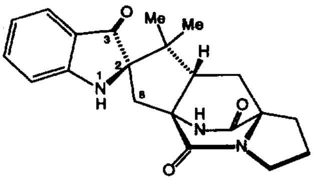
GRAPHICAL ABSTRACTS

Tetrahedron, **1993**, *49*, 8471

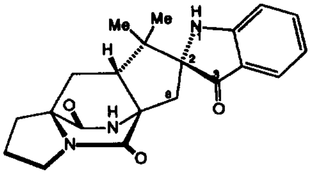
BIOSYNTHESIS OF BREVIANAMIDES A AND B: IN SEARCH OF THE BIOSYNTHETIC DIELS-ALDER CONSTRUCTION.

Juan F. Sanz-Cervera, Tomasz Glinka, and Robert M. Williams*
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

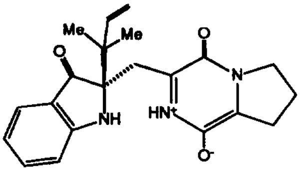
Studies on the biosynthesis of brevianamides A (1) and B (2). Compound **27** is proposed as a key biosynthetic intermediate.



1, *(+)-BREVIANAMIDE A*



2, *(+)-BREVIANAMIDE B*



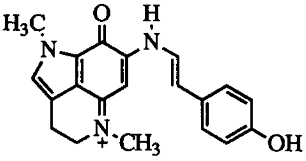
27

Tetrahedron, **1993**, *49*, 8483

MAKALUVAMINE G, A CYTOTOXIC PIGMENT FROM THE INDONESIAN SPONGE *HISTODERMELLA* SP.

John R. Carney and Paul J. Scheuer,* Deptartment of Chemistry, University of Hawaii at Manoa, 2545 The Mall, Honolulu, HI 96822 and Michelle Kelly-Borges, Harbor Branch Oceanographic Institute, 5600 Old Dixie Highway, Fort Pierce, FL 34936

Makaluvamine G (5) was isolated from the sponge *Histodermella* sp. The compound shows significant in vitro cytotoxicity to several human tumor cell lines and inhibits topoisomerase-I (IC_{50} = 3 μM), RNA (15 μM), DNA (15 μM) and protein (21 μM) synthesis.



5

Tetrahedron, **1993**, *49*, 8487

LITHIUM CARBENOIDS INDUCED RING ENLARGEMENT OF SILACYCLOBUTANE INTO 2-HALO-1-SILACYCLOPENTANE AND ITS USE IN ORGANIC SYNTHESIS

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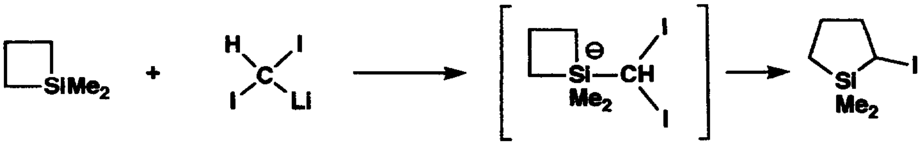
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan
Noorsaadah Abd. Rahman
Department of Chemistry, Faculty of Science, University of Malaya, 59100 Kuala Lumpur, Malaysia

An addition of lithium diisopropylamide to a solution of 1,1-dimethyl-1-silacyclobutane and dihalomethane provided the corresponding 1,1-dimethyl-2-halo-1-silacyclopentane in good yield.

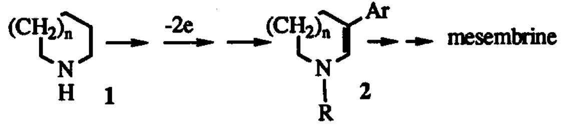


Tetrahedron, **1993**, *49*, 8503

A COVENIENT ROUTE TO β-ARYL-SUBSTITUTED CYCLIC ENAMINES AS KEY SYNTHETIC INTERMEDIATES OF *SCELETIUM* AND *AMARYLLIDACEAE* ALKALOIDS

Yoshihiro Matsumura,* Jun Terauchi, Takashi Yamamoto,
Takashi Konno, and Tatsuya Shono
Division of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University
Yoshida, Sakyo, Kyoto 606-01, Japan

β-Aryl-substituted cyclic amines 2 were prepared from corresponding cyclic amines 1 by utilizing anodic oxidation and they were used as building blocks for some alkaloids such as mesembrine.



