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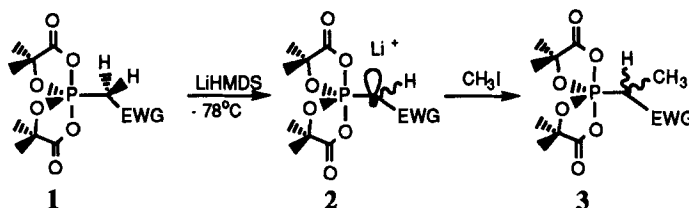
C-SPIROOXYPHOSPHORANYL (P^V) α -ANIONS. ALKYLATION AND OLEFINATION CHEMISTRY

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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**.



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 organophosphorus intermediates. These intermediates equilibrate to a mixture of pentacoordinated organophosphorus species, and they subsequently decompose to the *E*, *Z*-alkenes.

