On the mechanism of C ⇄ N migration of alkoxycarbonyl groups in reactions of pyridinium ylides with isocyanates

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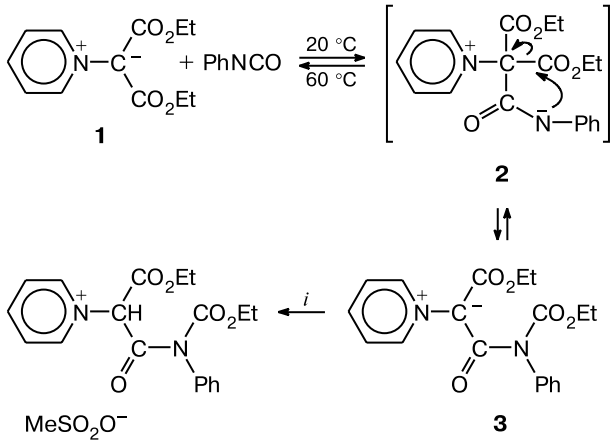
New examples of reversible C ⇄ N migrations of alkoxycarbonyl groups, which occur in the reactions of pyridinium and 3-(diethylcarbamoyl)pyridinium ylides, *viz.*, derivatives of dimethyl and diethyl malonates, with aryl isocyanates were studied. The mechanism of migration of the methoxycarbonyl group from the carbon atom to the nitrogen atom was considered on the basis of quantum-chemical calculations. The product of the primary attack of the isocyanate group by pyridinium ylide was established to be rearranged with low potential barriers to form carbamate without formation of cyclic intermediate compounds.

Key words: pyridinium ylides, aryl isocyanates, migrations of alkoxycarbonyl groups, C—N rearrangements, rearrangement mechanism, quantum-chemical calculations.

A new rearrangement occurring in the reaction of pyridinium ylide **1** with phenyl isocyanate has been described[1] (Scheme 1).

Scheme 1



i. $MeSO_2OH$.

The first step of the reaction in Scheme 1 gives (under the conditions of isocyanate excess) adduct **2** in which the intramolecular attack of the carbon atom of the ethoxycarbonyl group by the N-anion leads to the C—C bond cleavage and formation of the C—N bond. As a result, the phenyl isocyanate molecule is inserted into the C—C bond to form carbamate **3**.

Active medicines are known among pyridine derivatives and compounds containing carbamate fragments. Therefore, we introduced pyridinium ylides **4** and **8** into the reactions with substituted aryl isocyanates (Schemes 2 and 3) to obtain new carbamates with the pyridinium ring.

The introduction of previously unknown ylide **8** containing the fragment of widely used medicine *Cardiamin* into the considered transformations is of special interest (see Scheme 3). We synthesized ylide **8** by the alkylation of *N*,*N*-diethylnicotinamide with diethyl monobromomalonate followed by the treatment of the formed quaternary pyridinium salt with a solution of soda in the presence of chloroform. In a CH_2Cl_2 solution at room temperature, ylides **4** and **8** react with the corresponding isocyanate excess to form carbamates **6** and **10**. The conversion of these ylides to carbamates can easily be controlled by ^1H NMR on an instrument with a working frequency of 400 MHz, because the chemical shifts of protons of the pyridinium ring and alkoxy groups in the starting ylides and formed carbamates differ distinctly. According to the IR spectroscopic data, the anion charge in the starting ylides **4** and **8** is delocalized involving both CO_2Alk groups (bands of the conjugated CO_2Alk group appear at 1600—1660 cm^{-1}). However, in ylides **3**, **6**, and **10** only one CO_2Alk group is conjugated with the anion charge