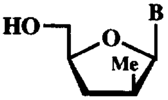
n= 0 ~ 2

Tetrahedron, **1993**, *49*, 8513

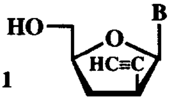
Nucleosides and Nucleotides. 120.
Stereoselective Radical Deoxygenation of *tert*-Alcohols in the Sugar Moiety of Nucleosides: Synthesis of 2',3'-Dideoxy-2'-*C*-methyl- and -2'-*C*-ethynyl-β-D-*threo*-pentofuranosyl Pyrimidines and Adenine as Potential Antiviral and Antitumor Agents

Akio Kakefuda,[a] Yuichi Yoshimura,[a] Takuma Sasaki,[b] and Akira Matsuda[a,*]
Faculty of Pharmaceutical Sciences, Hokkaido University,[a] Kita-12, Nishi-6, Kita-ku, Sapporo 060, Japan and Cancer Research Institute, Kanazawa University,[b] Takara-machi, Kanazawa 920, Japan

Synthesis of 1 and 2 was achieved via radical deoxygenation of the corresponding *tert*-methoxalyl ester.



1



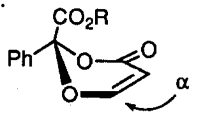
2

Tetrahedron, **1993**, *49*, 8529

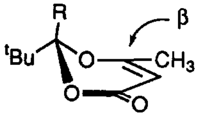
l-MENTHYL (*R*)-2-PHENYL-4-OXO-1,3-DIOXINE-2-CARBOXYLATE: DIASTEREOFACIAL SELECTIVITY FOR CONJUGATE ADDITION AND ITS EXPLANATION

Masayuki Sato, Masayuki Murakami, and Chikara Kaneko
Pharamaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan
Toshio Furuya
Tsukuba Research Laboratories, Yamanouchi Pharmaceutical Co. Ltd., 21 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

Conjugate addition of RMgX/CuI to A proceeds from the α-side. This selectivity is reverse to that observed in B. A possible reason for this difference is proposed.



A ($R=CH_3$, *l*-menthyl)

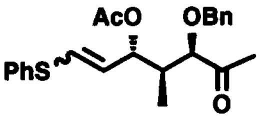


B ($R=H, CH_3$)

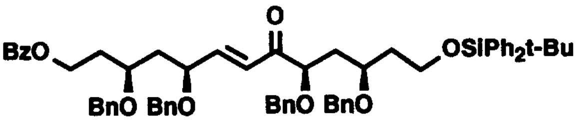
Tetrahedron, **1993**, *49*, 8541

A Carbohydrate Approach to Polyol Fragments of Amphotericin and the Trienomycin- and Mycotrienin Antibiotics

Alois Fürstner*, Judith Baumgartner
Institute of Organic Chemistry, Technical University, A-8010 Graz, Austria



C9-C14 fragment of trienomycin



C1-C13 fragment of amphoteronolide B

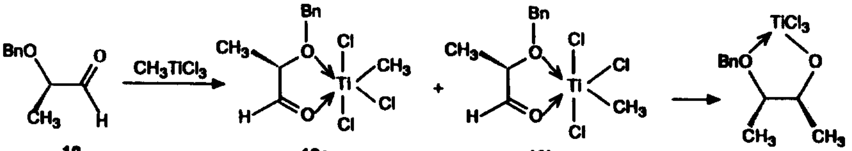
Synthesis of enantiomerically pure segments of macrolide antibiotics by reductive ring opening of deoxyhalo sugars with Zn/Ag-graphite.

Tetrahedron, **1993**, *49*, 8561

First Direct NMR Spectroscopic Observation of a Cram-Chelate Involving a Chiral α-Alkoxy Aldehyde

Manfred T. Reetz*, Burkhard Raguse and Thomas Seitz
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany
Fachbereich Chemie der Universität, Hans-Meerwein-Straße, 35043 Marburg, Germany

^{13}C-NMR spectroscopic evidence for the Cram-type chelates 13a/13b has been obtained.



