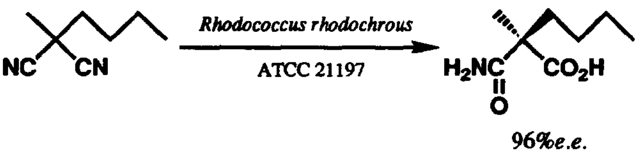
Tetrahedron: Asymmetry **1993**, *4*, 1081

Asymmetric Hydrolysis of a Disubstituted Malononitrile by the Aid of a Microorganism

Masahiro Yokoyama, Takeshi Sugai, and Hiromichi Ohta*
Department of Chemistry, Keio University, Hiyoshi 3-14-1, Yokohama 223, Japan



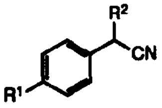
Rhodococcus rhodochrous ATCC 21197 hydrolyzed prochiral butylmethylmalononitrile to afford the corresponding amide–carboxylic acid with high *e.e.*

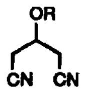
Tetrahedron: Asymmetry **1993**, *4*, 1085

STEREOSELECTIVE HYDROLYSIS OF NITRILES AND AMIDES UNDER MILD CONDITIONS USING A WHOLE CELL CATALYST.

Timothy Beard[a], Mark A. Cohen[a], Julian S. Parratt[a], Nicholas J. Turner*[a], John Crosby[b], and Jock Moilliet[b], [a]Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, U.K., [b]ICI Fine Chemicals Manufacturing Organisation, P.O. Box A38, Leeds Road, Huddersfield, Yorkshire, HD2 1FF, U.K.

Both racemic arylalkylnitriles and prochiral dinitriles have been hydrolysed to optically active amides and/or acids using an immobilised whole cell *Rhodococcus* sp.



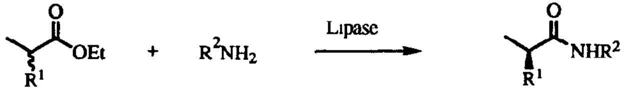


Tetrahedron: Asymmetry **1993**, *4*, 1105

LIPASE-CATALYZED SYNTHESIS OF OPTICALLY ACTIVE AMIDES IN ORGANIC MEDIA

Margarita Quirós, Víctor M. Sánchez, Rosario Brieva, Francisca Rebolledo and Vicente Gotor*
Departamento de Química Orgánica e Inorgánica. Universidad de Oviedo. 33071 Oviedo. Spain.

Lipases from *Candida cylindracea* and *Candida antarctica* catalyze the aminolysis of activated and nonactivated esters, respectively.

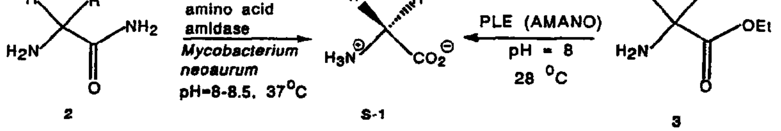


R^1 = Cl, Br, Et

Tetrahedron: Asymmetry **1993**, *4*, 1113

Enzymatic Resolution of α,α-Disubstituted α-Amino Acid Esters and Amides

Bernard Kaptein, Wilhelmus H.J. Boesten, Quirinus B. Broxterman, Piet J.H. Peters, Hans E. Schoemaker and Johan Kamphuis
DSM Research, Bio-organic Chemistry Section, Geleen, The Netherlands.

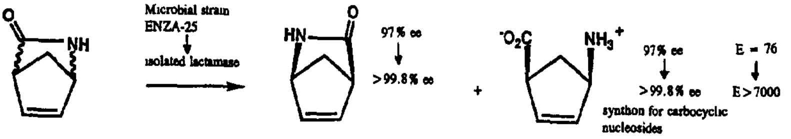


Enantiomerically pure (S)-disubstituted α-amino acids 1 are prepared by enzymatic resolution of the corresponding amides 2 and ethyl esters 3.

