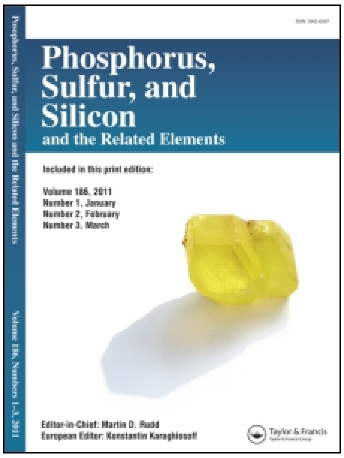

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Stereochemistry of Protiodesilylation of 3-Trimethylsilyl-2-Thiabicyclo[2.2.1]Heptenes, Heptanes and Derivatives

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STEREOCHEMISTRY OF PROTIODESILYLATION OF 3-TRIMETHYLSILYL-2-THIABICYCLO[2.2.1]HEPTENES, HEPTANES AND DERIVATIVES.

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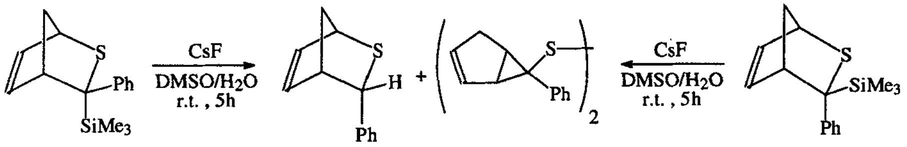
Abstract Some 3-trimethylsilyl-2-thiabicyclo[2.2.1]heptenes and heptanes of known configuration were protiodesilylated and the stereochemistry of the reaction was studied. Evidences for a carbanionic intermediate as well as the pivotal role played by the metal counter-ion are described.

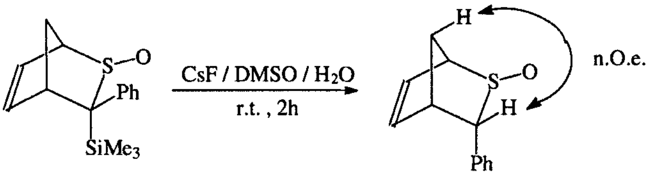
A variety of compounds containing the Si-C-S unit can be synthesised from silyl thioketones. Subsequent protiodesilylation of these compounds gives products formally derived from thioaldehydes[1]. In this context we examined the stereochemistry of cesium fluoride promoted protiodesilylation in stereochemically and conformationally defined systems 1 and 2, obtained by cycloaddition of phenyltrimethylsilyl thioketone with cyclopentadiene. The presence of a sulphur atom α to silicon that can be oxidised to sulphoxide 3 or sulphone 4 and 5, might modulate the stability of negatively charged intermediates. The protiodesilylation of both the endo 1 and exo 2 sulphides afforded stereospecifically the endo-phenyl derivative 6 beside the disulphide 7 in a 1:1 ratio (chart 1).



1 6 7 2

CHART 1

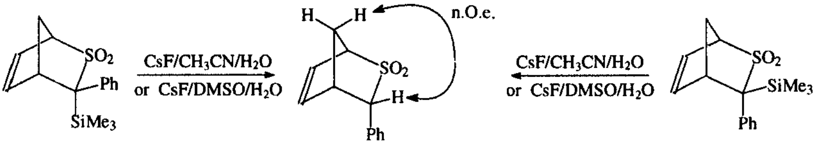
Protiodesilylation of 3-endo-silyl-2-exo-sulphoxide 3 gave the endo-phenyl derivative 8 with complete inversion at C-3 (chart 2).



3 8

CHART 2

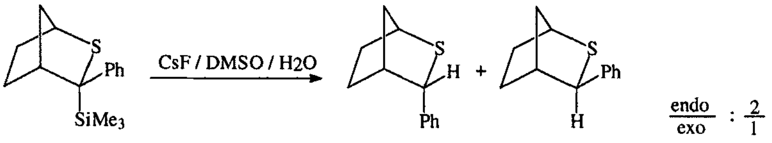
Protiodesilylation of both the endo 4 and the exo 5 S,S-dioxides produced only the endo-phenyl derivative 9 (chart 3). Configurations of 8 and 9 were determined by n.O.e. experiments.



4 9 5

CHART 3

The stereoconvergence observed in the cases so far described could simply be explained in terms of an attack of the proton donor from the sterically less hindered exo-side onto a common carbanionic intermediate. On the other hand, this model fails to explain the lack of stereospecificity we observed in the protiodesilylation of the corresponding thiabicycloheptane 10 (chart 4).



10 11

CHART 4

Therefore, the high stereospecificity observed on the desilylation of the unsaturated compounds can be better explained by taking into account an interaction between the carbon-carbon double bond and the cesium counter ion, that should occur preferentially on the endo-face, thus shielding this side of the molecule from the electrophile.

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