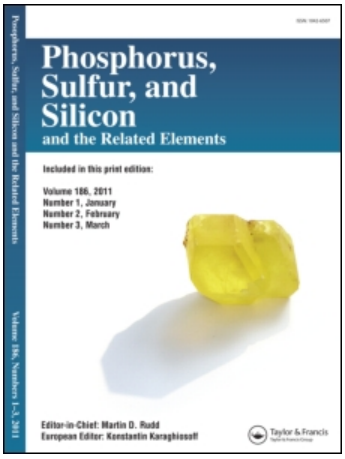

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New Free Radical Syntheses and Reactions of Functionalized Phosphonates

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NEW FREE RADICAL SYNTHESES AND REACTIONS OF FUNCTIONALIZED PHOSPHONATES

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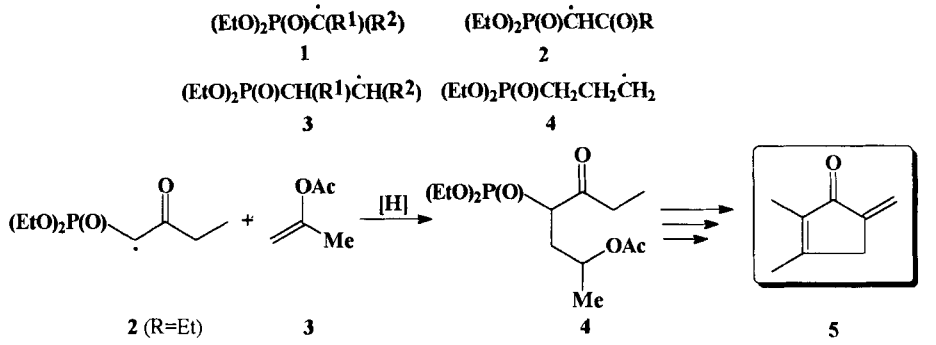
Abstract Reactions of α,β and γ-phosphonyl radicals with alkenes leading to the formation of the $P(C)_n$-C bonds (n=1÷3) and illustrated by a synthesis of Methylenomycin B are described. Desulfenylation and deselenylation reactions of α-heterosubstituted α-phosphoryl sulfides and selenides are also presented.

A new free radical approach to synthesis of functionalized phosphonates is based on the reactions of α,β and γ-phosphonyl radicals of the type **1-4** derived from α-phosphorylalkyl halides, sulfides and selenides with alkenes and alkynes. It leads to the formation of the new $P(C)_n$-C bonds (n=1÷3).



The utility of the elaborated approach is exemplified by the formal synthesis of Methylenomycin B. This synthesis is based on the free radical reaction of **2** (R=Et) with isopropenyl acetate **3**. New free radical desulfenylation and deselenylation reactions of the α-heterosubstituted (OR, $(EtO)_2P(O)$, SR, Cl) α-phosphoryl sulfides and selenides are also presented.