

GRAPHICAL ABSTRACTS

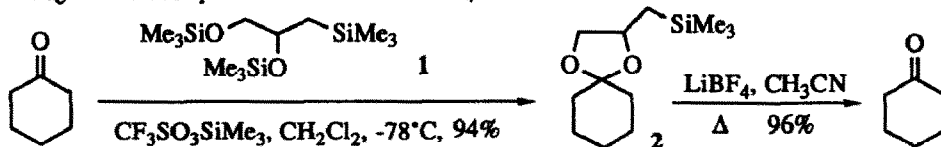
Tetrahedron Letters, 1994, 35, 969

The Protection of Ketones and Aldehydes as

4-Trimethylsilylmethyl-1,3-dioxolanes. Brett M. Lillic

and Mitchell A. Avery,* Department of Chemistry, University of North Dakota, P. O. Box 9024, Grand Forks, ND 58202-9024

Ketones and aldehydes can be protected with 2,3-bis(trimethylsilyloxy)trimethylsilylpropane **1** catalyzed by TMSOTf to provide ketals. Cleavage can be accomplished with either HF or LiBF₄.

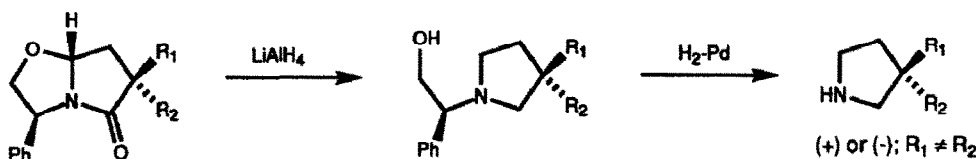


Tetrahedron Letters, 1994, 35, 973

A Synthesis of Enantiomerically Pure 3- and 3,3-Disubstituted Pyrrolidines

Larry J. Westrum and A. I. Meyers*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 U.S.A.



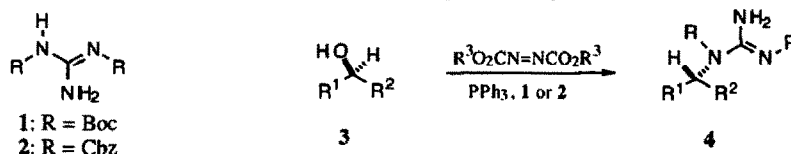
Tetrahedron Letters, 1994, 35, 977

Conversion of Alcohols to Protected Guanidines Using the

Mitsunobu Protocol. Dharmpal S. Dodd and Alan P. Kozikowski*

Neurochemistry Research, Mayo Foundation for Medical Education and Research, 4500 San Pablo Road, Jacksonville, FL 32224, USA.

An efficient method for the direct conversion of alcohols to guanidines is presented. Reaction of **1** and **2** with a variety of alcohols under the Mitsunobu conditions gave protected guanidines in high yield.



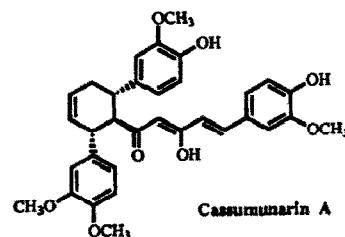
Tetrahedron Letters, 1994, 35, 981

NOVEL ANTIOXIDANTS, CASSUMUNARIN A, B, AND C, FROM ZINGIBER CASSUMUNAR

Akiko Jitoe, Tooshiya Masuda, and Tom J. Mabry

Department of Botany, University of Texas at Austin, Austin, Tx 78713, USA

Novel antioxidants, Cassumunarin A, B, and C, were isolated from *Zingiber cassumunar* and their structures were determined to be a new type of complex curcumin.



Asymmetric Allylboration of Acylsilanes

Tetrahedron Letters, 1994, 35, 985

John D. Buynak*, Bolin Geng, Shinian Uang, and J. Byron Strickland
Department of Chemistry, Southern Methodist University, Dallas, TX 75275, U.S.A.

Acylsilanes were asymmetrically allylbored in 2 - 92% e.e.

