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New Free Radical Syntheses and Reactions of Functionalized Phosphonates

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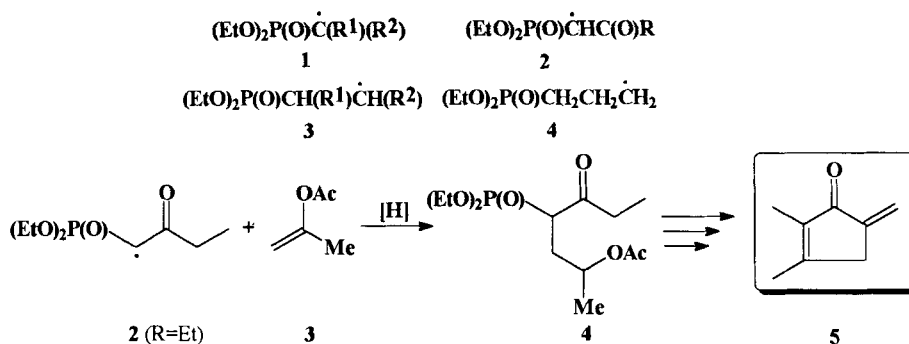
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PIOTR BAŁCZEWSKI, MARIAN MIKOŁAJCZYK

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 Methyleneomycin 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 Methylennomycin 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.