

A NEW BOOK FOR *Biochemists.*

Topics in Lipid Research From Structural Elucidation to Biological Function

Edited by R. A. Klein and B. Schmitz
Molteno Institute, University of Cambridge

Over the last decade many lipid chemists and biochemists have made a conscious effort to move from purely structural investigations to those which throw more light on the biological function of lipid molecules.

For many years lipids were considered to be molecules containing just C, H and O, related to fatty acids and hydrocarbons, with high oil-water partition coefficients; more recently, however, it has been realised that the more complex structures such as glycolipids and lipoproteins, and

indeed glycolipoproteins, are fascinating both as structural challenges and as functional elements of the cell.

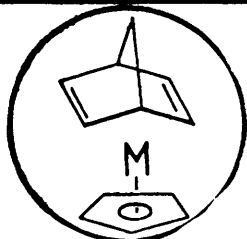
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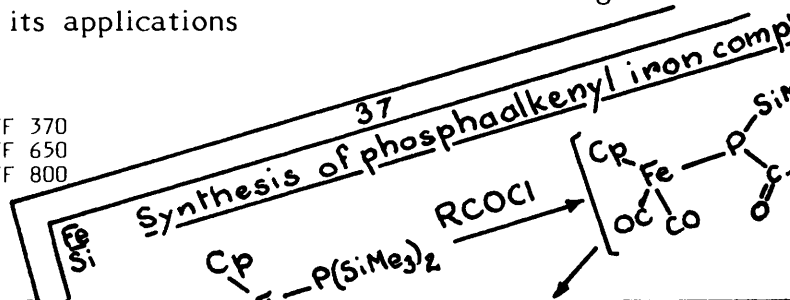
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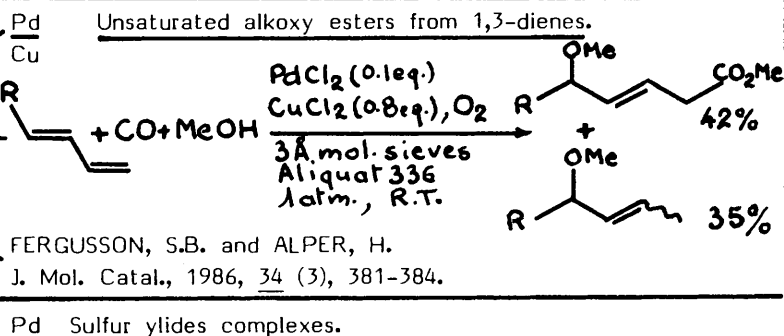
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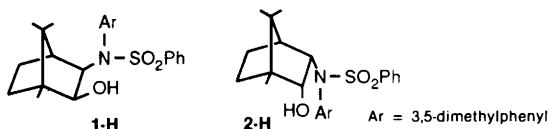
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Helmchen Chiral Auxiliaries

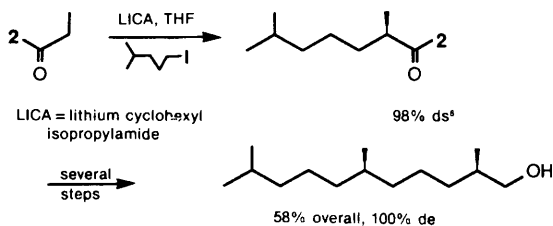


In 1981, Professor Helmchen's research group at the University of Stuttgart (now at the University of Heidelberg) discovered that esters prepared from chiral auxiliaries **1-H** and **2-H** displayed remarkable diastereoselectivity during alkylation reactions of their derived enolates.¹ Since *Z* and *E* enolates are known to form with high selectivity under appropriate reaction conditions [e.g., the *Z* enolate predominates in THF, whereas the *E* enolate is the major isomer in THF/HMPT (4:1)],² it is possible to prepare both diastereoisomeric adducts by utilizing the *same* chiral auxiliary and simply changing the reaction medium. The auxiliaries can be attached to and nondestructively removed from the substrates employing simple chemical reactions, resulting in the formation of chiral products with almost complete enantiomeric purity.

