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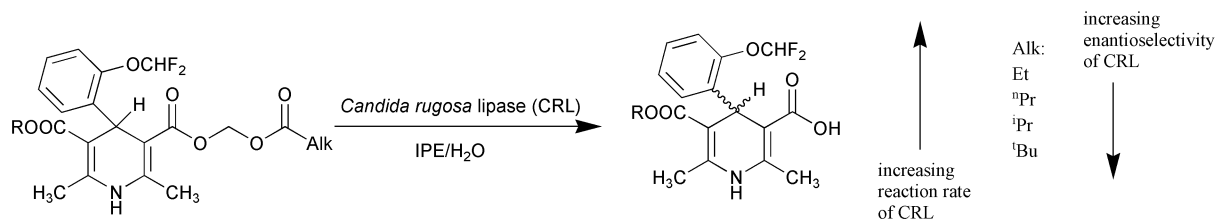
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Perkin 1 Abstracts: Biocatalysis in Organic Synthesis aims to cover recent literature concerning the applications of enzymes and micro-organisms as catalysts in organic synthesis. The abstracts will emphasise the key synthetic step(s) that are mediated by the biocatalyst. Emerging technologies for biocatalyst design and optimisation will also be included.

Kinetic resolution of substituted 1,4-dihydropyridine 3,5-diester

Lipase

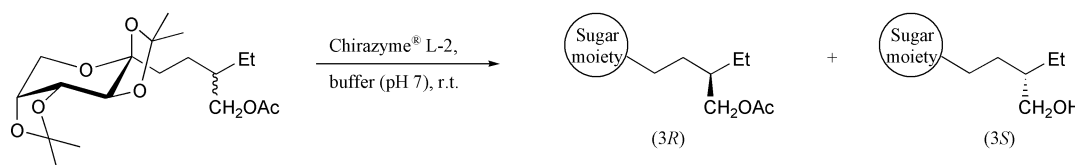


A. Sobolev, M. C. R. Franssen, B. Vigante, B. Cekavicus, R. Zhalubovskis, H. Kooijman, A. L. Spek, G. Duburs and A. de Groot, *J. Org. Chem.*, 2002, **67**, 401.

Seven acyloxymethyl esters of 5-methyl- and 5-(2-propoxyethyl)-4-[2-(difluoromethoxy)-phenyl]-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate were synthesized and subjected to *Candida rugosa* lipase (CRL) catalysed hydrolysis in wet diisopropyl ether.

Lipase catalysed resolution of a dec-6-ulose derivative

Lipase

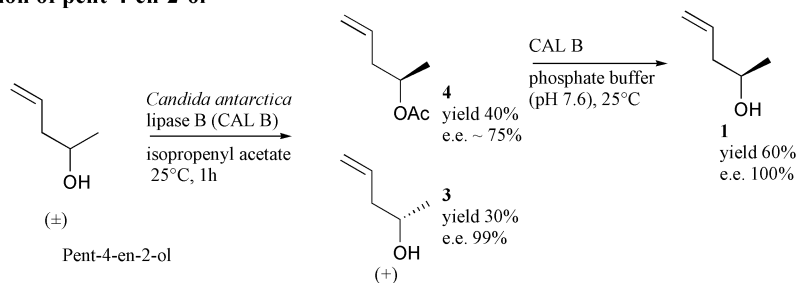


I. Izquierdo, M. T. Plaza, M. Rodríguez and J. A. Tamayo, *Eur. J. Org. Chem.*, 2002, 309.

The corresponding acetylation reaction using the racemic alcohol gave the 3*S* acetate and unreacted 3*R* alcohol but with poorer e.e. The products were intermediates in the synthesis of (-)-talaromycins C and E.

Resolution of pent-4-en-2-ol

Lipase

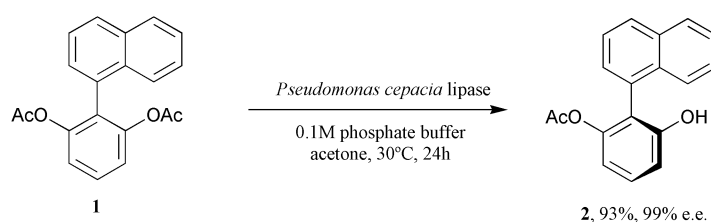


M. G. Banwell, K. A. Jolliffe, D. T. J. Loong, K. J. McRae and F. Vounatsos, *J. Chem. Soc., Perkin Trans. 1*, 2002, 22.

The enantiomerically pure alcohol 1 was used as an intermediate in the synthesis of (-)-cladospolide A.

