acyl-*N*-alkylamino)vinylphosphonium salts can be used as pure compounds (procedure A) or can be prepared *in situ* from the corresponding β-carbonyl phosphorus ylides **3** and imidoyl chlorides **4** (procedure B). We also showed that other nucleophiles than methanol can be used for the deacylation of β-(*N*-acyl-*N*-alkylamino)



1a-d

R = H; R^1, R^2, X: see Table I; R^3 = Ph; Nu = MeO, PhO or $PhCH_2S$

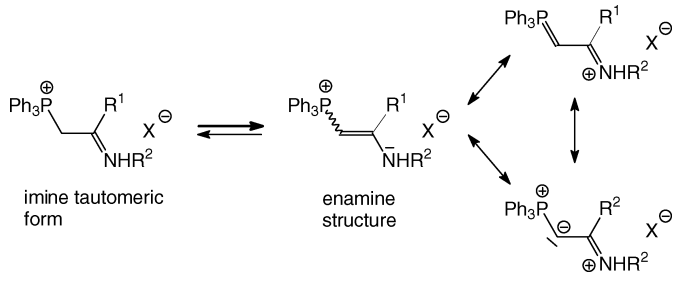
SCHEME 3

vinylphosphonium salts, e.g., phenol or benzyl mercaptan in THF (procedures C and D, respectively); methanol is the most versatile reagent, however. The work-up of the reaction mixture was very simple: after evaporation of the solvent, the residue was crystallized from acetonitrile.

The structure of the β-aminovinylphosphonium salts was confirmed by their spectroscopic properties (IR, ^1H and ^{13}C NMR) and satisfactory elemental analyses (Tables I and II). Only in the case of compound **1c** did we observe two sets of ^1H and ^{13}C NMR signals, probably due to the formation of a mixture of the *Z* and the *E* isomer. For comparison, we synthesised two β-aminovinylphosphonium salts using Schweizer's method (Table I, procedure E, compounds **1e** and **1f**). Their spectroscopic properties were very similar to the properties of the β-aminovinylphosphonium salts, obtained by deacylation of the corresponding β-(*N*-acyl-*N*-alkylamino)vinylphosphonium salts.

In the case of compounds **1a, 1d,** and **1f** a structure determination by single crystal X-ray diffraction was performed, which revealed the *E*-configuration at the C=C double bond (Figures 1–3).

Using ^1H and ^{31}P NMR spectroscopy Schweizer et al. observed the presence of an enamine-imine tautomeric equilibrium for some of the synthesized β-aminovinylphosphonium salts.[1] In the case of our compounds, we have not noticed in the ^1H NMR spectra any traces of signals of a CH_2 group connected to phosphorus (Scheme 4). Moreover,



R^1, R^2, X: see Table I

SCHEME 4

TABLE I Synthesis and Properties of β-Aminovinylphosphonium Salts

Phosphonium salts								Elemental analyses (calcd./found) (%)			
	R^1	R^2	X	Procedure	Yield (%)	M.p.(°C)	IR (cm^{-1})	C	H	N	P
1a	H	Me	Cl	B	84	295–296	1605	71.29/71.31	5.98/6.21	3.96/4.14	8.75/9.03
1b	Me	Me	Cl	A	94	306.5	1563	71.83/71.57	6.30/6.53	3.81/3.86	8.42/8.64
1b	Me	Me	Cl	C	77	306	1563	—	—	—	—
1b	Me	Me	Cl	D	95	307	1564	—	—	—	—
1c[a]	Ph	Me	Cl	B	82	209–211	1550	75.43/75.11	5.86/6.02	3.26/3.21	7.20/7.06
1d	Me	$PhCH_2$	Cl	B	47	267–268	1560	75.75/75.28	6.13/6.13	3.15/3.17	6.98/7.12
1e	Me	$PhCH_2$	Br	E	92	268.5–269	1562	68.86/68.26	5.57/5.32	2.87/3.00	6.34/6.45
1f	Me	Ph	Br	E	96	275–276[b]	1565	68.36/68.66	5.31/5.66	2.95/3.23	6.53/6.63