The synthetic utility of these reagents is clearly evident from the following asymmetric transformations.

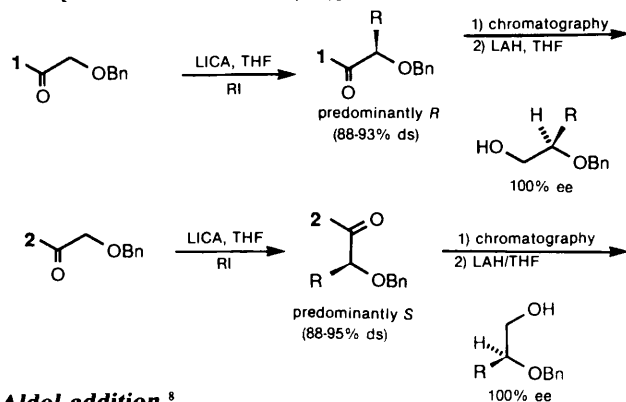
Enolate alkylation^{1,3,4} and cycloalkylation⁵

Synthesis of Vitamin E side chain:³



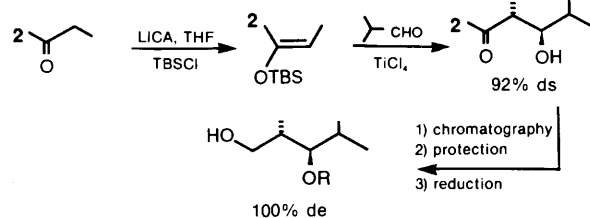
Synthesis of optically pure diols⁷

Unlike the enolate alkylation, the product ratio obtained from glycolate alkylation is the same regardless of the solvent composition [THF or THF/HMPT (4:1)]:



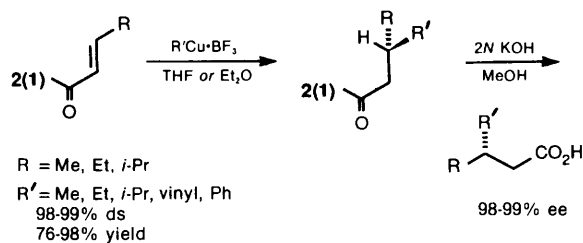
Aldol addition⁸

O-silyl ketene acetals derived from acetates and propionates undergo aldol addition under Mukaiyama conditions⁹ with a high degree of *anti*-diastereoselectivity:



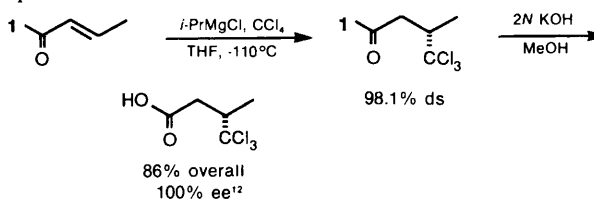
Conjugate addition¹⁰

Conjugate addition of a variety of organocopper reagents to α,β -unsaturated esters prepared from **1-H** and **2-H** also proceeds with high diastereoselectivity ($\geq 99:1$ in most cases):



Synthesis of enantiomerically pure (*S*)-3-trichloromethyl butanoic acid¹¹

An interesting application of the Helmchen auxiliary **1-H** is its use in a simple synthesis of (*S*)-3-trichloromethylbutanoic acid, a logical precursor to a number of polyhalogenated marine natural products.



These versatile reagents promise to find wide application in the field of asymmetric organic synthesis.

References and Notes:

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- (4) Helmchen, G.; Selim, A.; Dorsch, D.; Tauber, I. *ibid.* **1983**, *24*, 3213.
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- (6) ds = diastereoselectivity. For a definition of % ds, see Seebach, D.; Naef, R. *Helv. Chim. Acta* **1981**, *64*, 2704.
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- (10) Helmchen, G.; Wegner, G. *Tetrahedron Lett.* **1985**, *26*, 6051.
- (11) *Idem ibid.* **1985**, *26*, 6047.
- (12) A 100% enantiomeric purity was obtained for the intermediate ester after two recrystallizations.

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