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### Stereochemistry of Protodesilylation 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<sup>1</sup>. 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  $\alpha$  to silicon that can be oxidised to sulfoxide **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).

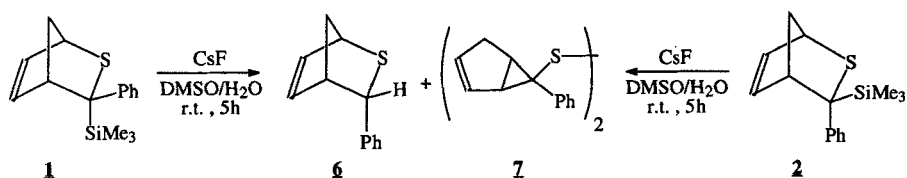


CHART 1

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

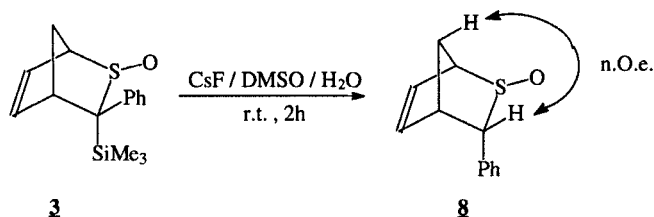


CHART 2

Protidesilylation 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.

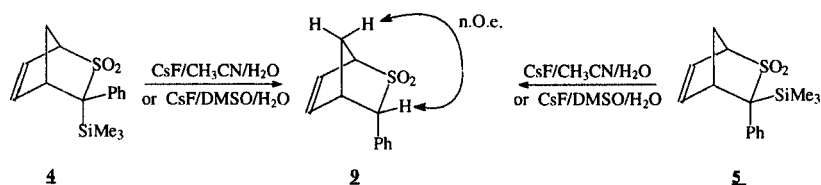


CHART 3

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 protidesilylation of the corresponding thiabicycloheptane 10 (chart 4).

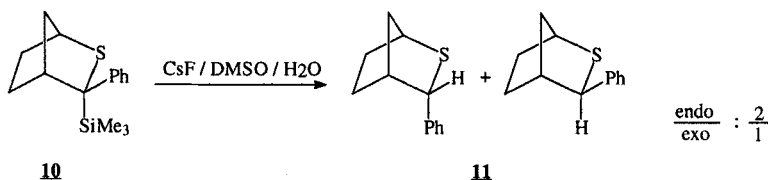


CHART 4

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.

## REFERENCES

1. B. F. Bonini, Phosphorus, Sulphur and Silicon, **74**, 31 (1993).