GRAPHICAL ABSTRACTS

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Synthesis of (R,R) and (S,S) Bicyclo[3.3.0]octane-2,6-dione Interactions between Non-Conjugated Chromophores Joëlle Pérard-Viret and André Rassat

URA CNRS 1679, Ecole Normale Supérieure, Département de chimie, Pans, France

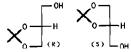
Synthesis of (R,R) and (S,S) Bicyclo[3.3.0]octane-2,6-dione by Resolution of the *diendo* Diol Intermediate with Menthyloxyacetic Acid. Study of the Dione by Circular Dichroism.

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SYNTHESIS OF (R)- AND (S)-ISOPROPYLIDENE GLYCEROL

M.Pallavicinia, E.Valotia*, L.Villa and O.Piccolob*

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Isopropylidene glycerol

The preparation of (R)- and (S)-isopropylidene glycerol of high optical purity (>98%) was accomplished through salt formation between their hydrogen phthalates with (S)- and (R)-1-methylbenzylamine respectively, selective crystallization of these salts and subsequent regeneration of the optically active compounds by saponification.

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ENZYMATIC ASYMMETRIZATION OF SOME PROCHIRAL AND MESO DIOLS THROUGH MONOACETYLATION WITH PIG

PANCREATIC LIPASE (PPL). Giuseppe Guanti,* Luca Banfi, and Renata Riva, Istituto di Chimica Organica, corso Europa 26, 16132 Genova (Italy).

A series of 2-substituted 1,3-propanediols and a meso diol have been asymmetrized through monoacetylation with crude PPL supported on celite, using vinyl acetate as both solvent and acylating agent. Under these conditions reactions are fast and reproducible and the enzyme can be recycled.

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ENZYMATIC RESOLUTION OF ETHYL ACETALS OF (R)-AND (S)-4-HYDROXYALK-2-YNALS

Pietro Allevi,* Mario Anastasia, Francesco Cajone, Pierangela Ciuffreda and Anna M. Sanvito

Dipartimento di Chimica e Biochimica Medica, via Saldini 50, 20133 Milano.

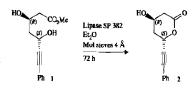
Several 4-hydroxyalk-2-ynals diethylacetals have been efficiently resolved by enatioselective acetylation mediated by *Pseudomonas fluorescens* lipase affording the acetylated (R)-enantiomers in preference.

SYNTHESIS OF (3R,5S)-3-HYDROXY-7-PHENYL-6-HEPTYN-5-OLIDE BY AN ENANTIOSELECTIVE

ENZYME-CATALYZED LACTONIZATION OF A RACEMIC 3.5-DIHYDROXY ESTER

Birgitta Henkel, Annamaric Kunath and Hans Schick*
Centre of Selective Organic Synthesis, Rudower Chaussee 5,
D-12489 Berlin-Adlershof, Germany

(3R,5S)-3-Hydroxy-7-phenyl-6-heptyn-5-olide (2) was obtained with a high enantiomeric excess by an enzyme-catalyzed enantioselective lactorization of the corresponding methyl $(3R^*,5S^*)$ -dihydroxyalkynoate (rae-1) followed by spontaneous crystallization.



BAKER'S YEAST-MEDIATED HYDROGENATION OF 2-SUBSTITUTED ALLYL ALCOHOLS: A BIOCATALYTIC ROUTE TO A NEW HIGHLY ENANTIOSELECTIVE SYNTHESIS OF

(R)-2-METHYL ALKANOLS
P. Ferraboschi, S. Casati, E. Santaniello*

Dipartimento di Chimica e Biochimica Medica, Universita' di Milano.

a. $R = (CH_3)_2C = CH + CH_2$ b. $R = CH_2 = CH + (CH_2)_3$ c. $R = PhCH_2$

The biohydrogenation of 2-substituted allyl alcohols 1a-c proceeds enantioselectively (95-98% ee) to afford (R)-2-methyl alkanols 2a-c.

