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Unusual Transformations of 2-Cyanoacrylates in Reactions with Trivalent Phosphorus Compounds

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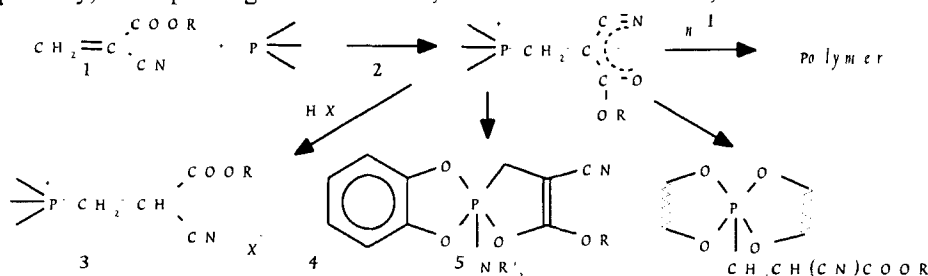
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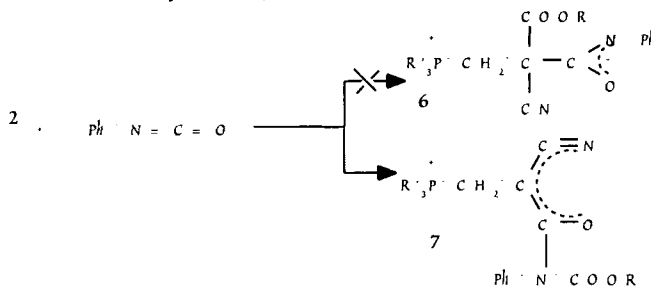
UNUSUAL TRANSFORMATIONS OF 2-CYANOACRYLATES IN REACTIONS WITH TRIVALENT PHOSPHORUS COMPOUNDS

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Cyanoacrylates **1** have existed for 40 years, but up till ¹ only polymerization processes, effected by various nucleophiles, including trivalent phosphorus compounds, have been known. We have shown that under established conditions **1** (**a** R=Me, **b** R=Et) reacts with trivalent phosphorus compounds not only *via* the anionic polymerization pathway, but depending on the structure, it forms stable adducts **2,4** or **5**.



Only strong nucleophiles react to form stable betaines **2**. Weak nucleophiles, e.g. Ph_3P , react reversible with **1**, and the equilibrium is shifted to the left. The reaction zwitterions **2** with electrophile, that locks a good leaving group, e.g. $\text{Ph-N}=\text{C}=\text{O}$, affords not the expected adduct of C-alkylation **6**, but isomeric zwitter-ion **7**.



The second possibility of the stabilization of the anionic charge is closing unsaturated ring **4**. Stereoeffects play an important role in its stabilization. Carboxylic acid esters with P-C bond, which are intramolecularly phosphorylated at oxygen, were unknown. Stabilization of the primary formed zwitter-ion is possible not only its intramolecular spirocyclization, but also by "trapping" of the anionic charge by an active hydrogen of the starting nucleophiles (adducts **5**). Trapping of the anionic charge in the initially formed zwitter-ion **2** can be carried out with introduction of an acid (adduct **3**).

[1] I.I. Kandror, I.O. Bragina, M.A. Galkina and Yu.G. Gololobov, *Izv. Akad. Nauk. Ser. Khim.*, 2798 (1990).