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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Phosphate-Phosphonate Rearrangement of Aliphatic Phosphates

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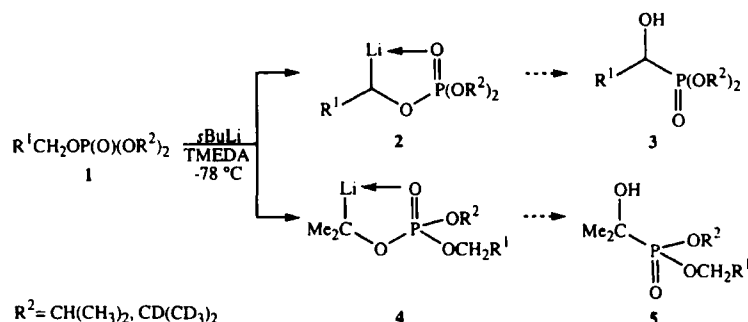
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## Phosphate-Phosphonate Rearrangement of Aliphatic Phosphates

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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  $-78^{\circ}\text{C}$ . The organo-lithiums **2** and **4** formed isomerize to  $\alpha$ -hydroxyphosphonates **3** and **5** (phosphate-phosphonate rearrangement).<sup>[1,2]</sup>



The portion of **5** depends on the substituents  $\text{R}^1$  and  $\text{R}^2$  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  $(\text{CD}_3)_2\text{CD}$  instead of an *i*Pr group for  $\text{R}^2$ . The rearrangement occurs with retention of configuration as proven with the phosphate of (*S*)-[1- $^2\text{H}_1$ ]hexanol. Replacing TMEDA by chiral diamines allows the synthesis of chiral, non-racemic  $\alpha$ -hydroxyphosphonates.

### References

- [1] G. Sturtz, J.-J. Yaouanc, *Synthesis*, **1980**, 289.
- [2] F. Hammerschmidt, S. Schmidt, *Monatsh. Chem.*, **1997**, 128, 1173.