Tetrahedron: Asymmetry **1993**, *4*, 1117

Development of the Biocatalytic Resolution of 2-azabicyclo[2.2.1]hept-5-en-3-one as an entry to Single-Enantiomer Carbocyclic Nucleosides

Stephen J C Taylor[a], Raymond McCague[a*], Richard Wisdom [a], Carol Lee[a], Karen Dickson[a], Graham Ruecroft[a], Fergal O'Brien[a], Jennifer Littlechild[b], Jennifer Bevan[b], Stanley M Roberts[b] and Christopher T Evans[a]
[a]Chiros Ltd, 283 Cambridge Science Park, Cambridge CB4 4WE, UK and [b]Department of Chemistry, Exeter University, Exeter, EX4 4QD, UK



Tetrahedron: Asymmetry **1993**, *4*, 1129

Enantioseparation of 5-Monosubstituted Hydantoins by Capillary Gas Chromatography - Investigation of Chemical and Enzymatic Racemization

H. Lickefett*[1], K. Krohn[2], W.A. König[3], B. Gehrcke[3] and C. Syldatk[1]

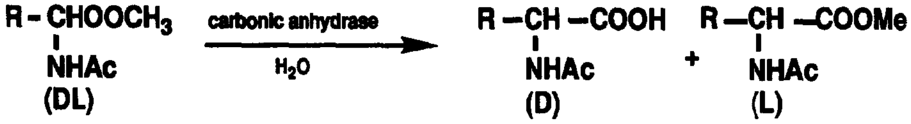
[1]Institut f. Biochemie u. Biotechnologie der TU Braunschweig Konstantin Uhde Str.5, W-3300 Braunschweig, Germany
[2] Fachbereich Chemie der Universitäts-GH-Paderborn Warburger Str.100, W-4790 Paderborn, Germany
[3] Institut f. organische Chemie der Universität Hamburg Martin-Luther-King-Platz 6, W-2000 Hamburg 13, Germany

The enantioseparation of different 5-monosubstituted hydantoins by capillary gas chromatography, using octakis(2,6-di-O-methyl-3-O-pentyl)-γ-cyclodextrin as chiral stationary phase was examined. The method described should allow not only to study chemical, but also enzymatic racemization processes of 5-monosubstituted alkyl-hydantoins.

Tetrahedron: Asymmetry **1993**, *4*, 1137

Selectivity in carbonic anhydrase catalysed hydrolysis of standard N-acetylamino acid methyl esters.

Robert Chênevert*, Rachid Bel Rhlid, Martin Létourneau, René Gagnon, and Linda D'Astous.
Département de Chimie, Université Laval, Québec, Canada G1K 7P4.

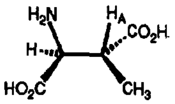


$$\underset{\text{(DL)}}{\underset{\text{NHAc}}{\text{R}-\underset{|}{\text{CH}}\text{OOCH}_3}} \xrightarrow[\text{H}_2\text{O}]{\text{carbonic anhydrase}} \underset{\text{(D)}}{\underset{\text{NHAc}}{\text{R}-\underset{|}{\text{CH}}-\text{COOH}}} + \underset{\text{(L)}}{\underset{\text{NHAc}}{\text{R}-\underset{|}{\text{CH}}-\text{COOMe}}}$$

Tetrahedron: Asymmetry **1993**, *4*, 1141

Syntheses of (2S,3R)- and (2S,3R)[3-^{2}H]-3-Methylaspartic acid: Slow Substrates for a *syn*-Elimination Reaction catalysed by Methylaspartase.

*Catherine H. Archer, Neil R. Thomas and David Gani**
Chemistry Department, The Purdie Building, The University,
St. Andrews, Fife, KY16 9ST, UK.



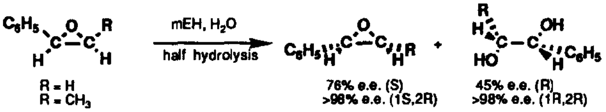
(2S,3R)- and (2S,3R)[3-^{2}H]-3-methylaspartic acid were prepared *via* enzymic and non-enzymic routes and were used to probe the mechanism of methylaspartase

Tetrahedron: Asymmetry **1993**, *4*, 1153

SUBSTRATE ENANTIOSELECTIVITY IN THE RABBIT LIVER MICROSOMAL EPOXIDE HYDROLASE CATALYZED HYDROLYSIS OF TRANS AND CIS-1-PHENYLPROPENE OXIDES. A COMPARISON WITH STYRENE OXIDE.

