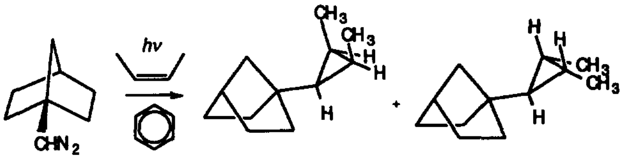
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1993**, *34*, 3967

THE STEREOCHEMISTRY OF ADDITION OF AN ALKYLCARBENE

Nanying Bian and Maitland Jones, Jr.
Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

1-Norbornylcarbene adds stereospecifically to the 2-butenes.

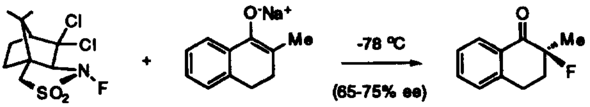


Tetrahedron Lett. **1993**, *34*, 3971

ASYMMETRIC FLUORINATION OF ENOLATES WITH N-FLUORO 2,10-(3,3-DICHLOROCAMPHORSULTAM)

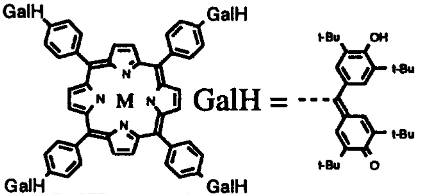
Franklin A. Davis* Ping Zhou and Christopher K. Murphy
Department of Chemistry, Drexel University, Philadelphia, PA 19104

Asymmetric fluorination with nonracemic N-fluoro dichlorocamphorsultam affords α-fluoro carbonyl compounds in good yield and up to 75% ee.



Tetrahedron Lett. **1993**, *34*, 3975

Preparation of *meso*-Tetra(4-galvinolphenyl)porphyrin — A Building Block for Molecular Magnetic Materials



$GalH_4TPPM$

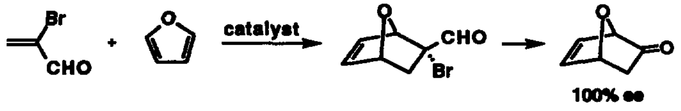
David A. Shultz,* David A. Knox, Larry W. Morgan, Kay Sandberg, and Gregory N. Tew
Department of Chemistry, Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204

The synthesis and electrochemistry of a free-radical substituted metalloporphyrin are described. The porphyrin is prepared in four steps in good yield. Voltammetry indicates that a stable pentaradical may be prepared.

Tetrahedron Lett. **1993**, *34*, 3979

CATALYTIC ENANTIOSELECTIVE DIELS-ALDER ADDITION TO FURAN PROVIDES A DIRECT SYNTHETIC ROUTE TO MANY CHIRAL NATURAL PRODUCTS

E. J. Corey and Teck-Peng Loh
Department of Chemistry
Harvard University
Cambridge, Massachusetts, 02138

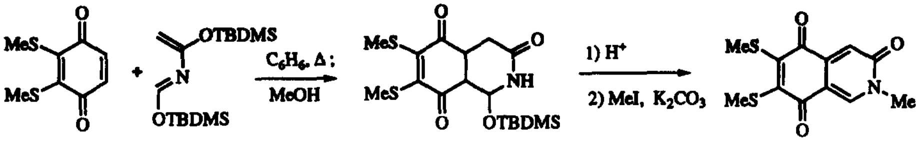


SYNTHESIS OF PERFRAGILIN B, A CYTOTOXIC ISOQUINOLINE QUINONE ISOLATED FROM THE BRYOZOAN *MEMBRANIPORA PERFRAGILIS*.

Tetrahedron Lett. **1993,** *34,* 3983

Aeri Park and Francis J. Schmitz*, Department of Chemistry and Biochemistry,University of Oklahoma, Norman, Oklahoma 73019-0370

Perfragilin B, a cytotoxic isoquinoline quinone has been synthesized.

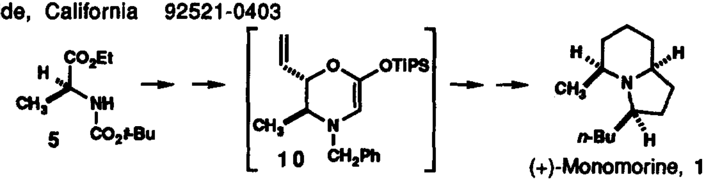


A General Route for the Synthesis of Enantiopure Indolizidine Alkaloids from α-Amino Acids. Total Synthesis of (+)-Monomorine

Tetrahedron Lett. **1993,** *34,* 3985

Steven R. Angle* and J. Guy Breitenbucher Department of Chemistry, University of California, Riverside, California 92521-0403

The total synthesis of the indolizidine alkaloid (+)-monomorine from amino ester **5** is reported. The key step is a conformationally restricted Claisen rearrangement of **10**.