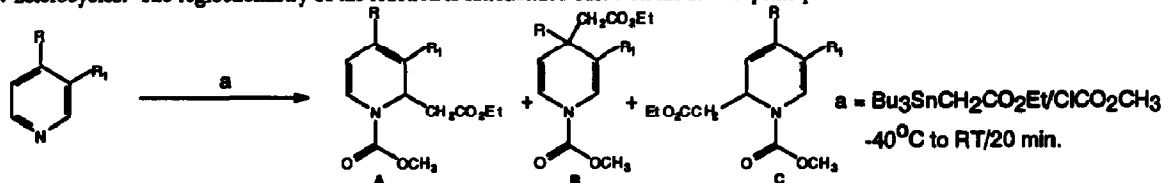


ETHYL (TRIBUTYLSTANNYL)ACETATE: A VERSATILE REAGENT FOR THE CARBOETHOXYMETHYLATION OF FUNCTIONALIZED PYRIDINES

Tetrahedron Letters, 1994, 35, 989

T.G. Murali Dhar* and Charles Gluchowski

Synaptic Pharmaceutical Corporation, 215 College Road, Paramus, NJ 07652. Ethyl (tributylstannyl)acetate adds chemoselectively to acylpyridinium salts to yield a variety of dihydropyridines which are useful precursors for the preparation of a variety of N-heterocycles. The regiochemistry of the reaction is rationalized based on the HSAB principle.



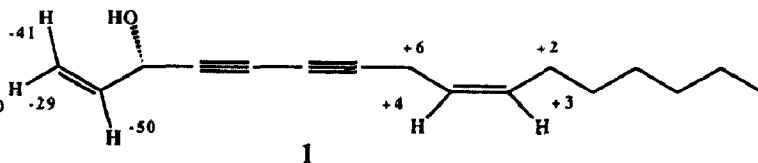
STEREOCHEMISTRY OF ENYNOLS - A CAVEAT ON THE EXCITON CHIRALITY METHOD

Tetrahedron Letters, 1994, 35, 993

Matthew W. Bernart, Yali F. Hallock, John H. Cardellina II and Michael R. Boyd*

Laboratory of Drug Discovery Research and Development, Developmental Therapeutics Program, Division of Cancer Treatment, National Cancer Institute, Bldg. 1052, Rm 121 Frederick, MD 21702-1201 USA

The exciton chirality method, as applied to secondary allylic alcohols, cannot be extended to secondary alcohols flanked by two chromophores.

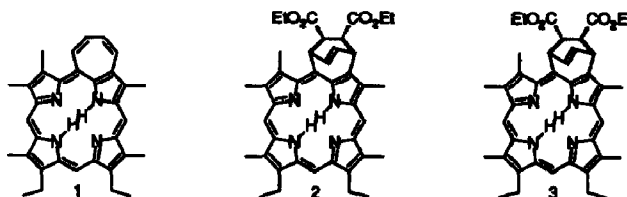


A NEW PORPHYRIN DERIVATIVE FOR USE AS A DIENE

IN THE DIELS-ALDER REACTION. Paul A. Liddell, Lori J. Demanche,

Shumin Li, Alisdair N. Macpherson, Ronald A. Nieman, Ana L. Moore,* Thomas A. Moore,* and Devens Gust,* Center for the Study of Early Events in Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA

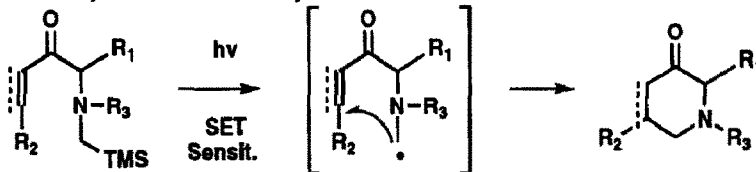
Porphyrin diene 1 has been synthesized from substituted pyrrole precursors, and undergoes the Diels-Alder reaction with diethyl fumarate to yield 2 and 3. The diene is thus a potential precursor for a variety of porphyrins bearing electron or energy donor or acceptor moieties.



A Novel Method for Synthesis of Functionalized

Piperidines. S. K. Khim, P. S. Mariano, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, 20742, USA

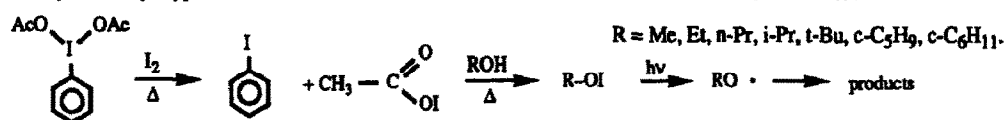
A new method for synthesis of functionalized piperidines which employs photoinduced radical cyclization reactions of α -silylamino-enones and -ynones is described.



ALKOXYL RADICALS FROM ALCOHOLS. SPECTROSCOPIC DETECTION OF INTERMEDIATE ALKYL AND ACYL HYPOIODITES IN THE SUAREZ AND BEEBE REACTIONS.

