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Novel Reaction of Iso(thio)cyanates.
Insertion Reaction of Iso(thio)cyanates into C-C Bond

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Abstract. Interaction of zwitter-ions **1** with arylisocyanates (**a-e**) and phenylisothiocyanate leads to the stable zwitter-ions **3(a-e)** and **4** which probably represent rearrangement products of the initially formed adducts **2**. The molecular structure of compounds **4** was confirmed by X-ray diffraction study. The formation of zwitter-ions **3** and **4** is a result of the insertion of iso(thio)cyanates into the C-C bond of the starting zwitter-ion **1**, under the action of the positively charged phosphorus atom (intramolecular electrophilic catalysis).

Quite a lot of the insertion reactions of isocyanates into carbon-element and element-element bonds[1] have been documented, whereas the insertion reactions of iso(thio)cyanates into the C-C bond were to our knowledge as yet unknown.

We have shown that zwitter-ion **1**[2] reacts with isocyanates (**a-e**) under mild conditions (r.t., solution in acetonitrile) and forms stable insertion products **3(a-e)**[3] with the yields of 80-90%, *Scheme 1.*

$$i\text{-}Pr_3P^+\text{-}CH_2\text{-}C^-(CN)\text{-}COOEt\ (\mathbf{1})\ +\ Ar\text{-}N{=}C{=}O\ \text{------>}$$

$$Ar = Ph(\mathbf{a}),\ 1\text{-}Nf(\mathbf{b}),\ p\text{-}ClC_6H_4(\mathbf{c}),\ m,p\text{-}2ClC_6H_3(\mathbf{d}),\ p\text{-}O_2NC_6H_4(\mathbf{e})$$

$$\text{------>}\ [i\text{-}Pr_3P^+\text{-}CH_2\text{-}C(CN)\text{-}(COOEt)\text{-}C(O)\text{-}N^-\text{-}Ar]\ (\mathbf{2})\ \text{------>}$$

$$\text{------>}\ i\text{-}Pr_3P^+\text{-}CH_2\text{-}C^-(CN)\text{-}C(O)\text{-}N(Ar)\text{-}COOEt\ (\mathbf{3})$$

Scheme 1

The structure of products **3** follows from the NMR (^1H, ^{13}C, ^{31}P), IR spectra and elemental analysis data. For all the compounds **3(a-e)** analyses on C, H, N, P, Cl were satisfactory.

The negative charge in **3** is not stabilized by the shift of a proton to anionic carbon as its basicity is significantly reduced because of the delocalization of the charge; the high degree of the delocalization was confirmed by the IR data[4].

The molecular structures of compounds **3f** and **3g** were established earlier[2,5] by X-ray diffraction studies. The X-ray results confirmed the structure of compounds **3f-g** but the place of insertion of the isocyanate moiety in **3f-g** could not be determined.

Alk$_3$P$^+$-CH$_2$-C$^-$(CN)-**C(O)-NR**-C(O)-OEt, Alk$_3$P$^+$-CH$_2$-C$^-$(CN)-C(O)-**NR-C(O)**-OEt

A **B**

3f (Alk = n-Pr, R = Ph), **3g** (Alk = i-Pr, R = Me)

The position of RNCO in compounds **3** is of primary importance as the formation of structure **A** is the result of migration of the COOEt substituent from carbon to the nitrogen atom in the intermediate **2**; structure **B** is produced by the shift of the OEt group to the carbon atom of the inserted isocyanate. The first case corresponds to the insertion reaction of RNCO into the C-C bond of zwitter-ion **1**, the second one reflects the insertion reaction of RNCO into the C-OEt bond of starting **1**.

We could find the place of insertion using phenylisothiocyanate (*Scheme 2*). The latter reacts with the zwitter-ion **1** under more severe conditions[6] and affords zwitter-ion **4**, the structure of which was determined by IR, NMR spectra[7] as well as the X-ray diffraction study[8].

i-Pr$_3$P$^+$-CH$_2$-C$^-$(CN)-COOEt + PhNCS ----> i-Pr$_3$P$^+$-CH$_2$-C$^-$(CN)-C(S)-NPh-COOEt

4

Scheme 2

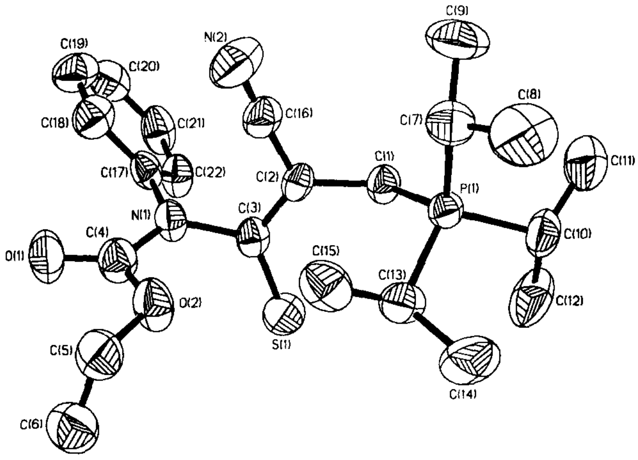

Figure 1. The structure of compound **4** in crystal (one of the three independent molecules is shown).

The molecular structure of compound **4** is shown in Fig.1. Details will be published elsewhere[8]. The main conclusion based on IR and the X-ray diffraction studies indicates that PhNCS is inserted into the C-C bond of the starting zwitter-ion **1.** As it is well known that the reactivities of isocyanates and isothiocyanates towards carbanions are similar, it is logical to state that the *Schemes 1* and *2* show the new type of insertion reactions of iso(thio)cyanates, *viz.* the insertion reaction into the C-C bond.

