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Highly Stereoselective Vinylogous Pummerer Rearrangement

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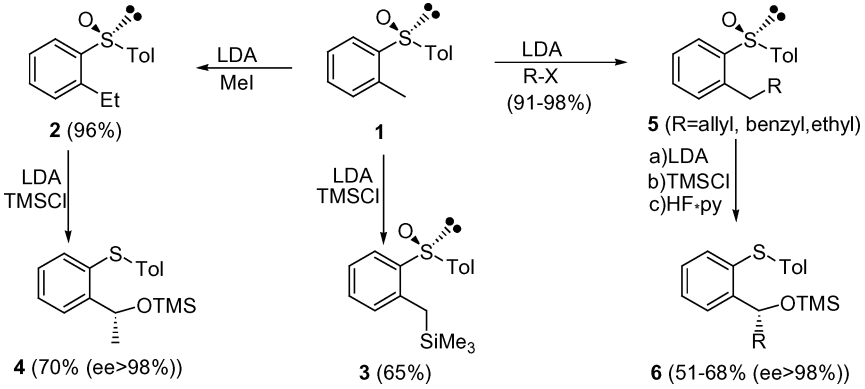
The Pummerer reaction has received considerable attention as a synthetically useful process.[1] Recently, our research groups have published an interesting example of a new asymmetric vinylogous tin-induced Pummerer rearrangement.[2] Now, we present our results dealing with an unprecedented vinylogous sila-Pummerer rearrangement,[3] which occurs in a completely stereoselective manner.



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It was observed that when an ortho-sulfinyl carbanion derived from sulfoxide **2**[4] was treated with LDA and TMSCl, the TMS-protected alcohol **4** was obtained with remarkably high enantioselectivity (ee > 98%) and good yield (70%).[5] By contrast, under identical conditions, sulfoxide **1** (R=H) was found to undergo a clean carbosilylation reaction at the benzylic position, furnishing compound **3** as the exclusive product. Steric hindrance at the carbanionic position accounts for the observed differences.

We studied the reactions of compounds **5** (prepared in high yields by reaction of **1** with LDA and the corresponding alkyl halide) with LDA and TMSCl, and observed the formation of the sila-Pummerer rearrangement products. These results reveal a wide scope for this new sila-Pummerer reaction.

REFERENCES

[1] M. Kennedy and M. A. McKervey in *Comprehensive Organic Synthesis*, B. M. Trost, Ed. (Pergamon: Oxford, 1991), Vol. 7, pp. 193–217; A. Padwa, D. E. Gunn, and H. M. Osterhout, *Synthesis*, 1353 (1997).
[2] J. L. García Ruano, J. Alemán, and A. Padwa, *Org. Lett*., **6,** 1757 (2004).
[3] E. Block and M. Aslam, *Tetrahedron*, **44**, 284 (1988) and references therein.
[4] J. L. García Ruano, M. C. Carreño, M. A. Toledo, J. M. Aguirre, M. T. Aranda, and J. Fisher, *Angew. Chem., Int. Ed. Eng*., **39,** 2736 (2000).
[5] J. L. García Ruano, J. Alemán, M. T. Aranda, M. J. Arevalo, and A. Padwa, *Org. Lett*. (submitted).