Letters to the Editor

A novel electrophilic rearrangement with migration of an alkoxycarbonyl group from carbon to a nitrogen anionic center

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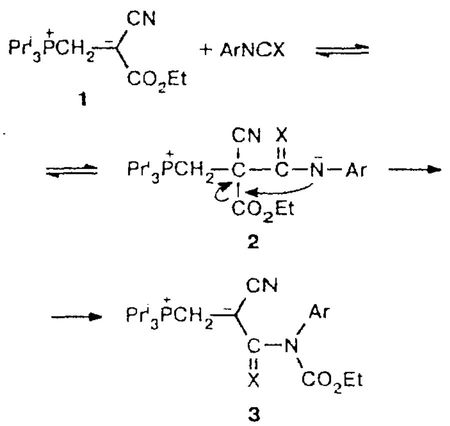
Among the known electrophilic rearrangements (migrations of electron-deficient species from one atom to another: O→C, C→O, C→C', O→O', N→N', O→N, N→O, S→N, S→O, and S→C; see, for example, Refs. 1 and 2), rearrangements of the C→N type had not been described before our publication.[3] Migrations of alkoxycarbonyl groups are especially rare; they have been found[4] only for the O→N case, because the shift of a group of this type from carbon to nitrogen requires cleavage of a relatively strong C—C bond. This event was reliably established[5] for the interaction of P-zwitterions **1** with aryl iso(thio)cyanates (Scheme 1). The second step of this process involves migration of the ethoxycarbonyl group from the C atom to the N-anionic center arising upon the reaction of carbanion **1** with aryl iso(thio)cyanate.

Scheme 1



It is known that reactions of carbanions with isocyanates are the basis for the synthesis of carboxamides, which can be isolated after acidification of a reaction mixture containing N-anions of type **2**. However, since N-anionic adduct **2** does not contain sufficiently active hydrogen atoms that would be able to protonate its N-anionic center and does contain an ethoxycarbonyl group, intramolecular transformations according to Scheme 1 become possible. This process is unusual, because a carbanion rather than the ethoxy anion (as in the case of aminolysis of esters) acts as the leaving group upon nucleophilic attack by the N atom on the carbonyl group. Apparently, this unique situation in which cleavage of a C—C bond is preferred over cleavage of a C—O bond is due to the efficient delocalization of the negative charge in the resulting carbanion **3**. The latter is indicated by the data of IR spectroscopy (change in the intensity and the positions of the absorption bands for the cyano and the carbonyl group at the carbanion center of the zwitterions **3**).[5]

To elucidate the role of the phosphonium group in the C→N rearrangements described here, we studied the

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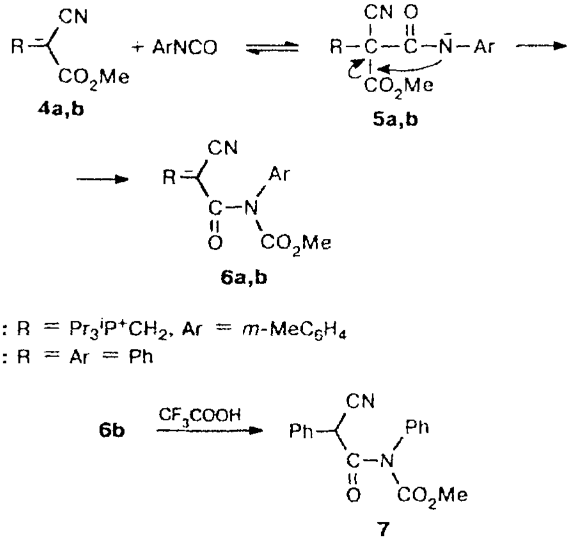
reactions of isocyanates with carbanions **4a,b** under similar conditions (Scheme 2). Compound **4a** (unlike carbanion **4b**) contains a phosphonium group, which can act as a catalytic center that accounts for the easy rearrangement. Zwitterion **4a** was synthesized by a known procedure,[6] and carbanion **4b** was prepared by treatment of methyl 2-cyano-2-phenylacetate with sodium hydride in THF.

Scheme 2



a: R = $Pr_3{}^iP^+CH_2$, Ar = *m*-MeC_6H_4
b: R = Ar = Ph

Realization of the reactions shown in Scheme 2 under mild conditions (a THF solution, 20 °C) has shown that in both cases the process affords carbamates **6a** and **6b**. Thus, the presence of a phosphonium group in the initial structure is not a necessary condition for the rearrangement of N-anions **2** and **5** into C-anions **3** and **6**. Therefore, the novel type of electrophilic rearrangement described here can be regarded as quite common in organic chemistry.

Zwitterion **6a** was isolated in a pure state. Carbanion **6b** was converted into crystalline carbamate **7** by treatment with CF_3COOH. The structures of compounds **6a** and **7** were determined by the data of elemental analysis, IR, Raman, and NMR spectroscopy, and mass spectrometry.