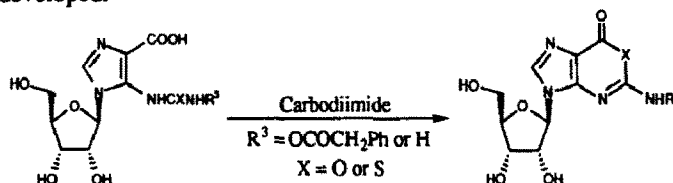
John L. Courtneidge, Janusz Lusztyk and Daniel Pagé, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Canada, K1A 0R6.

Acetyl and alkyl hypoiodites have been characterized as intermediates in the Suárez and Beebe reactions.

**A Novel Synthesis of Oxanosine and 1-Thiaguanosine.**

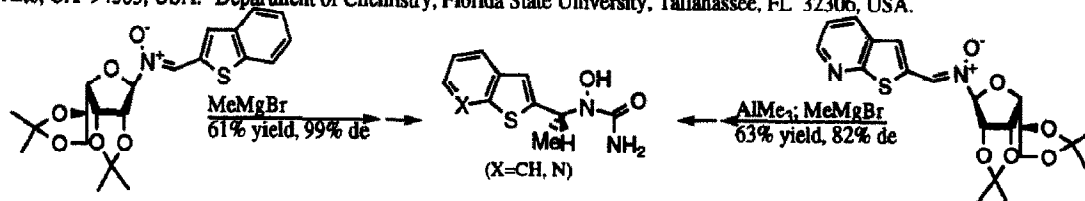
Kin-Chun Luk,* Douglas W. Moore, and Dennis D. Keith, Roche Research Center, Hoffmann-La Roche Inc., Nutley, NJ 07110.

A novel total synthesis of oxanosine and 1-thiaguanosine using carbodiimide mediated dehydration and cyclization of an urea-acid has been developed.

**ENANTIOSELECTIVE SYNTHESIS OF 5-LO INHIBITORS USING A**

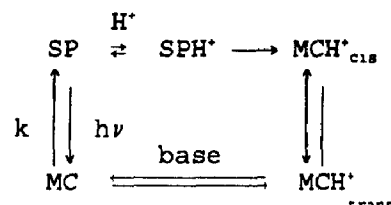
GULOFURANOSE AUXILIARY. John C. Rohloff,* Thomas V. Alfredson[†] and

Martin A. Schwartz.[‡] *Institute of Organic Chemistry and [†]Institute of Analytical Research, Syntex Discovery Research, Palo Alto, CA 94303, USA. [‡]Department of Chemistry, Florida State University, Tallahassee, FL 32306, USA.



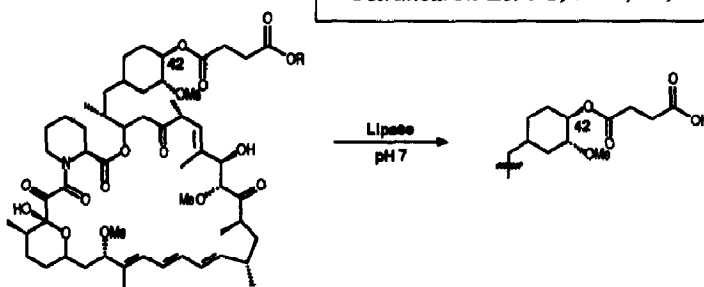
A NOVEL METHOD FOR MEASUREMENT OF THE MERCOPYRAN-SPIROPYRAN INTERCONVERSION IN NON-ACTIVATED 1,3,3-TRIMETHYLSPIRO-(2H-1-BENZOPYRAN-2,2'-INDOLINE) DERIVATIVES
 S.-R. Keum^a, K.-B. Lee^a, P.M. Kazmaier^b and E. Buncel^c. Depts. of Chemistry, ^aKorea University, Chung-Nam, South Korea 339-700; ^bXerox Research Centre of Canada, Mississauga, Canada; ^cQueen's University, Kingston, Canada.

A novel method for studying the merocyanine \rightleftharpoons spiropyran (MC \rightleftharpoons SP) interconversion is proposed: acid-induced ring opening of the SP followed by neutralization and stopped-flow measurement of ring closure of the resulting MC.



