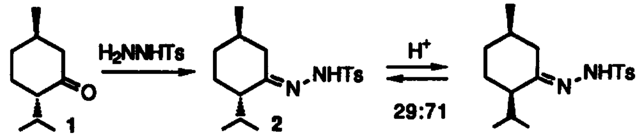
Tetrahedron Lett. **1993**, *34*, 4273

THE EPIMERIZATION OF α-CHIRAL HYDRAZONES: MENTHONETOSYLHYDRAZONE.

Charles M. Garner,*
Brett C. Mossman and Mark E. Prince, Department of Chemistry, Baylor University, Waco, TX 76798.

Epimerization of menthonetosylhydrazone (2) occurs much more readily than with the parent ketone (1), and leads to quite different equilibrium mixtures.

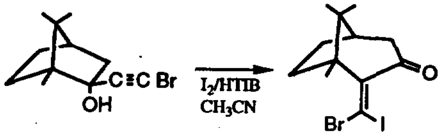


Tetrahedron Lett. **1993**, *34*, 4277

Ring Expansion of an α-Bromoalkynol Camphor by Means of Iodine and Koser's Reagent

Pakorn Bovonsombat and Edward McNelis*
Department of Chemistry, New York University, New York, New York 10003

The bromoethynyl adduct of camphor was treated with equimolar amounts of iodine and Koser's reagent to afford in good yield and in good stereospecificity a (Z)-bromoiodoenone, a synthon for enantiospecific syntheses.

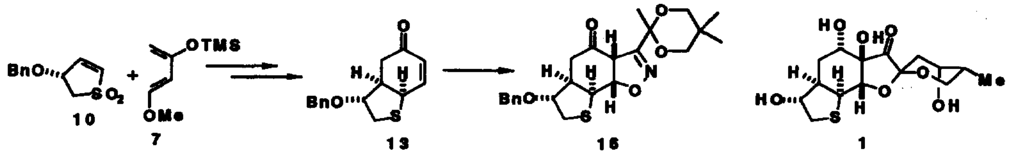


Tetrahedron Lett. **1993**, *34*, 4281

A NOVEL APPROACH TO BREYNOLIDE

Stephen F. Martin* and Dilon Daniel
Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712

A new synthetic approach to breynolide (1) features the preparation of 16 using Diels-Alder and dipolar cycloadditions as key steps.

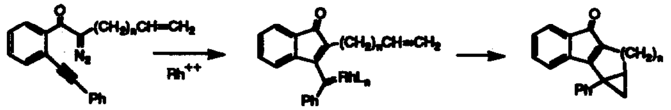


Tetrahedron Lett. **1993**, *34*, 4285

RHODIUM CARBENOID MEDIATED CYCLIZATIONS. INTRAMOLECULAR CYCLOPROPANATION AND C-H INSERTION REACTIONS DERIVED FROM TYPE II O-ALKYNYL SUBSTITUTED α-DIAZOACETOPHENONES

*Paul. H Mueller, Jamal M. Kassir, Mark A. Semones, M. David Weingarten, and Albert Padwa**
Department of Chemistry, Emory University Atlanta, GA 30322 USA

The rhodium(II) catalyzed reaction of o-alkynyl substituted α-diazo ketones gives rise to products derived from migration of the metal to the remote acetylenic carbon atom.

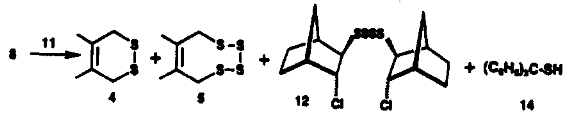


SULFENYL CHLORIDE CHEMISTRY. SULFUR TRANSFER TO DOUBLE BONDS.

Tetrahedron Lett. **1993**, *34*, 4289

Imad. A. Abu-Yousef, Rosemary C. Hynes and David N. Harpp*
Department of Chemistry
McGill University
Montreal, Quebec, Canada, H3A 2K6

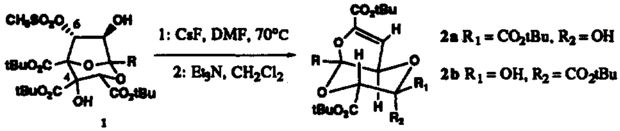
The reaction of norbornene and bicyclo[2.2.2.]octene with Ph_3CSCl and Ph_3SSCl resulted in 1,2 addition across the double bond. Subsequent rearrangement in the presence of 1,3-dimethylbutadiene gave evidence for a diatomic sulfur transfer (4, 5). The major product was bis-tetrasulfide 12.



Rearrangement of Zaragozic Acid A Derivatives.