One may assume that the rearrangement of the initially formed adduct **2** into more stable zwitter-ion **3** is promoted by the positively charged phosphorus atom which facilitates nucleophilic attack of the N-anion at the carboxylic group (intramolecular electrophilic catalysis)[9].

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3. Mixture of **1** (δp = 38.4 ppm) (0.005 mol), ArNCO (0.006 mol) and 2-3 ml CH_3CN held one day at r.t. ^{31}P NMR of reaction mixture exhibits the only signal, corresponding to compounds **3a-e**. Solvent was evaporated in vacuo and product was isolated by crystallization from THF or acetone. ^1H NMR (400.26 MHz), ^{13}C (100.68 MHz) and ^{31}P (162.02 MHz) spectra (δppm, internal reference TMS, $CDCl_3$ and 80% H_3PO_4 for ^1H, ^{13}C and ^{31}P spectra respectively) are fully consistent with the assigned structures. Selected physical properties and spectra data are as follow: **3a** yield 80%; m.p. 128-129 °C (ac); ^1H NMR 3.10 (d, CH_2P, JHP = 8.52 Hz); ^{31}P 41.35; ^{13}C NMR 17.31 (d, CH_2P, JCP = 44.2 Hz), 52.10 (d, C^-, JCP = 4.53), 139.68 (c, CN), 153.96 (c, COOEt), 167.57 (d, C(O)N, JCP = 3.22). **3b** yield 87%; m.p.180-181 °C (ac); ^1H NMR 3.16 (d, CH_2P, JHP = 8.07 at 55 °C); ^{31}P 41.12; ^{13}C 17.30 (d, CH_2P, JCP = 44.0), 50.77 (d, C^-, JCP = 4.13 Hz); 136.70 (c, CN), 154.65 (c, COOEt), 167.68 (d, C(O)N, JCP = 3.30). **3c** yield 85 %; m.p.142-143 °C (THF); ^1H NMR 3.14 (d, CH_2P, JHP = 8.58); ^{31}P 41.59; ^{13}C 17.07 (d, CH_2P, JCP = 47.4), 52.28 (d, C^-, JCP = 4.40), 141.14 (c, CN), 153.64 (c, COOEt), 166.89 (d, C(O)N), JCP = 3.10). **3d** yield 83%; m.p. 169-170 °C (ac); ^1H NMR 3.11 (d, CH_2P, JHP = 8.75); ^{31}P 41.63; ^{13}C NMR 16.88 (d, CH_2P, JCP = 44.5), 52.41 (d, C^-, JCP = 4.33), 139.46 (c, CN), 153.44 (c, COOEt), 166.39 (d, C(O)N, JCP = 3.52). **3e** yield 92%; m.p. 157-158 °C (ac); ^1H NMR 3.10 (d, CH_2P, JHP = 8.95); ^{31}P 41.49; ^{13}C 16.73 (d, CH_2P, JCP = 44.7), 52.96 (d, C^-, JCP = 4.33), 146.02 (c, CN), 153.07 (c, COOEt), 165.75 (d, C(O)N, JCP = 3.30).

4. Zwitter-ions **3** show a strong broad line at 1615-1640 cm^{-1} (C(O)N), 1715-1730 cm^{-1} (COOEt) and a narrow strong band at 2170-2180 cm^{-1} (CN).
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6. Mixture of **1** (O.01 mol) and PhNCS (O.O6 mol) was heated for 8h at 80-100 °C in dry nitrogen. After heating this mixture exhibited four signals in the ^{31}P NMR spectra (ppm) (28.38 - 8.3%, 45.34 - 83%, 57.94 - 4.2%, 73.23 - 4.2%). It was than washed by dry ether and the product was isolated by crystallization from THF. Yield 76%; m.p. 146-147 °C (THF) (In [7] the m.p. for **4** was erroneously reported as 50 °C); ^{1}H NMR 3.78 (d, CH$_2$P, JHP = 8.23); ^{31}P 44.38; ^{13}C 21.41 (d, CH$_2$P, JCP = 44.1), 61.43 (d, C$^-$, JCP = 3.60), 141.17 (c, CN), 153.22 (c, COOEt), 182.03 (d, C(S)N, JCP = 7.95); IR (KBr, cm^{-1}), 1500 (CS), 1720 (CO), 2185 (CN).
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8. Crystal data for **4**: $C_{22}H_{33}N_2O_2PS$, M = 420.53, monoclinic, space group P2$_1$/n, at 20°C a = 8.298(3), b = 38.256(12), c = 22.544(7) E, β = 99.37(3)°, V = 7061(4) E^3, Z = 12, d$_{calc}$ = 1.187 g/cm^3. Unit cell parameters and 11657 reflections were measured with an automated 4-circle Siemens P3/PC diffractometer (293 K, λMoK$_\alpha$, graphite monochromator, θ/2θ-scan, θ$_{max}$ = 25°). The structure was solved by direct method and refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms in the geometrically calculated positions were included in refinement with fixed positional and isotropic thermal (riding model) parameters. The final discrepancy factors are R$_1$ = 0.059 for 7651 unique reflections with I ≥ 2σ(I) and wR$_2$ = 0.150 for 9985 unique reflections. All calculation were carried out using SHELXTL PLUS (PC Version 5.0) programs.
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