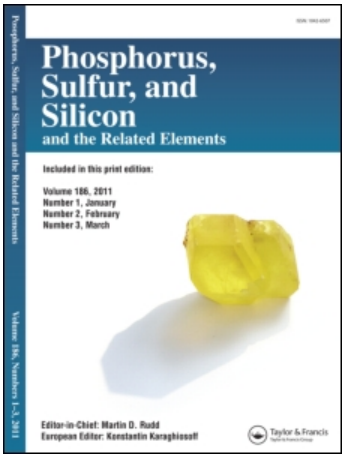

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Sulfur-Mediated Anti-Markovnikov Cyclization of 4- Alkenols

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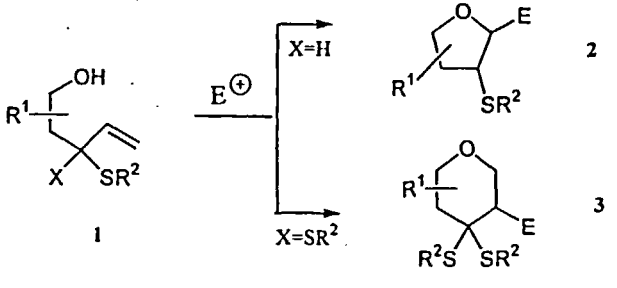
Cyclizations of 3-mono-vs. 3,3-disulfur-substituted 4-alkenols are discussed.

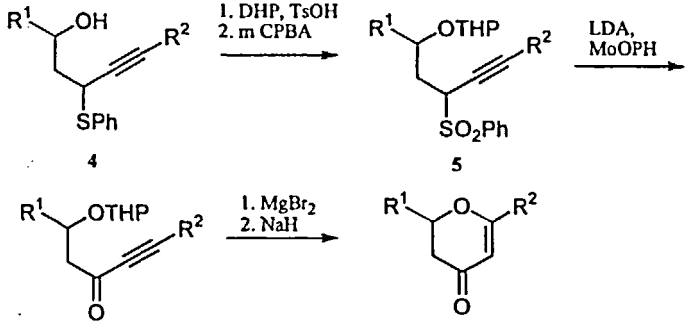
Keywords: regioselectivity; tetrahydrofurans; dihydropyrans; tetrahydropyrans

In the reaction of epoxides with lithiated allyl sulfides, regioselective C-C bond formation occurs to give 3-sulfur-functionalized 4-alkenols **1** (X =H) [1]. The action of electrophiles [proton, Hal^+, $Hg(OAc)^+$] on alkenols **1** (X=H) leads to the expected Markovnikov-controlled formation of functionalized tetrahydrofurans **2**. The ring-opening reaction of ep-



oxides has also been applied to lithiated unsaturated dithioacetals as nucleophiles giving the corresponding alcohols **1** ($X=SR^2$). The subsequent treatment of **1** ($X=SR^2$) with acid gives surprisingly not tetrahydrofurans **2**, but tetrahydropyrans **3** in an apparent anti-Markovnikov cyclization. Control experiments using independently synthesized **2** confirmed that tetrahydropyrans **3** are not secondary products of tetrahydrofurans **2**. Based on trapping reactions, we suggest initial protonation on sulfur to account for the unusual regioselectivity of the ring-closure reaction.

Alternatively, pyrones which are pheromones of moths [2], may be obtained from epoxide ring-opening products by Michael-type ring closure:



References

[1] E. Schaumann, A. Kirschning, F. Narjes, *J. Org. Chem.*, **56**, 717 (1991); E. Schaumann, F. Narjes, Phosphorus, *Sulfur and Silicon*, **74**, 395 (1993).

[2] a) V. Sinnwell, S. Schulz, W. Francke, R. Kittmann, D. Schneider, *Tetrahedron Lett.*, **26**, 1707 (1985) b) I. Kubo, T. Matsumoto, D. L. Wagner, J. N. Shoolery, *Tetrahedron Lett.*, **26**, 563 (1985).