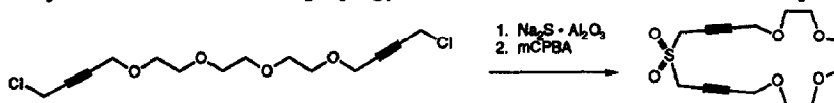
Lipase Mediated Hydrolysis of Rapamycin 42-Hemisuccinate Benzyl and Methyl Esters

Maciej Adamczyk,^{*} John C. Gebler,
 and Phillip G. Matingly
 Abbott Laboratories
 Abbott Diagnostics Division
 Abbott Park, IL 60064, USA



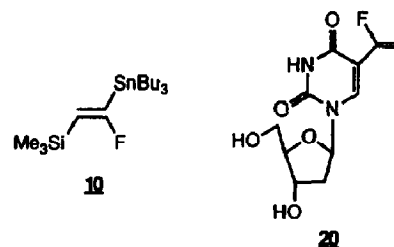
Synthesis of a DNA-Cleaving Bis(propargylic) Sulfone Crown Ether.
 Sean Michael Kerwin, Division of Medicinal Chemistry, College of Pharmacy, The University of Texas, Austin, TX 78712.

Macrocyclization of the bis(4-chloro-2-butyn-1-ol) ether of triethylene glycol with alumina-supported sodium sulfide followed by oxidation affords a bis(propargylic) sulfone crown ether that cleaves supercoiled DNA.



A NEW ROUTE TO 2-FLUORO-1-OLEFINS UTILIZING A SYNTHETIC EQUIVALENT FOR THE 1-FLUOROETHENE ANION. Donald P. Matthews, Raymond S. Gross, James R. McCarthy,^{*} Marion Merrell Dow Research Institute, 2110 E. Galbraith Road, Cincinnati, OH 45215

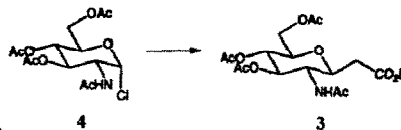
The preparation of (E)-tributyl(1-fluoro-2-trimethylsilyl)vinylstannane (**10**), a synthetic equivalent for the 1-fluoroethene anion, and its utility for the synthesis of nucleoside **20**, and other 2-fluoro-1-olefins is described.



SYNTHESIS OF C-GLYCOSIDES OF N-ACETYLGLUCOSAMINE BY DIRECT ALKYLATION OF 2-AMINO-2-DEOXY-2,3,4,6-TETRA-O-ACETYL GLUCOPYRANOSYL CHLORIDE

Tetrahedron Letters, 1994, 35, 1031

Kyung-II Kim and Rawle I. Hollingsworth*
Department of Chemistry and Biochemistry, Michigan State University
East Lansing, Michigan 48824, U.S.A.



The β -isomer of ethyl 2-acetamido-2-deoxy-3,4,6-tri-O-acetyl- β -D-glucopyranosylacetate (3) was prepared stereoselectively in two steps by reaction of 2-acetamido-2-deoxy-3,4,6- α -D-glucopyranosyl chloride (4) with potassium diethylmalonate and 18-crown-6, followed by decarboxylation.

Solid-Phase N-Glycopeptide Synthesis Using Allyl Side-Chain Protected Fmoc-Amino Acids.

Tetrahedron Letters, 1994, 35, 1033

Steven A. Kates,^a Beatriz G. de la Torre,^b Ramon Eritja,^b and Fernando Albericio^{a,*}

^aMillipore Corporation, 75A Wiggins Avenue, Bedford, MA 01730, USA.

^bCID-CSIC, Jordi Girona 18-26 08034 Barcelona, Spain

N-Glycopeptides are assembled *via* a mild, three-dimensional orthogonal solid-phase protection strategy (Fmoc/tBu/allyl), featuring selective deprotection of a carboxylic acid allyl ester with Pd(PPh₃)₄, coupling of the glycosylamine while the peptide is still attached to the resin, and final cleavage of the peptide from the resin.

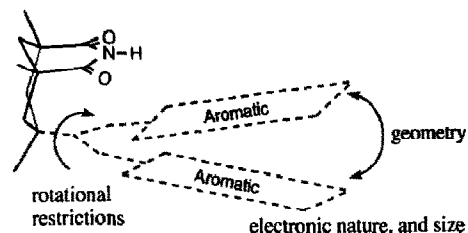


MOLECULAR RECOGNITION OF ADENINE : ROLE OF GEOMETRY, ELECTRONIC EFFECTS AND ROTATIONAL RESTRICTIONS

Tetrahedron Letters, 1994, 35, 1035

Ivan Huc, Julius Rebek, Jr.*, Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

New receptors for adenine have been synthesized. Their binding affinities have been measured and correlated to their structural features.

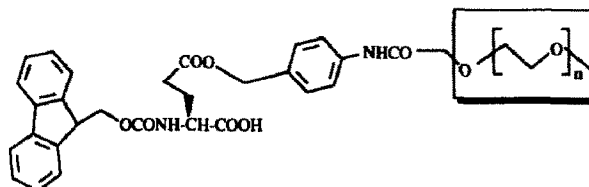


POLYETHYLENE GLYCOL BOUND BENZYL-AND FLUORENYL DERIVATIVES AS SOLUBILIZING SIDE-CHAIN PROTECTING GROUPS IN PEPTIDE SYNTHESIS.

