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Phosphorylated Allylchlorides: A Source of new Structures and Transformations

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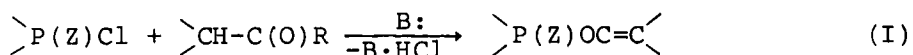
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PHOSPHORYLATED ALLYLCHLORIDES: A SOURCE OF NEW STRUCTURES AND TRANSFORMATIONS

Yu.G.GOLOLOBOV, A.S.OGANESYAN, G.D.KOLOMNIKOVA, and S.A.KUZNETSOVA
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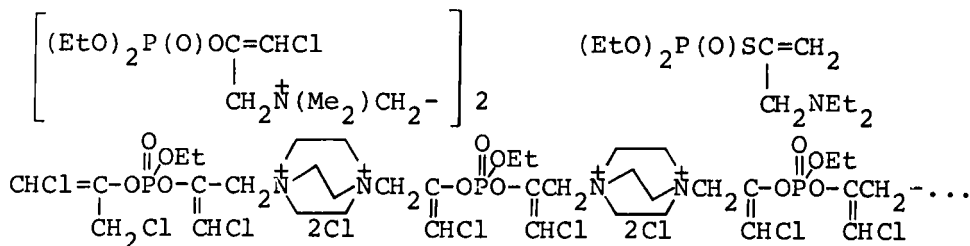
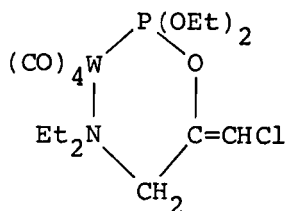
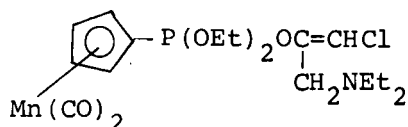
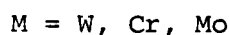
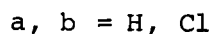
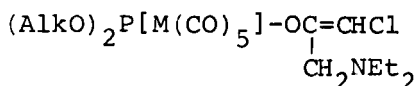
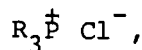
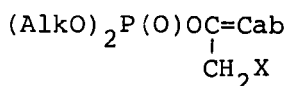
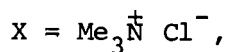
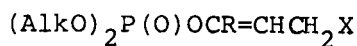
General methods have been elaborated for the synthesis of O (or S)-phosphorylated vinylcholines, including the corresponding betaines of mono-, bis- and polymer structures, 5-membered heterocycles with P, O, S, N atoms in the cycle and exo- CHX= (X=H, Cl) bond. The key substances, O-phosphorylated allylchlorides, were obtained either by the well known Perkov reaction or according to scheme (I), worked out by us. The scheme is based on the reactions of 3- or 4-coordinated phosphorus with substituted ketones in the presence of triethylamine (B:).



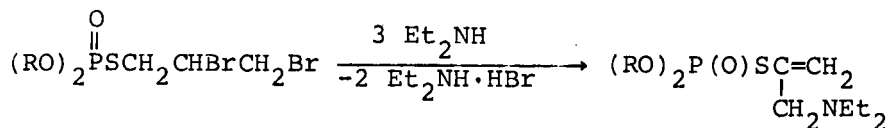
Z = lone pair of electrons, O, S; R = Alk, Ar

According to scheme (I) derivatives of trivalent phosphorus, di- and trivinyl esters of phosphorus acids, heterocycles with 2-, 3- and 4-coordinated phosphorus can be synthesized.¹

For example, use of 1,3-dichloroacetone leads to vinyl esters of phosphorus acids, which can be used in the synthesis of various types of enol derivatives with chloro-allyl fragments in the ester group, including complexes with platinum, molybdenum, manganese, tungsten, chromium, europium, praseodymium:



"Vinylthiocholines" can also be obtained by an unexpected reaction



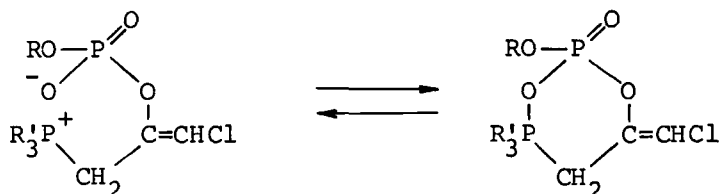
All vinylcholines obtained by this method are liable to dealkylation leading to a new type of betaines



In contrast to corresponding "nitrogen" betaines, P-betaines undergo 1-3 proton migration which yields betaines with positive charge at a multiple bond.



According to NMR data, P-betaines exist in THF media as a tautomeric mixture of betaines and isomeric phosphoranes



Betaines display a striking hydrolytic stability and a definite ability to inhibit esterases according to reversible and irreversible schemes.

1. Gololobov Yu.G., Balitski Yu.V., Danchenko M.N., Kim T.V., Kiselyova E.I., Kolodka T.V., Lysenko V.P., Malenko D.I., Maidanovich N.K., Nesterova L.I. - Proceedings of the VII Conference on Chemistry of Organophosphorus Compounds. Leningrad, 1987, p. 72.