Giuseppe Bellucci*, Cinzia Chiappe, Antonio Cordoni and Franco Marioni. Dipartimento di Chimica Bioorganica, Università di Pisa, Via Bonanno 33, 56126 - Pisa, Italy

cis-1-Phenylpropene oxide, but not *trans*-1-phenylpropene oxide, was subjected by microsomal epoxide hydrolase catalyzed hydrolysis to a kinetic resolution much more efficient than styrene oxide

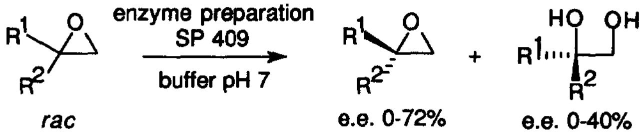


Tetrahedron: Asymmetry **1993**, *4*, 1161

ASYMMETRIC HYDROLYSIS OF EPOXIDES USING AN IMMOBILIZED ENZYME PREPARATION FROM *RHODOCOCCUS* SP.

P. Hechtberger, G. Wirnsberger, M. Mischitz, N. Klempier and K. Faber*
Institute of Organic Chemistry, Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria

An enzyme-catalyzed asymmetric hydrolysis of epoxides was achieved using an immobilized crude enzyme preparation derived from *Rhodococcus* sp.

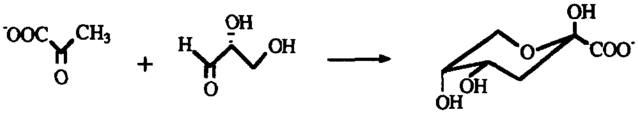


Tetrahedron: Asymmetry **1993**, *4*, 1165

Microbiological Aldolisations.
Synthesis of 2-Keto-3-Deoxy-D-Gluconate.

Claudine Augé and Véronique Delest
Institut de Chimie Moléculaire d'Orsay, URA CNRS 462, bât 420, 91405 Orsay cédex, France.

Aspergillus niger was used to catalyze a stereoselective aldolisation reaction between pyruvate and D-glyceraldehyde.



Tetrahedron: Asymmetry **1993**, *4*, 1169

AN EFFICIENT SYNTHESIS OF SEDOHEPTULOSE CATALYZED BY SPINACH TRANSKETOLASE.

Valérie DALMAS et Colette DEMUYNCK, Laboratoire de Chimie Organique Biologique, URA 485 du CNRS, Université Blaise Pascal, 63177 Aubière Cedex, France.

One step enzymatic synthesis of D-sedoheptulose.

Tetrahedron: Asymmetry **1993**, *4*, 1173

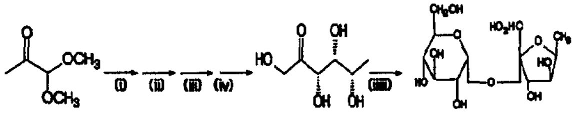
Combined chemoenzymatic synthesis of 2O-6-deoxy-L- sorbofuranosyl-D-glucose.

Jörg Peters, Hans-Peters Brockamp, Torsten Minuth, Marita Grothus, Alois Steigel, Maria-Regina Kula and Lothar Elling

Institut für Enzymtechnologie, Heinrich-Heine-Universität Düsseldorf, Postfach 2050, 5170 Jülich

Chemoenzymatic route for the synthesis of deoxy monosaccharides and disaccharides

(i) Carbonyl Reductase, Formate Dehydrogenase, NAD, NaHCOO
(ii) Dowex
(iii) Fructose-1,6-Bisphosphate Aldolase, Dihydroxyacetone phosphate
(iv) Acid Phosphatase
(iiii) Sucrose Synthase, UDP-Glucose

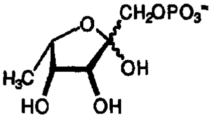


Tetrahedron: Asymmetry **1993**, *4*, 1183

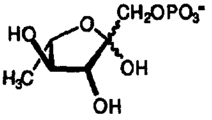
6-DEOXY-L-*LYXO*- AND 6-DEOXY-L-*ARABINO*-HEXULOSE 1-PHOSPHATES. ENZYMIC SYNTHESES BY ANTAGONISTIC METABOLIC PATHWAYS

Wolf-Dieter Fessner,* Achim Schneider, Oliver Eyrisch, Gudrun Sinerius, and Josefa Badía. Department of Organic Chemistry and Biochemistry, University of Freiburg, W-7800 Freiburg i. Br., Germany