Tetrahedron Lett. **1993**, *34*, 4293

Narindar N. Girotra*, Robert A. Reamer, and Mitree M. Ponpipom.
Merck Research Laboratories P. O. Box 2000, Rahway, New Jersey, 07065. *The C_6 mesylate of desacyl zaragozic acid A tris tBu ester has been observed to undergo rearrangement in the presence of CsF in DMF.*



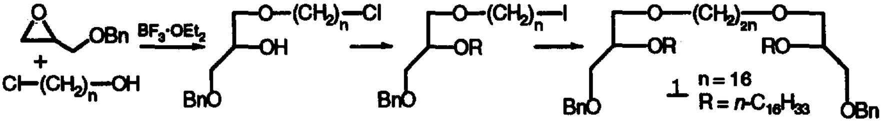
R = $C_6H_5CH_2CH(CH_3)CH(OAc)CH(=CH_2)CH_2CH_2$-

A New Approach to Archaebacterial Lipid Models

Tetrahedron Lett. **1993**, *34*, 4297

William F. Berkowitz,* Dongfeng Pan, and Robert Bittman*
Department of Chemistry and Biochemistry, Queens College of the City University of New York, Flushing, NY 11367

Archaebacterial lipid models (1) have been prepared from 1-(ω-iodoalkyl)-2-alkylglycerol diethers by silver- catalyzed coupling with the corresponding Grignard reagent.

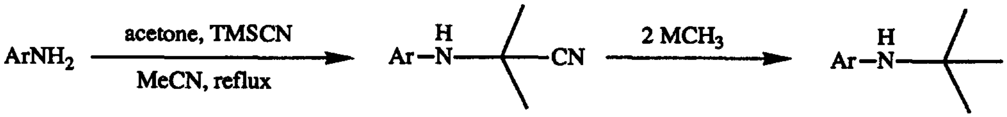


A Novel Method for the *t*-Butylation of Aromatic Amines

Tetrahedron Lett. **1993**, *34*, 4301

Michael J. Genin, Carolyn Biles and Donna L. Romero*
Upjohn Laboratories, Medicinal Chemistry Research, Kalamazoo, MI 49001.

A new method for the synthesis of *t*-butylamines from amines in two steps via α-aminonitriles, and its application to various arylamines is discussed.

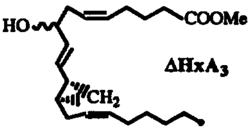


Tetrahedron Lett. **1993**, *34*, 4305

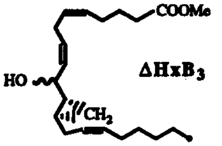
SYNTHESIS OF RACEMIC 11,12-CYCLOPROPYL ANALOGS OF HEPOXILINS A_3 AND B_3

Peter M. Demin[1] *and Cecil R. Pace-Asciak*[1,2]
[1]Research Institute, Hospital for Sick Children, Toronto, Canada M5G 1X8
[2]Department of Pharmacology, University of Toronto, Toronto, Canada M5S 1A8

Stable biologically active 11,12-cyclopropyl analogs of hepoxilins A_3 and B_3 (ΔHxA_3 and ΔHxB_3) were prepared via polyacetylenic intermediates



ΔHxA_3



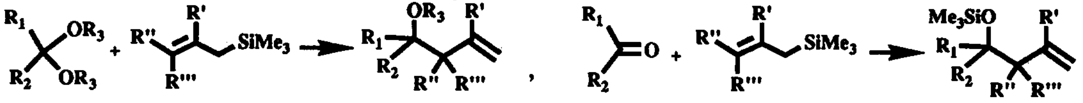
ΔHxB_3

Tetrahedron Lett. **1993**, *34*, 4309

HOMOGENEOUS CATALYSIS. USE OF THE $[TiCp_2(CF_3SO_3)_2]$ CATALYST FOR THE SAKURAI REACTION OF ALLYLIC SILANES WITH ORTHOESTERS, ACETALS, KETALS AND CARBONYL COMPOUNDS.

T. Keith Hollis, N.P. Robinson, John Whelan and B. Bosnich*
Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, U.S.A.

Allylic silanes add to orthoesters, acetals, ketals, ketones and benzaldehyde in the presence of 0.5 mol% catalyst in nitromethane. Controlled double allylations are performed with trimethyl orthoformate.

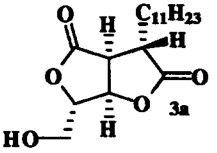


Tetrahedron Lett. **1993**, *34*, 4313

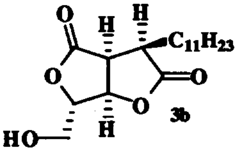
SYNTHESIS OF TWO RIGID DIACYLGLYCEROL ANALOGUES HAVING A PERHYDRO FURO[3,4-*b*]FURAN BIS-γ-BUTYROLACTONE SKELETON.2.

J. Lee[1], V. E. Marquez[1]*, N. E. Lewin,[2] and P. M. Blumberg[2]
[1]Laboratory of Medicinal Chemistry, Developmental Therapeutics Program, Division of Cancer Treatment and [2]Molecular Mechanisms of Tumor Promotion Section, Laboratory of Cellular Carcinogenesis and Tumor Promotion, National Cancer Institute, NIH, Bethesda, MD 20892.

