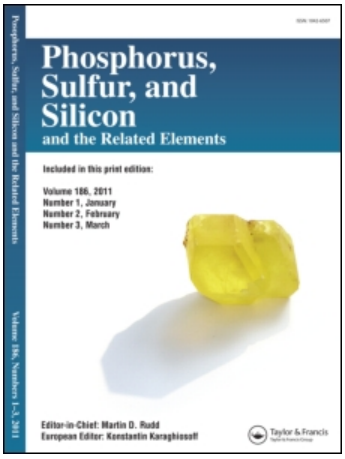


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Yuri G. Gololobov[a]; Tatiana O. Krylova[a]
[a] A.N. Nesmeyanov Institute of Organo-Element Compounds Russian Academy of Sciences, Moscow V-334, GSP-1, Russia

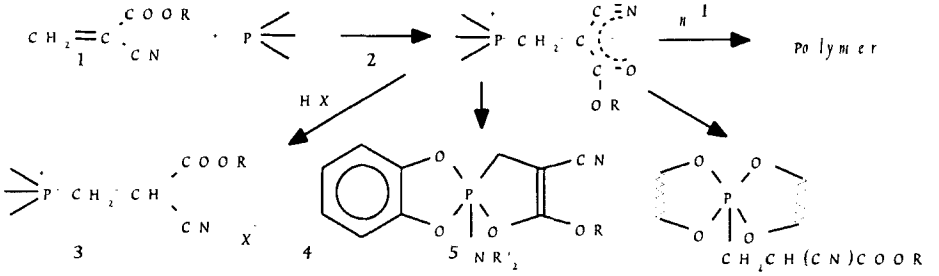
To cite this Article Gololobov, Yuri G. and Krylova, Tatiana O.(1996) 'Unusual Transformations of 2-Cyanoacrylates in Reactions with Trivalent Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 201
To link to this Article: DOI: 10.1080/10426509608054830
URL: http://dx.doi.org/10.1080/10426509608054830

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 201
Reprints available directly from the publisher
Photocopying permitted by license only

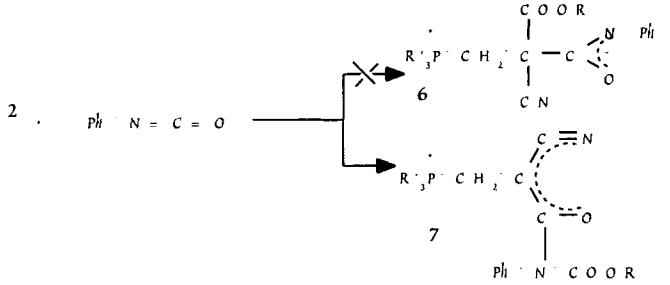
UNUSUAL TRANSFORMATIONS OF 2-CYANOACRYLATES IN REACTIONS WITH TRIVALENT PHOSPHORUS COMPOUNDS

YURI G. GOLOLOBOV and TATIANA O. KRYLOVA
A.N. Nesmeyanov Institute of Organo-Element Compounds
Russian Academy of Sciences,
Vavilov str., 28, Moscow V-334, 117813 GSP-1, Russia

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 zwitter-ions **2** with electrophile, that locks a good leaving group, e.g. Ph-N=C=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 intramoleculary 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).