The title compounds 1 and 2 are prepared from L-fucose and L-rhamnose by isomerization–phosphorylation, or by aldol addition of dihydroxyacetone phosphate to lactaldehyde using overexpressed enzymes from *E. coli.*



1



2

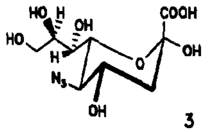
Tetrahedron: Asymmetry **1993**, *4*, 1193

Repetitive Batch as an Efficient Method for Preparative Scale Enzymic Synthesis of 5-Azido-Neuraminic Acid and ^{15}N-L-Glutamic Acid

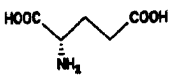
U. Kragl, A. Gödde, C. Wandrey, W. Kinzy, J.J. Cappon, J. Lugtenburg

Research Center Jülich, Germany; Ciba-Geigy AG, Switzerland; Leiden University, The Netherlands

- aldolase catalysed condensation of 2-azido-2-deoxy-mannose and pyruvate to form 3
- reductive amination with cofactor regeneration to form 6



3



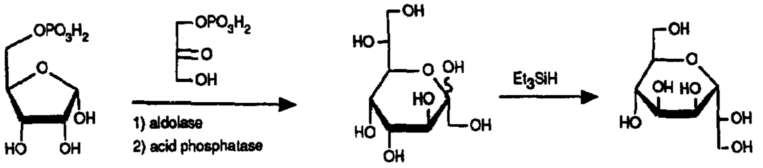
6

Tetrahedron: Asymmetry **1993**, *4*, 1203

SIMPLE AND STEREOSELECTIVE CHEMOENZYMATIC SYNTHESIS OF AN α-C-MANNOSIDE

Francesco Nicotra,* Luigi Panza, Giovanni Russo and Alessia Verani

Aldolase-catalyzed reaction of D-ribose 5-phosphate with dihydroxyacetone phosphate and reduction of the product with triethylsilane affords an α-C-D-mannopyranoside (3), through a stereoselective procedure which does not require any protective step.

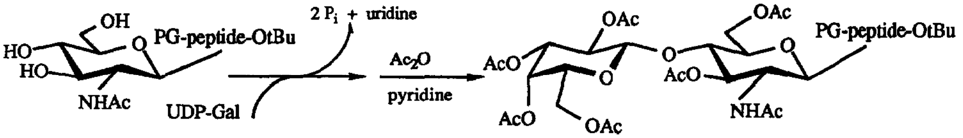


Tetrahedron: Asymmetry **1993,** *4,* 1205

Synthetic O-Glycopeptides as Model Substrates for Glycosyltransferases

Michael Schultz and Horst Kunz*
Institut für Organische Chemie, Universität Mainz, Becherweg 18-20, D-6500 Mainz, Germany

O-glycosylation of N-urethane (Teoc, Aloc) protected glucosamine derived bromo- or thioglycosides yields O-glycopeptides which are selectively galactosylated with β-1,4-galactosyltransferase (EC 2.4.1.22).

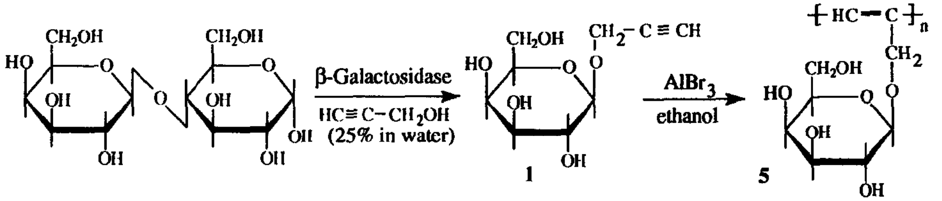


Tetrahedron: Asymmetry **1993,** *4,* 1221

ENZYMATIC DERIVATIZATION OF SACCHARIDES AND THEIR CHEMICAL POLYMERIZATION

Alexander M. Blinkovsky and Jonathan S. Dordick
Department of Chemical and Biochemical Engineering and Center for Biocatalysis and Bioprocessing, University of Iowa, Iowa City, IA 52242, USA

A chemoenzymatic route to a β-D-galactopyranoside-based acetylene polymer is described.