The stereoselective synthesis of two rigid diacylglycerol analogues starting from L-arabinose is described. The bicyclic bis-butyrolactone structure was accomplished via intramolecular radical cyclization. Both **3a** and **3b** showed poor binding affinity for PK-C.



3a



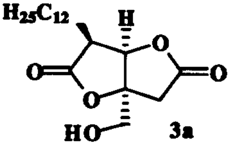
3b

Tetrahedron Lett. **1993**, *34*, 4317

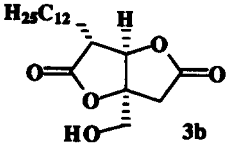
SYNTHESIS OF TWO RIGID DIACYLGLYCEROL ANALOGUES HAVING A PERHYDRO FURO[3,2-*b*]FURAN BIS-γ-BUTYROLACTONE SKELETON.3.

J. Lee[1], V. E. Marquez[1]*, A. Bahador[2], M. G. Kazanietz[2], and P. M. Blumberg[2]
[1]Laboratory of Medicinal Chemistry, Developmental Therapeutics Program, Division of Cancer Treatment and [2]Molecular Mechanisms of Tumor Promotion Section, Laboratory of Cellular Carcinogenesis and Tumor Promotion, National Cancer Institute, NIH, Bethesda, MD 20892.

The stereoselective synthesis of two new bis-γ-butyrolactones starting from 1,2:5,6-di-O-isopropylidene-α-D-allofuranose was completed in 22 steps. One of the isomers (**3a**) showed very good binding affinity towards PK-C.



3a

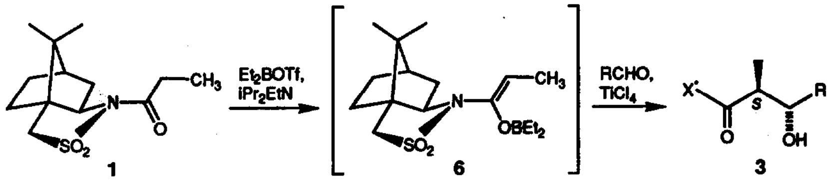


3b

Tetrahedron Lett. **1993**, *34*, 4321

EFFICIENT ASYMMETRIC SYNTHESIS OF ANTI-ALDOLS FROM BORNANESULTAM DERIVED BORYL ENOLATES

Wolfgang Oppolzer* and Philippe Lienard
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Switzerland

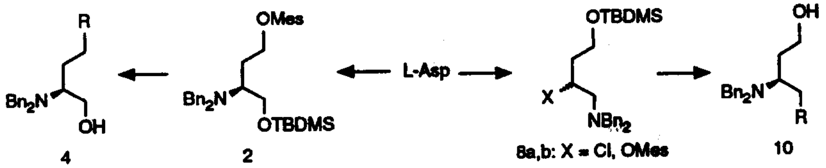


Tetrahedron Lett. **1993**, *34*, 4325

PRACTICAL EPC SYNTHESIS OF 1,2- AND 1,3- AMINO ALCOHOLS

Peter Gmeiner*, Annerose Kärtner and Dagmar Junge; Institut für Pharmazie und Lebensmittelchemie der Ludwig-Maximilians-Universität, Sophienstraße 10, D-8000 München 2, Germany

Starting from L-aspartic acid enantiomerically pure 1,2- and 1,3-amino alcohols (**4**, **10**) have been prepared using **2** and **8** as the key intermediates.

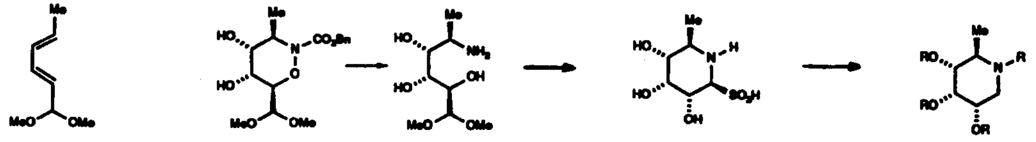


Tetrahedron Lett. **1993**, *34*, 4327

A STRAIGHTFORWARD SYNTHESIS OF THE (±)5-AMINO-5,6-DIDEOXYALLOSE-BISULFITE β-ANOMER AND OF ITS 1-DEOXY DERIVATIVE

Albert DEFOIN, Hervé SARAZIN, Jacques STREITH, E.N.S.C.Mu.
Université de Haute-Alsace, 3, rue Alfred Werner, 68093 MULHOUSE CEDEX, FRANCE.