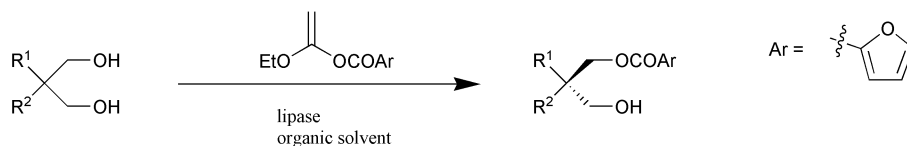
Desymmetrisation of axially chiral biaryls

Lipase



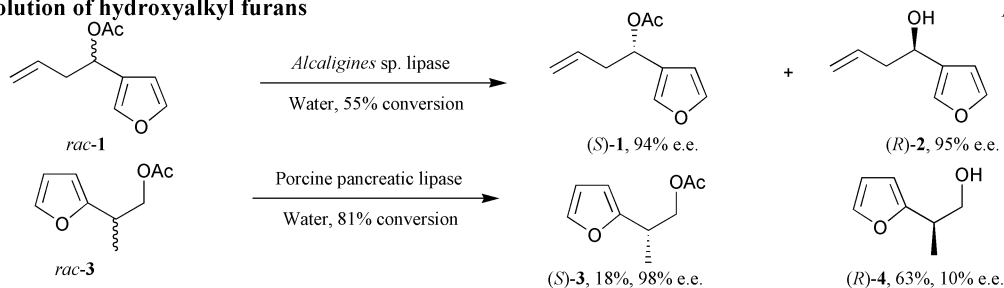
T. Matsumoto, T. Konegawa, T. Nakamura and K. Suzuki, *Synlett*, 2002, 122.

The enzymatic desymmetrisation of biaryl compounds was reported. A series of four diacetates of type 1 were successfully desymmetrised using lipases from either *Pseudomonas cepacia* or *Candida antarctica*.

Lipase-catalysed enantioselective desymmetrization of pro-chiral and meso diols
Lipase


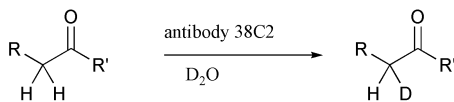
S. Akai, T. Naka, T. Fujita, Y. Takebe, T. Tsujino and Y. Kita, *J. Org. Chem.*, 2002, **67**, 411.

An efficient lipase-catalysed desymmetrization of prochiral 2,2-disubstituted propane-1,3-diols was developed using 1-ethoxyvinyl 2-furoate, for which well-known methods, using vinyl or isopropenyl acetate, had limited success due to the low reactivity and easy racemisation of products through acyl group migration.

Kinetic resolution of hydroxyalkyl furans
Lipase/esterase


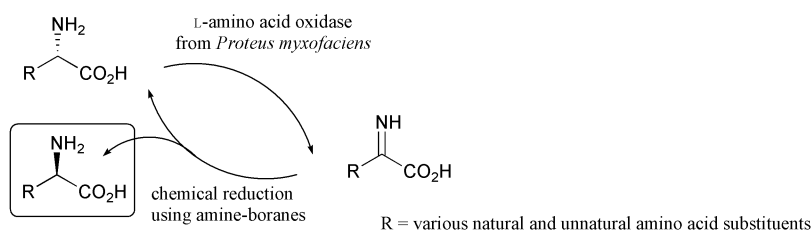
A. Bierstedt, J. Stöling, R. Fröhlich and P. Metz, *Tetrahedron: Asymmetry*, 2001, **12**, 3399.

A series of lipases was screened for the ability to resolve alcohols **2** and **4** via transesterification or hydrolysis of the corresponding acetates **1** and **3**. The latter approach, illustrated, gave the best results.