Tetrahedron Letters, 1994, 35, 1039

A. Zier[†], D. Ryan, and M. Mutter*
Section de Chimie, Université de Lausanne,
Rue de la Barre 2, CH-1005 Lausanne,
Switzerland.

The covalent attachment of PEG to commonly used protecting groups results in increased solvation of fully protected peptides.

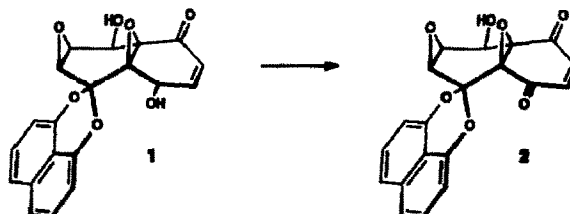


**CLADOSPIRONE BISEPOXIDE - A NOVEL FUNGAL METABOLITE
STRUCTURE DETERMINATION.**

Tetrahedron Letters, 1994, 35, 1043

Regina Thiergardt, Paul Hug†, Greta Rihs†, Heinrich H. Peter, Pharmaceutical Research Department, Microbial Chemistry and Central Function Research† Ciba Geigy Ltd., 4002 Basle, Switzerland

The structure elucidation of the novel metabolite 1 and its derivative 2 is described.



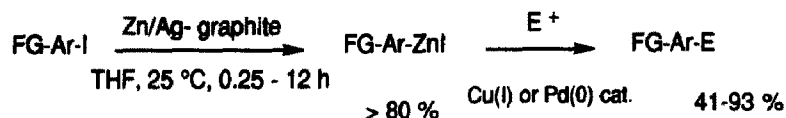
A Convenient Preparation of Functionalized Arylzinc Compounds by the Reaction of Zinc/Silver-Graphite with Aryl Iodides.

Tetrahedron Letters, 1994, 35, 1047

Alois Fürstner^{1*}, Robert Singer² and Paul Knochel^{2*}

¹ Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D - 45470 Mülheim/Ruhr, Germany

² Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany

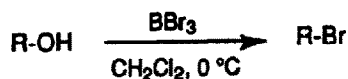


BROMINATION OF ALCOHOLS BY BORON TRIBROMIDE.

Tetrahedron Letters, 1994, 35, 1051

Joëlle D. Pelletier and Donald Poirier* Medicinal Chemistry Division, Molecular Endocrinology Laboratory, CHUL Research Center and Laval University, Québec, G1V 4G2, Canada.

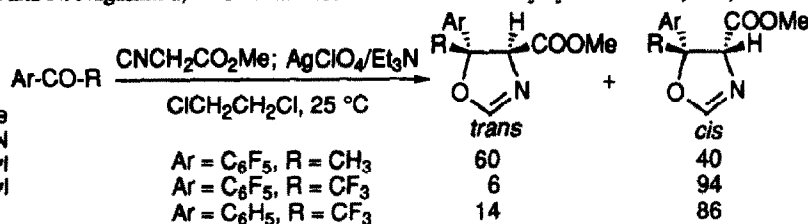
Boron tribromide was used as a brominating agent for the conversion of alcohols to bromides. Tertiary alcohols were more reactive than secondary alcohols which were more reactive than primary alcohols.



Highly Diastereoselective Aldol Reaction of Fluoroalkyl Aryl Ketones with Methyl Isocyanoacetate Catalyzed by Silver(I)/Triethylamine

Tetrahedron Letters, 1994, 35, 1055

V. A. Soloshonok and T. Hayashi,* *Catalysis Research Center, Hokkaido University, Sapporo 060, Japan;* K. Ishikawa and N. Nagashima, *Central Research Laboratories of Ajinomoto Co., Inc., Suzukicho, Kawasaki 210, Japan*



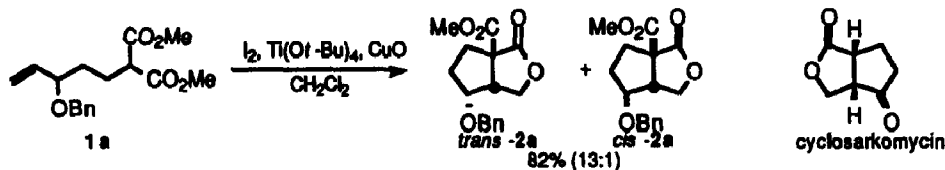
The remarkable difference in the diastereoselectivity of AgClO₄/Et₃N-catalyzed reaction of aryl fluoroalkyl and aryl alkyl ketones with methyl isocyanoacetate was disclosed.