[a]A mixture of stereoisomers in a ratio of 74:26; and [b]Lit. m.p. 262–263°C.[1]

TABLE II Spectroscopic Properties of the β-Aminovinylphosphonium Salts 1a–f

		^{13} C-NMR ($CDCl_3$, δ (ppm)/J_{PC} (Hz))						
				Ph_3P^+				
	^{1} H-NMR ($CDCl_3$, δ (ppm))	C=N	P^+—C	C—i	C—o	C—m	C—p	Other carbon atoms
1a	9.57 (s, br, 1H, NH), 7.8–7.4 (m, 15H, Ph), 7.03 (ddd, $J_1 = J_2 = 13.8$ Hz, $J_3 = 7.2$ Hz, 1H, CHN), 4.07 (dd, $J_1 = J_2 = 14.7$ Hz, 1H, PCH), 2.96 (d, $J = 4.8$ Hz, 3H, Me)	155.7/17.0	54.9/120.4	122.3/92.7	132.9/10.0	129.7/12.5	133.9/3.0	29.4 (NMe)
1b	9.60 (s, br, 1H, NH), 7.6–7.5 (m, 15H, Ph), 3.56 (d, $J = 15.0$ Hz, 1H, CH), 2.94 (d, $J = 4.8$ Hz, 3H, NMe), 1.89 (s, 3H, CMe)	166.5/15.0	52.4/123.6	123.7/91.0	132.8/10.3	129.8/12.4	133.7/2.8	30.2 (NMe), 21.9/4.6 (CMe)
1c[a]	8.56 (s, br, 1H, NH), 7.7–6.6 (m, 20H, Ph), 4.07 (d, $J = 12.3$ Hz, 1H, CH), 3.16 (d, $J = 4.8$ Hz, 3H, Me)	168.6/14.0	55.6/125.4	123.7/92.7	132.7/10.0	129.4/12.6	133.3/2.5	129.7, 128.4, 127.5 (Ph), 31.1 (Me)
1c[b]	9.92 (s, br, 1H, NH), 7.7–6.6 (m, 20H, Ph), 5.74 (d, $J = 14.4$ Hz, 1H, CH), 2.51 (d, $J = 5.1$ Hz, 3H, Me)	170.6/14.6	57.9/125.9	124.5/92.2	132.8/11.3	129.1/12.6	134.6/3.5	129.7, 128.4, 127.5 (Ph), 31.0 (Me)
1d	10.13 (s, br, 1H, NH), 7.8–7.2 (m, 20H, Ph), 4.54 (d, $J = 5.4$ Hz, 2H, CH_2), 3.60 (d, $J = 13.8$ Hz, 1H, CH), 1.89 (s, 3H, Me)	165.5/14.0	56.0/122.4	123.4/91.1	132.6/10.5	129.7/12.6	133.7/2.5	137.1, 128.3, 127.3, 127.0, (Ph), 47.2 (CH_2), 21.8/4.9 (Me)
1e	9.43 (s, br, 1H, NH), 7.7–7.2 (m, 20H, Ph), 4.54 (d, $J = 5.7$ Hz, 2H, CH_2), 3.64 (d, $J = 14.1$ Hz, 1H, CH), 1.89 (s, 3H, Me)	165.2/13.5	56.7/121.9	123.2/91.7	132.6/10.0	129.7/12.6	133.7/3.0	136.9, 128.4, 127.4, 127.1 (Ph), 47.1 (CH_2), 21.8/5.0 (Me)
1f	10.5 (s, br, 1H, NH), 7.8–7.1 (m, 20H, Ph), 4.64 (s, br, 1H, CH), 2.07 (s, 3H, Me)	164.5/14.0	58.5/120.4	123.0/91.7	132.8/10.0	130.0/12.6	134.0/3.0	138.4, 129.2, 125.7, 124.6 (Ph), 22.3 (Me)

[a]Major stereoisomer; and [b]minor stereoisomer.