Regioselective Addition of Organocopper-Magnesium Reagents to Chiral Dienylic Cyclic Carbonates

Suk-Ku Karig,* Dong-Gyu Cho, Jea-Uk Chung, and Dae-Yeun Kim Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, Korea

Enantioselective Synthesis of Cinnamyl-1-Phenyl-2-Propenyl Ether: A Metabolite of Marine Green Algal Species Caulerpa Racemosa

U.V. Mallavadhani and Y.R. Rao Regional Research Laboratory Bhubaneswar-751 013, India.

The enantioselective synthesis of title compound has been achieved using a new enzyme-acyl system (PPL/VL) and a mild PT catalysed etherification.

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Chiral Recognition of Olefins by ¹H NMR Spectroscopy in the Presence of a Chiral Dirhodium Complex

Klaudia Wypchlo and Helmut Duddeck, Universität Hannover,

Institut für Organische Chemie, Schneiderberg 1B, D-30167 Hannover, Germany

New method for the determination of the enantiomeric purity of olefins Examples: α-pinene, limonene, 4-vinyl-1-cyclohexene and carvone; camphene fails

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Sulfur Derivatives of Ephedra Alkaloids; New and Highly Efficient Chiral Catalysts.

Robert P. Hof, Martin A. Poelert, Nathalie C.M.W. Peper, Richard M. Kellogg, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

(R)-1-phenylpropanol (89% c.c.)

Asymmetric Michael Additions of Homochiral Magnesium Amides

Tetrahedron: Asymmetry 1994, 5, 35

Mark E. Bunnage, a Stephen G. Davies, a* Christopher J. Goodwin, b and Iain A.S. Waltersa

mark E. Dulmage, "Supplied O. Davies," Chilotophie J. Dodown, and said Sci. Whitesa a The Dyson Perrins Laboratory, South Parks Road, Oxford, OX 13 QY, UK. b Fisons ple, Pharmaceutical Division, Research and Development Laboratories, Bakewell Road, Loughborough, LEI I ORH, UK.

The first asymmetric Michael addition of a homochiral magnesium amide is presented. Methylation of the resultant β-amino magnesium enolate was found to occur with excellent stereoselectivity, providing a direct synthesis of homochiral syn-α-methyl-β-amino acids.

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STEREOSELECTIVE SYNTHESIS OF NEW HOMOCHIRAL POLYFUNCTIONAL SIDE-CHAIN CYCLOPENTANE DERIVATIVES

Miguel Díaz, Javier Ibarzo, and Rosa M. Ortufto*

Departament de Química, Universitat Autônoma de Barcelona, 08193 Bellatera, Barcelona, Spain.

The new epoxycompound shown has been synthesized stereoselectively. This product is an useful intermediate in the synthesis of hydroxyesters, polyols or aminoalcohols.

PREPARATION OF CHIRAL INDANONES AND DIHYDROCOUMARINS; APPLICATION TO SYNTHESIS OF (+) 3-(2,6-DIMETHOXYPHENYL)PENTANOIC ACID Tetrahedron: Asymmetry 1994, 5, 41

Elie Stephan*, Richard Rocher, Jeanine Aubouet, Guy Pourcelot and Pierre Cresson Synthese Organique, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05

chiral B-aryl carboxylic acids are prepared and transformed into following compounds:

(i)intramolecular acylation (ii) CF3CO3H (iii) KOH,PhCOCl (iv)intramol.acylation (v)MCPBA (vi)NaOH,Me2SO4

Enantioselective Catalysis by 1-(1-Isoquinolinyl)-2naphthalenemethanol; an Atropisomerically Chiral

N-O Chelating Ligand

Robert W. Baker,* Simon O. Rea, Melvyn V. Sargent,* Elisabeth M. C. Schenkelaars, Brian W. Skelton and Allan H. White Department of Chemistry, University of Western Australia, Nedlands, Western Australia, 6009.

