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C–N Migration of Allyl- and Propargyloxycarbonyl Groups

Yu. G. Gololobov, N. G. Senchenya, O. A. Linchenko, P. V. Petrovskii, and I. A. Garbuzova

Nesmeyanov Institute of Organoelement Compounds, Russan Academy of Sciences, ul. Vavilova 28, Moscow, 119334 Russia
e-mail: yugol@ineos.ac.ru

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Abstract—Reactions of triisopropylphosphine with allyl- and propargyl-2-cyanoacrylates give corresponding 1,3-zwitterions. Under the action of phenyl- or 1-naphthylisocyanates the zwitterions exert C–N migration of allyl- or propargyloxycarbonyl groups affording carbamates. Atropisomerism at room temperature was established for the carbamate formed from 1-naphthylisocyanate.
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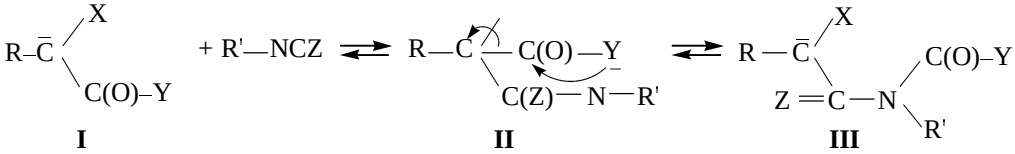
Intramolecular 1,3-migrations of alkoxycarbonyl and acetyl groups from carbon to nitrogen atom taking place in the reaction of carbanions, zwitterions, or ylides with isocyanates (Scheme 1) have been described for saturated ethers only [1–4].

Kinetical studies of this process [5] and the results of quantumchemical calculations [6] point to second order of the general reaction, that is the first order by each reagent. Reaction mechanism includes nucleophilic attack of the carbanion on the electrophilic carbon atom of the isocyanate group with the subsequent attack of carbonyl carbon atom by the nucleophilic nitrogen atom which leads to cleavage of the weaken C–C bond without intermediate formation of four-membered ring.

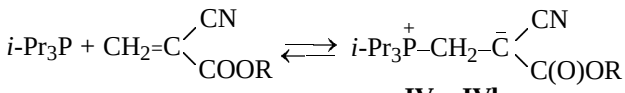
Scheme 1.



R = Ar, Py^+, isoquinolin$^+$, $Alk_3P^+CH_2$; Alk = *n*-Pr, *i*-Pr, *n*-Bu, Et_2N, [(Ph)(Bu)Et_2N], *n*-Bu_3P^+CHPh; X = CN, C(O)OEt, C(O)Me; Y = Me, OAlk; Alk = Me, Et; R' = Me, cyclo-C_6H_{11}, Ph, *p*-$NO_2C_6H_4$, *p*-ClC_6H_4, *m*,*p*-$Cl_2C_6H_3$, *m*-Tol, *m*,*m*-$Me_2C_6H_3$, *o*-FC_6H_4, *o*-ClC_6H_4, *o*-BrC_6H_4, *o*-IC_6H_4, *o*-$MeOC_6H_4$, *o*-$CF_3C_6H_4$, *o*-Tol, *o*,*p*-$Me_2C_6H_3$, *o*-EtC_6H_4, *o*-*i*-PrC_6H_4, *o*-PhC_6H_4; R' = 1-naphthyl; Z = O, S.

In this report we consider reactions of arylisocyanate with earlier unknown 1,3-zwitter-ions **IVa** and **IVb** prepared from triisopropylphosphine and allyl- or propargyl-2- cyanoacrylates respectively (Scheme 2).

Scheme 2.



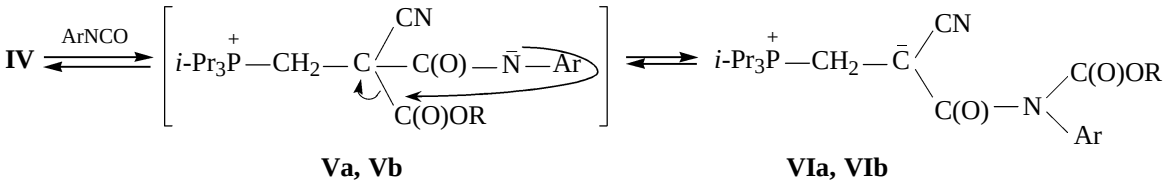
IVa, IVb

R = CH_2–CH^c=C(H^a)(H^b) (**a**), CH_2–C≡CH (**b**).