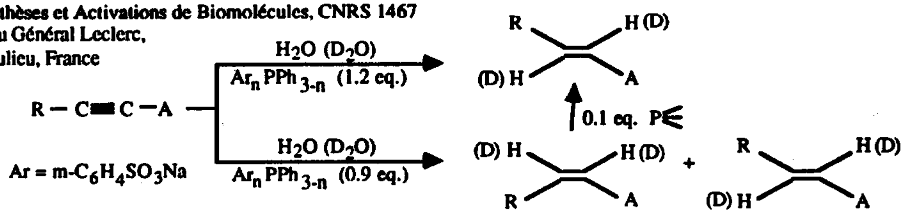
The amino-dideoxyallose bisulfite and its 1-deoxy derivative were synthesized in good yield from (E,E)-hexadienal dimethylacetal.



Tetrahedron Lett. **1993**, *34*, 4331

Chemistry in Water - Part VI. Catalytic Isomerization and Stereochemistry of Reduction of Acetylenics Mediated by Water-Soluble Phosphines.

Chantal Larpent *and Gérard Meignan
Laboratoire de Synthèses et Activations de Biomolécules, CNRS 1467
ENSCR, Avenue du Général Leclerc,
35700 Rennes-Beaulieu, France

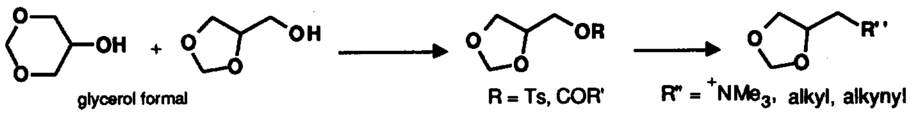


Tetrahedron Lett. **1993**, *34*, 4335

4-SUBSTITUTED DIOXOLANES BY CHEMOSELECTIVE REACTIONS ON GLYCEROL FORMAL

Jean-Louis Gras[a]*, Hervé Dulphy[a], Christophe Marot[b], Patrick Rollin[b]
a) Laboratoire de Synthèse Organique, associé au CNRS, Faculté des Sciences de Saint-Jérôme D12 - F-13397 - Marseille Cedex 20
b) Laboratoire de Chimie Bioorganique et Analytique, associé au CNRS, Université d'Orléans, B.P. 6759, F-45067 Orléans Cedex 2

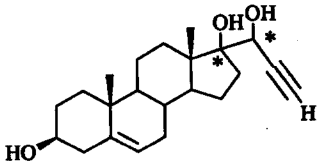
Glycerol formal is a direct source for 4-substituted-1,3-dioxolanes, through reactions chemoselectively performed on the mixture of alcohols.



Tetrahedron Lett. **1993**, *34*, 4337

21,24-Dinorchol-5-en-22-yne-3β,17,20-triol : Stereoselective Synthesis of the Four Diastereomers as Inhibitors of Ecdysone Biosynthesis

Antony Mauvais[1], Charles Hetru[2], and Bang Luu[1]*
[1]Laboratoire de Chimie Organique des Substances Naturelles, associé au CNRS, Université Louis Pasteur, 5 rue Blaise Pascal, 67084 Strasbourg, France,
[2]Laboratoire de Biologie Générale, Université Louis Pasteur, associé au CNRS, 12 rue de l'Université, 67000 Strasbourg, France.



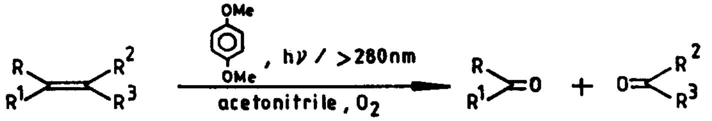
The four diastereomers are obtained through stereoselective condensations on silylated hydroxy-aldehydes.

Tetrahedron Lett. **1993**, *34*, 4341

Novel Photooxidation of Alkenes Sensitized by p-Dimethoxybenzene

Uday T. Bhalerao* and Madabhushi Sridhar
Organic Division II, Indian Institute of Chemical Technology, Hyderabad-500 007, INDIA.

p-Dimethoxybenzene catalyses photooxidation of alkenes to carbonyls.

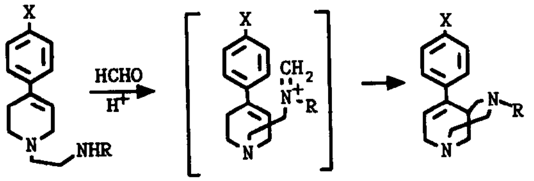


Tetrahedron Lett. **1993**, *34*, 4343

INTRAMOLECULAR CYCLIZATION WITH IMINIUM IONS. SYNTHESIS OF 1.4-DIAZABICYCLO(4.3.1)DECENE DERIVATIVES.

Emese Csuzdi, István Pallagi, Sándor Sólyom, Institute for Drug Research, H-1325 Budapest, P.O. Box 82. Hungary

Intramolecular cyclization between an iminium ion and a conjugated double bond as nucleophil terminator.