Deuteration of carbonyl compounds
Aldolase


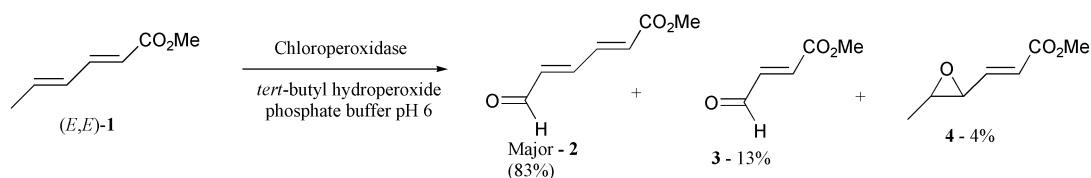
A. Shulman, D. Sitry, H. Shulman and E. Keinan, *Chem. Eur. J.*, 2002, **8**, 229.

The aldolase antibody 38C2 catalysed deuteration was studied for a variety of ketones, aldehydes and bifunctional ketones. From these studies it was concluded that the antibody 38C2 is able to accept a wide range of substrates, with high rates and rate enhancement values. It was possible to determine aspects of the mechanism and mapping of the active site from the rate information. The mechanism of the 38C2 catalysed aldol reaction was also discussed.

Deracemisation of DL-amino acids using an amino acid oxidase
Amino Acid Oxidase


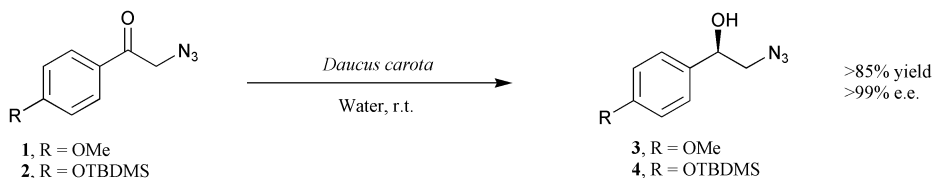
F.-R. Alexandre, D. P. Pantaleone, P. P. Taylor, I. G. Fotheringham, D. J. Ager and N. J. Turner, *Tetrahedron Lett.*, 2002, **43**, 707.

The deracemisation of DL- α -amino acids using amino acid oxidase and amine-boranes as chemical reducing agents is reported. Starting from the racemate, a range of D-amino acids were obtained in yields of up to 90% and e.e. >99%.

Chloroperoxidase-catalysed oxidation of conjugated dienoic esters
Chloroperoxidase


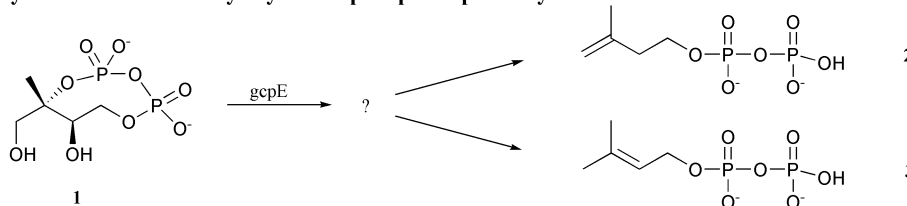
D. J. Bougioukou and I. Smonou, *Tetrahedron Lett.*, 2002, **43**, 339.

The chloroperoxidase catalysed oxidations of the isomeric conjugated dienoic esters methyl (2*E*,4*E*)-**1**, methyl (2*Z*,4*E*), methyl (2*Z*,4*Z*) and methyl (2*E*,4*Z*)-hexadienoate are reported.

Asymmetric reduction of azidoketones
Daucus carota


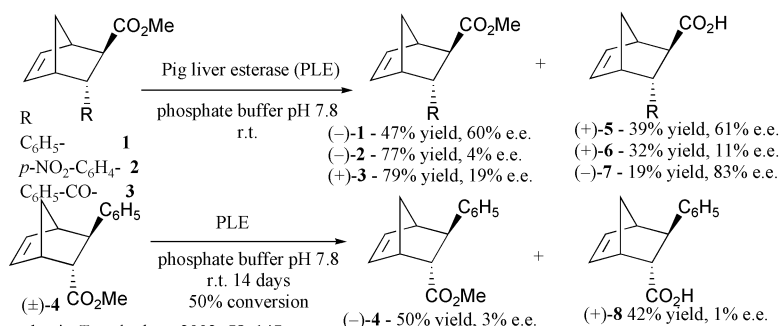
J. S. Yadav, P. T. Reddy, S. Nanda and A. Bhaskar Rao, *Tetrahedron: Asymmetry*, 2001, **12**, 3381.