5

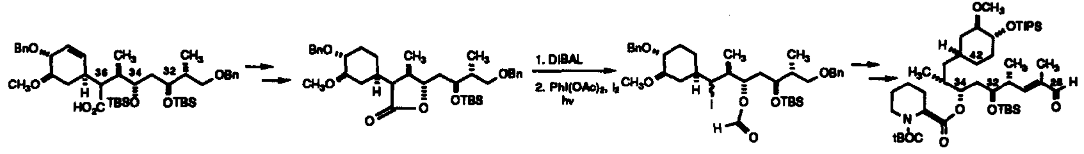
10

(+)-Monomorine, 1

AN APPLICATION OF THE SUÁREZ REACTION TO THE REGIOSPECIFIC AND STEREOSPECIFIC SYNTHESIS OF THE C_{28}-C_{42} SEGMENT OF RAPAMYCIN

Tetrahedron Lett. **1993,** *34,* 3989

*Cheryl M. Hayward, Matthew J. Fisher, Daniel Yohannes, and Samuel J. Danishefsky**
Department of Chemistry, Yale University, New Haven, CT 06511-8118 USA



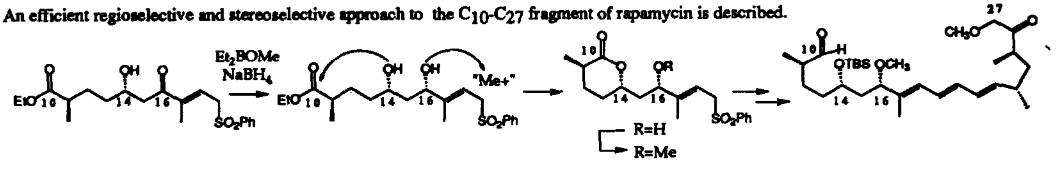
Specific lactonization of a TBS ether followed by iodinative scission of a γ-lactol allowed for differentiation of the C_{32} and C_{34} hydroxyl groups en route to the C_{28}-C_{42} fragment of rapamycin.

AN APPLICATION OF THE EVANS-PRASAD 1,3-SYN DIOL SYNTHESIS TO A STEREOSPECIFIC SYNTHESIS OF THE C_{10}-C_{27} SEGMENT OF RAPAMYCIN

Tetrahedron Lett. **1993,** *34,* 3993

Raymond F. Horvath, Robert G. Linde II, Cheryl M. Hayward, Jesus Joglar,
*Daniel Yohannes and Samuel J. Danishefsky**
Department of Chemistry, Yale University New Haven, CT 06511-8118 USA

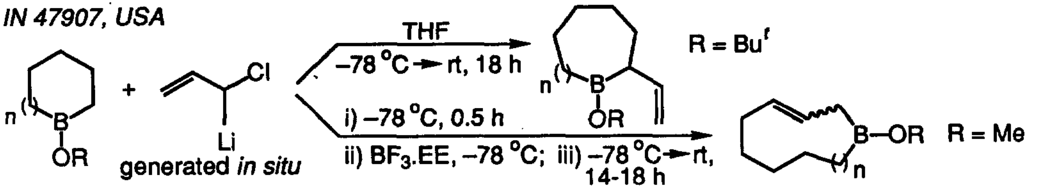
An efficient regioselective and stereoselective approach to the C_{10}-C_{27} fragment of rapamycin is described.



Tetrahedron Lett. **1993**, *34*, 3997

Three-Carbon Ring Expansion of Boracyclanes

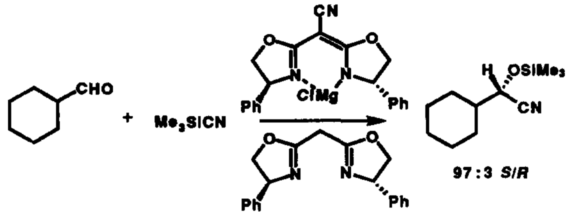
Herbert C. Brown* and Seetharaman Jayaraman
H.C. Brown and R.B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette IN 47907, USA