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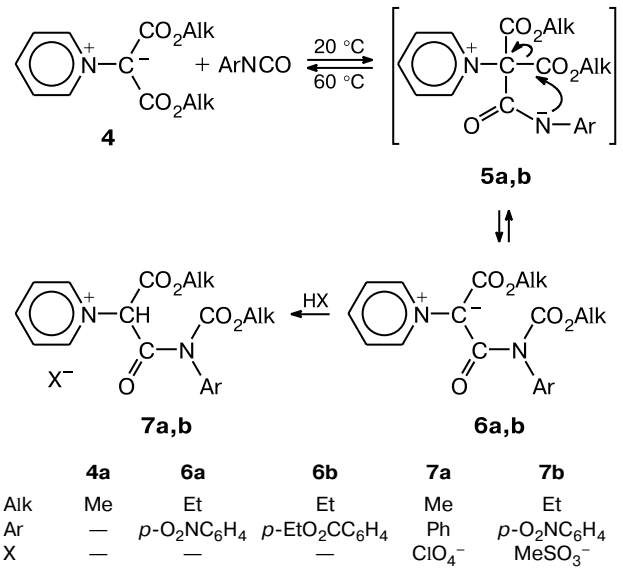
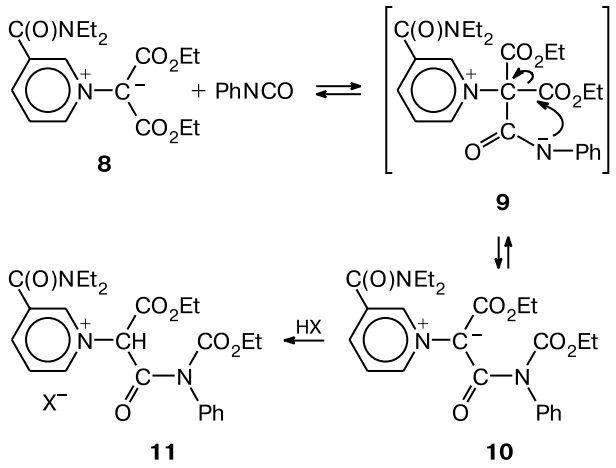
Scheme 2



	4a	6a	6b	7a	7b
Alk	Me	Et	Et	Me	Et
Ar	—	p-$O_2NC_6H_4$	p-$EtO_2CC_6H_4$	Ph	p-$O_2NC_6H_4$
X	—	—	—	ClO_4^-	$MeSO_3^-$

Scheme 3

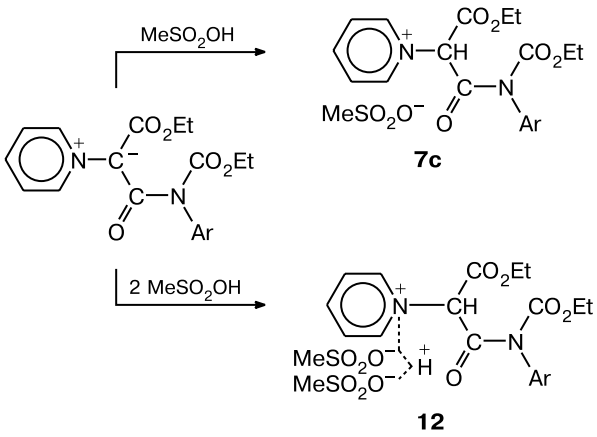


(ν_{CO} 1580—1590 cm^{-1}). At the same time, the band of the non-conjugated CO_2Alk groups is manifested at ~1720 cm^{-1}.[2]

The reactions of isocyanates **1**, **4**, and **8** are reversible, and the conversion of the latter to carbamates **3**, **6**, and **10** substantially depends on the steric and electronic characteristics of radicals at the isocyanate group. For example, cyclohexyl isocyanate, being even in fivefold excess, reacts with ylide **1** very slowly and, according to the ^{1}H NMR spectroscopic data,[2] an equilibrium mixture of ylide **1** (64%) and the corresponding carbamate (36%) is achieved at room temperature for 30 days. *ortho*-Substituents in aryl isocyanates[2] substantially hinder the processes shown in Scheme 2. At the same time, *p*-nitrophenyl isocyanate (70% excess) reacts completely with ylide **1** for 1 day to form carbamate **6a**. According to the ^{1}H NMR data, the crystalline carbamates described, being dissolved in $CDCl_3$, are significantly decomposed to the starting ylides after several weeks. An attempt to recrystallize carbamates **3**, **6**, and **10** (obtained by crystallization at low temperatures) from boiling acetone results in their complete decomposition, and the initial pyridinium ylides are the products of "recrystallization." Yellow solutions of the considered ylides in methylene dichloride immediately become colorless upon addition of strong acids, because the corresponding colorless salts stable to heating and storage are formed.

