Reversible C ⇌ N migration of the ethoxycarbonyl group in pyridinium ylides

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Previously,[1] we described C ⇌ N migrations of alkoxycarbonyl groups in a series of organic carbanions and P-zwitterions. For the purpose of further studying rearrangements of this type, the reaction of phenyl isocyanate (a 20% solution in $CHCl_3$, 20 °C, 24 h) with pyridinium ylide **1** (prepared from *N*-(diethoxycarbonylmethyl)-pyridinium bromide[2]) was investigated (Scheme 1).

In the first stage, obviously, an intermediate **2** is formed. The C—C bond undergoes cleavage, and the ethoxycarbonyl group migrates towards the negatively charged N atom to give ylide **3**. The structure of the latter was concluded from the data of elemental analysis and IR and ^1H NMR spectroscopy, as well as from its transformation into pyridinium salt **4** in CH_2Cl_2. The IR spectrum of compound **3** contains both the bands of the carbonyl group conjugated with the carbanionic center (at 1594—1620 cm^{-1}) and those of the NCOOEt group (1708 and 1715 cm^{-1}). According to ^1H NMR spectral data, the COOEt groups in ylide **3**, unlike those in the starting ylide **1**, are nonequivalent (signal ratio 1 : 1).

When heated to 100 °C, dry ylide **3** decomposes to give the starting compound **1** (in 60% yield) and poly(phenylisocyanate), thus suggesting that the rearrangement is reversible. Similar migration occurs upon heating ylide **3** in $CDCl_3$ (60 °C) or upon recrystallization from boiling acetone.

IR spectra were recorded on a Karl Zeiss M-82 instrument (KBr). ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.26 MHz) in $CDCl_3$.

Pyridinium (*N*-ethoxycarbonyl-*N*-phenylcarbamoyl)ethoxycarbonylmethylide (3), yield 96%, m.p. 106—109 °C (crystallization without heating from a THF—hexane—acetone mixture, 10 : 5 : 1). Found (%): C, 63.84; H, 5.69; N, 7.77. $C_{19}H_{20}N_2O_5$. Calculated (%): C, 64.04; H, 5.62; N, 7.87. ^1H NMR, δ: 1.21 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 1.26 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 4.14 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.2 Hz); 4.22 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.2 Hz); 7.25—7.30 (m, 5 H, Ph); 7.21 (t, 2 H, H(3) Py, H(5) Py, J = 7.2 Hz); 8.15 (t, 1 H, H(4) Py, J = 7.6 Hz); 8.57 (d, 2 H, H(2) Py, H(6) Py, J = 5.6 Hz).

***N*-[(*N*-Ethoxycarbonyl-*N*-phenylcarbamoyl)ethoxycarbonylmethyl]pyridinium methosulfate (4)**, yield 50%, m.p. 135—137 °C (from a MeCN—hexane mixture). Found (%): C, 52.70; H, 5.25; N, 6.06. $C_{20}H_{24}N_2O_8S$. Calculated (%): C, 53.10; H, 5.31; N, 6.19. IR, ν/cm^{-1}: 1745, 1708 (C=O). ^1H NMR, δ: 1.15 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 1.29 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 2.77 (s, 3 H, CH_3S); 4.23 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.2 Hz); 4.24 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.2 Hz); 7.30—7.40 (m, 5 H, Ph); 7.78 (s, 1 H, CH); 7.95 (t, 2 H, H(3) Py, H(5) Py, J = 5.6 Hz, J = 7.8 Hz); 8.43 (t, 1 H, H(4) Py, J = 7.8 Hz); 9.13 (d, 2 H, H(2) Py, H(6) Py, J = 5.6 Hz).

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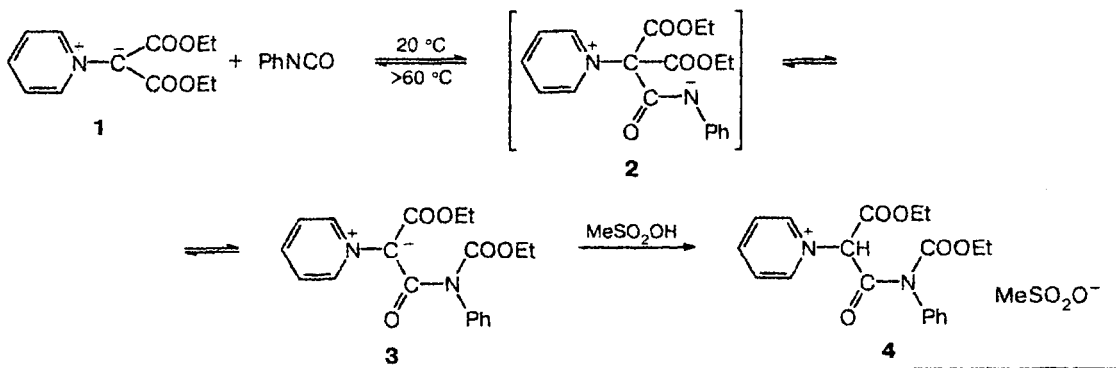
Scheme 1



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