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The Synthesis, Structure and Properties of Phosphire-Nium Halogenides

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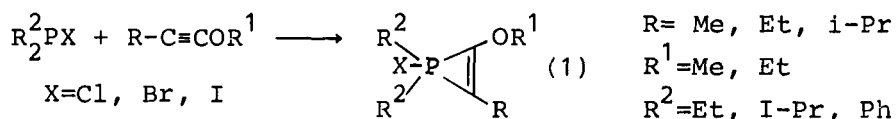
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THE SYNTHESIS, STRUCTURE AND PROPERTIES OF PHOSPHIRENIUM HALOGENIDES

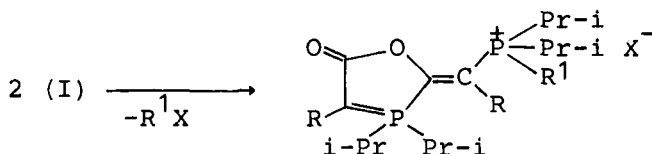
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In the study of electrophilic addition of organoelement halogenides to alkoxyacetylenes¹ it has been found that in the absence of catalysts dialkyl(phenyl)halogenphosphines add to internal alkoxyacetylenes, which results in the formation of stable phosphirenes (I) of a new type.



For phosphirene (I) unusual values of the NMR parameters (δ_{P} , δ_{C} , J_{PC}) have been found, which are not typical for known phosphonium salts. The analysis of these values as well as δ_{P} concentration and temperature dependence allows us to suppose the presence of equilibrium with the pentacoordinated form for chloro- and bromoderivatives in the solution. The stability of phosphirenes (I) is dependent on the nature of the halogens atom and the character of alkyl radicals at the phosphorus atom and at the olefinic carbon. Spontaneous cyclodimerization is observed in the solution for several bromo- and iodophosphirenes with the formation of a new type cyclic ylides. The structure of ylides has been established by X-ray analysis.



1. M.A.Kazankova, I.L.Rodionov, E.V.Luzikova, I.F.Lutsenko, in: Chemistry and Application of Phosphororganic compounds. Proceedings of the VIII-th All Union Conference on Chemistry of Phosphororganic Compounds, p. 82, Moscow, Nauka, 1987.