In Vitro Cytotoxicity of Gold(I) and Platinum(II) Compounds containing Asymmetric [2-(Methylsulfinyl)ethyl]diphenylarsine and its Phosphorus Analogue

Simon Y.M. Chooi, Pak-Hing Leung, K.Y. Sim, K.S. Tan and O.L. Kon National University of Singapore, Singapore 0511

The synthesis of novel gold(I) compounds containing the optically active and racemic forms of Ph2ECH2CH2S(O)Me (E = As, P) is described. In vitro cytotoxicity evaluation in three human tumour models showed the gold-phosphine compounds to be remarkably potent.

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EASY PREPARATION OF ENANTIOPURE C.-SYMMETRICAL AMINO ALCOHOLS DERIVED FROM m-XYLYLENÉ DIAMINE.

José M. Andrés, María A. Martínez, Rafael Pedrosa* and Alfonso Pérez-Encabo.

Condensation of isophthaldehyde with chiral amino alcohols or with a-amino acids followed by reduction and further transformations, leads to enantiopure C2-symmetrical amino alcohols in good chemical yields.

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ENANTIOSELECTIVE ETHYLATION OF ALDEHYDES CATALYZED BY CHIRAL C.-SYMMETRICAL α -HYDROXY- α -XYLYLENE DIAMINES

Lock M. Andréa Moria A. Morinon Defeat Dedecort and Alfance Direct Engels

José M. Andrés, María A. Martínez, Rafael Pedrosa* and Alfonso Pérez-Encabo.

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Valladolid, 47011-Valladolid (Spain)

Chiral C₂-symmetric aminoalcohols 1A-I are excellent catalysts for enantioselective addition of diethylzing

to aromatic and aliphatic aldehydes 2-5. The best experimental conditions and pattern substitution on the catalyst to achieve the highest chemical yield and e.e. have been studied

Enzymatic Preparation of Optically Active Silylmethanol Derivatives Having A Stereogenic Silicon Atom by Hydrolasecatalyzed Enantioselective Esterification

ToshiakiFukui, Takuo Kawamoto, and Atsuo Tanaka, Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

Enzymatic resolution of silylalkanols having a stereogenic silicon atom.

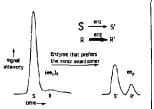
KINETIC RESOLUTIONS CONCENTRATE THE MINOR ENANTIOMER AND AID MEASUREMENT OF HIGH ENAN-

TIOMERIC PURITY. Gaétan Caron, George W.-M. Tseng, and

Romas J. Kazlauskas,* Department of Chemistry, McGill University, 801

Sherbrooke St. W., Montréal, Québec H3A 2K6, Canada

A kinetic resolution aids measurement of small amounts of the minor enantiomer because it concentrates the minor enantiomer into the product. The original enantiomeric purity can be calculated from the extent of conversion and the enantioselectivity of the kinetic resolution. We validated this method with the lipsase-catalyzed acetylation of menthol. As an example of its use, we measured 98.5% ee for a commercial sample of (+)-naproxen using simple optical rotation after concentrating the minor enantiomer.



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IMPROVEMENT OF ENANTIOSELECTIVE ENZYMATIC ESTER HYDROLYSIS IN ORGANIC SOLVENTS

Tetrahedron: Asymmetry 1994, 5, 93

J.L.L. Rakels, A.J.J. Straathof and J.J. Heijnen

Department of Biochemical Engineering, Delft University of Technology Julianalaan 67, 2628 BC Delft, The Netherlands

Abstract: Yield and enantiomeric excess significantly increased by ion-pair formation of a non-reactive amine with product carboxylic acid during kinetic resolution of a chiral ester.