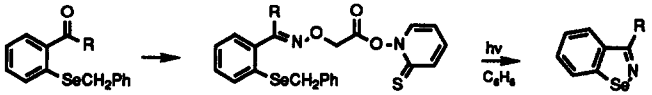


Tetrahedron Lett. **1993**, *34*, 4347

Homolytic Substitution by Iminyl Radical at Selenium: A Free-Radical Route to 1,2-Benzoselenazoles

Mei C. Fong and Carl H. Schiesser*
School of Biological and Chemical Sciences, Deakin University, Geelong, Victoria, Australia, 3217
and School of Chemistry, University of Melbourne, Parkville, Victoria, Australia, 3052

Thiohydroxamic esters derived from the O-carboxymethyl oxime derivatives of 2-(benzylseleno)benzaldehyde, 2-(benzylseleno)-acetophenone and 2-(benzylseleno)propiophenone decompose smoothly, upon irradiation, to give 1,2-benzoselenzaoles.



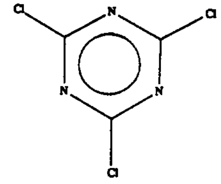
Tetrahedron Lett. **1993**, *34*, 4349

EVIDENCE FOR ANISOTROPY IN CHLORINE/NITROGEN INTERACTIONS IN THE CYANURIC CHLORIDE CRYSTAL STRUCTURE

Stephen J. Maginn[a]*, Richard G. Compton[b], Mark S. Harding[b], Colin M. Brennan[c], Robert Docherty[c]

a. Zeneca FCMO, PO Box 11, The Heath, Runcorn, Cheshire WA7 4QE
b. Physical Chemistry Laboratory, Oxford University, South Parks Rd., Oxford OX1 3QZ
c. Zeneca Specialties Research Centre, Blackley, Manchester M9 3DA

Current isotropic interatomic potential models cannot account for the observed non-linearity in intermolecular Cl--N interactions in the cyanuric chloride structure.

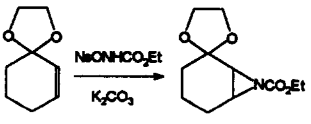


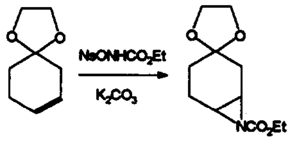
Tetrahedron Lett. **1993**, *34*, 4353

A FACILE AZIRIDINATION OF ALLYLIC AND HOMOALLYLIC CYCLIC ACETALS.

Stefania Fioravanti, M.Antonietta Loreto, Lucio Pellacani and Paolo A.Tardella, Dipartimento di Chimica, Università "La Sapienza", P.le Aldo Moro 2, I-00185 Roma, Italy

Reactions of $NsONHCO_2Et$ in the presence of solid K_2CO_3 gave aziridination of allylic and homoallylic cyclic acetals in short times and in good yields.

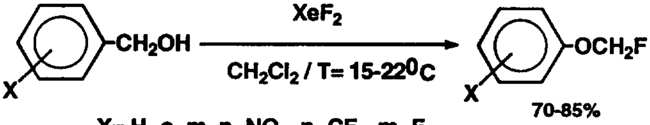




Tetrahedron Lett. **1993**, *34*, 4355

ROOM TEMPERATURE REACTIONS OF XeF_2 WITH PHENYL SUBSTITUTED ALCOHOLS.

Stojan Stavber and Marko Zupan; Laboratory for Organic and Bioorganic Chemistry, "Jožef Stefan Institute", and Department of Chemistry,University of Ljubljana, Jamova 39, 61000 Ljubljana, Slovenia



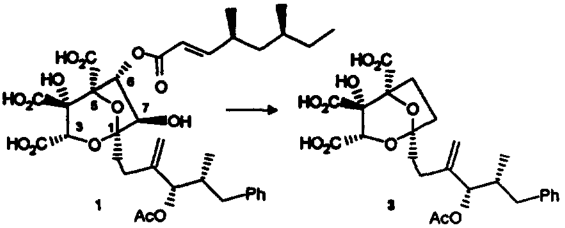
X= H, o, m, p- NO_2 ,p- CF_3, m- F

Tetrahedron Lett. **1993**, *34*, 4357

STRUCTURALLY SIMPLIFIED SQUALESTATINS: A CONVENIENT ROUTE TO A 6,7-UNSUBSTITUTED DERIVATIVE.

Michael G. Lester, Gerard M. P. Giblin, Graham G. A. Inglis, Panayiotis A. Procopiou, Barry C. Ross, Nigel S. Watson.
Glaxo Group Research Ltd, Greenford, Middlesex, UB6 OHE.

