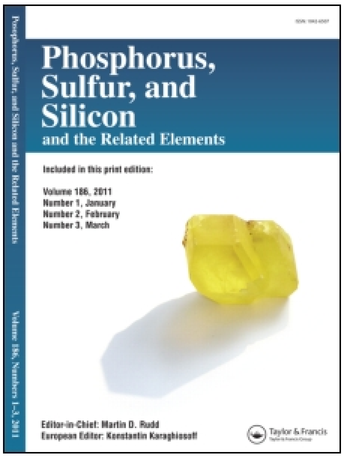

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Phosphate-Phosphonate Rearrangement of Aliphatic Phosphates

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Phosphate-Phosphonate Rearrangement of Aliphatic Phosphates

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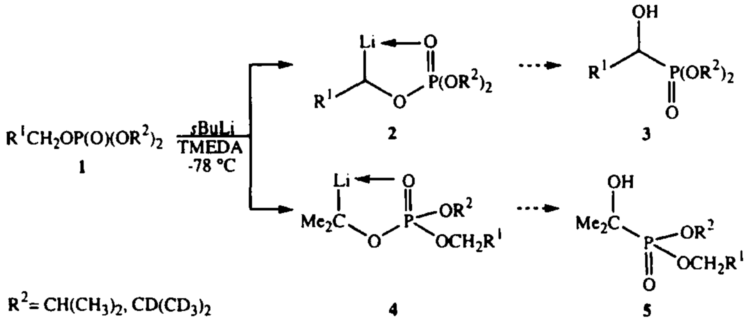
Phosphorylation of various aliphatic alcohols gives phosphates **1** which are deprotonated by *s*BuLi/TMEDA in diethyl ether, THF or hexane at −78 °C. The organo-lithiums **2** and **4** formed isomerize to α-hydroxyphosphonates **3** and **5** (phosphate-phosphonate rearrangement).[1,2]



The portion of **5** depends on the substituents R^1 and R^2 and represents the acidification of a secondary alcohol for deprotonation by the phosphoryl group. The formation of byproduct **5** can be prevented by using *t*Bu or $(CD_3)_2CD$ instead of an *i*Pr group for R^2. The rearrangement occurs with retention of configuration as proven with the phosphate of (*S*)-[1-$^2H_1$]hexanol. Replacing TMEDA by chiral diamines allows the synthesis of chiral, non-racemic α-hydroxyphosphonates.

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[2] F. Hammerschmidt, S. Schmidt, *Monatsh. Chem.*, **1997**, *128*, 1173.