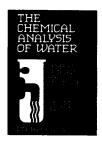


The Chemical Analysis of Water: General Principles and Techniques 2nd Edition



by A. L. Wilson and D. T. E. Hunt, Water Research Centre, Medmenham

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This new edition covers the considerable developments which have taken place in the eleven years since the first edition was published, in the measurement of water quality with particular reference to methods for estimating and controlling possible errors in analytical results.

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Oppolzer's Chiral Auxiliaries

These chiral auxiliaries display excellent π -topological differentiation on reactions of their acryloyl (e.g., Diels-Alder, conjugate addition, hydrogenation)¹⁻⁶ as well as their enolate derivatives.^{5,7,9} Thus, chiral products are obtained in >90% diastereomeric excess (de) many of which can be purified to virtually 100% de by recrystallization. The auxiliaries are easily attached to the substrates and nondestructively removed from the products (e.g., by hydrolysis, transesterification and reduction) to give synthetically useful building blocks in high enantiomeric purity.

The following reaction schemes highlight a variety of recent asymmetric transformations which are directed by Oppolzer's auxiliaries.

Intermolecular Diels-Alder reaction 1-4

Preparation of a virtually pure chiral loganin precursor:

Intramolecular Diels-Alder reaction3

Conjugate addition⁵

Enolate alkylation⁵

Southern corn rootworm pheromone

Asymmetric α -acetoxylation

Synthesis of chiral α-hydroxyacids and glycols:⁷

Asymmetric α -halogenation

Synthesis of chiral halohydrins and epoxides:9

α-Amino acid synthesis10

Following this protocol, the combination of $C(\beta)$ -alkylation (conjugate addition) with $C(\alpha)$ -halogenation provided the uncommon amino acid L-allo-isoleucine [(2S) - 99.3% ee, (3R) - 97.8% ee], an essential precursor in the synthesis of the psychotropic ergot peptide epicriptine.

Asymmetric hydrogenation⁶

A series of β , β -dialkylacrylamides prepared from auxiliary 3 gave reduced products of high diastereomeric excess on simple hydrogenation with H_2 and Pd/C.

References and notes:

1) Oppolzer, W. Angew. Chem., Int. Ed. Engl. 1984, 23, 876. 2) Oppolzer, W.; Chapuis, C., Bernardinelli, G. Helv. Chim. Acta 1984,67, 1397. 3) Oppolzer, W.; Dupuis, D.; Tetrahedron Lett. 1985, 26, 5437. 4) Vanderwalle, M. et al. Tetrahedron, in press. 5) Oppolzer, W.; Dudfield, P.; Stevenson, T.; Godel, T. Helv. Chim. Acta 1985, 68, 212. 6) Oppolzer, W.; Mills, R.J.; Reglier, M. Tetrahedron Lett. 1986, 27, 183. 7) Oppolzer, W.; Dudfield, P. Helv. Chim. Acta 1985, 68, 216. 8) Acyl derivatives of auxiliaries 1 and 2 were prepared from the acid chloride with AgCN and those employing auxiliaries 3 and 4 were prepared with NaH and the acid chloride. 9) Oppolzer, W.; Dudfield, P. Tetrahedron Lett. 1985, 26, 5037. 10) Oppolzer, W.; Pedrosa, R.; Moretti, R. ibid. 1986, 27, 831.

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