NMR spectra were recorded on a Bruker AMX-400 instrument in $CDCl_3$ or acetone-d_6. IR spectra were measured on a Carl Zeiss M-82 spectrometer in KBr tablets, Raman spectra were run on a KR U1000, T64000 instrument (an argon laser with an excitation wavelength of 514.5 nm was used), and mass spectra were recorded on a Kratos MS 890 instrument.

1-[*N*-(*m*-Tolyl)-*N*-methoxycarbonylcarbamoyl]-2-(triisopropylphosphonio)-1-cyanoethan-1-ide (6a). A solution of zwitterion **4a** (1 g, 3.69 mmol) and *m*-MeC_6H_4NCO (0.95 mL, 3.69 mmol) in CH_2Cl_2 (2 mL) was kept at 20 °C until the signal with δP 38.7, typical of the initial zwitterion **4a**, disappeared from the ^{31}P NMR spectrum of the reaction mixture (5 days). The resulting ^{31}P NMR spectrum consisted of 90% of a signal with δP 41.24. The solvent was evaporated *in vacuo*, and the residue was crystallized from dry THF to give compound **6a** as colorless crystals, yield 0.77 g (50%), m.p. 127 °C. Found (%): C, 65.39; H, 8.30; N, 7.10; P, 7.30. $C_{22}H_{33}N_2O_3P$. Calculated (%): C, 65.4; H, 8.2; N, 6.9; P, 7.7. IR, ν/cm^{-1}: 1710 (COOMe); 1645 (C(O)N); 2185 (CN conjug.). ^{31}P NMR, δ: 41.46. ^1H NMR ($CDCl_3$), δ: 1.43 (m, 18 H, $C\underline{H}_3CH$); 2.28 (s, 3 H,$C\underline{H}_3C_6H_4$); 2.64 (m, 3 H, $C\underline{H}CH_3$); 3.14 (d, 2 H, CH_2P, J_{HP} = 8.4 Hz); 3.71 (s, 3 H, CH_3O); 6.95—7.27 (m, 4 H, C_6H_4).

Methyl [*N*-phenyl-*N*-(2-phenyl-2-cyanoacetyl)]carbamate (7). A powder of 50% NaH (0.9 g, 10.2 mmol) in a polymeric coating was added with stirring in an atmosphere of dry nitrogen to a solution of ester **4b** (3 g, 10.2 mmol) in 20 mL of dry THF cooled to 4 °C. After 15 min, a solution of PhNCO (1.86 mL) in 10 mL of THF was added dropwise, and the mixture was stirred for 2.5 h at 20 °C. A solution of CF_3COOH (1.27 mL) in 10 mL of Et_2O was added to the reaction solution at 4 °C. The precipitated sodium trifluoroacetate was filtered off, the solvent was evaporated *in vacuo*, and the residue was extracted with Et_2O. The ethereal solution was concentrated *in vacuo*, and the precipitated crystals were recrystallized from a hexane—THF mixture. Yield 1.4 g (50%), m.p. 114—116 °C. Found (%): C, 69.39; H, 4.90; N, 9.53. $C_{17}H_{14}N_2O_3$. Calculated (%): C, 69.37; H, 4.79; N, 9.52. IR, ν/cm^{-1}: 2975 (H—CCN); 2265 (CN); 1780 (COOMe); 1705 (C(O)N). Raman spectrum, ν/cm^{-1}: 2962 (H—CCN); 2251 (CN); 1755, 1695 (CO). ^1H NMR, δ: 3.67 (s, 3 H, CH_3O); 6.53 (s, 1 H, HCCN); 7.13—7.56 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 44.69 (HC—CN); 54.42 (CH_3); 116.19 (CN); 127.7—136.69 (Ph); 153.86 (COOMe); 167.18 (C(O)N). MS, *m/z* (I_{rel} (%)): 294 $[M]^+$ (0.67), 150 (14.47), 143 (38.87).

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References

1. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, *Molekulyarnyi dizain tautomernykh sistem* [*Molecular Design of Tautomeric Systems*], Izd. Rost. Univ., 1977 (in Russian).
2. K. V. Vatsuro and G. L. Mishchenko, *Imennye reaktsii v organicheskoi khimii* [*Named Reactions in Organic Chemistry*], Khimiya, Moscow, 1976 (in Russian).
3. Yu. G. Gololobov, G. D. Kolomnikova, and T. O. Krylova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 186 [*Russ. Chem. Bull.*, 1995, **44**, 181 (Engl. Transl.)].
4. L. V. Pavlova and F. Yu. Rachinskii, *Usp. Khim.*, 1968, **37**, 1370 [*Russ. Chem. Rev.*, 1968, **37** (Engl. Transl.)].
5. Yu. G. Gololobov, N. A. Kardanov, V. N. Khroustaliev, and P. V. Petrovskii, *Tetrahedron Lett.*, 1997, **38**, 7437.
6. Yu. G. Gololobov, V. A. Pinchuk, H. Thonnessen, P. Jones, and R. Schmutzler, *Phosp., Sulf., and Silicon*, 1966, **115**, 19.

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