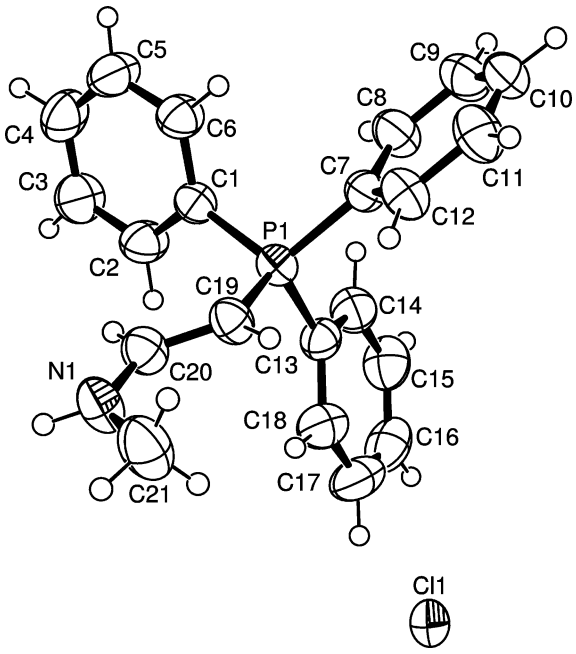


FIGURE 1 ORTEP-Plot of the molecular structure of 2-(*N*-methylamino)-vinyltriphenyphosphonium chloride **1a** in the crystal. Thermal ellipsoids are drawn at 50% probability level.

our attempts to exchange mobile protons of the investigated compounds in MeCN-D_2O solution at room temperature revealed, when monitored by ^1H NMR, an immediate exchange of the NH proton and no exchange of the proton of the PCH group even after 24 h (Table III). This means, that in practice the enamine-imine tautomeric transformation does not occur under these conditions. Only after addition of DBU we observed a fast exchange of the PCH group proton; it should be mentioned, however, that the exchange of these protons in the presence of a strong base does not necessarily need an enamine-imine equilibrium. It seems, that the enamine-imine tautomeric equilibrium claimed by Schweizer can exist only in the case of β-aminovinylphosphonium salts with special structure, *e.g.* derived from hydrazine.

The presence of a strong electron-donating amino group and a strong electron-withdrawing phosphonium group at opposite sides of the vinylic double bond of β-aminovinylphosphonium salts implicates the strong push-pull resonance stabilization of these compounds. Consequently, apart from the enamine structure, the β-iminium ylide resonance structures must be taken into account (Scheme 4). We have tried

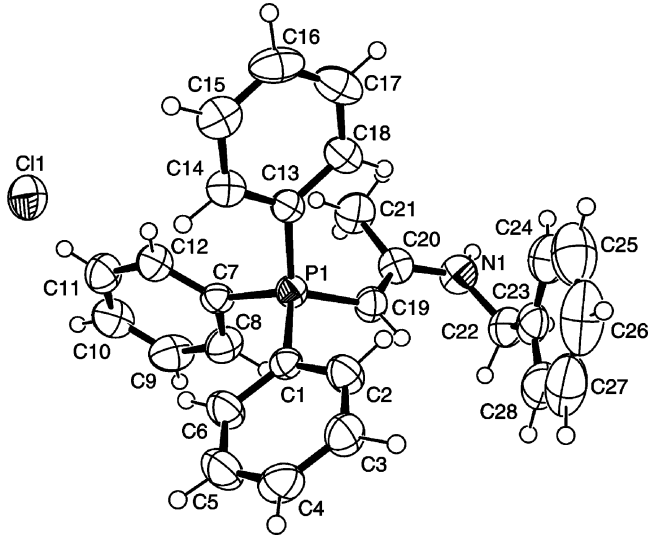


FIGURE 2 ORTEP-Plot of the molecular structure of 2-(*N*-benzylamino)-l-propenyltriphenyphosphonium chloride **1d** in the crystal. Thermal ellipsoids are drawn at 50% probability level.

