



## Efficient and practical aerobic radical addition of thiophosphites to alkenes

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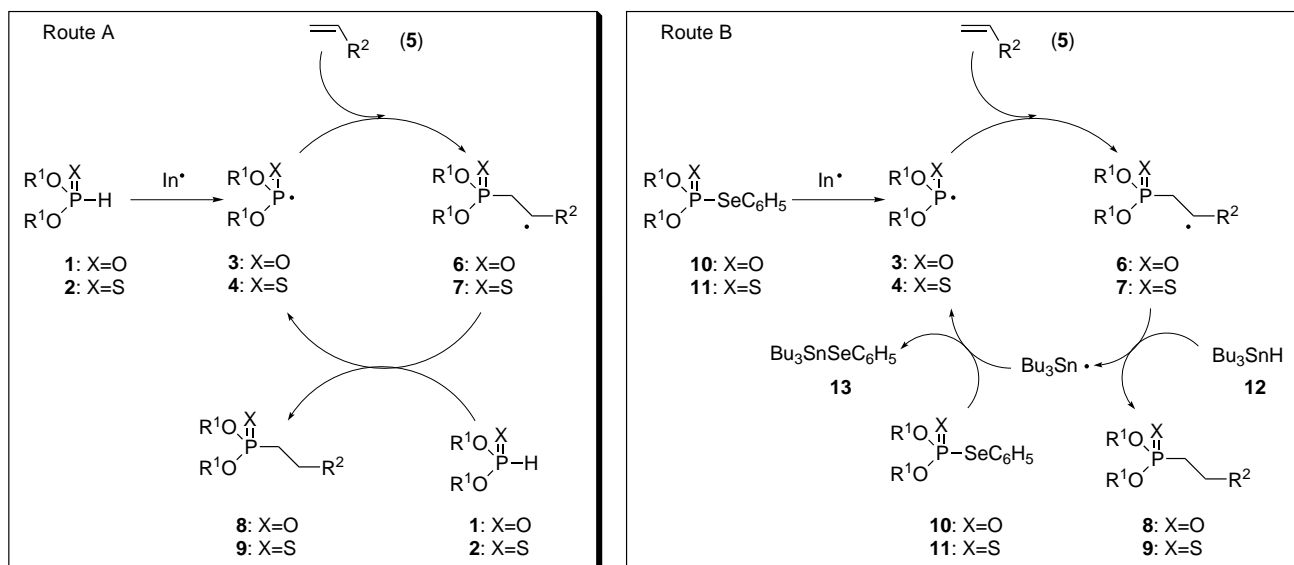
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**Abstract**—Thiophosphites, but not phosphites, add onto alkenes under very mild conditions when treated with triethylborane and oxygen, and deliver the expected adducts in high isolated yields. This method, featuring a high atom economy, complements those described in literature and can be used to initiate tandem cascade processes. © 2001 Published by Elsevier Science Ltd.

The formation of carbon–phosphorus bonds has been an area of intense investigation for decades due to the implication of organophosphorus compounds as ligands of metals, as close analogues of phosphate esters, and because of their involvement in reactions such as the Wittig (and related) olefination. Thus, these C–P bonds have traditionally been created by nucleophilic substitution of halides (including Arbuzov transformations) or by addition of phosphorus-centered radical onto alkenes (chain process).

In particular, phosphonyl and phosphonothioyl radicals (**3**) and (**4**) have been used to produce phosphonates (**8**) and phosphonothioates (**9**), respectively, which can be considered as non-hydrolyzable analogues of monoesters of the phosphate group. Radical (**3**) or (**4**) have been typically generated (i) from the corresponding phosphites (**1**) or thiophosphites (**2**) in the presence of peroxides (Scheme 1, route A), or (ii) from selenophosphates (**10**) or selenophosphorothioates (**11**) and trialkyltin hydride (**12**) in the presence of a radical initiator (route B).<sup>1,2</sup>



**Scheme 1.** ( $\text{R}^1 = \text{alkyl}$ ;  $\text{R}^2 = \text{alkyl, aryl, ...}$ ).

**Keywords:** boron; phosphonothioate; thiophosphite; radical addition; cascade radical cyclization.

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