10 **13a** **13b** **14**

Tetrahedron, **1993**, *49*, 8569

SYNTHESIS AND ELECTROCHEMICAL INVESTIGATION OF β-ALKYLOXY SUBSTITUTED meso-TETRAPHENYL-PORPHYRINS

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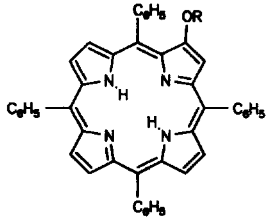
Institut für Chemie der Medizinischen Universität zu Lübeck, Ratzeburger Allee 160, 23538 Lübeck, Germany
José A. S. Cavaleiro,* Maria da Graça P. M. S. Neves and Maria de Fátima Condesso
Department of Chemistry, University of Aveiro, 3800 Aveiro, Portugal

The synthesis of alkyloxy substituted porphyrins is described. The electrochemical properties of the synthesized compounds were investigated by cyclic voltammetry.

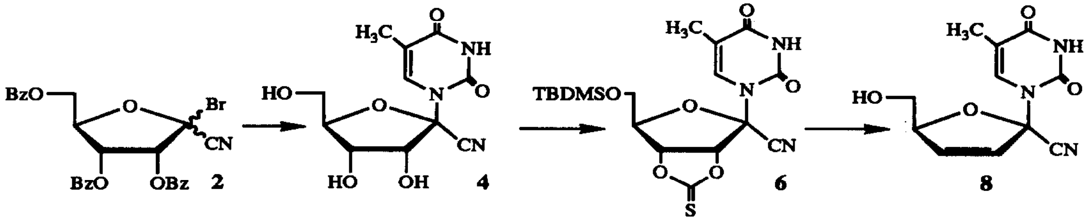


Tetrahedron, **1993**, *49*, 8579

SYNTHESIS AND STRUCTURE DETERMINATION OF THE FIRST 1'-*C*-CYANO-β-D-NUCLEOSIDES

V.Uteza, G.R.Chen, J.Le Quan Tuoi, G.Descotes, B.Fenet and A.Grouiller*, Université Lyon I, 69622 Villeurbanne Cedex, (France)

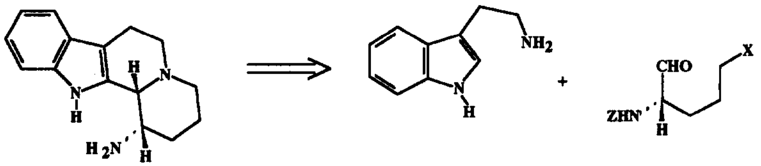
The 1'-*C* -cyanonucleoside **4**, obtained from the *C* -1 *gem* disubstituted sugar **2**, was converted in four steps into the olefinic nucleoside **8**.



Tetrahedron, **1993**, *49*, 8589

STEREOSPECIFIC PICTET-SPENGLER REACTION: SYNTHESIS OF CIS (+)-(1S,12bR)-1-AMINOINDOLOQUINOLIZIDINE FROM A PURE α-(S)-AMINO-ALDEHYDE DERIVATIVE

Patricia Melnyk, Pierre Ducrot, Claude Thal*
ICSN, CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette, France



Pictet-Spengler reaction provides cis (+)-1-(S)-aminoindolo[2,3-a]quinolizidine in an enantio- and diastereoselective manner, using an α-aminoaldehyde derived from L-glutamic acid.

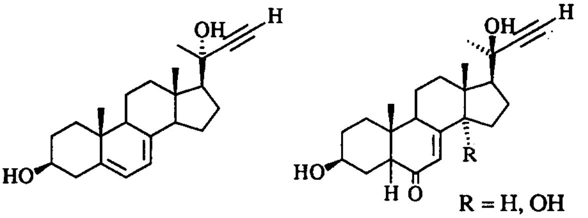
Tetrahedron, **1993**, *49*, 8597

INHIBITION OF ECDYSONE BIOSYNTHESIS : PREPARATION OF ACETYLENIC INTERMEDIATES

Antony Mauvais[1], Charles Hetru[2], Jean-Pierre Roussel[2] and Bang Luu[1]*

[1]Laboratoire de Chimie Organique des Substances Naturelles, CNRS URA 31, 5 rue Blaise Pascal, 67000 Strasbourg. [2]Laboratoire de Biologie Générale, CNRS URA 1490, 12 rue de l'Université, 67000 Strasbourg, France.

The synthesis of a $\Delta^{4,7}$ pregnadiene and its hydroboration-oxidation leads to inhibitors analogue of ecdysone precursors.