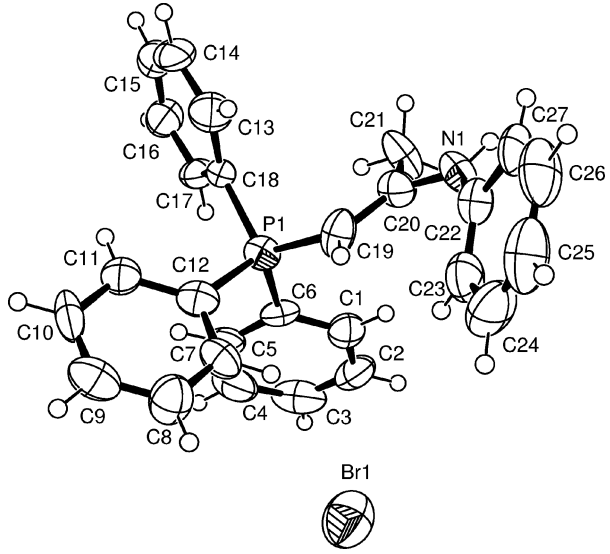


FIGURE 3 ORTEP-Plot of the molecular structure of 2-(*N*-phenylamino)-l-propenyltriphenyphosphonium bromide **1f** in the crystal. Thermal ellipsoids are drawn at 50% probability level.

TABLE III H/D Exchange of the Mobile Protons of β-Aminovinylphosphonium Salts in MeCN-D_2O Solution

	Time for the full H/D exchange (min)		
	Without base		In the presence of DBU
	N-H	C_α-H	C_α-H
1a	<5	–[a]	<5
1b	<4	–[a]	<2
1d	<3	–[b]	<2

[a]No isotopic exchange after 1 h; and [b]no isotopic exchange after 24 h.

to evaluate the contribution of enamine and β-iminium ylide structures basing on the spectroscopic properties of β-aminovinylphosphonium salts as well as on the X-ray data.

A comparison of the chemical shifts of the proton at the α-carbon atom of β-aminovinylphosphonium salts **1a, 1b,** and **1d** (Table II) with those of the parent β-(*N*-benzoylamino)vinylphosphonium chlorides[4] reveals, that in the case of the β-aminovinylphosphonium salts the considered protons are shielded at least by 2.65–3.42 ppm. Using the well-known equation for the chemical shifts δ of olefinic protons postulated by Pascual et al.[7,8]

$$\delta = 5.25 + \sum_i Z_i, \tag{1}$$

where Z_i are the respective shielding increments of the substituents in *gem*, *cis,* and *trans* position with respect to the olefinic protons, the following expression for the expected difference Δ of the chemical shifts of the α-protons in β-(*N*-acyloamino)vinylphosphonium salts and β-aminovinylphosphonium salts is obtained:

$$\Delta^{E,E} = Z^{cis}_{RCONH} - Z^{cis}_{RNH}, \tag{2}$$

for both phosphonium salts of *E*-configuration, and

$$\Delta^{Z,E} = Z^{trans}_{RCONH} + Z^{cis}_{Alkyl} - Z^{cis}_{RNH} - Z^{trans}_{Alkyl}, \tag{3}$$

for the β-(*N*-acyloamino)vinylphosphonium salt of *Z*-configuration and the β-aminovinylphosphonium salt of *E*-configuration. Substituting for Z^{cis}_{RCONH}, Z^{trans}_{RCONH}, Z^{cis}_{RNH}, Z^{cis}_{Alkyl} and Z^{trans}_{Alkyl} the corresponding increment values (−0.57, −0.72, −1.26, −0.22, −0.28),[9] the values 0.69 and 0.60 ppm are obtained as the expected shielding effect caused by exchange of the acylamino group for the amino group. Therefore, the observed strong shielding effect (2.65–3.42 ppm) cannot be simply explained

as the result of substitution of the less electron-donating acylamino group by a more electron-donating amino group; to account for such a strong shielding effect, we have to assume a high contribution of the β-iminium ylide structures, and the strong shielding effect typical for ylides due to the increased electron density at the ylidic carbon atom. Moreover, the range of the chemical shifts for the protons at the ylidic carbon atom for the investigated compounds (3.56–4.64 ppm) is typical for resonance-stabilized phosphonium ylides, e.g., $Ph_3P{=}CHC{\equiv}N$ (3.71 ppm), $Ph_3P{=}CHCOMe$ (3.19 ppm) or $Ph_3P{=}CHCOPh$ (4.43 ppm).[10]