Cultures of *Daucus carota*, a plant-derived biocatalyst, were reported to reduce azidoketones **1** and **2** to the chiral alcohols **3** and **4** with high yield and high enantioselectivity. Alcohols **3** and **4** were then used in stereoselective syntheses of naturally occurring hydroxyamides such as (*R*)-(-)-denopamine.

Isoprenoid biosynthesis via the methylerythritol phosphate pathway
Escherichia coli


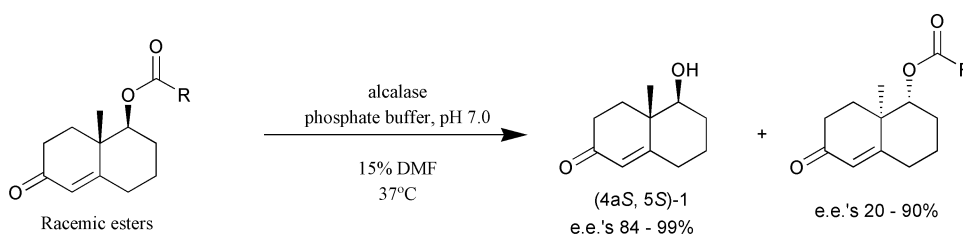
M. Seemann, N. Campos, M. Rodríguez-Concepcion, J.-F. Hoeffler, C. Grosdemange-Billiard, A. Boronat and M. Rohmer, *Tetrahedron Lett.*, 2002, **43**, 775.

A study of the unknown genes in the 2-*C*-methyl-D-erythritol (ME) phosphate pathway to isoprenoids is reported. The *gcpE* gene was found to be necessary for the metabolism of ME cyclophosphate, **1**, and the subsequent biosynthesis of isoprenoid precursors isopentenyl pyrophosphate, **2**, and dimethylallyl pyrophosphate, **3**.

Kinetic resolution of aromatic substituted norbornene monoesters
Esterase


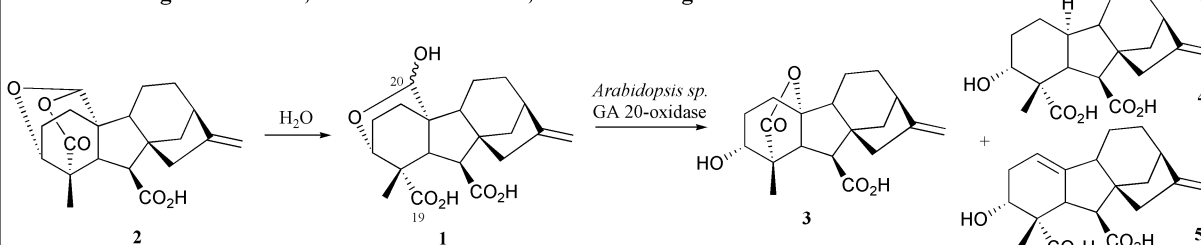
M. Mamaghani, *Tetrahedron*, 2002, **58**, 147.

The effect of co-solvents on the reaction time was considerable and no detrimental effect on e.e.'s was observed.

Resolution of racemic esters
Esterase


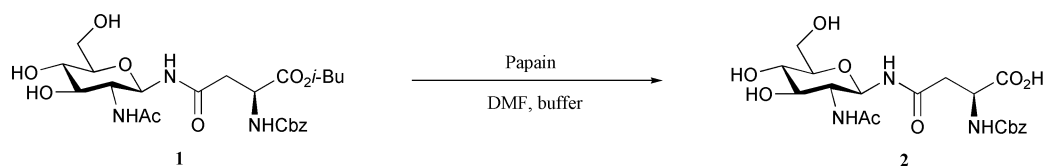
L.-C. Lo, J.-J. Shie and T.-C. Chou, *J. Org. Chem.*, 2002, **67**, 282.

A convenient method for the chemoenzymatic preparation of (4a*S*, 5*S*)-(**1**) has been developed using the enantioselective alcalase. Four different esters were compared, and the butanoate ester was found to be the best substrate.