DIASTEREOSELECTIVE IODOCARBOCYCLIZATION OF 4-PENTENYLMALONATE DERIVATIVES: APPLICATION TO CYCLOSARKOMYCIN SYNTHESIS

Tetrahedron Letters, 1994, 35, 1059

Osamu Kitagawa, Tadashi Inoue, and Takeo Taguchi*

Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

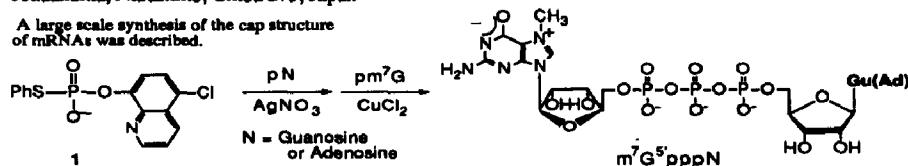


One-pot reaction for the synthesis of m⁷G⁵pppG and m⁷G⁵pppA by using an activatable bifunctional phosphorylating reagent

Tetrahedron Letters, 1994, 35, 1063

Koichiro Fukuoka, Fuminori Suda, Ryo Suzuki, Hiroshi Takaku, Masahide Ishikawa and Tsujiaki Hata*
 Department of Life Chemistry, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 227, Japan
 † Laboratory of Bioorganic Chemistry, Department of Industrial Chemistry, Chiba Institute of Technology, Tsudanuma, Narashino, Chiba 275, Japan

A large scale synthesis of the cap structure of mRNAs was described.



First Total Synthesis of a Barnacle Hatching Factor 8(R)-Hydroxy-eicosa-5(Z),9(E),11(Z),14(Z),17(Z)-pentaenoic acid.

Tetrahedron Letters, 1994, 35, 1067

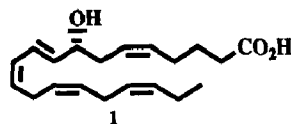
Tony K. M. Shing,^a K. H. Gibson,^b Jonathan R. Wiley,^c C. Ian F. Watt^c

^a Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong

^b Chemistry Department II, ICI pharmaceutical Division, Alderley Park, Macclesfield, Cheshire SK10 4TG, U.K.

^c Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

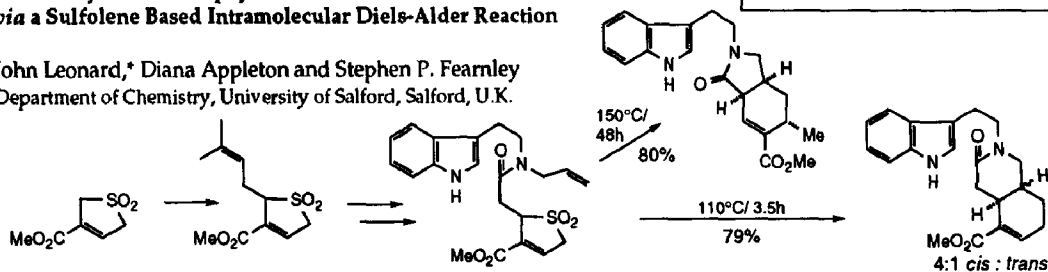
The first total synthesis of a barnacle hatching factor (BHF) establishes its constitution and absolute stereochemistry as 8(R)-Hydroxy-eicosa-5(Z),9(E),11(Z),14(Z),17(Z)-pentaenoic acid **1**.



A Short Synthesis of Apoyohimbins via a Sulfolene Based Intramolecular Diels-Alder Reaction

Tetrahedron Letters, 1994, 35, 1071

John Leonard,^{*} Diana Appleton and Stephen P. Fearnley
 Department of Chemistry, University of Salford, Salford, U.K.