Similarly to the case of methyl or ethyl 2-cyanoacrylate [7], allyl and propargyl esters react under certain conditions with triisopropylphosphine to form crystalline 1,3-zwitter-ions **IVa** and **IVb** in 40–50% yield. Structure of the zwitter-ions **IVa** and **IVb** follows from the elemental analysis and IR and NMR spectral data. IR spectra of compounds **IVa** and **IVb** contain strong bands of cyano- and ester groups conjugated with the anionic charge. The ^{31}P NMR spectrum of a zwitter-ion **IVa** and **IVb** contains a singlet at 38–39 ppm. In ^{1}H NMR spectra of each zwitter-ion the doublet of CH_2P group protons is revealed (compare [2]).

Zwitter-ions **IVa** and **IVb** readily react with an arylisocyanate excess (**IVa** with 1-naphthylisocyanate, **IVb** with phenylisocyanate) according to the general scheme of the isocyanate molecule insertion [4] by the starting zwitter-ion C–C bond (Scheme 3).

Scheme 3.



Va, Vb **VIa, VIb**

R = CH_2–CH=CH_2, Ar = 1-$C_{10}H_7$ (**a**); R = CH_2–C≡CH, Ar = Ph (**b**).

Carbamates **VIa** and **VIb** resulting from the transfer of corresponding unsaturated alkoxycarbonyl group from carbon to nitrogen exhibit spectral characteristics typical of this type compounds [1].

But it must be noted that ^{1}H NMR spectrum of carbamate **VIa** at 20°C contains broad signals of methyl protons of the isopropyl groups and methylene protons of CH_2 group at phosphorus, while the signals of other protons exhibit expected multiplicity. At 55°C all proton signals are well resolved (see figure).