It is interesting to mention that the carbamates described form mono-salts with an equimolar amount of acid, and crystalline bis-salts of the type **12** are formed with excess methanesulfonic acid (Scheme 4). The structures of bis-salts **12** formed are discussed in Ref. 2.

Scheme 4



The mechanism of rearrangement of intermediate adducts **5** to carbamates **6** is of substantial interest. In chemical sense, the second step of the reaction presented in Schemes 1, 2, and 3 is nucleophilic substitution. As known, the reactions of nitrogen-containing bases with carboxylates usually result in the displacement of the alkoxy group and formation of the corresponding amides. However, in the transformations described, the carbanion acts as the leaving group, *i.e.*, the C—C bond is cleaved instead of C—O, which is likely a unique example in the organic chemistry. Perhaps, the preferential cleavage of the C—C bond instead of C—O occurs due to the following factors. On the one hand, the electron-withdrawing influence of the alkoxycarbonyl group and positive charge of the pyridinium ring weakens the C—C bond. On the other hand, the C—C bond cleavage induces the formation of carbanion (**3**, **6**, or **10**), whose delocalization of the anion charge is likely higher than that in the starting carbanion (**1**, **4**, or **8**), which is confirmed by the IR spectroscopic data. For example, in the rearrangement

product **6A** the conjugated ethoxycarbonyl group appears at 1591 cm^{-1}, while in the starting ylide **4** this band is observed at 1658 cm^{-1}.

What is the route of transformation of intermediates **2**, **5**, and **9** to rearrangement products **3**, **6**, and **10**? Whether an intermediate four-membered compound (of the type **15** or **16**, Scheme 5) is formed or the new C—N bond is formed along with the synchronous cleavage of the old C—C bond? In the study of similar transformations of isocyanates with phosphorus-containing zwitterions, the authors[3] failed to detect the formation of products of the intermediate steps using ^{31}P NMR and kinetic measurements.[4] Therefore, the authors[4] proposed the mechanism of direct nucleophilic substitution at the sp^2-hybridized carbon atom. This mechanism is similar to that established for the nucleophilic substitution at the olefinic carbon atom of some types of unsaturated compounds.[5]

In order to study the rearrangement mechanism and, in particular, to determine the structure of the adduct formed in the first step of the reactions (see Schemes 1—3), the starting pyridinium ylide **4a**, adduct **13**, and carbamate **14**, as well as possible intermediates azetidinones **15** and **16** (see Scheme 5), were calculated by the quantum-chemical AM1,[6] PM3,[7] and DFT-B3LYP/6-31G* [8] methods.

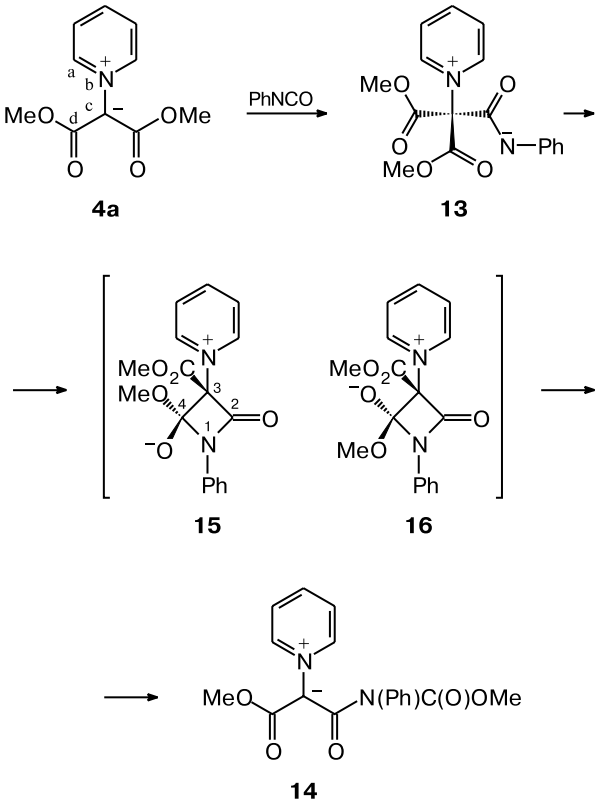
The published data on the structure of starting ylide **4A** are lacking. According to the calculations, the system is not planar. The δ(a—b—c—d) torsion angle is 18.6° (PM3), 31.5 (AM1), and 50.5° (DFT), respectively. The rotation barriers are low (PM3: $\Delta\Delta H_f = 4.6$; AM1: $\Delta\Delta H_f = 4.8$ kcal mol^{-1}). The reaction of ylide **4A** (see Scheme 5) with phenyl isocyanate giving adduct **13** is slightly endothermic (DFT: 5.1 kcal mol^{-1}).