The shielding effect observed for the α-carbon atom in the ^{13}C NMR spectra of β-aminovinylphosphonium salts **1a**, **1b**, and **1d** is even more striking if compared with that of the parentβ-(*N*-benzoylamino)vinylphosphonium chlorides[4] and amounts to 28.6–47.0 ppm. The increase of the $^1J_{PC}$ coupling constant from about 95–100 Hz for β-(*N*-acyloamino)vinylphosphonium salts[4] to more than 120 Hz for the corresponding β-aminovinylphosphonium salts (Table II) also indicates a change of the phosphonium salt structure to the ylide structure. The range of chemical shifts for the α-carbon atom of β-aminovinylphosphonium salts (52.4–58.5 ppm) as well as the range of one bond C-P coupling constants (120.4–125.9 Hz) is close to the corresponding values for other resonance-stabilized phosphonium ylides, e.g. $Ph_3P{=}CHCOPh$ (50.4 ppm/112 Hz).[10]

Also the P-C_α bond distance determined by single crystal X-ray diffraction can be used as an indication of ylide or phosphonium salt structure of the investigated compounds (Table IV). The typical P-C_α bond distance for phosphonium salts is about 1.80 Å.[10] An inspection of the data in Table IV shows the P-C_α bond lengths to be in the range 1.725–1.730 Å, which is close to the typical range of this bond for resonance-stabilized ylides, e.g., $Ph_3P{=}CHCHO$ (1.709 Å),[10] $Ph_3P{=}CHCOPh$ (1.711 Å)[11] or $Ph_3P{=}CH(CN)_2$(1.753 Å).[10] On the other

TABLE IV Lengths of Some Bonds of the β-Aminovinylphosphonium Salts 1a, d, and f

	Bond lengths (Å)			
	P–C_α	C_α–C_β	C_β–N	N–R^2
1a	1.725 (3)	1.352 (4)	1.325 (3)	1.429 (4)
1d	1.729 (3)	1.371 (4)	1.336 (4)	1.453 (4)
1f	1.730 (13)	1.367 (16)	1.380 (16)	1.391 (16)

TABLE V Crystal Data and Structure Refinement Details for Compounds 1a, d, and f

	Compound		
	1a	**1d**	**1f**
Empirical formula	$C_{21}H_{21}ClNP$	$C_{28}H_{27}ClNP$	$C_{27}H_{25}BrNP$
Formula weight	353.81	443.93	474.36
Crystal shape	Colourless needle 0.5 × 0.3 × 0.2 mm	Colourless plate 0.5 × 0.4 × 0.2 mm	Colourless needle 0.7 × 0.3 × 0.1 mm
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, P2/1c	Orthorhombic, $Pca2_1$
Unit cell dimensions	a = 10.782 (2) Å b = 13.720 (3) Å c = 13.127 (3) Å β = 102.55(3)°	a = 9.874 (2) Å b = 17.301 (4) Å c = 14.390 (3) Å β = 102.99(3)°	a = 18.305 (5) Å b = 9.562 (5) Å c = 13.382 (5) Å
Volume	V = 1895.5 (7) $Å^3$	V = 2395.3 (8) $Å^3$	V = 2342.3 (16) $Å^3$
Z, Calculated density	4, 1.240 g/cm^3	4, 1.231 g/cm^3	4, 1.345 g/cm^3
Absorption coefficient	0.287 mm^{-1}	0.242 mm^{-1}	1.837 mm^{-1}
Theta max.	25.06°	25.06°	25.55°
Index ranges	$-12 \le h \le 12$ $0 \le k \le 16$ $0 \le l \le 15$	$-11 \le h \le 11$ $0 \le k \le 20$ $0 \le l \le 17$	$0 \le h \le 22$ $0 \le k \le 11$ $0 \le l \le 16$
Reflections collected	3513	4425	2290
Independent reflections	3361 [R_{int} = 0.0392]	4244 [R_{int} = 0.0732]	2290
Data/restraints/parameters	3361/0/294	4244/6/380	2290/1/272
Goodness on fit on F^2	0.937	0.888	0.874
Data to parameter ratio	11.4 : 1	11.2 : 1	8.4 : 1
Final R indices [I > 2σ (I)]	R1 = 0.0376 wR2 = 0.0909	R1 = 0.0411 wR2 = 0.0911	R1 = 0.0567 wR2 = 0.1313
R indices (all data)	R1 = 0.1157 wR2 = 0.1084	R1 = 0.1646 wR2 = 0.1151	R1 = 0.2291 wR2 = 0.1771
Largest diff. peak and hole	0.241; −0.212 e $Ä^{-3}$	0.244; −0.239 e $Ä^{-3}$	0.418; −0.500 e $Ä^{-3}$

