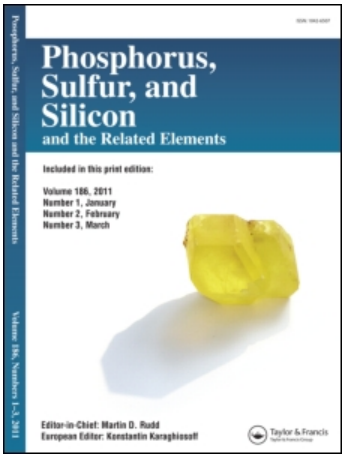

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C-Spirooxyphosphoranyl (P^v) α-Anions. Alkylation and Olefination Chemistry

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C-SPIROOXYPHOSPHORANYL (P^V) α-ANIONS. ALKYLATION AND OLEFINATION CHEMISTRY

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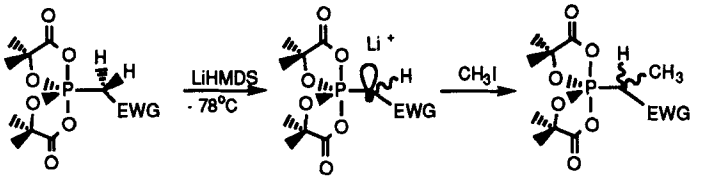
Abstract The chemical features of C-spirooxyphosphoranyl α-anions are investigated toward alkylation and olefination reactions. Proposed mechanistic pathways are based on low temperature ^{31}P-NMR data.

Key Words : spirooxyphosphorane, α-phosphoranyl carbanion, alkylation, olefination.

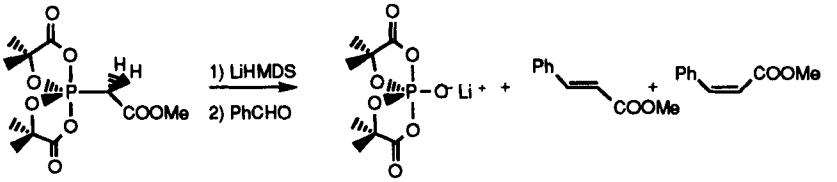
The C-spirooxyphosphorane **1** is selectively deprotonated by LiHMDS at -78°C to obtain one diastereomeric lithiated α-anion **2**.



1 **2** **3**

To examine the reactivity of **2**, the alkylation of these species (EWG = phenyl, α-naphthyl) was performed by addition of CH_3I at -78°C. A diastereomeric alkylated product (**3**) was obtained with low selectivity (9% d.e.). NMR studies suggest that this low selectivity is the result of the epimerization of anion **2** *via* an "ylide-like" form.

Alternatively, the deprotonation of methylester phosphorane **4** (EWG = COOMe) followed by the addition of benzaldehyde showed that the titled species could undergo olefination reaction. In fact, besides phosphorane **5**, a mixture of *E*-**6** and *Z*-**6** is observed with a ratio *E*/*Z* =60/40 (GC-MS). A mechanistic rationale is proposed based on an evaluation of the ^{31}P-NMR data which indicate the presence of a diastereomeric mixture of hexacoordinated organophosporus intermediates. These intermediates equilibrate to a mixture of pentacoordinated organophosphorus species, and they subsequently decompose to the *E*, *Z*-alkenes.



4 **5** ***E*-6** ***Z*-6**