The mechanism of the subsequent rearrangement of adduct **13** to carbamate **14** is unknown. The primary formation of azetidinones **5** or **16** followed by ring opening and formation of the resulting carbamate **14** could be assumed.

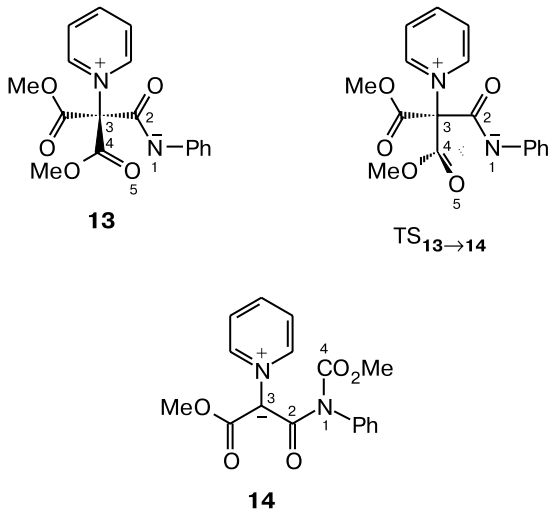
However, despite the detailed study at the semiempirical level (AM1, PM3) of the potential energy surfaces (PES) of azetidinones, we found no local minima corresponding to structures **15** and **16**. This is seen from the data in Fig. 1, which presents the PES of **15** in the region $1.45 \le r(1—4) \le 1.95$ Å (PM3). The absence of local energy minima in the corresponding vector map (Fig. 2), which represents the gradient field of PES, is seen more clearly. The results of PES studies for structure **16** are similar. At the DFT level (B3LYP/6-31G*), the rearrangement of adduct **13** to carbamate **14** (Scheme 6) is exothermic (ΔE = 17.9 kcal mol^{-1}). The energy of the transition state is low (the potential barriers of the direct and inverse reactions are 7.5 and 25.4 kcal mol^{-1}, respectively).

Thus, the quantum-chemical calculations have confirmed the primary formation of adduct **13** in the reac-

Scheme 5



Scheme 6



Atom	*d*/Å		
	13	$TS_{13\rightarrow14}$	**14**
1—2	1.306	1.333	1.458
1—4	2.555	1.790	1.381
2—3	1.537	1.548	1.437
3—4	1.591	1.625	3.162
4—5	1.209	1.230	—