Tetrahedron Lett. **1993**, *34*, 4001

ENANTIOSELECTIVE CONVERSION OF ALDEHYDES TO CYANOHYDRINS BY A CATALYTIC SYSTEM WITH SEPARATE CHIRAL BINDING SITES FOR ALDEHYDE AND CYANIDE COMPONENTS

E. J. Corey and Zhe Wang
Department of Chemistry
Harvard University
Cambridge, Massachusetts, 02138

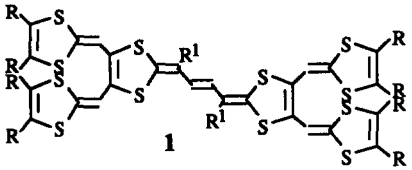


Tetrahedron Lett. **1993**, *34*, 4005

VINYLOGS OF TETRATHIAFULVALENE (TTF) BEARING FOUR 1,4-DITHIAFULVEN-6-YL SUBSTITUENTS : NOVEL HIGHLY EXTENDED AND SULFUR-RICH π-DONORS

Ahmed Belyasmine,[a] Pierre Frère,[a] Alain Gorgues,[a]* Michel Jubault,[a] Guy Duguay,[b] and Piétrick Hudhomme[b]
[a] Laboratoire de Chimie Organique Fondamentale et Appliquée, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France
[b] Laboratoire de Synthèse Organique, Université de Nantes, 2 rue de la Houssinière, 44072 Nantes, France

The title compounds **1** [R^1 = H (**a**), Ph (**b**), pMe-Ph (**c**); R or R-R = CO$_2$Me (α), (CH=CH)$_2$ (β), H (γ)] are synthesized in three steps from the monoacetal of acetylenedicarbaldehyde and 3-thioxo-1,2-dithioles via fourfold Wittig reactions. Their cyclovoltammograms show they behave as very strong π-donors with the potential to afford conducting salts.



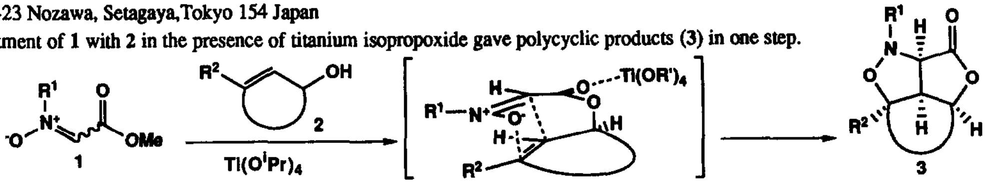
1

Tetrahedron Lett. **1993**, *34*, 4009

ONE STEP BICYCLIZATION BY WAY OF TANDEM TRANS-ESTERIFICATION, INTRAMOLECULAR 1,3-DIPOLAR CYCLOADDITION OF α-METHOXYCARBONYLNITRONES WITH ALLYL ALCOHOLS IN THE PRESENCE OF TITANIUM ISOPROPOXIDE.

Osamu Tamura,* Tatsuya Yamaguchi, Katsuhide Noe, and Masanori Sakamoto, Meiji College of Pharmacy, 1-35-23 Nozawa, Setagaya,Tokyo 154 Japan

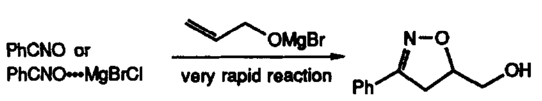
Treatment of 1 with 2 in the presence of titanium isopropoxide gave polycyclic products (3) in one step.



Tetrahedron Lett. **1993**, *34*, 4011

A Highly Effective Quenching Method of 1,3-Dipolar Cycloadditions of Nitrile Oxides or Nitrile Oxide/Lewis Acid Complexes by Use of 2-Propenyloxymagnesium Bromide

Shuji Kanemasa* and Masaki Nishiuchi
Institute of Advanced Material Study, Kyushu University, Kasugakoen, Kasuga 816, Japan

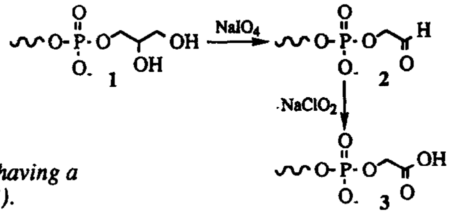


2-Propenyloxymagnesium bromide can be a highly effective quenching agent for the nitrile oxide cycloadditions using any of ever known dipolarophiles.