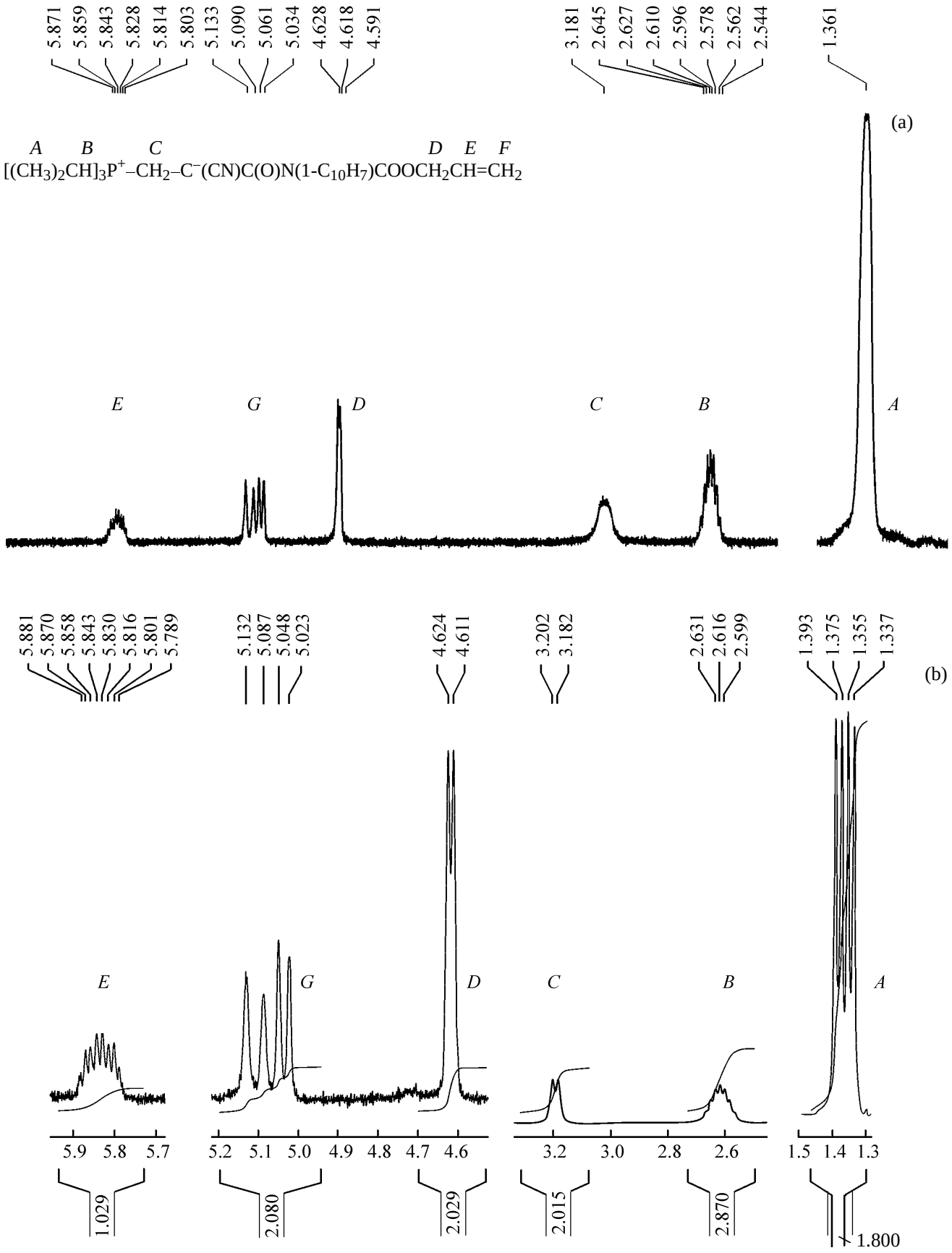
These facts can be explained taking into account the hindered rotation of 1-naphthyl radical around the C–N bond in the carbamate fragment of compound **VIa**. Such hindering even at room temperature creates enantiomeric asymmetry in the molecule leading to location of the isopropyl and methylene group protons at phosphorus in the different surrounding making them diastereotopic. Such type of atropoisomerism has been considered in detail [8]. Increase in temperature to 55°C makes rotation of 1-naphthyl radical at the nitrogen atom free, and the asymmetry of molecule disappears, as is reflected by the ^{1}H NMR spectrum. Previously by means of coalescent method the barrier of rotation around C–N bond ($\Delta G_c^{\neq}$ 63.0 ± 0.1 kJ mol^{-1}) and the coalescence temperature (T_c 32 ± 4°C) were evaluated for the analog of compound **VIa** with ethoxy ester group [8]. The barrier of rotation of 1-naphthyl radical around C–N bond in compound **VIa** is probably close by the value.

Hence, in the above-considered transformations the ester groups formed by allyl and propargyl alcohols migrate from the carbon atom to nitrogen similarly to their saturated analogs to form corresponding unsaturated carbamates. Compounds **VIa** and **VIb** can be used as the starting reagents in the synthesis of carbamates of more complex structure by modification of the molecule at the multiple bonds.

EXPERIMENTAL

IR spectra were registered on a Magna IR-750 Nicolet Fourier spectrometer with the resolution 2 cm^{-1} for a suspension in vaseline oil. ^{1}H and ^{31}P NMR spectra were taken on a Bruker AMX-400 spectrometer (400.13 MHz for ^{1}H and 161.98 MHz for ^{31}P) in $CDCl_3$ against internal TMS and external 85% phosphoric acid respectively. Reactions were carried out under dry nitrogen. Solvents were used after purification and drying. Allyl and propargyl 2-cyanoacrylates were prepared according to the procedure [9].