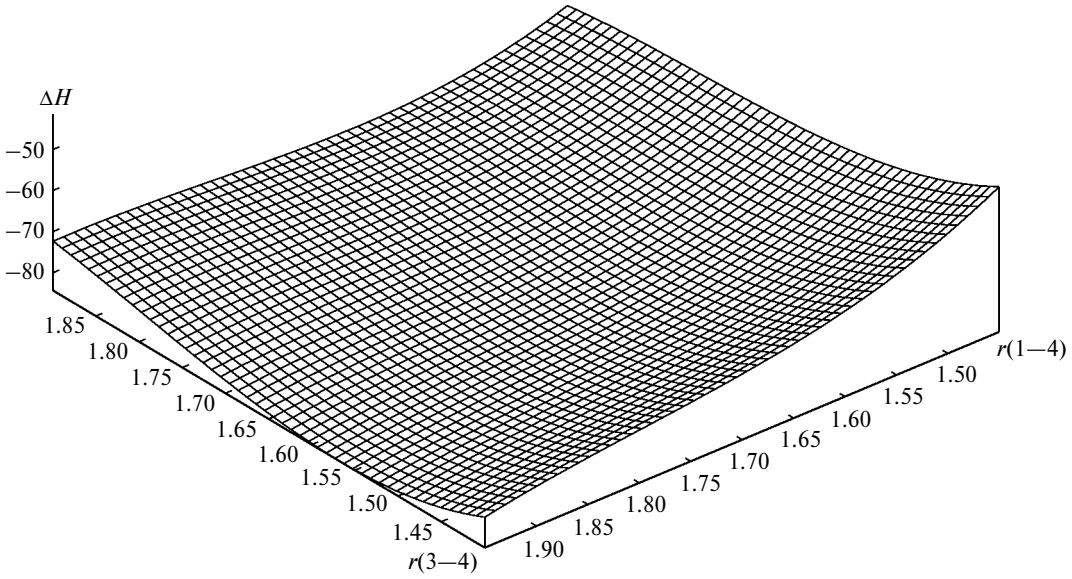


Fig. 1. Potential energy surface of azetidinone **15**.

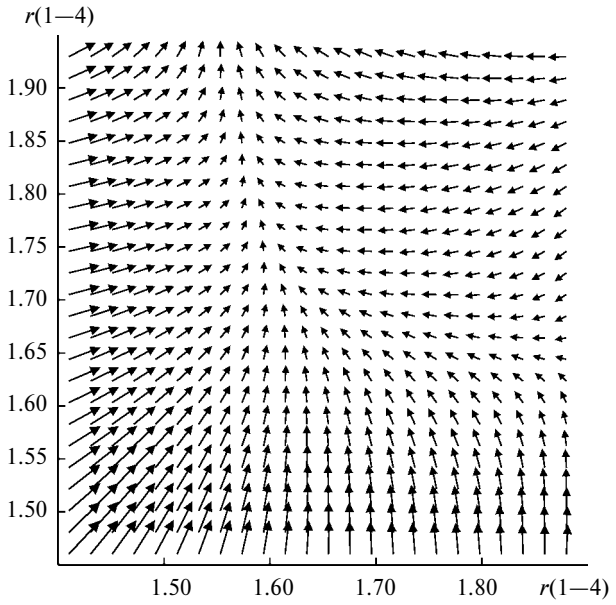


Fig. 2. Vector map of the PES of azetidinone **15**.

tions of ylide **4A** with phenyl isocyanate and its direct (without formation of cyclic intermediate compounds) rearrangement to carbamate **14**, which occurs with low potential barriers.

Experimental

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX-400 spectrometer (400.26 MHz) using $CDCl_3$ as the solvent. IR spectra were recorded on a Karl Zeiss M-82 instrument in KBr pellets.

Reagents available from Aldrich were used. THF was dried over KOH and distilled above metallic sodium in dry nitrogen atmosphere. Ylide **1** was synthesized according to a known procedure[9] (m.p. 171—172 °C, the ^{13}C NMR spectrum is presented in Ref. 2). Ylide **4a** was synthesized by a previously described method[10] (m.p. 191—192 °C) (*cf.* Ref. 9: m.p. 183—184 °C). ^{1}H NMR of **4a**, δ: 3.70 (s, 6 H, CH_3); 7.71 (t, 1 H, CH, J = 7.6 Hz); 8.12 (m, 2 H, CH); 8.57 (d, 2 H, CH, J = 5.6 Hz), Py. ^{13}C NMR, δ: 49.5 (CH_3); 96.3 (C^-); 124.9 (CH); 140.6 (CH); 149.1 (CH); 164.2 ($\underline{C}O_2Me$).