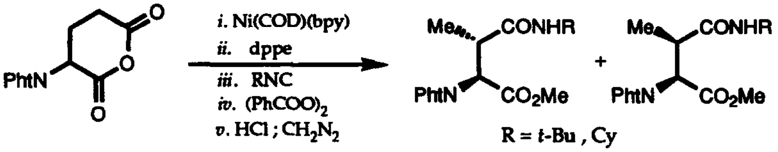
An efficient conversion of the potent squalene synthase inhibitor, Squalestatin 1, into a 6,7-unsubstituted analogue 3 by deoxygenation of an intermediate *6R,7S*-diol, is described.



Tetrahedron Lett. **1993**, *34*, 4361

SYNTHESIS OF PROTECTED 3-METHYLASPARTIC ACIDS FROM GLUTAMIC ANHYDRIDE *VIA* NICKELACYCLES

Ana M. Castaño[a] and Antonio M. Echavarren*[,a,b]
[a] Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006, Madrid, Spain
[b] Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.

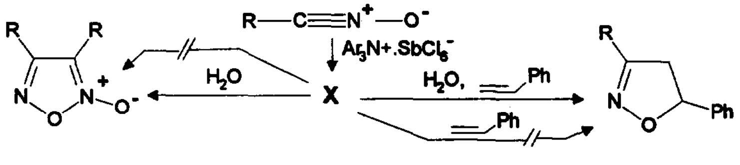


Tetrahedron Lett. **1993**, *34*, 4363

NEW ASPECTS OF NITRILE OXIDES CHEMISTRY.

Sergio Auricchio,* Aldo Ricca, G. Battista Romeo, and Ada M. Truscello.
Dipartimento di Chimica, Politecnico di Milano, via Mancinelli 7, 20131 Milano.

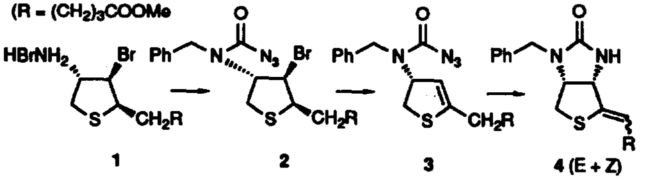
Reactivity of nitrile oxides towards both dimerization and cycloaddition with dipolarophiles can be inhibited by catalytic amount of tris-(4-bromophenyl)-aminium hexachloroantimonate and subsequently restored.



Tetrahedron Lett. **1993**, *34*, 4365

A NOVEL ENANTIOSELECTIVE SYNTHESIS OF (+)-BIOTIN

Frederik D. Deroose and Pierre J. De Clercq*
University of Ghent, Department of Organic Chemistry, Krijgslaan, 281 (S.4), B-9000 GENT (Belgium)

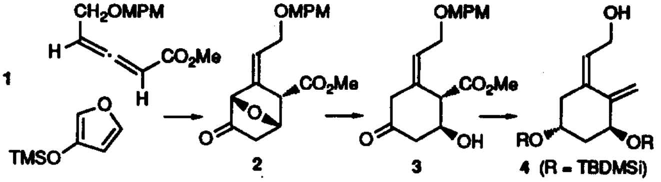


An enantioselective synthesis of (+)-biotin from L-cysteine (14 steps) is reported based on the unprecedented intramolecular cycloaddition of 3 to 4. The preparation of 1 is analogous to work described by Confalone, et al., *J. Am. Chem. Soc.* **1977**, *99*, 7020.

A NOVEL SYNTHESIS OF AN A-RING PRECURSOR TO 1α-HYDROXYVITAMIN D

Tetrahedron Lett. **1993**, *34*, 4369

Johny De Schrijver and Pierre J. De Clercq*
University of Ghent, Department of Organic Chemistry, Krijgslaan, 281 (S.4), B-9000 GENT (Belgium)



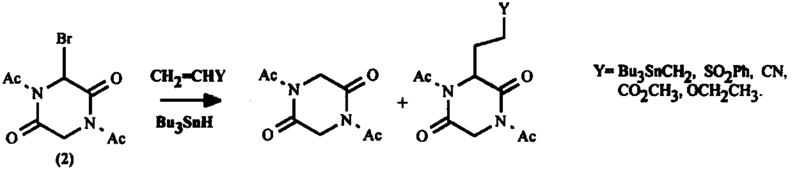
DA-reaction of allene **1** with 3-trimethylsilyloxyfuran and hydrolysis to **2**; followed by SmI_2 reductive opening to **3** are the key-steps in the synthesis of (±)-**4**, a synthon for 1α-OH vit D derivatives.

RADICAL ADDITIONS OF SIMPLE PIPERAZINE-2,5-DIONES.

Tetrahedron Lett. **1993**, *34*, 4373

Christina L.L. Chai* and Dennis M. Page, Department of Chemistry,
P.O. Box 600, Victoria University of Wellington, Wellington, New Zealand.