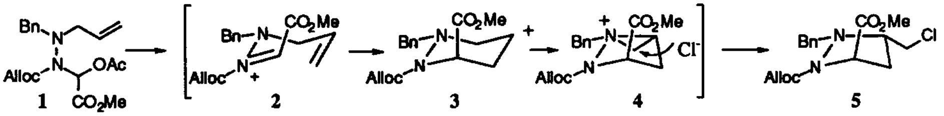


Tetrahedron, **1993**, *49*, 8605

SYNTHESIS OF CYCLIC α-HYDRAZINO ACID DERIVATIVES VIA *N*-ACYLHYDRAZONIUM IONS

Floris P.J.T. Rutjes, N. Miranda Teerhuis, Henk Hiemstra* and W. Nico Speckamp*
Laboratory of Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The synthesis of cyclic α-hydrazino esters of different ring sizes is described. Cyclization occurs via the highly reactive *N*-acylhydrazonium ion **2**, to give the cyclic cationic intermediate **3**. This species might either rearrange via the aziridinium intermediate **4** to afford the five-membered ring **5**, or when stabilized, directly lead to the cyclic α-hydrazino ester.



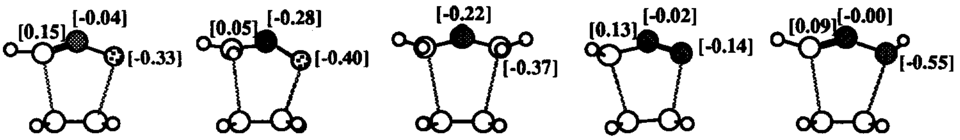
Variation of the π-nucleophiles furnishes various functionalized α-hydrazino esters. A deprotection seqenence that leads to the free cyclic α-hydrazino acids is also detailed.

Tetrahedron, **1993**, *49*, 8629

ELECTROSTATIC EFFECTS IN 1,3-DIPOLAR CYCLOADDITION REACTIONS TO CHIRAL ALLYL ETHERS: A RATIONALE FOR THE EXPERIMENTALLY OBSERVED DIASTEREOSELECTIVITIES

Annunziata, R.; Benaglia, M.; Cinquini, M.; Raimondi, L.*
Centro CNR and Dipartimento di Chimica Organica e Industriale - Università di Milano (Italy)

A rationale is provided for differences in stereoselectivities for 1,3-dipolar cycloadditions based on T.S.s charge distribution. This was evaluated with two different methods (Mulliken and CHELPG) on the *ab initio* located RHF/3-21G transition structures for model reactions. The trend observed in *ab initio* charge distributions offers a rationale for the experimentally observed diastereoselectivities and allows predictions of reactivity.

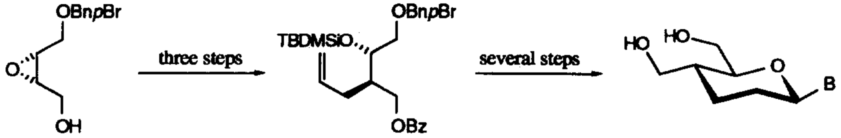


Tetrahedron, **1993**, *49*, 8637

SYNTHESIS OF 4-*C*-HYDROXYMETHYL HEXOPYRANOSYL NUCLEOSIDES AS POTENTIAL INHIBITORS OF HIV.

Magnus Björsne, Björn Classon, Ingemar Kvarnström and Bertil Samuelsson*
Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

4-*C*-Hydroxymethyl hexopyranoside nucleosides are synthesised using a Sharpless epoxidation procedure followed by a regioselective epoxide opening with allylmagnesium bromide giving the required chirality of the hexopyranoside moiety.



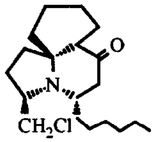
Tetrahedron, **1993**, *49*, 8645

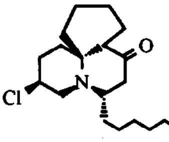
CYLINDRICINES A AND B, NOVEL ALKALOIDS FROM THE ASCIDIAN *CLAVELINA CYLINDRICA*

Adrian J. Blackman* and Caiping Li, Chemistry Dept., Uni. of Tasmania, P.O. Box 252C, Hobart, Tas 7001.
David C. R. Hockless, Brian W. Skelton and Allan H. White, Chemistry Dept., Uni. of Western Australia, Nedlands, W.A. 6009.

The ascidian *Clavelina cylindrica* has given cylindricine A, the first pyrrolo[2.1-j]-quinoline known from nature and cylindricine B, the first example of the new pyrido-[2.1-j]quinoline ring system. Single crystal X-ray studies support the structures.