 $R_1^*COOR_2 + H_2O \rightleftharpoons R_1^*COOH + R_2OH$

 R_1 COOH + RNH, \rightarrow RNH₃ R_1 COO

 R_1COOR_2 + $H_2O \rightleftharpoons R_1COOH + R_2$ OH

and

R,COOH + RNH, → RNH, R,COO -

Asymmetric Synthesis of D- and L-2-Deoxy-4-thioriboses

Jun'ichi Uenishi,* Mitsuhiro Motoyama and Keiji Takahashi

Department of Chemistry, Faculty of Science, Okayama University of Science Ridaicho, Okayama, 700, Japan

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D- and L-2-deoxy-4-thioriboses, 12 and 17 were prepared in 4 steps from optically active epoxy alcohols 8 and 15 respectively.

Tetrahedron: Asymmetry 1994, 5, 111

Synthesis of (-)- and (+)-esermethale via chemical resolution of 1,3-dimethyl-3-(2-aminoethyl)-5-methoxyoxindole

M Pallovicini, E Valoti*, L.Villa and F.Lianza

Istituto di Chimica Formaceutica e Tossicologica, Universita di Milano, viale Abruzzi 42, 1-20131 Milano, Italia

- a) GH₃I, TBAB, GH₂GI₂, aq 1.5% NaOH, b) H₂, PtO₂, HGI, MeOH,
- c) D-tartaric acid, KOH, H2O, d) CICOOMe, Et3N, CH2Cl2,
- e) LiAlH₄, THF, f) L-tartaric acid, KOH, H₂O

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A Simple Enantioselective Synthesis of γ-Valerolactone

John A. O'Neill^a, Stephen D. Lindell^b, Thomas J. Simpson^a and Christine L. Willis^{a,*}

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK Schering Agrochemicals Ltd., Chesterford Park, Saffron Walden, Essex CB10 1XL

32% overall yield

A simple enantioselective synthesis of y-valerolactone is described which may be simply adapted for the efficient incorporation of a carbon-13 label.

Chiral Pool Synthesis of trans-(2S,3S)-3-Hydroxyproline and Castanodiol from S-Pyroglutamic Acid

Tetrahedron: Asymmetry 1994, 5, 119

Claus Herdeis,^a Hans Peter Hubmann^a and Herman Lotter^b

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^bInstitut für Pharmazeutische Biologie der Universität, 80333 Munchen, Karlstrasse 29, Germany

STEREOCONTROLLED SYNTHETIC ENTRIES TO

HOMOCHIRAL HYDROXYLATED NORBORNENE DERIVATIVES. FORMAL SYNTHESIS OF SOME CARBOCYCLIC NUCLEOSIDES

Miguel Díaz, Javier Ibarzo, José M. Jiménez, and Rosa M. Ortuño* Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellatera, Barcelona, Spain.

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DIRECT CHIRAL HPLC SEPARATION OF ENANTIOMERS OF FLUORINATED N-ARYLAMINO-I-ARYLMETHYLPHOSPHONATE ESTERS. SUBSTITUENT EFFECTS ON THE ENANTIOSELECTIVITY.

Salvatore Caccamese^a, Grazia Principato^a, Ulrike Gruss^b, Gerahard Hagele^b, Salvatore Failla^c.

^aDipartimento di Scienze Chimiche, Università di Catania, viale A. Doria 6, 95123 Catania, Italy

blassmat für Anorganische Chemie und Strukturchemie, Heinrich-Heine Universität, Universitätssir. 1, D 4000, Dusseldorf, Germany

Cistituto Chimico della Facoltà di Ingegneria, Università di Catania, viale A. Doria 6, 95125 Catania, Italy The chiral separation on Chiralcel OD strongly depends on the substitution pattern in the

N-aryl and/or in the C-aryl moieties and improves markedly with the polarity of the fluorinated substituent.

A chiral recognition model between (R)-o-Burke 1 and the enantiomers of an analyte afforded to propose the absolute configuration of the optical isomers and to relate it to the chiroptical behaviour.

Y+H, 2-CF3, 2-OCF3, 2-F, 3-F, 4-F, 3-CF3 4-CF3, 3,4-F2 X=H, 3,4-F2, 4-OCF3