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Synthesis and properties of β-(*N*-acylamino)vinylphosphonium salts. A novel intramolecular [1,3] O-to-N migration of the vinyl group

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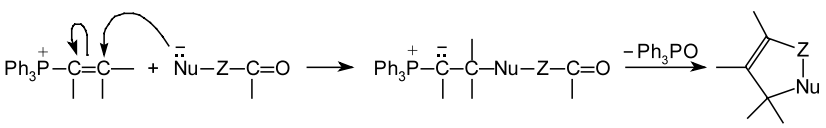
Abstract—A reaction of β-carbonyl phosphorus ylides with imidoyl halides gives hitherto unknown β-(*N*-acylamino)vinylphosphonium salts. The key step of the reaction probably involves an intramolecular [1,3] O-to-N migration of the vinyl group, converting the primary *O*-imidoylation product into a β-(*N*-acylamino)vinylphosphonium salt.

In 1964 Schweizer[1] realised that the addition of nucleophiles with a carbonyl function to vinylphosphonium salts results in phosphorus ylides **2**, which can undergo the intramolecular Wittig reaction to carbo- or heterocyclic systems (Scheme 1).

For many years this idea has attracted significant attention of synthetic chemists; many carbo- and heterocyclic systems have been synthesised in this way.[2]

Recently, we have developed a method for the synthesis of hitherto unknown β-(*N*-acylamino)vinylphosphonium salts **7** by imidoylation of β-carbonyl phosphorus ylides **4** with imidoyl halides **5** (Scheme 2). Treatment of the ylide with an imidoyl halide in acetonitrile at room temperature for 24 h results in vinylphosphonium salts **7** as stable, crystalline compounds, usually in good yields.[3] The structures of the β-(*N*-acylamino)vinylphosphonium salts were confirmed by their spectroscopic properties (IR, ^{1}H and ^{13}C NMR)[4–6] and satisfactory elemental analyses,[7] as well as, in the case of the compound **7d**, by a single crystal X-ray structure determination,[8] which revealed its *Z*-configuration (Table 1).

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 type of [1,3] sigmatropic migration is well-known in the literature;[9] e.g. *O*-imidoylated car-



Scheme 1.

Keywords: β-(*N*-acylamino)vinylphosphonium salts; β-carbonyl ylides; imidoylation; imidoyl halides; rearrangement.

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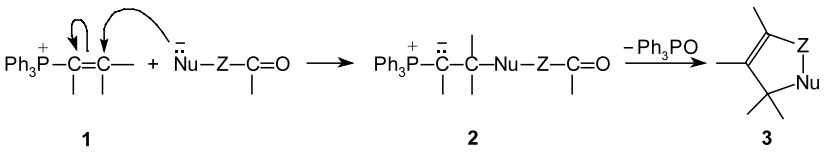

Scheme 2.

Table 1. Synthesis of β-(*N*-acylamino)vinylphosphonium salts **7**

Ylide **4**		Imidoyl halide **5**			β-(*N*-Acylamino)vinylphosphonium salt **7**		
R^1	R^2	R^3	R^4	X	No.	Yield (%)	Mp (°C)
H	H	Me	Ph	I	**7a**	91	133–134
H	H	Ph	Me	Cl	**7b**	71	238–239
H	H	Ph	$PhCH_2$	Cl	**7c**	64	273–275
H	Me	Ph	Me	Cl	**7d**	66	140–141
H	Me	Ph	Me	I	**7e**	85	182–183
H	Me	Ph	Ph	Cl	**7f**	72	192–193
H	Me	Ph	$PhCH_2$	Cl	**7g**	87	175–177
Me	H	Ph	Me	Cl	**7h**	99	Resin

boxamides undergo a similar rearrangement.[10] An analogous rearrangement also probably takes place in the case of well-known acylations of β-carbonyl ylides; however, being a degenerate rearrangement, it cannot be directly observed.

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), synthesis of *N*-acylynamines (by β-elimination of Ph_3P and HX if $R^2=H$) or *N*-vinylamides (by hydro-de-phosphonation of phosphonium salts **7**).