Tetrahedron: Asymmetry **1993,** *4,* 1229

DERIVATIVES OF THE PRODUCT OF BAKER'S YEAST REDUCTION OF ETHYL 2-ALKYL 3-OXOBUTANOATES AS PRECURSORS OF FREE RADICAL CHIRONS OF THE 2(S)-HYDROXYALKYL MOIETY

M. Hamdani, B. De Jeso, H. Deleuze and B. Maillard , LCOO,Associé au CNRS . F-33405 TALENCE-CEDEX

$$CH_3C(O)CHRCO_2Et \longrightarrow CH_3CH(OH)CHRCO_2Et \longrightarrow \longrightarrow CH_3CH(OP)CHR \longrightarrow$$

Tetrahedron: Asymmetry **1993,** *4,* 1233

THE PRODUCT OF BAKER' S YEAST REDUCTION OF ETHYL 2-CHLORO 3-OXOBUTANOATE AS A PRECURSOR OF THE 1-ETHOXYCARBONYL 2(S)-HYDROXYPROPYL RADICAL

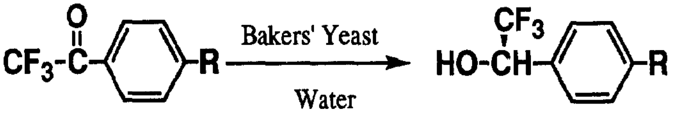
M. Hamdani, B. De Jeso, H. Deleuze, A. Saux and B. Maillard, LCOO,Associé CNRS, F-33405 TALENCE-CEDEX

$$CH_3C(O)CHClCO_2Et \longrightarrow CH_3CH(OH)CHClCO_2Et \xrightarrow{Bu_3Sn^{\bullet}} CH_3CH(OH)\dot{C}HCO_2Et \longrightarrow$$

Tetrahedron: Asymmetry **1993, *4*,** 1237

Stereocontrolled Synthesis of *p*-Substituted Trifluoromethylbenzylic Alcohol Derivatives of High Optical Purity by the Bakers' Yeast Reduction

Tamotsu FUJISAWA*, Kouji ICHIKAWA, and Makoto SHIMIZU
Department of Chemistry for Materials, Mie University, Tsu, Mie 514, Japan



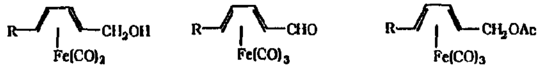
R = CO_2H, CO_2Me, $COCF_3$,
or $C(SCH_2)_2CF_3$

Tetrahedron: Asymmetry **1993, *4*,** 1241

Asymmetric Biochemical Reduction, Acylation and Hydrolysis in the (Diene)Fe(CO)$_3$ Series: Experimental Results and Molecular Modelling Studies

James A.S. Howell, Michael G. Palin,
Chemistry Department, Keele University, Keele, Staffordshire ST5 5BG, Great Britain
Gérard Jaouen, Siden Top, Hassane El Hafa, Jean Michel Cense
Ecole Nationale Superieure de Chimie, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

The complexes below have been obtained in enriched or homochiral form using biochemical reduction or acylation procedures.



(3) R = Me, (+)-(2S)
e.e. 76-78%
(4) R = CO_2Me, (-)-(2S)
e.e. 76%
(14) R = CHO, (-)-(2R)
e.e. 90%

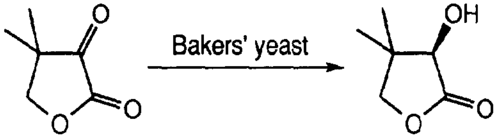
(1) R = Me, (-)-(2R)
e.e. >99%
(2) R = CO_2Me, (+)-(2R)
e.e. 90%

(5) R = Me, (-)-(2R)
e e. 70%
(11) R = CH_2OH
e.e. 56%

Tetrahedron: Asymmetry **1993, *4*,** 1253

Asymmetric Reduction of Ketopantolactone by Baker's Yeast

Kaoru Nakamura, Shin-ichi Kondo, Yasushi Kawai, and Atsuyoshi Ohno
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan



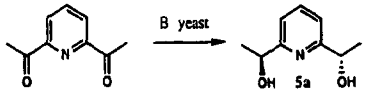
without β-CD	73% e.e.	(41% yield)
with β-CD	93% e.e.	(39% yield)

Tetrahedron: Asymmetry **1993, *4*,** 1255

PREPARATION OF HIGHLY ENANTIOPURE PYRIDYLETHANOLS BY BAKER'S YEAST REDUCTIONS.

