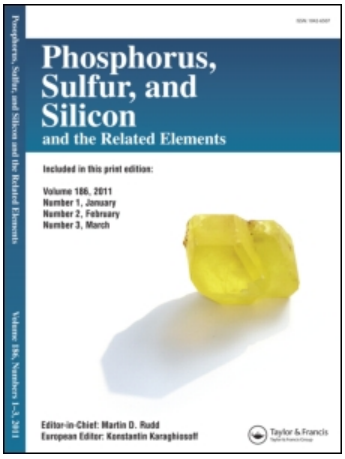


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# Synthesis, Reactions and Applications of Phosphorus Containing Carbon Centered Radicals

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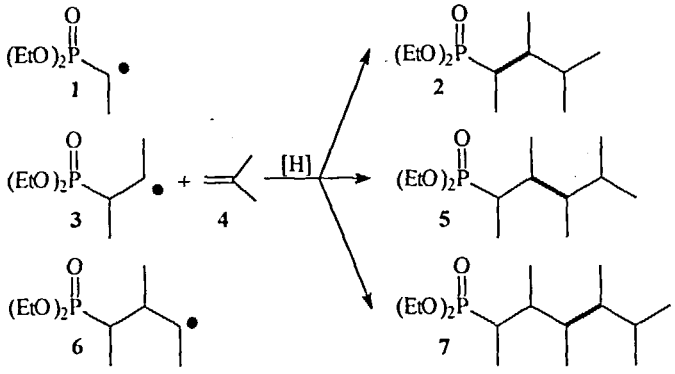
A general method for synthesis of $C_n$-C (n=1, 2...) phosphonate bonds involving a reaction of 1-diethoxy-phosphorylalkan-1-, -2-and -3-yl radicals **1, 3, 6** with alkenes **4**, a new example of functional group interconversion in 1-heterosubstituted phosphonates and synthesis of useful phosphoroorganic compounds and methylenomycin B are described.

*Keywords:* phosphonate; 1-diethoxyphophorylalkan-1-; -2-and -3-yl radicals; alkene; tri-n-butyltin hydride; methylenomycin B

## INTRODUCTION

A rich family of phosphonates and their derivatives constitutes a very important class of organophosphorus compounds. A wide and practical application in organic synthesis, medicine, agriculture and technology possess phosphonates having a high degree of structural functionalization. In this paper we propose one of the possible solutions to the problem of functionalization of phosphonates harnessing the dynamically developing area of radical reactions. The new idea is based on the reaction of the phosphorylated $C_n$ (n=1, 2, 3) radicals **1**, **3**, **6** with alkenes **4** resulting in the formation of the new $C_n$-C bonds in phosphonates **2**, **5**, **7**[1,2] (Scheme 1).