hand, the C_β—N bond lengths for compounds **1a** and **1d** (1.325 and 1.336 Å, respectively) are much shorter if compared with a typical C—N single bond (1.47 Å)[12] and with the C_β—N bond in 2-(*N*-benzoyl-*N*-methylamino)-1-propenyltriphenylphosphonium chloride (1.415 Å),[4] which indicates a considerable contribution of the β-iminium ylide resonance structure. The situation is somewhat different in the case of compound **1f**; the C_β—N bond is in this case considerably longer (1.380 Å), whereas the N-C bond to the phenyl ring is shorter (1.391 Å) than the corresponding N-Me bonds in compounds **1a** and **1d** (1.429 and 1.453 Å, respectively). It seems that this phenomenon can be explained taking into account the competitive resonance structures with the electron pair of the nitrogen atom partly spread over the benzene ring.

The C_α-C_β bonds of the investigated compounds are much shorter than a typical $C_{sp}2$- $C_{sp}2$ single bond (1.48 Å),[13] but markedly longer than a $C_{sp}2$-$C_{sp}2$ double bond (1.32 Å).[13] It is noteworthy, that the lengths of the C_α-C_β bonds in resonance-stabilized β-keto ylides range from 1.35 to 1.48 Å, with most being near 1.40 Å.[10]

CONCLUSIONS

Deacylation of easily accessible β-(*N*-acylamino)vinylphosphonium salts with methanol offers a convenient way for the synthesis of β-aminovinylphosphonium salts. It seems, that at least the *N*-alkyl derivatives of the investigated compounds should be considered as strongly resonance-stabilized β-iminium ylides rather than β-aminovinylphosphonium salts. In the case of *N*-aryl derivatives, the β-iminium ylide structures are probably less pronounced.

EXPERIMENTAL

General

Melting points are determined in capillary tubes with a Stuart Scientific SMP3 melting point apparatus, and are uncorrected. IR spectra were recorded with 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.

Single crystals of **1a, 1b,** and **1d,** suitable for X-ray measurements, were obtained by slow evaporation of the solvent from solutions of these compounds in acetonitrile. Data collection was performed on a KUMA KM4 four-circle diffractometer, Zr foil filtered MoK_α radiation, $\omega/2\Theta$

scan mode, Θ range 2.5–25.5°; temperature of the measured crystals: 293 K (Table V). The structures were solved by direct methods using the SHELX-97 program[14] and refined by full-matrix least squares with the SHELXL97 program.[15] All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated according to the standard geometry, and refined as a riding model with isotropic thermal parameters.[15] Software used to prepare material for publication: Ortep-3.[16] Crystallographic data for the structures **1a**, **1d**, and **1f**, were deposited with the Cambridge Crystallographic Data Centre as supplementary publications number CCDC 279686, 279687 and 279688, respectively.[1]

