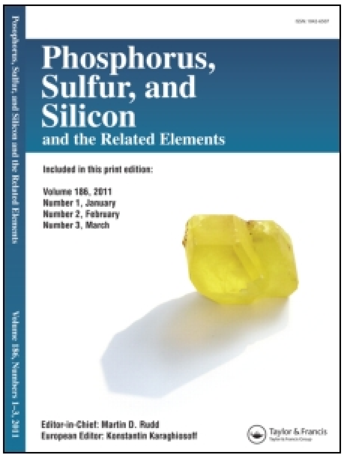

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Chemistry of Dialkyl Alkenylphosphonates - Synthetic Implications

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CHEMISTRY OF DIALKYL ALKENYLPHOSPHONATES - SYNTHETIC IMPLICATIONS

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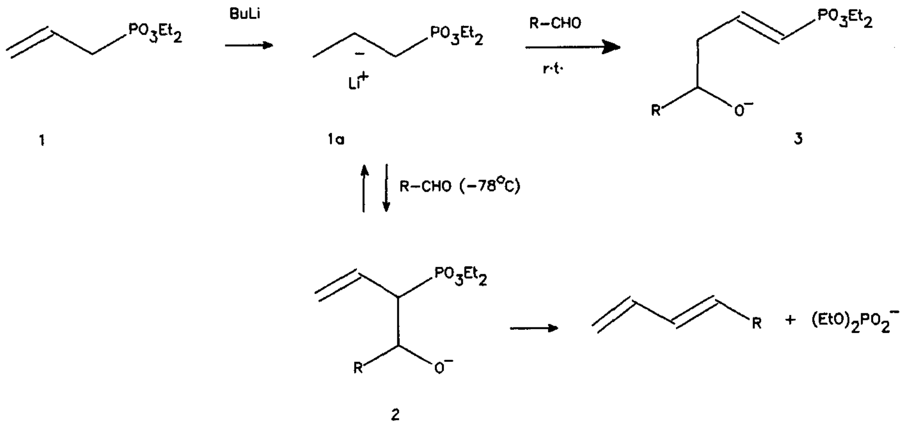
Abstract Reactions of lithiated diethyl allylphosphonates, derived from propene or cyclohexene, with aldehydes and *α,β*-unsaturated ketones or esters are described.

The reactions of lithiated esters of alk-2-enylphosphonic acids with carbon electrophiles are described. Diethyl prop-2-enylphosphonate (**1**) was first chosen as a model substrate and its reactions with carbonyl compounds were studied. The reaction with aldehydes[1] led to the formation of *α*-adducts (**2**) as kinetic, and of *γ*-adducts (**3**) as thermodynamic products; the former products could either isomerize to **3** *via* the reversal of the condensation step, or undergo fragmentation to the corresponding diene (Scheme 1).