3-(*N,N*-Diethylaminocarbonyl)pyridinium bis(ethoxycarbonyl)methylide (8). Diethyl bromomalonate (1.83 g, 7.7 mmol) was added to *N,N*-diethylnicotinamide (1.24 g, 6.9 mmol), and the mixture was left for 15 days at ~20 °C in a closed flask. Then a very viscous oil that formed was dissolved in chloroform, and soda (0.94 g) was added to a saturated aqueous solution. The chloroform solution was dried over $MgSO_4$, evaporated, and left in a refrigerator. A precipitated crystalline product was filtered off and washed with ether. A yellow crystalline substance was obtained in 90.4% yield (1.70 g), m.p. 168—169 °C. Found (%): C, 60.80; H, 7.24; N, 8.30. $C_{17}H_{24}N_2O_5$. Calculated (%): C, 60.71; H, 7.14; N, 8.33. ^{1}H NMR, δ: 1.17, 1.23 (both m, 3 H each, $NCH_2C\underline{H}_3$); 1.27 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.36, 3.53 (both m, 2 H each, $NC\underline{H}_2CH_3$); 4.15 (q, 4 H, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.70 (m, 1 H, CH), 8.11 (d, 1 H, CH, J = 8.0 Hz), 8.58 (m, 2 H, CH), Py. ^{13}C NMR, δ: 12.4, 14.1, 14.5 ($OCH_2\underline{C}H_3$); 39.9, 43.5 ($N\underline{C}H_2CH_3$); 58.8 ($O\underline{C}H_2CH_3$); 97.8 (C^-); 125.2 (CH); 134.7, 139.1 (CH); 147.2 (CH); 149.5 (CH); 164.1, 164.6 ($\underline{C}O$). IR, ν/cm^{-1}: 1640 (C(O)N); 1588 (C—CO_2Et conjug.).

3-(Diethylaminocarbonyl)-1-bis(ethoxycarbonyl)methylpyridinium perchlorate. 70% $HClO_4$ (0.106 g) was added dropwise to a solution of ylide **8** (0.25 g, 0.74 mmol) in ethanol (4 mL). Then the reaction mixture was added with vigorous stirring to ether (50 mL), and the resulting solution was left in a refrigerator for a week. A precipitate formed was washed with hexane and dissolved in a minimum amount of CH_2Cl_2, and the resulting solu-

tion was added dropwise to hexane. Precipitated crystals were dried *in vacuo*. Low-melting hygroscopic white crystals were obtained in 65% yield. Found (%): C, 46.91; H, 5.76; N, 6.23. $C_{17}H_{25}N_2O_9Cl$. Calculated (%): C, 46.79; H, 5.73; N, 6.42. ^{1}H NMR, δ: 1.16—1.19, 1.25 (both m, 3 H each, $NCH_2C\underline{H}_3$); 1.35 (t, 6 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.31—3.39, 3.52—3.57 (both m, 2 H each, $NC\underline{H}_2CH_3$); 4.38 (m, 4 H, $OC\underline{H}_2CH_3$); 6.57 (s, 1 H, CH—N); 8.21 (m, 1 H, CH), 8.57 (d, 1 H, CH, J = 6.8 Hz), 9.02 (s, 1 H, CH), 9.11 (m, 1 H, CH), Py.

Pyridinium [*N*-ethoxycarbonyl-*N*-(4-nitrophenyl)carbamoyl]ethoxycarbonylmethylide (6a). *p*-Nitrophenyl isocyanate (1.5 g, 12.6 mmol) was added to ylide **1** (2 g, 8.44 mmol) dissolved in $CHCl_3$, and the solution was left at ~20 °C for 1 day. Then the solvent was evaporated, a residue was dissolved in a minimum amount of acetone, and the resulting solution was left for 16 h in a refrigerator. Yellow crystals formed were filtered off. The yield of the product was 62%, m.p. 58—60 °C. Found (%): C, 56.97; H, 4.73; N, 10.44. $C_{19}H_{19}N_3O_7$. Calculated (%): C, 56.86; H, 4.77; N, 10.47. ^{1}H NMR, δ: 1.12, 1.30 (both t, 3 H each, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 4.05, 4.28 (both q, 2 H each, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.71, 8.17 (both d, 2 H each, CH, Ph, J = 8.2 Hz); 7.85 (m, 2 H, CH), 8.26 (t, 1 H, CH, J = 7.6 Hz), 8.63 (d, 2 H, CH, J = 5.6 Hz), Py. ^{13}C NMR, δ: 10.6 ($OCH_2\underline{C}H_3$); 55.6 ($O\underline{C}H_2CH_3$); 57.6 ($O\underline{C}H_2CH_3$); 103.4 (C(—)); 121.7—122.2 (Ph); 124.7 (CH); 135.7 (N—C (Ph)); 138.4 (CH); 145.1 (CH); 150.0 (159.0 ($N\underline{C}O_2Et$); 160.2 ($\underline{C}O_2Et$). IR, ν/cm^{-1}: 1591 (C—$\underline{C(O)}$OEt); 1720 (N—$\underline{C(O)}$OEt).

