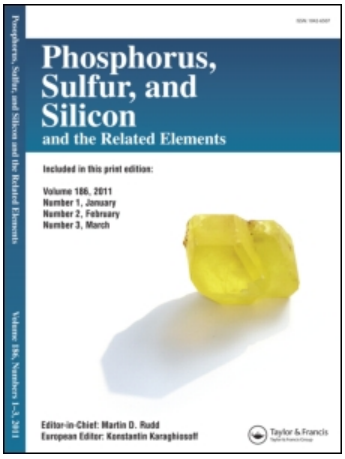

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P-Zwitterions from Trialkylphosphines and 2-Cyanoacrylates

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The recent developments in the chemistry of P-zwitterions **2** are discussed. They include unusual reactions of **2** with $HgCl_2$, ArN_3, TosNCO and Alk(Ar)NCX (X=O,S). The insertion reactions of alkyiso(thio)cyanates into C-C bond are considered. A novel type of the intramolecular electrophilic rearrangements is described.

Keywords: P-zwitterions; isocyanates; electrophilic rearrangements; insertion reaction

RESULTS AND DISCUSSION

Trialkylphosphines react with alkyl-2-cyanoacrylates at such a high rate that,under slow addition of dilute **1** solution to Alk_3P stable P-zwitterions **2** are formed [1].

$$R_3P + \underset{\mathbf{1}}{CH_2{=}C(CN)COOAlk} \dashrightarrow \underset{\mathbf{2}}{R_3\overset{+}{P}CH_2\overset{-}{C}(CN)COOAlk} \qquad (I)$$

R = n-Pr, i-Pr, n-Bu, Et_2N ; Alk = Me, Et

The structure of **2** was confirmed by NMR (^{1}H,^{13}C,^{31}P), IR spectroscopy [2] and X-Ray investigation of **2a** (R=i-Pr,Alk=Et) [3]. The anionic charge in zwitterions **2** is significantly delocalized, which is revealed by X-Ray analisis and IR spectra data. The anionic charge in **2** is not stabilized by the shift of a proton to anionic carbon, because its basicity is significantly reduced. But alkylation [4] of **2** occurs at the central carbon atom of the pentade anion and leads to **3**

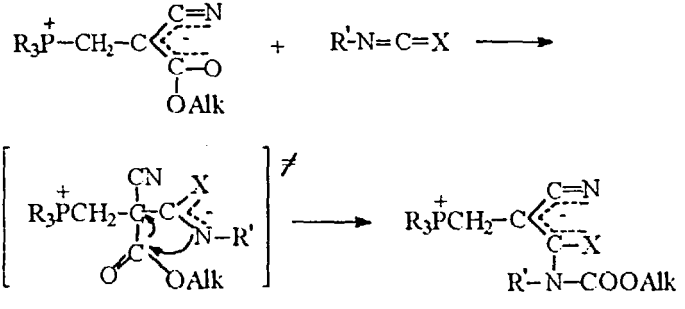
$R_3P^+CH_2C(CN)(COOAlk)Alk^{\cdot}\ Hal^-$ **3**

P-zwitterions **2** are displayed as "hidden" trialkylphosphines in the reactions with $HgCl_2$, ArN_3 and p-$MeC_6H_4SO_2NCO$. In the all last cases zwitterion **2a** stands out **1** (that is polymerized immidiately) and compounds **4-6** are formed.

i-Pr_3PHgCl_2 **4** i-Pr_3P=NAr **5** i-$Pr_3P^+C(O)N^-Tos$ **6**

The structure of **6** was confirmed by IR and NMR spectroscopy and single-crystal X-Ray analysis. **6** was also obtained by the direct reaction of i-Pr_3P with tosyl isocyanate [5].

With alkyl- and aryliso(thio)cyanates the zwitterionic species **2**, react specifically. These reactions are proceeding as a process of insertion of iso(thio)cyanates into C-C bond of phosphabetaine anionic part [6].



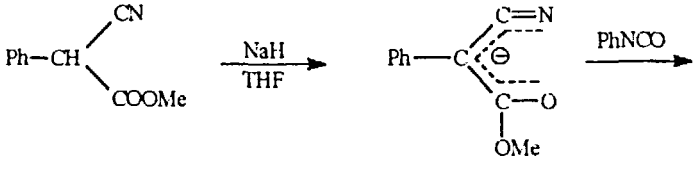
8 **9**

R= n-Pr, i-Pr, n-Bu, Et_2N; Alk= Me, Et

R'= Me, c-C_6H_{11}, Ph, 1-$C_{10}H_7$, m-MeC_6H_4, m-ClC_6H_4, m,p-$Cl_2C_6H_3$, p-$NO_2C_6H_4$; X = O, S

Kinetics and mechanism of this unusual reaction have been studied[6] by the method of spectrophotometry in different solvents at 20-60°C. It was established that the reaction is carrying out by the total second order - the first by each of reagents. Most probably, the nucleophilic attack of phosphabetaine anionic center on the carbon atom of isocyanate group and nucleophilic attack of nitrogen atom on the carbon atom of carbethoxy group, leading to a rupture of C-C bond, are carrying out relatively synchronously in the frame of one transition state by concerted mechanism. The driving force of carbethoxy group migration from carbon to the nitrogen atom may be conditioned by sufficient steric hindrance of activated complex 8, and also by energetic gain from the more effective delocalization of anionic charge in the forming product 9.

This type of rearrangements involving the migration of alkoxycarbonyl group from a saturated carbon to an anionic nitrogen centre is of the general character, because the same rearrangemen takes place in the time of using carbanions 11 without phosphonium group and mobile hydrogen in molecule as well [7].



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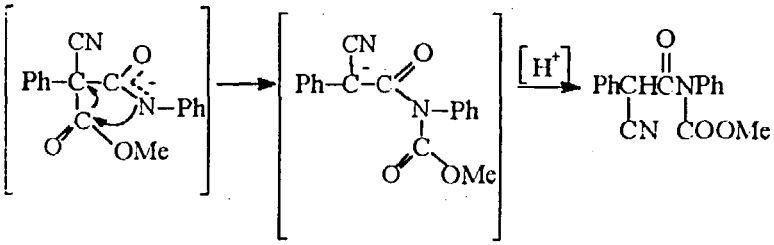

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