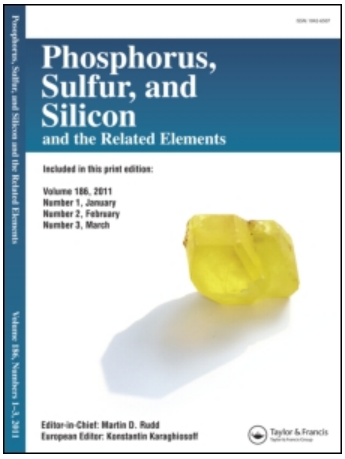

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Sulfur-Functionalized Allyl Anions as Synthetic Building-Blocks

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SULFUR-FUNCTIONALIZED ALLYL ANIONS AS SYNTHETIC BUILDING-BLOCKS

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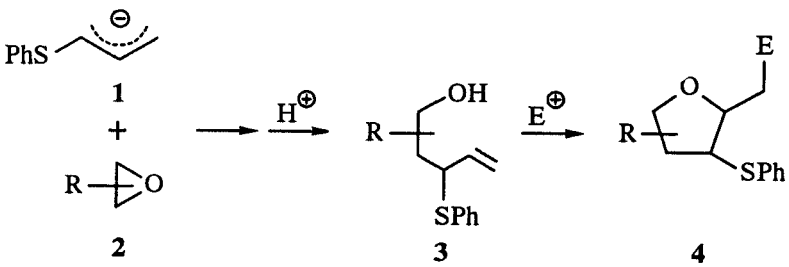
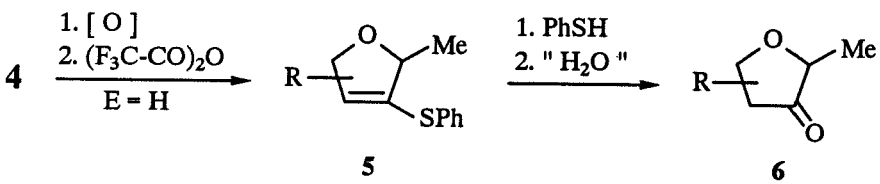
Abstract Ring-opening of epoxides by functionalized allyl anions **1,7,9** is used in the synthesis of furan and pyran derivatives.

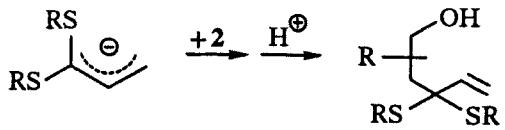
The anion of allyl phenyl sulfide **1** gives a smooth and highly regioselective ring-opening reaction with epoxides **2**:[1]



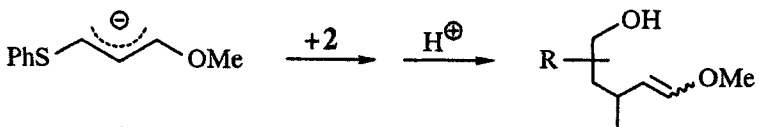
Addition of electrophiles to the unsaturated alcohols **3** leads to cyclization. Products **4** may be subjected to a Pummerer reaction giving in most cases 2,5-dihydrofurans **5**. The latent carbonyl group in **5** can be liberated by consecutive thiophenol addition and hydrolysis.



Alternatively, the latent carbonyl function may already be present in the anionic 3-carbon-building-block, e.g. in the form of a thioacetal group as in **7** or as an enolether as in **9**.[2]

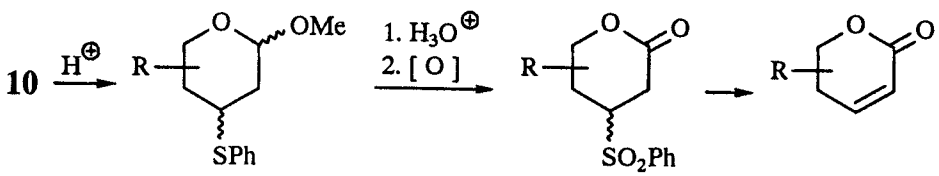


7 **8**



9 **10**

Due to the directing effect of the methoxy group, products **10** cyclize to pyrans **11**. Here, the acetal moiety may be cleaved to a hemiacetal and from there oxidation provides lactones **12**. Treatment with base leads to ready elimination giving unsaturated lactones **13**.



11 **12** **13**

The utility of the approach is demonstrated by an asymmetric synthesis of S-(+)-parasorbic acid.[2]

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1. E. Schaumann, F. Narjes, Phosphorus, Sulfur and Silicon **74**, 395 (1993)
2. F. Narjes, R. Tiedemann, E. Schaumann, Synlett, **1994**, in the press.