David Bailey[a], David O'Hagan[a]*, Ulrich Dyer[b] and R. Brian Lamont[c]
[a] University of Durham, Department of Chemistry, Science Laboratories, South Rd. Durham, DH1 3LE, UK.
[b] Glaxo Group Research Ltd., Park Road, Ware, Hertfordshire, SG12 ODP, UK.
[c] Glaxo Group Research Ltd., Greenford Road, Greenford, Middlesex, UB6 OHE, UK.

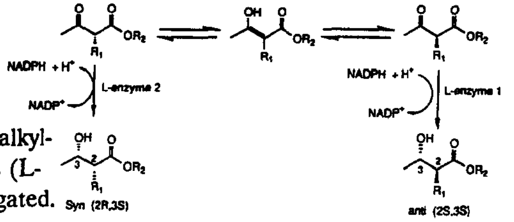
The double reduction of 2,6-diacetylpyridine with Bakers' yeast lead to 5a in essentially homochiral form (>99.92%ee).



Tetrahedron: Asymmetry **1993, *4*,** 1259

Stereochemical control of yeast reductions. 6. Diastereoselectivity of 2-alkyl-3-oxobutanoate oxido-reductases.

Woan-Ru Shieh and Charles J. Sih*
School of Pharmacy, University of Wisconsin-Madison,
425 N. Charter St., Madison, WI 53706 U.S.A.



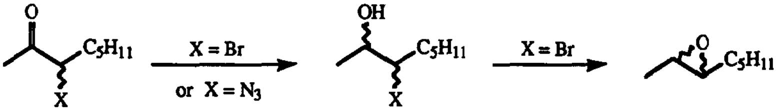
The stereoselective reductions of a variety of 2-alkyl-3-oxobutanoic esters by two purified L-oxidoreductases (L-enzyme 1 and 2) from Bakers' yeast have been investigated.

Tetrahedron: Asymmetry **1993, *4*,** 1271

CHEMOENZYMATIC SYNTHESIS OF "α-BICHIRAL" SYNTHONS APPLICATION TO THE PREPARATION OF CHIRAL EPOXIDES.

P.Besse and H.Veschambre, Laboratoire de Chimie Organique Biologique, URA 485 du CNRS, Université Blaise Pascal 63177 Aubière Cedex, France.

Synthesis of all the chiral isomers of 3-bromo-2-octanol, 3-azido-2-octanol and 2,3-epoxyoctane.

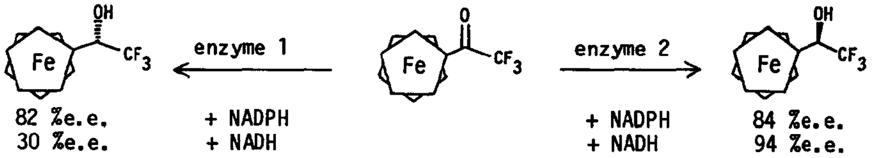


Tetrahedron: Asymmetry **1993, *4*,** 1287

STEREOSELECTIVITY IN THE MICROBIAL REDUCTION OF (TRIFLUOROACETYL)FERROCENE AND 2-FLUOROACETOPHENONES

Y. Yamazaki* and H. Kobayashi, National Institute of Bioscience and Human-Technology, AIST, Tsukuba, Ibaraki 305, Japan

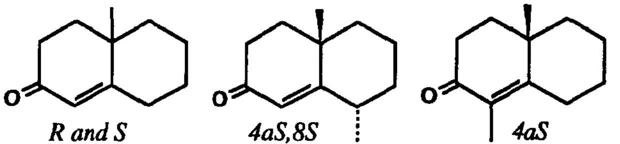
Rhodotorula rubra has at least 2 oxidoreductases with the diametric stereoselectivity.



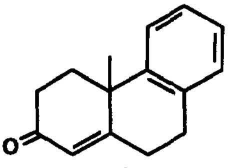
Tetrahedron: Asymmetry **1993, *4*,** 1295

MICROBIAL HYDROXYLATION AND FUNCTIONALIZATION OF SYNTHETIC POLYCYCLIC ENONES.

