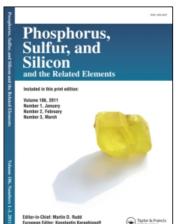
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Reactions of Sterically Protected 1-Halo- and 1-Pseudohalo-2-Phosphaethenyl-Lithiums

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Reactions of Sterically Protected 1-Halo- and 1-Pseudohalo-2-Phosphaethenyl-Lithiums

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Phosphorus analogs of alkylidenecarbenoid, Ar-P=C(X)Li, where X equals halogen or pseudohalogen atom, such as Cl, Br, or SPh, have been generated by use of the 2,4,6-tri-t-butylphenyl group (abbreviated to Ar in the Scheme) as a protecting group for low coordinated organophosphorus compounds. The reaction with methyl iodide and with some aldehydes or ketones, at low temperature, gave the corresponding alkylation products^[1]. The reaction with copper salts gave 1,4-diphosphabutadiene (1) or 1,4-diphosphabutatriene (2), depending upon the substituent $X^{[2,3]}$, as well as reaction conditions, such as reaction temperature and time, solvent, presence or absence of oxygen. Upon warming the phosphaethenyllithiums, thus generated, the chloro derivative of E-configuration gave a phosphaalkyne (3) via [1,2]-aromatic migration^[4], whereas the bromo derivative of Z-configuration gave a 1-phospha-3,4-dihydronaphthalene derivative (4), that is a formal C-H insertion product of a phosphinidenecarbene intermediate^[5].

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