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3. General procedure: To a solution of imidoyl halide **5** (2.4 mmol) in MeCN (3.6 cm^3) 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 cm^3). 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, v/v).
4. The most characteristic amide carbonyl frequency falls in the range 1690–1660 cm^{-1}.
5. **^{1}H NMR spectral data of 7a–h** (300 MHz, $CDCl_3$, δ): **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); **7b**: 7.8–7.2 (m, 22H, Ph and CH), 3.78 (s, 3H, Me); **7c**: 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); **7d**: 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); **7e**: (in DMSO-d_6): 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); **7f**: 7.9–6.5 (m, 26H, Ph and CH), 2.45 (s, 3H, Me); **7g**: 7.85–7.22 (m, 25H, Ph), 6.25 (d, 1H, CH, $J_{P-H}=14.4$ Hz), 5.52 (s, 2H, CH_2), 1.66 (s, 3H, CH_3); **7h**: 7.88–7.18 (m, 20H, Ph), 6.91 (d, 1H, $J_{P-H}=20.4$ Hz, CH), 3.75 (s, 3H, NMe), 2.42 (d, 3H, $J_{P-H}=15.6$ Hz, CMe).
6. **^{13}C NMR spectra of 7a–h** (75 MHz, $CDCl_3$, δ (ppm)/J_{C-P} (Hz)): **7a**: 176.6 (C=O); 86.1/99.5 (C_α), 151.1/17.6 (C_β); 119.2/91.1, 133.7/10.7, 130.2/13.1, 134.5/3.0 (Ph_3P, C-1, C-2, C-3, C-4); 135.6, 122.5, 128.7, 125.2 (Ph, C-1, C-2, C-3, C-4); 25.5 (Me); **7b**: 170.9 (C=O); 83.5/100.5 (C_α), 150.8/17.8 (C_β); 119.4/91.4, 133.8/10.6, 130.2/12.9, 134.7/3.0 (Ph_3P, C-1, C-2, C-3, C-4); 132.8, 128.6, 127.8, 131.3 (Ph, C-1, C-2, C-3, C-4); 34.5 (Me); **7c**: 171.6 (C=O); 85.1/100.5, (C_α) 149.7/17.8, (C_β) 119.1/91.8, 133.8/11.0, 130.2/12.9, 134.7/3.0 (Ph_3P, C-1, C-2, C-3, C-4); 136.2, 133.0, 131.5, 128.9, 128.8, 128.6, 128.1, 127.5 (PhCO+ $PhCH_2$); 47.9 (CH_2); **7d**: 170.4 (C=O); 99.4/97.6, (C_α) 161.6/8.6, (C_β) 120.6/92.5, 133.8/10.3, 130.0/12.8, 134.3/3.1 (Ph_3P, C-1, C-2, C-3, C-4); 133.2, 128.4, 127.0, 131.0 (Ph, C-1, C-2, C-3, C-4); 37.8 (NMe); 26.1/15.4 (CMe); **7e**: (in DMSO-d_6): 169.2 (C=O); 98.2/94.9, (C_α) 160.9/8.0, (C_β) 120.6/92.5, 133.5/10.7, 129.7/12.8, 134.1/3.0 (Ph_3P, C-1, C-2, C-3, C-4); 133.3, 128.0, 127.1, 130.7 (Ph, C-1, C-2, C-3, C-4); 36.7 (NMe); 24.8/15.5 (CMe); **7f**: 170.3 (C=O); 98.2/94.4, (C_α) 161.0/5.2, (C_β) 120.1.1/91.8, 134.1/10.3, 130.0/13.0, 134.0/3.0 (Ph_3P, C-1, C-2, C-3, C-4); 133.0, 127.8, 127.3, 130.8 (Ph, C-1, C-2, C-3, C-4); 27.4/15.5 (CMe); **7g**: 172.1 (C=O); 98.8/95.9, (C_α) 164.4/10.6, (C_β) 119.0/90.6, 133.2/10.9, 130.6/13.3, 135.1/3.1 (Ph_3P,

C-1, C-2, C-3, C-4); 136.8, 135.7, 131.9, 129.00, 128.98, 128.6, 128.5, 127.8 (PhCO+PhCH$_2$); 52.3 (CH$_2$); 24.3/5.3 (Me); **7h**: 171.8 (C=O); 95.0/91.9 (C_α), 149.5/25.8 (C_β); 117.5/89.3, 133.7/10.2, 130.5/12.6, 135.1/2.6 (Ph$_3$P, C-1, C-2, C-3, C-4); 132.0, 128.7, 127.9, 131.1 (Ph, C-1, C-2, C-3, C-4); 36.0 (NMe), 16.6/8.3 (CMe).

7. **Elemental analyses for 7a–h** (formula: C, H, N, P–calcd/found): **7a**: $C_{28}H_{25}INOP$: 61.21/61.12, 4.59/4.66, 2.55/2.41, 5.64/5.77; **7b**: $C_{28}H_{25}ClNOP$: 73.44/73.51, 5.50/5.74, 3.06/3.00, 6.76/6.63; **7c**: $C_{34}H_{29}ClNOP$: 76.47/76.70, 5.47/5.30, 2.62/2.78, 5.80/6.00; **7d**: $C_{29}H_{27}ClNOP$: 73.80/73.54, 5.77/5.92, 2.97/2.91, 6.56/6.42; **7e**: $C_{29}H_{27}INOP$: 61.71/62.09, 4.83/4.59, 2.49/2.74, 5.50/5.42; **7f**: $C_{34}H_{29}ClNOP$: 76.47/76.21, 5.47/5.22, 2.62/2.32, 5.80/5.61; **7g**: $C_{35}H_{31}ClNOP$: 76.70/76.48, 5.70/5.91, 2.56/2.62, 5.65/5.48; **7h**: $C_{29}H_{27}ClNOP$: 73.80/73.51, 5.77/6.01, 2.97/3.04, 6.56/6.36.
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