A.Hammoumi[a], J.-P.Girault[a], R. Azerad*[a], G.Revial[b] and J. d'Angelo[c].
a) Lab.Chimie Biochimie Pharmacol.Toxicol., Univ.R.Descartes, 45 rue des Sts-Pères, 75270 Paris Cedex 06; b) Lab.Chimie, ESPCI, 10 rue Vauquelin, 75005 Paris; c) Lab.Chimie Organique, Fac.de Pharmacie, 5 rue J.B.Clément, 92296 Chatenay-Malabry (France).



R and S *4aS,8S* *4aS*



R and S

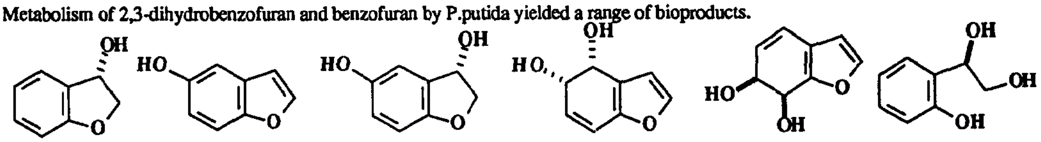
The hydroxylation patterns of substituted enantiomerically pure 4a-methyl-octalenones by fungi (and particularly *Mucor plumbeus*) have been determined.

Tetrahedron: Asymmetry **1993,** *4,* 1307

STRUCTURES AND STEREOCHEMICAL ASSIGNMENTS OF SOME NOVEL CHIRAL SYNTHONS DERIVED FROM THE BIOTRANSFORMATION OF 2,3-DIHYDROBENZOFURAN AND BENZOFURAN BY PSEUDOMONAS PUTIDA.

Derek R.Boyd,*[a] Narain D Sharma,[a] Rosemary Boyle,[a] John.F.Malone,[a] Jagdeep Chima,[b] and Howard Dalton.*[b]
[a] School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, U.K.
[b] Department of Biological Sciences, University of Warwick, Coventry CV4 7AL,U.K.

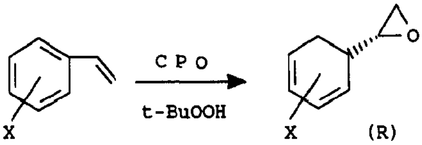
Metabolism of 2,3-dihydrobenzofuran and benzofuran by P.putida yielded a range of bioproducts.



Tetrahedron: Asymmetry **1993,** *4,* 1325

ENANTIOSELECTIVE EPOXIDATION OF STYRENE DERIVATIVES BY CHLOROPEROXIDASE CATALYSIS

S.Colonna[a], N.Gaggero[a], L.Casella[b], G.Carrea[c] and P.Pasta[c]
[a])Dipartimento di Chim. Org. e Industr., Centro C.N.R., Milano, Italy
[b])Dipartimento di Chimica Generale, Pavia, Italy
[c])Istituto di Chimica degli Ormoni, C.N.R., Italy

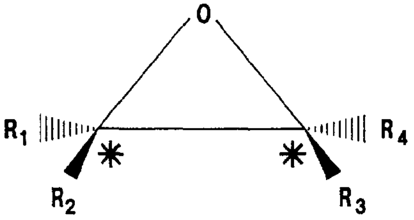


e.e. 28-68%
X = H, p-Cl, p-Br, p-NO_2, m-Cl, o-Cl

Tetrahedron: Asymmetry **1993,** *4,* 1331

BIOFORMATION OF OPTICALLY PURE EPOXIDES

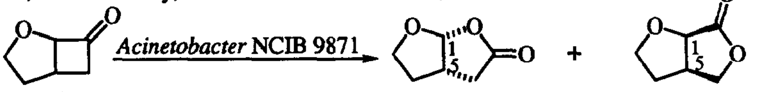
J.A.M. de Bont
Division of Industrial Microbiology,
Department of Food Science,
Wageningen Agricultural University,
P.O. Box 8129, 6700 EV Wageningen,
The Netherlands.



Tetrahedron: Asymmetry **1993,** *4,* 1341

Microbiological Transformations 25: Enantioselective Baeyer-Villiger Oxidation as a Tool for the Synthesis of Enantiopure Bicyclic Furofuran and Pyrofuran Chirons.