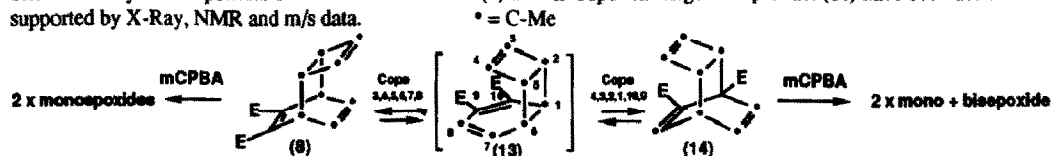


DIMETHYL OCTAMETHYLTRICYCLO[4.2.2.0^{2,5}]DECA-3,7,9-TRIENE-7,8-DICARBOXYLATE (COOKSON'S DIESTER) REVISITED: COPE REARRANGEMENT AND EPOXIDATION SITE SELECTIVITY

Ronald N. Warriner,* Gordon M. Eelsey, Ian G. Pitt, Edward R.T. Tiekink and Richard A. Russell

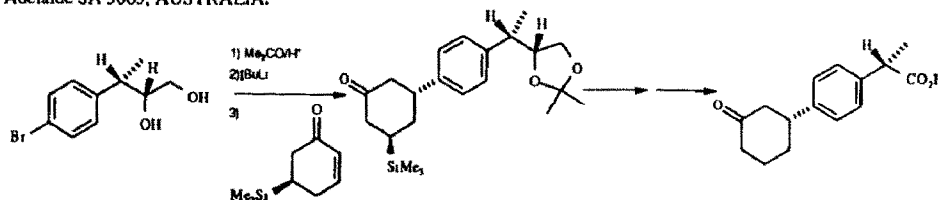
Centre for Molecular Architecture, University of Central Queensland, Rockhampton, Queensland, Australia, 4702.

Site selectivity in the epoxidation of Cookson's diester (8) and its Cope rearrangement product (14) have been determined and structures supported by X-Ray, NMR and m/s data.



CONCERNING THE ENANTIOSELECTIVE SYNTHESIS OF THE ISOMERS OF THE ARYLPROPANOIC ACID NSAID XIMOPROFEN.

Ralph A. Massy-Westropp*, David P.G. Hamon and Josephine L. Newton, Department of Chemistry, University of Adelaide, Adelaide SA 5005, AUSTRALIA.



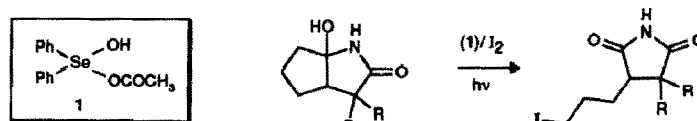
All four stereoisomers of the keto acid precursors of ximoprofen were prepared by this route

A SELENURANE DERIVATIVE PROMOTES β -FRAGMENTATION OF CARBINOLAMIDES LEADING TO CYCLIC IMIDES

Rosa L. Dorta, Cosme G. Francisco, Ernesto Suárez*

Instituto de Productos Naturales y Agrobiología del C.S.I.C., Carretera de La Esperanza 2, 38206-La Laguna, Tenerife, Spain

The alkoxy radical intermediates generated by reaction of carbinolamides with diphenylselenium hydroxyacetate (1) in the presence of iodine and under irradiation with visible light undergo β -fragmentation to afford 3,4-substituted cyclic imides (R = alkyl) in good yields.

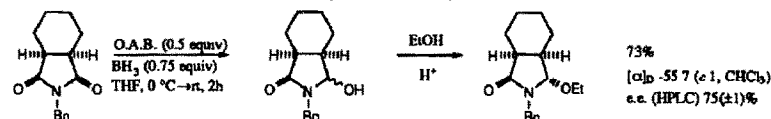


OXAZABOROLIDINE CATALYZED ENANTIOSELECTIVE REDUCTIONS OF CYCLIC MESO-IMIDES

R. Romagnoli[§], E.C. Roos[§], H. Hiemstra[§], M.J. Moolenaar[§], W.N. Speckamp[§], B. Kaptein[†] and H.E. Schoemaker[†]

[§]Department of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

[†]DSM Research, Department of Bio-Organic Chemistry, P.O. Box 18, 6160 MD Geleen, The Netherlands



Enantioselective reductions of various *meso*-imides using α, α -diphenyl-L-prolinol derived oxazaborolidine (O.A.B.) as chiral catalyst, and subsequent transformations into diastereomerically pure ethoxylactams and lactones (e.e.'s 75-89%), are described.

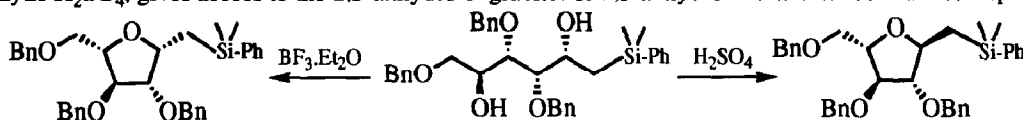
**SILICON-DIRECTED STEREOCONTROLLED
CYCLIZATION. POSSIBLE ROUTE TO
FUNCTIONALIZED TETRAHYDROFURANS.**

Tetrahedron Letters, 1994, 35, 1091

F.L. van Delft, G.A. van der Marel and J.H. van Boom*

Gorlaeus Laboratories, P.O.Box 9502, 2300 RA Leiden, The Netherlands

Cyclization of 3,4,6-tri-*O*-benzyl-1-deoxy-1-phenyldimethylsilyl-L-glucitol using a slight excess of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or catalytic H_2SO_4 , gives access to the 2,5-anhydro-L-glucitol or 2,5-anhydro-L-mannitol derivative, respectively.



