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Photoinduced Halophosphination of Unsaturated Compounds

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PHOTOINDUCED HALOPHOSPHINATION OF UNSATURATED COMPOUNDS

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Comprehensive studies of photoinduced addition of phosphorus trihalides to unsaturated compounds, i.e. alkenes, alkynes, alkadienes, and enynes, were carried out. The addition of phosphorus trihalides to unsaturated C-C bonds is proved to be a radical chain process, the total reaction rate increasing with the increase of electron density on the unsaturated C-C bond. The photoinduced reaction of alkenes with PBr_3 goes via Br atom attack on the least substituted C-atom of an unsaturated C-C bond and mainly results in the formation of dibromophosphines with a phosphorus atom in the second position of the carbon chain - (1-2)-addition. In the case of polysubstituted alkenes an alternative direction of the reaction is realized, namely the photoinduced substitutional dibromophosphination to alkyl group. The reaction with alkynes results only in the formation of the products of (1-2)-addition. The regioselectivity of the addition of phosphorous trihalide fragments to the substrate containing a heteroatom at the unsaturated C-C bond is determined by the stability of the secondary halogenoalkenyl(alkyl) radical.