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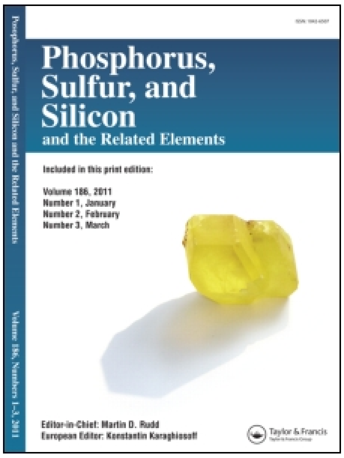

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About the Mechanism of the Reaction Cuprous Dialkyl Thiophosphates with the Alkynyl Halides

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ABOUT THE MECHANISM OF THE REACTION CUPROUS DIALKYL THIOPHOSPHATES WITH THE ALKYNYL HALIDES

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Cuprous dialkyl thiophosphates are convenient reagents for the synthesis of the organophosphorus compounds with the α-acetylenic bond in the alkthiolic radical, and for steric hindered S-propargyl thiophosphates. X-ray investigation established that the crystal is constructed of the tetramer molecules $Cu_4[(EtO)_2PSO]_4$.[1] The tetramer is a tetrahedral claster of Cu atoms coordinated with four three-dentant chelate-bridged diethyl thiophosphate ligands. Firmly coordinated diethyl thiophosphate ligand in the copper complex does not possess nucleophilic properties and does not react with alkyl bromide. EPR spectroscopy established that the ethynylation of cuprous dialkyl thiophosphate by the substituted ethynyl bromides proceeds via the paramagnetic cupric complex formation. The latter, being unstable under usual conditions, decomposes with the formation of substituted S-ethynyl thiophosphates and CuBr.[2] Sterically hindered halides of the propargyl type are not liable to Sn2 reaction with the potassium salts of dialkyl thiophosphoric acids, but they readily react with the cuprous salts of these acids yielding S-propargyl thiophosphates. This process is a redox one and it proceeds via the paramagnetic cupric complex formation.

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