Pyridinium [*N*-ethoxycarbonyl-*N*-(4-ethoxycarbonylphenyl)carbamoyl]ethoxycarbonylmethylide (6b). *p*-Ethoxycarbonylphenyl isocyanate (1.6 g, 8.4 mmol) was added to ylide **1** (1.0 g, 4.2 mmol) dissolved in $CHCl_3$, and the resulting mixture was left for 1 day at ~20 °C in a closed flask. Then the reaction mixture was added with stirring to petroleum ether, and an oil precipitated was separated and stored *in vacuo*. The oil was dissolved in an acetone—ether mixture, and the resulting solution was left for several days in a refrigerator. Crystals with m.p. 105—107 °C were obtained in 52.2% yield (0.94 g). Found (%): C, 62.42; H, 5.60; N, 6.53. $C_{22}H_{24}O_7N_2$. Calculated (%): C, 61.68; H, 5.61; N, 6.54. ^{1}H NMR, δ: 1.14, 1.27, 1.35 (all t, 3 H each, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 4.06, 4.24, 4.32 (all q, 2 H each, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.58 (d, 2 H, CH, Ph, J = 8.2 Hz); 7.78 (m, 2 H, CH), 8.18 (t, 1 H, CH, J = 7.6 Hz), 8.61 (d, 2 H, CH, J = 5.6 Hz), Py. IR, ν/cm^{-1}: 1727 (Ph—$\underline{C(O)}$OEt); 1706 (N—$\underline{C(O)}$OEt); 1598 (CO_2Et conjug.).

3-(*N,N*-Diethylaminocarbonyl)pyridinium (*N*-ethoxycarbonyl-*N*-phenylcarbamoyl)ethoxycarbonylmethylide (10). Phenyl isocyanate (0.54 g, 4.5 mmol) was added to ylide **8** (0.5 g, 1.5 mmol) dissolved in anhydrous CH_2Cl_2, and the mixture was left at ~20 °C for 5 days. Then the reaction mixture was added dropwise with stirring to a mixture of diethyl and petroleum ethers, and the resulting solution was left to stay in cold for several hours. A precipitate formed was filtered off, washed with ether, and stored *in vacuo*. A yellow crystalline substance was obtained in 94% yield (0.64 g), m.p. 125—127 °C. Found (%): C, 62.92; H, 6.40; N, 9.11. $C_{24}H_{29}N_3O_6$. Calculated (%): C, 63.30; H, 6.37; N, 9.23. ^{1}H NMR, δ: 1.15—1.29 (m, 6 H, $CH_2C\underline{H}_3$); 1.21 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.6 Hz); 1.25 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.33, 3.53 (both m, 2 H each, $NC\underline{H}_2CH_3$); 4.14, 4.21 (both q, 2 H each, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.31 (t, 2 H, CH, J = 7.6 Hz), 7.45 (d, 2 H, CH, J = 7.6 Hz), 7.75 (t, 1 H, CH, J = 7.6 Hz), Ph; 8.16 (d, 1 H, CH, J = 8.0 Hz); 7.16 (m, 1 H, CH), 8.65 (m, 2 H, CH), Py. IR, ν/cm^{-1}: 1714 (N—C(O)OEt), 1641 (C(O)N), 1580 (C—C(O)Et).

