

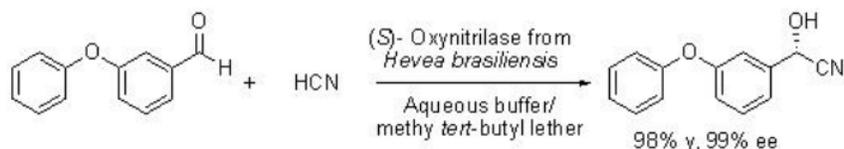
11.2: Formation of Carbon-Carbon Bonds

Biocatalysts are turned out to be versatile catalysts for carbon-carbon bond forming and reduction reactions in organic synthesis.

Carbon-carbon bond formation belongs to the heart of organic synthesis. The biocatalyzed route provides effective tool for the construction of carbon-carbon with excellent enantioselectivity.

Hydrocyanation of Aldehydes

The biocatalytic hydrocyanation of aldehydes is one of the oldest methods in organic synthesis. One of the well-established technologies for the large-scale hydrocyanation of aldehydes is the oxynitrilase (Griengl process) catalyzed production of (*S*)-phenoxybenzaldehyde cyanohydrins, which is an important intermediate for the industrial pyrethroid manufacture (Scheme 11.2.1). This method is turned out to be useful for the reactions of numerous aldehydes.

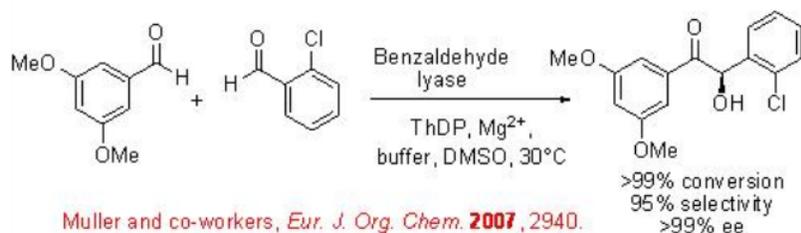


A. Liese, K. Seelbach, C. Wandrey, *Industrial Biotransformations Weinheim: Wiley-VCH, 2006*.

Scheme 11.2.1

Benzoin Condensation

The development of an asymmetric cross-benzoin condensation *via* enzymatic cross-coupling reactions is a synthetically useful process. Highly enantiomerically enriched mixed benzoin condensation can be obtained from two different substituted benzaldehydes using benzaldehyde lyase as a catalyst (Scheme 11.2.2). One of the aldehydes acts as acceptor, whereas the other one acts as donor.

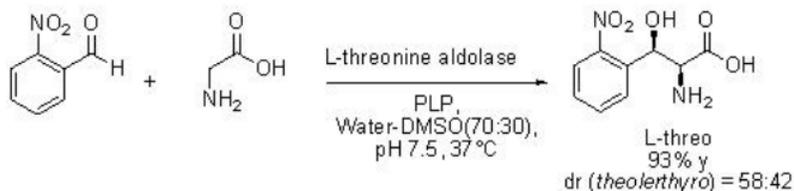


Muller and co-workers, *Eur. J. Org. Chem.* **2007**, 2940.

Scheme 11.2.2

Aldol Reaction

The biocatalytic aldol reactions are highly specific with respect to donor component, whereas a broad substrate scope is observed for the acceptor molecules. One of the examples is the reaction of glycine (donor) with substituted benzaldehyde (acceptor) employing threonine aldolases to give α -amino β -hydroxy acids with excellent enantioselectivity (Scheme 11.2.3).



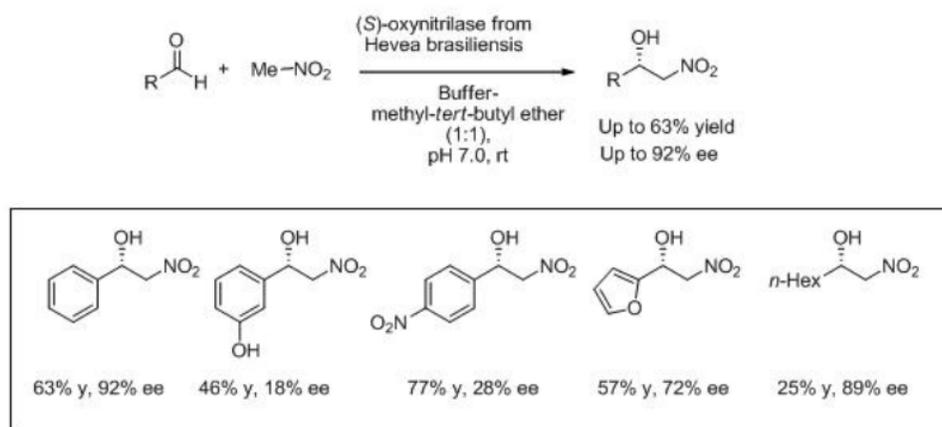
T. Kimura, et al., *J. Am. Chem. Soc.* **1997**, 119, 11734.

Scheme 11.2.3

Nitroaldol Reaction

Enzymes are also useful for the non-natural reactions. For example, using (*S*)-oxynitrilase the reaction of nitromethane with a broad range of aldehydes can be accomplished with excellent enantioselectivity (Scheme 11.2.4). Nitroalkane acts donor, whereas the

aldehydes are acceptors.



T. Purkarthofer et al., *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 3454.

Scheme 11.2.4

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