Metabolism of gibberellin 3 α ,20-hemiacetal and 19,20 lactol analogues
Oxidase


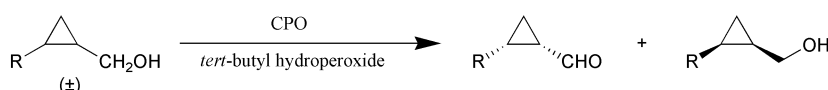
J. Ward, P. Gaskin, R. G. S. Brown, G. S. Jackson, P. Hedden, A. L. Phillips, C. L. Willis and M. H. Beal, *J. Chem. Soc., Perkin Trans. 1*, 2002, 232.

Compounds **1** and **2** were synthesised in order to investigate the structural requirements for oxidative cleavage of the carbon-20 by *Arabidopsis sp.* GA 20-oxidase clone AtGA20ox2 (At2353). It was concluded that **2** is initially converted to **1** by the enzyme. A mechanism was proposed taking into account the minor products **4** and **5**. Similar studies pointed to the requirement for a carboxy group at C-19.

Chemoenzymatic synthesis of GlcNAc-Cbz-Asn
Papain


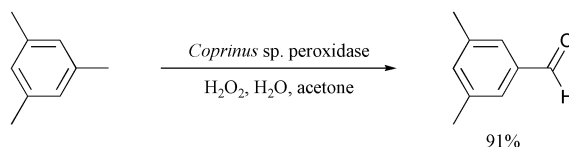
Y. Tokuda, Y. Takahashi, K. Matoishi, Y. Ito and T. Sugai, *Synlett*, 2002, 57.

Papain-catalysed hydrolysis was used as the final step in the synthesis of GlcNAc-CBz-Asn **2**, to effect mild hydrolysis of the isobutyl ester **1**.

Enantioselective oxidation of *cis*-cyclopropylmethanols by chloroperoxidase
Peroxidase


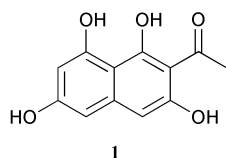
The reported chloroperoxidase (CPO) oxidation represents the first example for a heme enzyme which enantioselectively oxidises cyclopropylmethanols. CPO oxidation of *cis*-cyclopropanes shows much higher enantioselectivity than with the *trans*-isomers.

S. Hu and J. S. Dordick, *J. Org. Chem.*, 2002, **67**, 314.

Benzylic biooxidation of substituted toluenes by peroxidase
Peroxidase


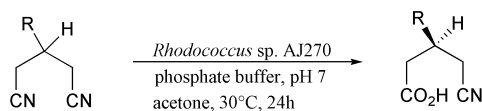
A number of substituted toluenes were oxidised to the corresponding benzaldehydes with *Coprinus sp.* peroxidase. The oxidation of the aromatic methyl group occurred chemoselectively under mild conditions, with only minor amounts of the respective benzoic acid being formed.

R. Russ, T. Zelinski and T. Anke, *Tetrahedron Lett.*, 2002, **43**, 791.

Synthesis of a novel hexaketide naphthalene
Polyketide synthase


A study of the mechanisms of polyketide synthase catalysed reactions is reported. A novel chimeric mutant polyketide synthase, SW-B, was constructed and was found to catalyse the synthesis of a novel hexaketide, 2-acetyl-1,3,6,8-tetrahydroxynaphthalene, **1**.

A. Watanabe and Y. Ebizuka, *Tetrahedron Lett.*, 2002, **43**, 843.

Desymmetrisation of prochiral dinitriles
Rhodococcus sp.


e.g. R = 4-F-C₆H₄, 4-CH₃-C₆H₄, 4-MeO-C₆H₄, C₆H₅CH₂

yields of up to 90%
e.e.'s of up to 95%

M.-X. Wang, C.-S. Liu and J.-S. Li, *Tetrahedron: Asymmetry*, 2001, **12**, 3367.

A study of the hydrolysis of 3-aryl- and 3-alkyl-substituted glutaronitriles catalysed by *Rhodococcus sp.* AJ270 cells is reported. The corresponding optically active (4S)-(+)-3-aryl- and (-)-3-alkyl-4-cyanobutanoic acids were obtained. The enantioselectivity of the process was greatly enhanced by the presence of additives such as acetone.