1-[Methoxycarbonyl-(*N*-methoxycarbonyl-*N*-phenylcarbamoyl)methyl]pyridinium perchlorate (7a). Phenyl isocyanate (0.71 g, 6.0 mmol) was added to ylide **4a** (0.25 g, 1.2 mmol) dissolved in $CDCl_3$ (1 mL), and the mixture was left at ~20 °C for 5 days. Then the reaction mixture was added dropwise with stirring to petroleum ether. A precipitate formed was filtered off, washed with ether, and stored *in vacuo*. The product was obtained in 99% yield (0.44 g). 70% $HClO_4$ (0.17 g) was added to the obtained unpurified ylide dissolved in a minimum amount of ethanol, and the mixture was slightly heated until a yellow precipitate dissolved. Then the resulting transparent colorless mixture was added dropwise to a stirred mixture of diethyl and petroleum ethers. A precipitate formed was filtered off and washed with ether. A crystalline substance with m.p. 88—91 °C was obtained in 84.3% yield (0.43 g). Found (%): C, 47.43; H, 3.91; N, 6.55. $C_{17}H_{17}O_9N_2Cl$. Calculated (%): C, 47.66; H, 3.97; N, 6.54. ^{1}H NMR, δ: 3.78, 3.93 (both s, 3 H each, CH_3); 7.38 (m, 5 H, CH), 7.51 (s, 1 H, CH), Ph; 7.97 (t, 1 H, CH, J = 7.6 Hz), 8.47 (m, 2 H, CH), 8.85 (d, 2 H, CH, J = 5.6 Hz), Py.

***N*-Ethoxycarbonylcarbamoyl-*N*-(4-nitrophenyl)ethoxycarbonylmethylpyridinium methanesulfonate (7b).** An equimolar amount of $MeSO_2OH$ was added dropwise to a stirred solution of ylide **6a** (0.10 g, 0.25 mmol) in CH_2Cl_2 (2 mL). The resulting colorless solution was concentrated, and a solid residue was washed with ether and recrystallized from an ether—THF mixture. The yield was 70%, m.p. 120—122 °C. Found (%): C, 47.47; H, 4.72; N, 7.93; S, 6.64. $C_{20}H_{23}N_3O_{10}S$. Calculated (%): C, 48.29; H, 4.66; N, 8.45; S, 6.44. ^{1}H NMR, δ: 1.18, 1.31 (both t, 3 H each, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 2.78 (s, 3 H, CH_3S); 4.25—4.45 (m, 4 H, $OC\underline{H}_2CH_3$); 7.68, 8.25 (both d, 2 H each, CH, Ph, J = 8.8 Hz); 7.99 (s, 1 H, CH); 8.02 (m, 2 H, CH), 8.52 (t, 1 H, CH, J = 7.6 Hz); 9.27 (d, 2 H, CH, J = 5.6 Hz), Py. IR, ν/cm^{-1}: 1750 ($\underline{C(O)}$OEt); 1711, (N—$\underline{C(O)}$OEt).

3-(*N,N*-Diethylaminocarbonyl)-(*N*-phenyl-*N*-ethoxycarbonylcarbamoyl)ethoxycarbonylmethylpyridinium iodide (11). 35% HCl was added dropwise to a solution of ylide **8** (0.4 g, 0.88 mmol) in acetonitrile (5 mL) until the mixture became colorless. Then an equimolar amount of NaI (0.132 g) dissolved in acetonitrile was added to the reaction mixture. A residue was filtered off and concentrated *in vacuo*. The resulting salt was washed with a hexane—acetone mixture and precipitated from acetone to hexane. A yellow crystalline substance with m.p. 74—76 °C was obtained in 98% yield (0.42 g). Found (%): N, 6.74. $C_{24}H_{30}N_3O_6I$. Calculated (%): N, 7.20. ^{1}H NMR, δ: 1.11 (t, 3 H, $NCH_2C\underline{H}_3$, J = 7.0 Hz); 1.19 (t, 3 H, $NCH_2C\underline{H}_3$, J = 7.2 Hz); 1.24 (t, 3 H, $OCH_2C\underline{H}_3$, J = 6.8 Hz); 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 3.31, 3.52 (both m, 2 H each, $NC\underline{H}_2CH_3$); 4.47—4.13 (m, 4 H, $OC\underline{H}_2CH_3$); 7.41—7.34 (m, 3 H, CH); 7.46—7.44 (m, 2 H, CH), Ph; 8.13 (s, CHN); 8.18 (m, 1 H, CH); 8.55 (d, 1 H, CH, J = 8.9 Hz); 9.05 (s, 1 H, CH); 9.89 (d, 1 H, CH, J = 6.0 Hz). IR, ν/cm^{-1}: 1740 ($CHCO_2Et$), 1709 (NCO_2Et), 1639, ($\underline{C(O)}NEt_2$).

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