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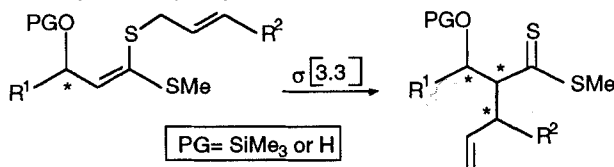
DIASTEREOSELECTIVE THIO-CLAISEN REARRANGEMENT OF S-ALLYLIC α -SILYLOXYKETENE DITHIOACETALS

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Introduction

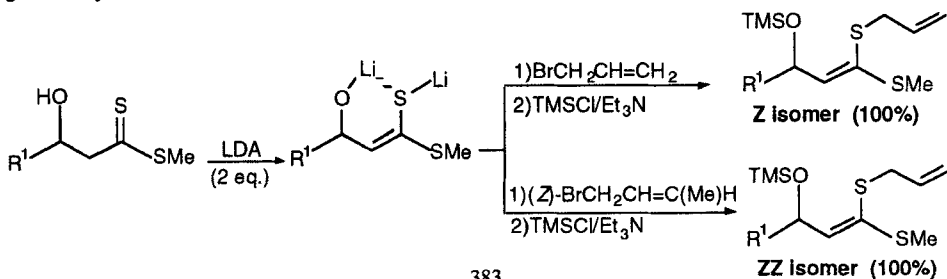
In continuing with the development of the use of the thio-Claisen rearrangement¹ for the diastereoselective formation of carbon-carbon bonds, we wish to report herein the rearrangement of S-allylic α -silyloxyketene dithioacetals (PG= SiMe₃).



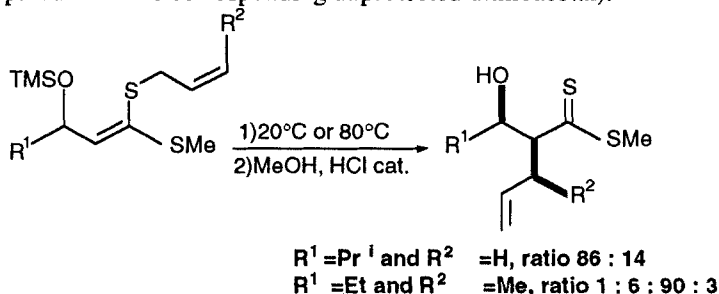
We have previously observed that the corresponding hydroxy analogues (PG= H) undergo, under mild neutral conditions (20-80°C), a thio-Claisen rearrangement to give rise to diastereoisomeric α -allyl- β -hydroxydithioesters.²⁻⁴ Moderate to high diastereoselections were achieved as a result of an asymmetric 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).

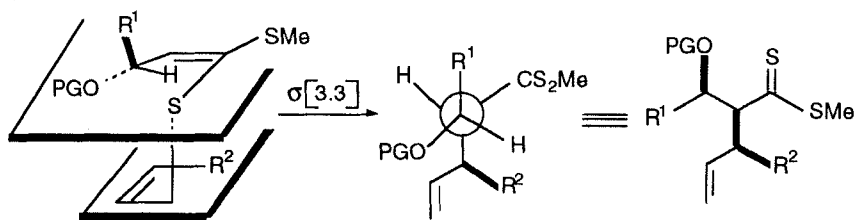


The stereochemical outcomes can be summarized as followed:

The rearrangement of the S-allylic ketene dithioacetal ($R^1 = \text{Pr}^i$, $R^2 = \text{H}$) 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 ($R^1 = \text{Et}$, $R^2 = \text{Me}$), 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 state⁴:



References

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4. P. Beslin. and S. Perrio *Tetrahedron* 1993, **49**, 3131-3142.