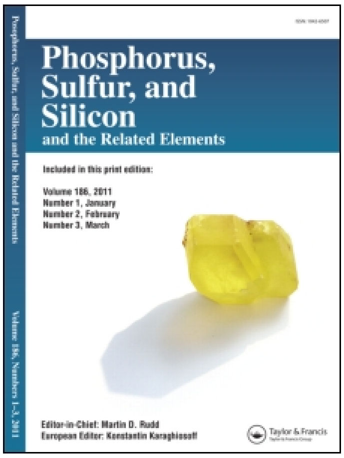

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Diastereoselective Thio-Claisen Rearrangement of S-Allylic α-Silyloxyketene Dithioacetals

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DIASTEREOSELECTIVE THIO-CLAISEN REARRANGEMENT OF S-ALLYLIC α-SILYLOXYKETENE DITHIOACETALS

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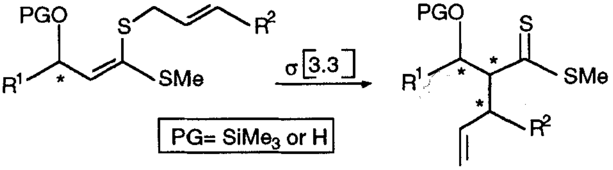
Introduction

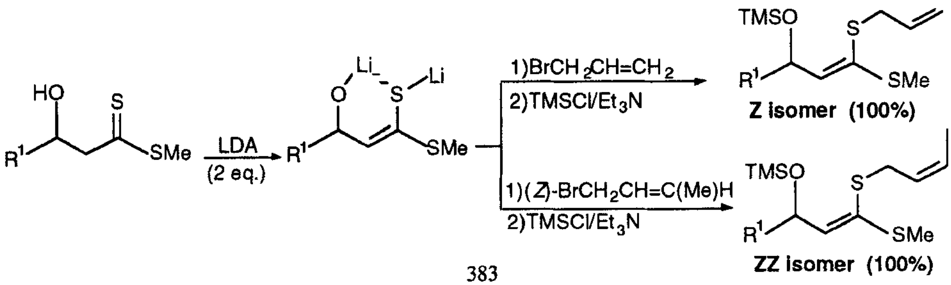
In continuing with the development of the use of the thio-Claisen rearrangement[1] for the diastereoselective formation of carbon-carbon bonds, we wish to report herein the rearrangement of S-allylic α-silyloxyketene dithioacetals (PG= $SiMe_3$).



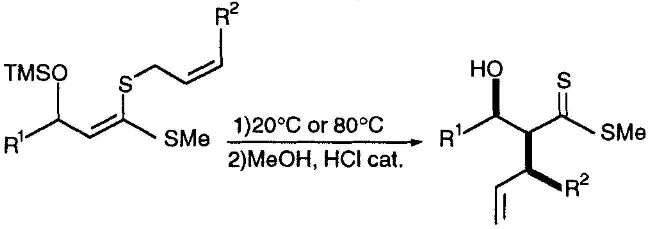
We have previously observed that the corresponding hydroxy analogues (PG= H) undergo, under mild neutral conditions (20-80°C), a thio-Claisen rearrangement to give rise to diastereoisomeric α–allyl-β-hydroxydithioesters.[2-4] Moderate to high diastereoselections were achieved as a result of an asymmetric induction of the remote hydroxy substituted chiral centre. Both steric and stereoelectronic factors were invoked.

Results

Deprotonation of β-hydroxydithioesters by LDA (2.2 eq.), followed by S-alkylation *in situ* with an allylic halide [allyl bromide or (*Z*)-but-2-enyl bromide] and quenching with TMSCl afforded the required O-protected dithioacetals. According to the ^1H NMR spectra, a single isomer was produced. This is ascribed to the rigid chelated structure of the dianionic intermediate; the alkylation occurs next with a net retention of the geometry.



The rearrangement was performed either at room temperature in an ethereal solution or in refluxing cyclohexane (80°C) and followed by removal of the protecting silicon group. The diastereoisomeric distribution of the resulting mixture was determined by HPLC analysis (the products were identified by comparison with a sample prepared from the corresponding unprotected dithioacetal).



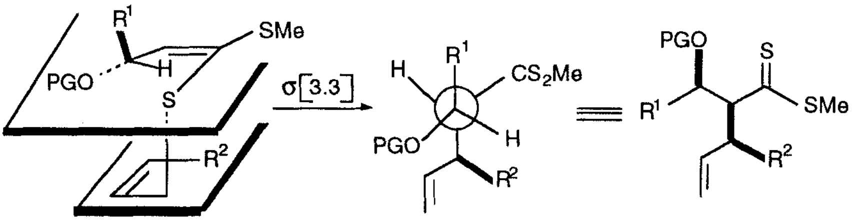
R^1 =Pr^i and R^2 =H, ratio 86 : 14
R^1 =Et and R^2 =Me, ratio 1 : 6 : 90 : 3

The stereochemical outcomes can be summarized as followed:

The rearrangement of the S-allylic ketene dithioacetal (R^1= Pr^i, R^2= H) lead to a mixture consisting mainly of the **syn** diastereoisomer (syn/anti ratio 86 : 14). The diastereoselectivity has not increased (a 96: 4 ratio was observed with the corresponding hydroxy species).

Starting with the S-crotylic ketene dithioacetal (R^1= Et, R^2= Me), four diastereoisomers were detected (ratio 1 : 6 : 90 : 3) and it is the **syn-syn** diastereoisomer which is predominant (90%). The diastereoselectivity has improved (with the hydroxy analogue, it was formed at only 78%).

The rearrangement is believed to take place by way of the following transition state[4] :



References

1. P. Metzner *Synthesis* 1992, 1185-1200.
2. P. Beslin. and S. Perrio *J. Chem. Soc., Chem. Commun.* 1989, 414-415.
3. P. Beslin. and S. Perrio *Tetrahedron* 1992, **48**, 4135-4146.
4. P. Beslin. and S. Perrio *Tetrahedron* 1993, **49**, 3131-3142.