1-Allyloxycarbonyl-2-triisopropylphosphonio-1-cyanoethan-1-ide (IVa). To a solution of 4 g of triisopropylphosphine in 70 ml of petroleum ether a solution of 5.5 g of allyl 2-cyanoacrylate in 1 : 1 mixture of diethyl and petroleum ethers (70 ml) containing one drop of methanesulfonic acid was added dropwise at stirring with magnetic stirrer and cooling with ice water. White grainy precipitate began to form immediately. After the addition of cyanoacrylate was complete the reaction mixture was heated to room temperature and filtered. Obtained precipitate, 4.3 g,



Fragments of ^{1}H NMR spectra of compound **VIa** at (a) 20°C and (b) 55°C.

was dissolved at heating in a minimum amount of acetone, the obtained solution was filtered and left at room temperature for a day. Precipitated crystals were filtered off to give 3.5 g (47.3%) of compound **IVa**, mp 123–124°C. IR spectrum, ν, cm^{-1}: 2143 (CN), 1619 (C=O), allyl group was not identified. ^1H NMR spectrum, ($CDCl_3$), δ, ppm: 1.29 d.d [18H, $(CH_3)_2C$, $^3J_{HP}$ 14.8 Hz, $^3J_{HH}$ 7.2 Hz], 2.56 d.sept (3H, CH, $^2J_{HP}$ 12.4 Hz, $^3J_{HH}$ 7.2 Hz), 3.05 d (2H, CH_2P, $^2J_{HP}$ 6.4 Hz), 4.37 d.t (2H, CH_2O, $^3J_{HH}$ 5.2 Hz), 4.92 d.q (1H, H^b, $^3J_{HH}$ 10.4 Hz, $^2J_{HH}$ 1.6, $^4J_{HH}$ 1.6 Hz), 5.12 d.q (1H, H^a, $^3J_{HH}$ 17.2 Hz, $^2J_{HH}$ 1.6 Hz), 5.77 d.d.t (1H, H^c, $^3J_{H^cH^a}$ 17.2 Hz, $^3J_{H^cH^b}$ 10.4 Hz, $^3J_{HH}$ 5.2 Hz). ^{21}P NMR spectrum ($CDCl_3$), δ_P, ppm: 38.81. Found, %: C 64.85, 64.76; H 9.17, 9.21; N 4.75, 4.71. $C_{16}H_{28}NO_2P$. Calculated, %: C 64.62; H 9.49; N 4.71.

1-Propargyloxycarbonyl-2-triisopropylphosphonio-1-cyanoethan-1-ide (IVb). Under the conditions of the above-described experiment from 4 g of triisopropylphosphine and 5.4 g of propargyl 2-cyanoacrylate 3.8 g (32.2%) of zwitter-ion **IVb** was obtained, mp 122–124°C. IR spectrum, ν, cm^{-1}: 1621 (C=O), 2116 (C≡C), 2160 (CN), 3222 (≡CH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 d.d [18H, $(CH_2)_2C$, $^3J_{HP}$ 14.8 Hz, $^3J_{HH}$ 7.2 Hz], 2.27 t (1H, CH≡, $^4J_{HH}$ 2.0 Hz), 2.67 d.sept (3H, CH, $^2J_{HP}$ 12.4 Hz, $^3J_{HH}$ 7.2), 3.16 d (2H, CH_2P, $^2J_{HP}$ 6.4), 4.58 d (2H, CH_2O, $^4J_{HH}$ 2.0 Hz). ^{31}P NMR spectrum, ($CDCl_3$), δ_P, ppm: 39.18. Found, %: C 65.15, 65.30; H 9.90, 8.91; N 4.71, 4.75; P 10.59, 10.48. $C_{16}H_{26}NO_2P$. Calculated, %: C 65.08; H 8.87; N 4.75; P 10.49.