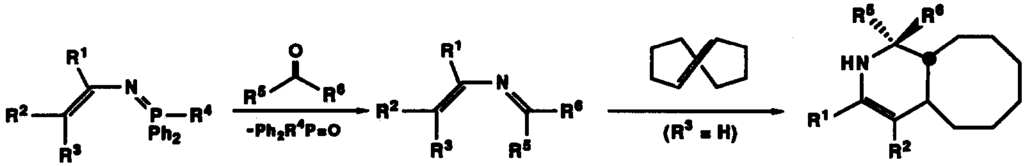
The behaviour of the captodative radical derived from the piperazine-2,5-dione (2) towards a variety of alkenes is investigated.



PREPARATION AND REACTIVITY OF ELECTRON-POOR 2-AZADIENES. DIELS-ALDER REACTION WITH *TRANS*-CYCLOOCTENE.

Tetrahedron Lett. **1993**, *34*, 4377

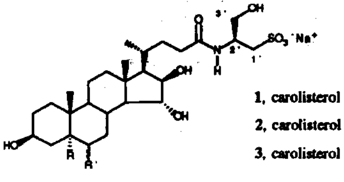
Francisco Palacios*, Itziar Perez de Heredia and Gloria Rubiales. Departamento de Química Orgánica . Facultad de Farmacia. Universidad del País Vasco. Aptdo. 450, 01007 Vitoria, SPAIN.



A NOVEL GROUP OF POLYHYDROXYCHOLANIC ACID DERIVATIVES FROM THE DEEP WATER STARFISH *STYRACASTER CAROLI*

Tetrahedron Lett. **1993**, *34*, 4381

Francesco De Riccardis, Luigi Minale* and Raffaele Riccio - Dipartimento di Chimica delle Sostanze Naturali, Università di Napoli "Federico II", Napoli, Italy; Maria Iorizzi - Università degli Studi del Molise, Facoltà di Agraria, Campobasso, Italy; Cécile Debitus and Daniel Duhet - ORSTOM, Centre de Nouméa, New Caledonia; Claude Monniot - Museum Nationale d'Histoire Naturelle, Paris, France.



1, carolisterol A R=OH; R'=◄OH
2, carolisterol B R=OH; R'==O
3, carolisterol C R=H; R'=⋯OH

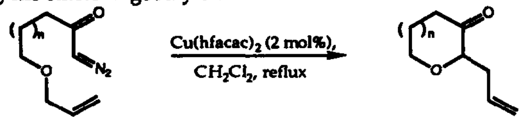
Three novel polyhydroxysteroid constituents have been isolated from the starfish *Styracaster caroli* collected at a depth of 2000 m off New Caledonia. These, designated carolisterols A - C (1 - 3), are characterized by a polyhydroxycholanic acid moiety, in which the 24-carboxylic acid function is found as an amide derivative of D-cysteinolic acid.

Tetrahedron Lett. **1993**, *34*, 4385

SYNTHESIS OF CYCLIC ETHERS FROM COPPER CARBENOIDS BY FORMATION AND REARRANGEMENT OF OXONIUM YLIDES

J. Stephen Clark and Steven A. Krowiak, Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK, and Leslie J. Street, Merck Sharp and Dohme Research Laboratories, Neuroscience Research Centre, Terlings Park Eastwick Road, Harlow, Essex, CM20 2QR, UK

Intramolecular insertion of allyl ethers into copper carbenoids, followed by rearrangement of the resulting ylide-type species, affords cyclic ethers in good yield.



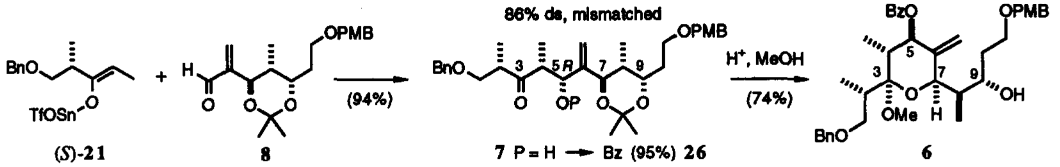
n = 1, 83%
n = 2, 76%
n = 3, 40%

Tetrahedron Lett. **1993**, *34*, 4389

STUDIES IN BIOMIMETIC POLYETHER SYNTHESIS: SYNTHESIS OF AN A-RING SUBUNIT OF ETHEROMYCIN.

I. Paterson,* R. D. Tillyer, and G. R. Ryan, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

The acid-promoted cyclisation behaviour of a series of potential C_1–C_{11} segments of etheromycin were studied. Formation of the A-ring derivative **6** can be efficiently accomplished by the sequence shown below.



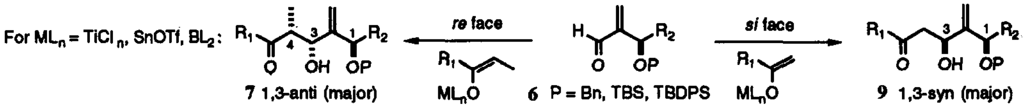
(*S*)-**21** **8** **7** P = H → Bz (95%) **26** **6**

Tetrahedron Lett. **1993**, *34*, 4393

1,3-ASYMMETRIC INDUCTION IN THE ALDOL REACTIONS OF α-METHYLENE-β-ALKOXY ALDEHYDES.