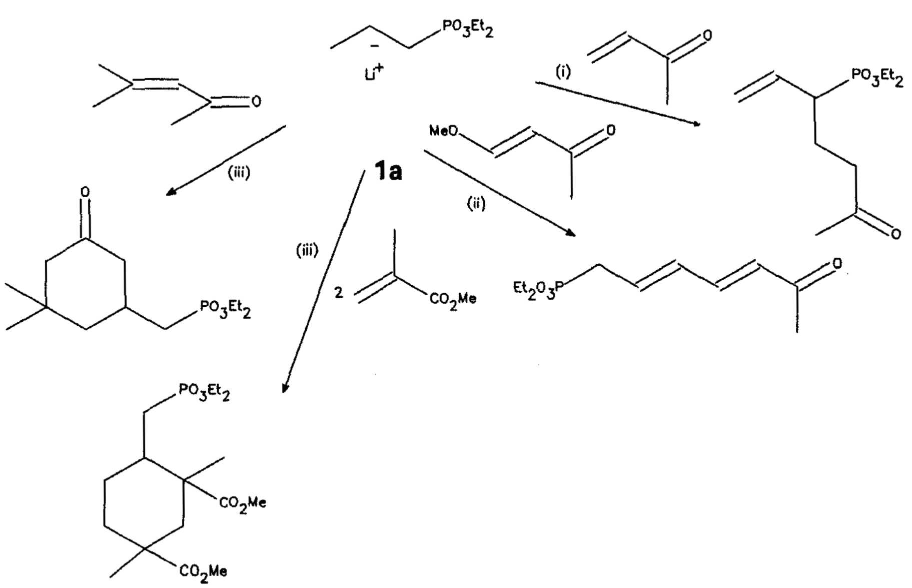


Scheme 1

1-Vinyl-2-hydroxyalkylphosphonates **2** are formed as a pair of diastereoisomers in a ratio not far from 1:1. For the p-nitrobenzaldehyde *α*-adduct (**2a**, R = p-$O_2NC_6H_4$) both diastereomers were separated and isolated in pure state, and the relative configurations of the chiral centers were determined by ^{1}H NMR spectroscopy. Structural assignments obtained from solution data were confirmed by the X-ray determination of the molecular structure of both stereoisomers of **2a**.[2]

The reactions of lithiated **1** with *α,β*-unsaturated ketones and carboxylic esters were also studied,[3] and were found to proceed according to the following patterns:

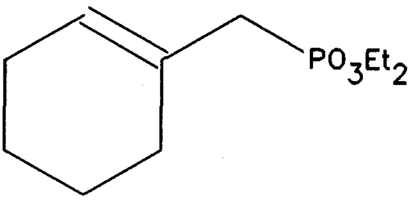
(i) simple nucleophilic addition; (ii) addition - elimination; (iii) multiple addition. Examples of these reactions are given in Scheme 2.



Scheme 2

The mechanisms of the transformations (i) - (iii) are discussed in terms of the nucleophilic reactivity of carbons *α* and *γ* in **1a**, and the electrophilic reactivity of carbon *β* in the intermediate *α,β*-unsaturated phosphonate.

The reaction with aldehydes was then studied using two phosphonates (**4**, **5**) derived from cyclohexene.



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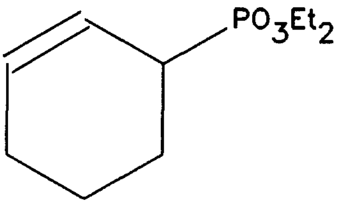
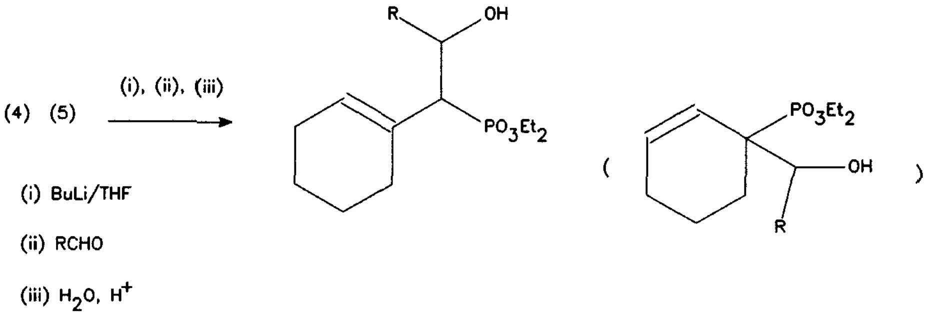


5

Lithiated **4** adds exclusively, and lithiated **5** almost exclusively *via* their *α*-carbon atoms (Scheme 3).



6 **7**

Scheme 3

Products **6** and **7**, upon deprotonation, undergo fragmentation involving the reversal of the addition (recovery of **4** or **5** and of the aldehyde) or the cleavage of the P—C bond (extrusion of the diethylphosphate ion) yielding the corresponding diene. The former fragmentation (reversal of the condensation) represents the major limitation to the synthetic application of the reaction.

For the adduct **6** derived from isobutyric and phenylacetic aldehyde, and for **7** derived from benzaldehyde, one crystalline stereoisomer was isolated in pure state from each pair of diastereoisomers. The molecular structures determined by X-ray diffraction were compared with those deduced from the NMR spectroscopy, showing, as for the stereoisomers of **2a**, close similarity between the solid state structure and the preferred conformation in the solution. The attempts were made to correlate the relative configuration of the chiral centers with the reactivity of a given stereoisomer towards diene formation by analyzing steric factors operating in the transition states for both fragmentation pathways.

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