1-[*N*-Allyloxycarbonylcarbamoyl-*N*-(1-naphthyl)]-2-(triisopropylphosphonio)-1-cyanoethan-1-yl (VIa). A mixture of 0.5 g of zwitter-ion **IVa**, 0.84 g of 1-naphthylisocyanate and 2 ml of CH_2Cl_2 was kept in a closed flask at room temperature for 2 weeks. After that reaction mixture was added dropwise with stirring to 50 ml of hexane, and the precipitate obtained was washed with Et_2O. It was trice crystallised from acetone-ether mixture. Yield 0.34 g (43%), mp 1213122°C. IR spectrum, ν, cm^{-1}: 2158 (C≡N), 1700 (C=O esterial), 1608 (C=O conjugated). ^1H NMR spectrum ($CDCl_3$, 55°C), δ, ppm: 1.37 d.d [18H, $(CH_3)_2C$, $^3J_{HP}$ 15.8 Hz, $^3J_{HH}$ 7.2 Hz], 2.60 d.sept (3H, CH, $^2J_{HP}$ 12.5 Hz, $^2J_{HH}$ 7.2 Hz), 3.19 d (2H, CH_2P, $^2J_{HP}$ 6.5), 4.62 d (2H, CH_2O, $^3J_{HH}$ 4.0 Hz), 5.05 d (1H, $^3J_{HH}$ 10.8 Hz), 5.09 d (1H, H^a, $^3J_{HH}$ 17.2 Hz), 5.87 d.d.t (1H, H^c, $^3J_{H^cH^a}$ 17.2 Hz, $^3J_{H^cH^b}$ 10.8 Hz, $^3J_{HH}$ 4.0 Hz), 7.46 m (3H, H_{arom}), 7.70 m (3H, H_{arom}), 8.40 d (1Hm CH_{peri} arom., $^3J_{HH}$ 8.4 Hz). ^1H NMR spectrum ($CDCl_3$, 20°C), δ, ppm: 1.37 br.s [18H, (CH_3)$_2$C, Δν 32 Hz), 2.50 d.sept (3H, CH, $^2J_{HP}$ 12.5, $^3J_{HH}$ 7.2), 3.19 br.s (2H, CH_2P, Δν 34 Hz), 3.19 d (2H, CH_2P, $^2J_{HP}$ 6.5 Hz), 4.62 d (2H, CH_2O, $^3J_{HH}$ 4.0 Hz), 5.05 d (1H, H^b, $^3J_{HH}$ 10.8 Hz), 5.09 d (1H, H^a, $^3J_{HH}$ 17.2 Hz), 5.87 d.d.t (1H, H^c, $^3J_{H^cH^a}$ 17.2 Hz, $^3J_{H^cH^b}$ 10.8 Hz, $^3J_{HH}$ 4.0 Hz), 7.46 m (3H, H_{arom}), 7.70 m (3H, H_{arom}), 8.40 d (1H, CH_{peri} arom., $^3J_{HH}$ 8.4 Hz). ^{31}P NMR spectrum, ($CDCl_3$), δ_P, ppm: 41.27. Found, %: C 68.97, 68.66; H 7.12, 7.20; N 5.76, 5.78. $C_{27}H_{35}N_2O_3P$. Calculated, %: C 69.53; H 7.51; N 6.01.

1-[*N*-(1-phenyl)-*N*-propargyloxycarbonylcarbamoyl]-2-(triisopropylphosphonio)-1-cyanoethan-1-yl (VIb). A solution of 0.5 g of zwitter-ion **VIb**, and 5.9 g of phenylisocyanate in 3 ml of CH_2Cl_2 was kept in a closed flask for four days at room temperature. After that reaction mixture was treated as described above. Yield of zwitter-ion **VIb** 0.33 g (42%), mp 121-123°C. IR spectrum, ν, cm^{-1}: 3227 (CH≡), 2166 (C≡N), 1704 (C=O esterial), 1616 (C=O conjugated). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 d.d [18H, $(CH_3)_2C$, $^3J_{HP}$ 15.2 Hz, $^3J_{HH}$ 7.2 Hz], 2.40 t (1H, CH≡, $^4J_{HH}$ 1.9 Hz), 2.63 d.sept (3H, CH, $^2J_{HP}$ 12.4 Hz, $^3J_{HH}$ 7.2 Hz), 3.12 d (2H, CH_2P, $^2J_{HP}$ 6.4 Hz), 4.72 d (2H, CH_2O, $^4J_{HH}$ 1.9 Hz), 7.14 t (1H, H_p arom., $^3J_{HH}$ 6.6 Hz), 7.27 m (2H, H_m arom.), 7.47 d (2H, H_o arom., $^3J_{HH}$ 7.6 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 41.87. Found, %: C 66.75, 66.48; H 7.64, 7,56; N 6.55, 6.60. $C_{23}H_{32}N_2O_3P$. Calculated, %: C 66.67, H 7.49; N 6.76.

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