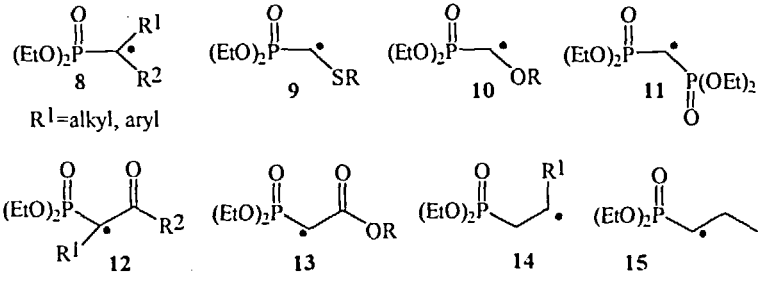



SCHEME 1

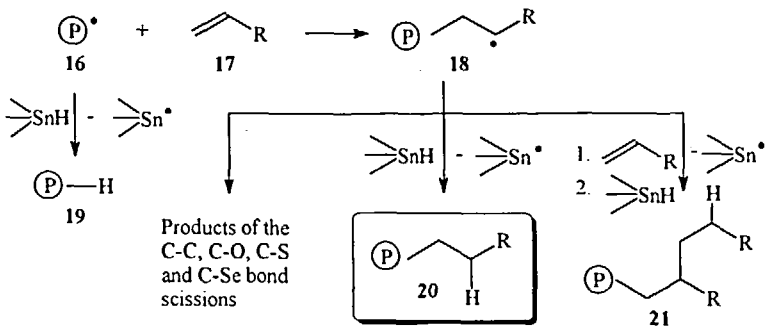


## RESULTS

New radicals **8-15** were synthesized in reactions involving homolysis of the C-X (Cl, Br, I, Se, S) bonds and reacted with alkenes under reductive conditions (≡SnH or ≡SiH/AIBN, UV light or $Et_3B,O_2$/- 78÷110°C) to give different reaction products: **19**, **20**, **21** or products of the C-C or C-heteroatom bond scissions (Scheme 2 and 3).



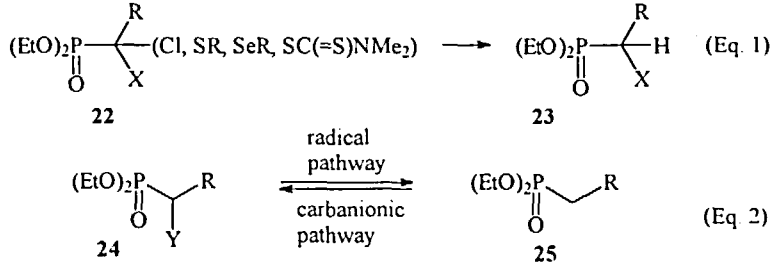

SCHEME 2




(P)- 1-diethoxyphosphorylalkan-1-, 2- or -3-yl residue

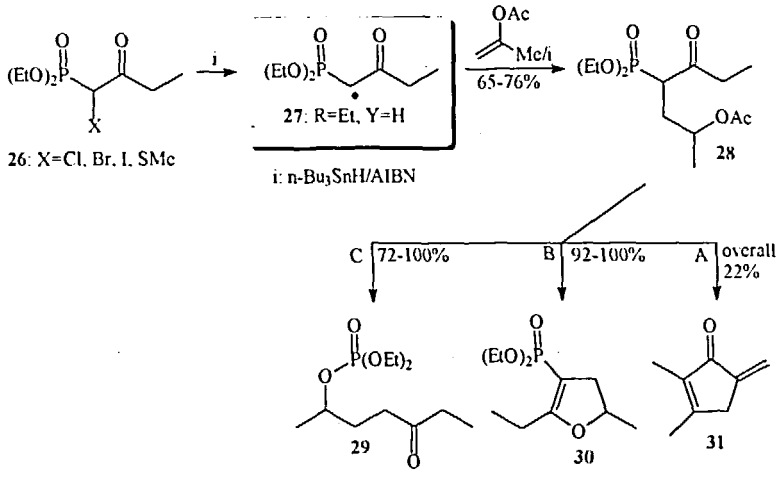
SCHEME 3

The effective synthesis of functionalized phosphonates **20** using iodoalkylphosphonates (homolysis of the C-I bond) and the $Et_3B/O_2$ reagent system at - 78°C realized the idea of the phosphonate bond synthesis depicted in Scheme 1. In the absence of alkene, products of type **19** could be obtained as major reaction products in high yields what led to the elaboration of the general method of dehalogenation and depseudohalogenation of heterosubstituted phosphonates **(22-23)** (Scheme 4, Eq. 1).




SCHEME 4

Considering synthesis of 1-thio- and 1-seleno-substituted phosphonates **24** via carbanionic pathway (addition of RSSR, RSeSeR, S or Se) our method constitutes a new example of functional group interconversion leading to the reduced phosphonates **25** (Scheme 4, Eq. 2).




SCHEME 5

The utilization of radical reactions of phosphonates was further demonstrated in synthesis of the model antibiotic methylenomycin B - **31** and other useful organophosphorus compounds **28**, **29**, **30** in high reaction yields. The overall yield of methylenomycin B - **31** exceeded 20%.

## *References*

[1] P. Bałczewski and M. Mikołajczyk, *Reviews on Heteroatom Chemistry*, 1998 in press.
[2] P. Bałczewski and W.M. Pietrzykowski, *Tetrahedron*, **53**, 7291 (1997). Part VII of the series: *Phosphorus containing radicals.*