F. Petit and R. Furstoss,
Groupe de Chimie Organique et Bioorganique, URA CNRS 1320, Faculte des Sciences de Luminy, case 901, 163, av. de Luminy, F-13288 Marseille Cedex 9, France



+/-

E.e. 90% (1R,5S)

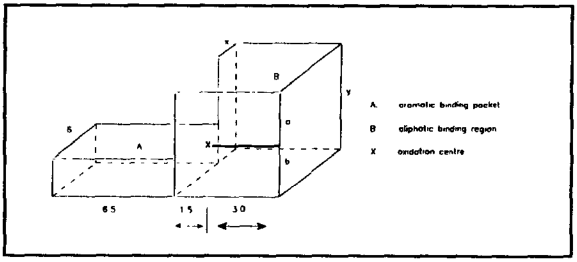
E.e. 98% (1R,5S)

Side Chain Hydroxylation of Aromatic Compounds by Fungi. Part 5. Exploring the Benzylic Hydroxylase of *Mortierella isabellina*

Tetrahedron: Asymmetry **1993**, *4*, 1353

H.L. Holland, M. Kinderman, S. Kumaresan, T. Stefanac. Dept. of Chemistry, Brock University, St. Catharines, Ont., L2S 3A1, Canada

The benzylic hydroxylase enzyme of *Mortierella isabellina* ATCC 42613 has been explored by examination of the hydroxylation of several substrates, and an active site model is proposed.

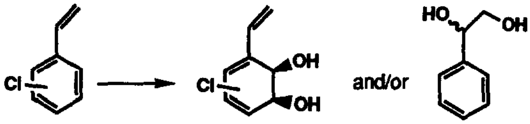


NEW DIOL METABOLITES DERIVED BY BIOOXIDATION OF CHLOROSTYRENES WITH *PSEUDOMONAS* PUTIDA: DETERMINATION OF ABSOLUTE STEREOCHEMISTRY AND ENANTIOMERIC EXCESS BY CONVERGENT SYNTHESES.

Tetrahedron: Asymmetry **1993**, *4*, 1365

Tomas Hudlicky,* Eric E. Boros, and Christie H. Boros, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212 USA

The absolute stereochemistry was determined for metabolites of the three isomeric chlorostyrenes subjected to biooxidation by *Pseudomonas putida* 39D.

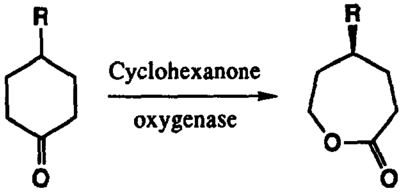


The Enzymatic Baeyer-Villiger Oxidation: A Study Of 4-Substituted Cyclohexanones

Tetrahedron: Asymmetry **1993**, *4*, 1387

Michael J. Taschner*, Donald J. Black, and Quin-Zene Chen
Department of Chemistry, The University of Akron,
Akron, Ohio 44325-3601

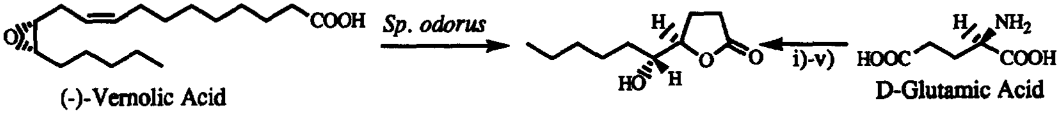
A study of the enzymatic Baeyer-Villiger oxidation of a number of 4-substituted cyclohexanones utilizing the enzyme cyclohexanone oxygenase (E.C. 1.14.13.-), isolated from the bacteria Acinetobacter NCIB 9871, is described.



Microbial Transformation of (-)-Vernolic Acid into (4R,5R)-5-Hydroxy-γ-decalactone

Tetrahedron: Asymmetry **1993**, *4*, 1391

Wolfgang Albrecht and Roland Tressl
Technische Universität Berlin, Institut für Biotechnologie, Fachgebiet Chemisch-technische Analyse, Seestr. 13, 1000 Berlin 65, Germany



i) $NaNO_2/HCl$, ii) $SOCl_2$, iii) $Pd/BaSO_4;H_2$, iv) $C_5H_{11}MgBr$ v) chromatographic separation