I. Paterson,* S. Bower, and R. D. Tillyer, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

The sense and level of 1,3-asymmetric induction in the aldol reactions of acyclic ketones with α-methylene-β-alkoxy aldehydes varies with the enolate structure and the β-hydroxyl protecting group in the aldehyde. The product allylic alcohols can often be obtained with high diastereoselectivity.



7 1,3-anti (major) 69–95% ds

6 P = Bn, TBS, TBDPS; R_2 = ^{i}Pr, ^{n}Pr

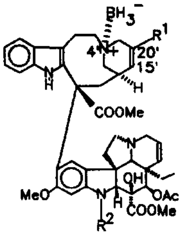
9 1,3-syn (major) 76–89% ds

Tetrahedron Lett. **1993**, *34*, 4397

BORANE COMPLEXES OF VINBLASTINE TYPE DIINDOLE DERIVATIVES

M. Balázs,[a] *Cs. Szántay Jr.,*[b] *H. Bölcskei*[b] *and Cs. Szántay*[a]
[a] Central Research Institute for Chemistry, Hungarian Academy of Sciences
H-1025 Budapest, POB 17, Hungary.
[b] Chemical Works of Gedeon Richter Ltd.

In the course of investigating the ferric chloride mediated coupling of catharanthine with vindoline and their derivatives, the borane complexes of 15',20'-anhydrovinblastine (AVLB), 20'-deethyl-AVLB and N-demethyl-AVLB (9,10,11) have been synthesized. The corresponding bases have also been obtained in high yield.



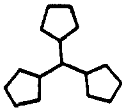
	R^1	R^2
9	Et	Me
10	H	Me
11	Et	H

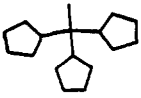
Tetrahedron Lett. **1993**, *34*, 4399

DEGENERACIES IN MOLECULAR GRAPH SPECTRA

T.P.Radhakrishnan, School of Chemistry,
University of Hyderabad, Hyderabad - 500 134, India.

Unusual degeneracies in the eigen value spectrum of systems like 1 and 2 are explained on the basis of the molecular graph decomposition.


1

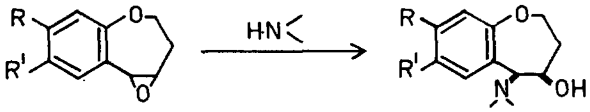

2

Tetrahedron Lett. **1993**, *34*, 4403

REGIO- AND STEREOSELECTIVE EPOXIDE RING OPENING REACTIONS OF 4,5-EPOXY-2,3,4,5-TETRAHYDRO-1-BENZOXEPINES WITH SECONDARY AMINES

V.K. Tandon* and Animesh Chandra
Department of Chemistry, Lucknow University, Lucknow, India

A Regio-and Stereoselective synthesis of cis-5-t-amino-2,3,4,5-tetrahydro-1-benzoxepin-4-ols via epoxide ring opening reactions with secondary amines.

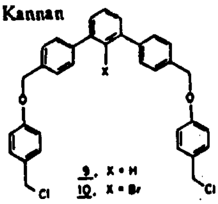


Tetrahedron Lett. **1993**, *34*, 4407

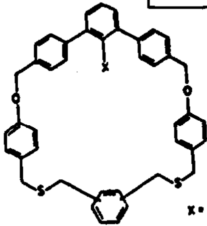
SYNTHESIS OF DITHIACYCLOPHANES WITH LARGE CAVITY

Perumal Rajakumar* and Arunachalam Kannan
Department of Organic Chemistry,
University of Madras,
Madras, Tamilnadu-600 025, INDIA.

Coupling of the dichlorides 9 & 10 with xylenedithiols and m-terphenyldithiol under high dilution technique in presence of KOH in benzene-ethanol afforded the cyclophanes of the class 1 & 2

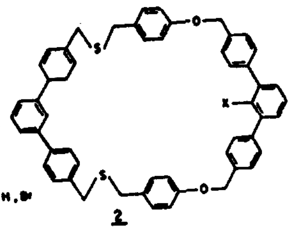


9, X = H
10, X = Br



1

X = H, Br



2

Tetrahedron Lett. **1993**, *34*, 4411

CLEAVAGE OF RESIN-BOUND PEPTIDE ESTERS WITH AMMONIA VAPOUR. SIMULTANEOUS MULTIPLE SYNTHESIS OF PEPTIDE AMIDES.

Andrew M. Bray, Robert M. Valerio and N. Joe Maeji.
Chiron Mimotopes Pty. Ltd., 11 Duerdin St., Clayton, Victoria 3168, Australia