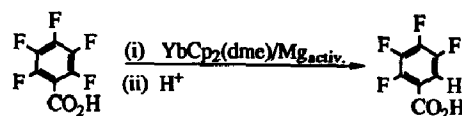
**REGIOSPECIFIC REPLACEMENT OF FLUORINE BY
HYDROGEN IN AN AROMATIC RING INDUCED BY
A RARE EARTH ORGANOMETALLIC**

Tetrahedron Letters, 1994, 35, 1095

Glen B. Deacon, Craig M. Forsyth and Junhui Sun

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

2,3,4,5-Tetrafluorobenzoic acid has been obtained in near quantitative yield from reaction of $\text{C}_6\text{F}_5\text{CO}_2\text{H}$ with $\text{YbCp}_2(\text{dme})$ and activated magnesium followed by hydrolysis, and there is catalytic turnover in ytterbium on addition of a cyclopentadiene source.



**Enantioselective Synthesis of Spiro[4.4]non- and
Spiro[4.5]dec-2-ene-1,6-diones**

Tetrahedron Letters, 1994, 35, 1099

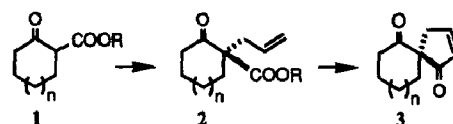
B. Chitkul, Y. Pinyopronpanich, C. Thebtaranonth, Y. Thebtaranonth*

Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand

W.C. Taylor

Department of Organic Chemistry, University of Sydney, N.S.W. 2006, Australia

Spiro[4.4]non- and spiro[4.5]dec-2-ene-1,6-diones [3, $n = 0$ and 1] were prepared in moderate to high enantiomeric purities *via* asymmetric allylation followed by carbanionic cyclization.

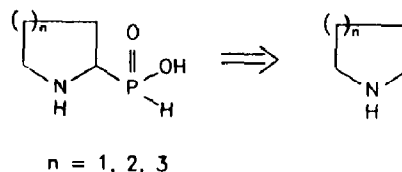


**A NEW METHOD FOR THE PREPARATION OF
2-PYRROLIDINYLPHOSPHINIC ACID AND HOMOLOGUES.**

Tetrahedron Letters, 1994, 35, 1103

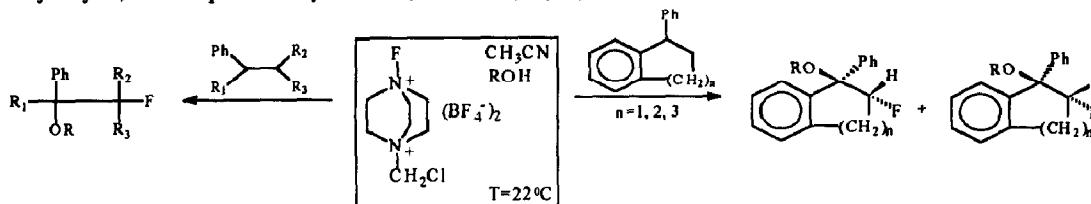
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Oxydation of pyrrolidine with persulphate, treatment with bis(trimethylsilyl) phosphonite and hydrolysis in aqueous methanol affords 2-pyrrolidinylphosphinic acid. The same procedure was used to prepare the 6- and 7-ring homologue.



A MILD, SELECTIVE METHOD FOR PREPARATION OF VICINAL FLUORO ETHERS USING "F-TEDA-BF₄".

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SYNTHESIS OF BIDENTATE MIXED DONOR PHOSPHORUS / NITROGEN LIGANDS. Leslie D. Field* and Ian J. Luck,

Department of Organic Chemistry, University of Sydney, Sydney N.S.W. 2006 Australia

(CH₃)₂PCH₂CH₂CH₂N(CH₃)₂ was synthesised by the photochemical addition of (CH₃)₂P-H to CH₂=CHCH₂N(CH₃)₂.
 (CH₃)₂PCH₂CH₂N(CH₃)₂ was synthesised by the reaction of sodium dimethylphosphide with (CH₃)₂NCH₂CH₂Cl.