Starting Materials

Commercial grade acetonitrile and CH_2Cl_2 were distilled and dried over molecular sieves (4 Å). The following reagents were of commercial quality (Aldrich): triphenylphosphoranylideneacetaldehyde, triphenylphosphoranylideneacetone and propargyltriphenylphosphonium bromide. The following compounds were synthesized as described in the literature: *N*-methylbenzimidoyl chloride,[17] *N*-benzylbenzimidoyl chloride,[18] triphenylphosphoranylideneacetophenone,[19] and 2-(*N*-benzoyl-*N*-methylamino)-1-propenyltriphenylphosphonium chloride.[4]

Synthesis of 2-(*N*-Methylamino)-1-propenyltriphenylphosphonium Chloride (1b) from 2-(*N*-Benzoyl-*N*-methylamino)-1-propenyltriphenylphosphonium Chloride (2b) and Methanol (Procedure A)

To a solution of 2-(*N*-benzoyl-*N*-methylamino)-1-propenyltripheny lphosphonium chloride **1b** (0.943 g, 2.0 mmol) in methanol (5.0 mL) DBU (0.08 mL, 0.5 mmol) was added and the mixture was left at room temperature for 24 h. After evaporation of the methanol the residue was extracted with benzene (4 × 4 mL), and the crude product was recrystallized from acetonitrile (20 mL).

Synthesis of β-Aminovinylphosphonium Chlorides 1 from Ylides 3, Imidoyl Chlorides 4, and Methanol (Procedure B)

To a solution of the imidoyl chloride **4** (2.4 mmol) in MeCN (3.6 mL) the ylide **3** (2 mmol) was added and the mixture was left at room

[1]A complete listing of the atomic coordinates can be obtained free of charge, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+int) 44-1223 336 033; e-mail: deposit@ccdc.cam.ac.uk], on quoting the depository numbers, the names of the authors, and the journal citation.

temperature for 24 h. The solvent was evaporated, the residue was dissolved in methanol (5.0 mL), DBU (0.08 mL, 0.5 mmol) was added, and the mixture was left at room temperature for 24 h. The reaction mixture was worked up as described above (Procedure A).

Synthesis of β-(*N*-Methylamino)-1-propenyltriphenylphosphonium Chloride (1b) from 2-(*N*-Benzoyl-*N*-methylamino)-1-propenyltriphenylphosphonium Chloride (2b) and Phenol (Procedure C) or Benzylmercaptan (Procedure D)

To a solution of 2-(*N*-benzoyl-*N*-methylamino)-1-propenyltripheny lphosphonium chloride **2b** (0.943 g, 2.0 mmol) in THF (5.0 mL) phenol or benzylmarcaptan (4 mmol) and DBU (0.08 mL, 0.5 mmol) was added and the mixture was left at room temperature for 24 h. After evaporation of THF the residue was extracted with benzene (4 × 4 mL), and the crude product was recrystallized from acetonitrile (20 mL).

Synthesis of β-Aminovinylphosphonium Bromides 1e and 1f from 2-Propynyltriphenylphosphonium Bromide (Procedure E)

To a solution of propargyltriphenylphosphonium bromide (0.602 g, 2 mmol) in acetonitrile (20 mL), aniline or benzylamine (2 mmol) was added, the mixture was heated under reflux for 3 h, and left at room temperature for 24 h. The precipitated crystals were filtered and recrystallized from acetonitrile (35 and 45 mL, respectively).

H/D Exchange of Mobile Protons in β-Aminovinylphosphonium Salts 1

A solution of the β-aminovinylphosphonium salt (0.1 mmol) in CD_3CN (0.5 mL) was added to a mixture of CD_3CN (0.45 mL) and D_2O (0.05 mL) in a NMR tube at room temperature. In some experiments, DBU (0.024 g, 0.16 mmol) was added to this mixture. The progress of H/D exchange was monitored by means of ^1H NMR spectroscopy.

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