Cylindricine A





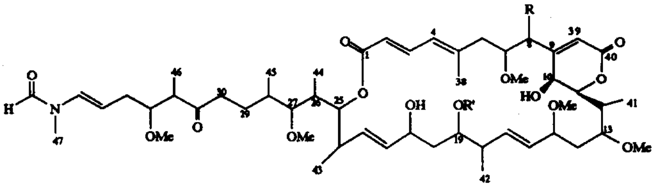
Cylindricine B

Tetrahedron, **1993**, *49*, 8657

Three New Potent Cytotoxic Macrolides Closely Related to Sphinxolide from the New Caledonian Sponge *Neosiphonia superstes.*

M.V. D'Auria, L.Gomez Paloma, L. Minale* and A. Zampella,
Dipartimento di Chimica delle Sostanze Naturali, via D. Montesano 49, 80131, Napoli, ITALY
J.F. Verbist and C. Roussakis, *Faculté de Pharmacie, 1, Rue Gaston Veil 44035 Nantes Cedex, FRANCE.*
Cécile Debitus, *Centre ORSTOM, B.P. A5, Nouméa, NOUVELLE CALEDONIE.*

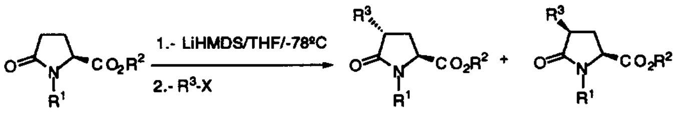
Three new potent cytotoxic macrolides closely related to sphinxolide (2 R=H, R'=H; 3 R=OMe, R'=Me; 4 R=H, R'=Me) have been isolated from the sponge *Neosiphonia superstes*. Their structure elucidation and activity against several human carcinoma cells is reported.



Tetrahedron, **1993**, *49*, 8665

STEREOSELECTIVE REACTIONS OF LITHIUM ENOLATES DERIVED FROM N-BOC PROTECTED PYROGLUTAMIC ESTERS.

Jesús Ezquerra*[1], Concepción Pedregal[1], Almudena Rubio[1], Belén Yruretagoyena[1], Ana Escribano[2] and Francisco Sánchez-Ferrando[3].
1.- Centro de Investigación Lilly, S. A., Paraje de la Cruz S/N. 28130 Valdeolmos. Madrid. Spain.
2.- Departamento de Química Orgánica, Universidad Autónoma de Madrid. Cantoblanco, 28049 Madrid. Spain.
3.- Departament de Química. Universitat Autònoma de Barcelona. Bellaterra. 08193 Barcelona. Spain



Lithium enolates of **1a** and **1b** react with reactive electrophiles in good yields without epimerization of the chiral centre. The stereoselectivity of the proccess is not dependent on the ester group bulkiness.

1a, R^1= BOC, R^2= Et
1b, R^1= BOC, R^2= ^{t}Bu

2a-p

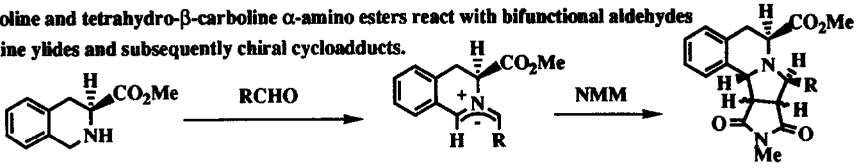
3a-p

Tetrahedron, **1993**, *49*, 8679

X=Y-ZH SYSTEMS AS POTENTIAL 1,3-DIPOLES. PART 40.[1]
CHIRAL AZOMETHINE YLIDES FROM HOMOCHIRAL CYCLIC α-AMINO ESTERS. UNUSUAL REGIOSPECIFIC DEPROTONATION OF IMINIUM IONS.

R. Grigg,* Z. Rankovic, M. Thornton-Pett and A. Somasunderam; School of Chemistry, Leeds University, Leeds LS2 9JT.

Chiral tetrahydroisoquinoline and tetrahydro-β-carboline α-amino esters react with bifunctional aldehydes to furnish chiral azomethine ylides and subsequently chiral cycloadducts.



Tetrahedron, **1993**, *49*, 8691

Reaction of Phosphonium Ylides with 4-Triphenylmethyl-1,2-benzoquinone

Fayez H. Osman, * Naglaa M. Abd El-Rahman and Fatma A. El-Samahy

Department of Pesticide Chemistry, National Research Centre, Dokki, Cairo 12622, Egypt.