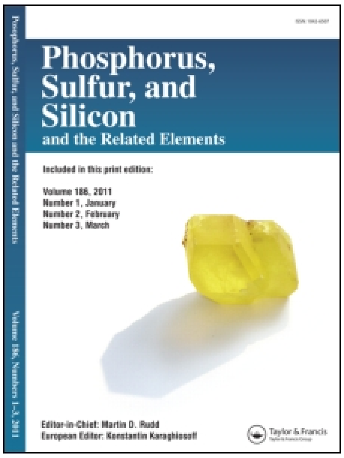

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Metalated 2-Alkenylsulfoximines: Reactivity and NMR-Spectroscopic Studies

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METALATED 2-ALKENYLSULFOXIMINES: REACTIVITY AND NMR-SPECTROSCOPIC STUDIES

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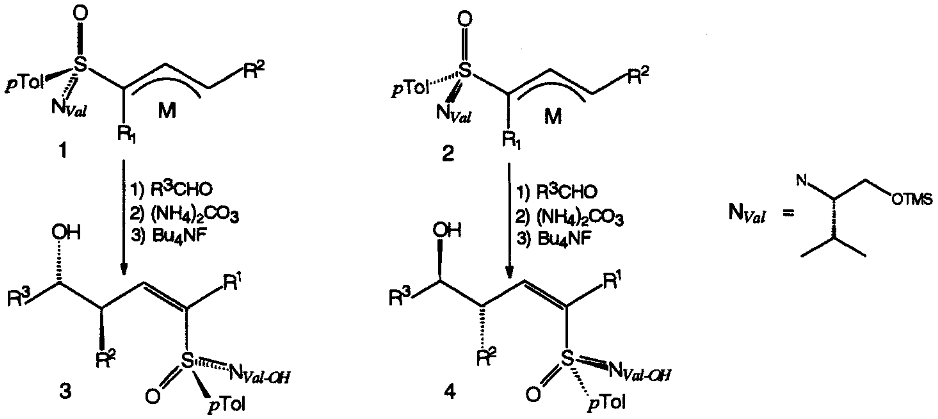
Abstract: Enantiomerically pure, metalated 2-Alkenylsulfoximines were used to prepare γ-hydroxyvinylsulfoximines yielding very high diastereomeric excesses. Experiments with epimeric mixtures and NMR-spectroscopic studies of the lithiated intermediates demonstrate their configurational lability as opposed to the assumed configurational stability of the titanium compound.

The majority of synthetic methods at hand today, for the stereocontrolled construction of carbon frameworks, are applications of polar organometallic chemistry. There are few modern synthesis' of natural products not relying on carbon nucleophiles in their stereochemical key-steps. So their is a need to develop new, even more efficient methods and to think about models to rationalize the stereochemical outcome of these reactions.

For a new asymmetric reaction the direction and extend of the attainable asymmetric induction should be predictable. For the practical implementation of such reagent-controlled asymmetric conversions electrophilic substitutions on enantiomerically pure and configurationally stable organometallics are a promising solution. Here stereocontrol is dominated by the reaction mechanism and not by substrate dependend steric effects.

We describe here for the first time the application of this concept to enantiomerically pure, *acceptor substituted* 2-alkenylmetal compounds being a chiral sulfimidoyl group responsible for facile deprotonation and high asymmetric induction during the transmetalation und hydroxyalkylation steps. (scheme 1).[1,2]



SCHEME 1 Asymmetric γ-hydroxyalkylation of metalated 2-Alkenyl-sulfoximines.

The sulfoximines 1 and 2 combine two - at first sight - incompatible properties: Acidification of protons in α-position by an electron withdrawing group within a conjugated π-system and stereocontrol through electrophilic substitution (S_E2') at a uniformly configured carbon atom. This is attained by a diastereoface differentiating transmetalation on the *configurationally labile* lithiosulfoximines (scheme 1, M=Li) leading to the corresponding 2-alkenyltitanium compounds (scheme 1, $M=TiL_3$), which can be transformed to enantio- and diastereomerically pure γ-hydroxyvinylsulfoximines 3 und 4 (scheme 1, 10 examples, *ds* ≥ 97%). Multidimensional NMR spectroscopy and distance geometry calculations allow for the simultanous determination of configuration and conformation of molecules in solution.[3,4,5] In accordance with the given interpretation of the stereochemical outcome of the reaction, the NOESY data (195K, THF-d^8) from the lithium species do not fulfil the geometric requirements for a single structure. From the distance geometry calculations we derive the existance of two (or more) rapidly interconverting isomers, supporting the results from the hydroxyalkylation reactions.

REFERENCES

1. M. Reggelin, H. Weinberger, Tetrahedron Letters, 33, 6959 (1992).
2. M. Reggelin, H. Weinberger, Angew. Chem. Int. Ed. Engl., 33, 444-446 (1994).
3. M. Reggelin, H. Hoffmann, M. Köck, D.F. Mierke, J. Am. Chem. Soc., 114, 3272-3277 (1991).
4. D. F. Mierke, M. Reggelin, J. Org. Chem., 57, 6365-6367 (1992).
5. M. Reggelin, M. Köck, K. Conde-Frieboes, D.F. Mierke, Angew. Chem. Int. Ed. Engl. 33, 753-755 (1994).