Tetrahedron Lett. **1993**, *34*, 4015

A Convenient Synthesis of Oligonucleotides with a 3'-Phosphoglycolate and 3'-Phosphoglycaldehyde Terminus

Hidehito Urata and Masao Akagi*
Osaka University of Pharmaceutical Sciences
2-10-65 Kawai, Matsubara, Osaka 580, Japan



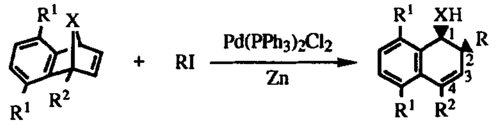
A simple and rapid synthesis method of oligonucleotides with a 3'-phosphoglycerol terminus (1) has been developed. These modified oligonucleotides were oxidized to corresponding oligonucleotides having a 3'-phosphoglycaldehyde (2) and a 3'-phosphoglycolate terminus (3).

Tetrahedron Lett. **1993**, *34*, 4019

PALLADIUM-CATALYZED STEREOSELECTIVE REDUCTIVE COUPLING REACTIONS OF ORGANIC HALIDES WITH 7-HETEROATOM NORBORNADIENES.

Jiun-Pey Duan and Chien-Hong Cheng*, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

Organic halides react with 7-heteroatom benzonorbornadiene derivatives in the presence of $Pd(PPh_3)_2Cl_2$ and zinc powder to give *cis*-1,2-dihydro-1-naphthol or methyl N-(*cis*-1,2-dihydro-1-naphthyl)carbamate derivatives stereoselectively.

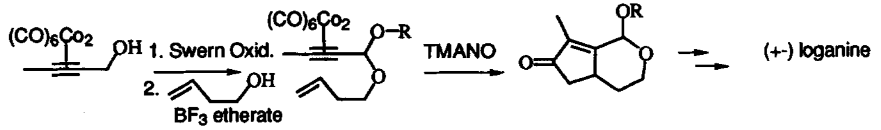


X = O, NCO_2Me

Tetrahedron Lett. **1993**, *34*, 4023

PREPARATION OF BICYCLICLACTOLS FROM ALLYL AND/OR HOMOALLYL PROPARGYL ACETAL-COBALT COMPLEXES AND ITS APPLICATION TO THE FORMAL SYNTHESIS OF (+-) LOGANINE

N. Jeong,[1] B. Y.Lee,[2] S. M. Lee,[2] Y. K. Chung,[2] and S.-G. Lee[3], 1. Hanhyo Inst. of Tech., Shihungshi, Kyungkido, 2. Seoul National University, Seoul, 3. Korea Research Inst. of Chemical Tech., Deajeon, KOREA

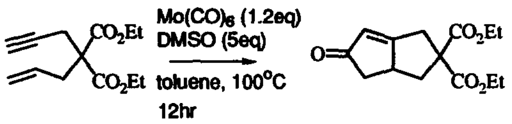


Tetrahedron Lett. **1993**, *34*, 4027

MOLYBDENIUM MEDIATED PREPARATION OF CYCLOPENTENONES

N. Jeong,[1] S.J. Lee,[1] B. Y.Lee,[2] Y. K. Chung,[2] 1. Hanhyo Inst. of Tech., Shihungshi, Kyungkido, 2. Seoul National University, Seoul, Korea.

Cocyclization of alkynes, alkenes and carbon monoxide was achived in the presence of a stoichiometric amount of molybdenium hexacarbonyl and excess of dimethylsulfoxide.

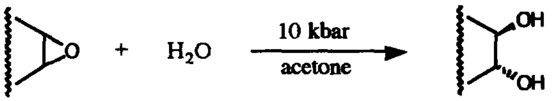


Tetrahedron Lett. **1993**, *34*, 4031

High Pressure-Promoted Uncatalyzed Hydrolysis of Epoxides

Hiyoshizo Kotsuki,* Masanori Kataoka, and Hitoshi Nishizawa
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan

A variety of epoxides are efficiently hydrolyzed to diols with water under high pressure conditions.

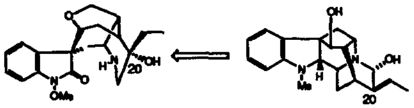


Tetrahedron Lett. **1993**, *34*, 4035

A First Synthesis of 20-Hydroxydihydrorankinidine, a New Oxindole Alkaloid from *Gelsemium elegans* Benth.

Chada Phisalaphong, Hiromitsu Takayama, and Shin-ichiro Sakai,*
Faculty of Pharmaceutical Sciences, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, 263 Japan

A new *Gelsemium* alkaloid, 20-hydroxydihydrorankinidine, having a humantenine-type *N*a-methoxyoxindole skeleton, was prepared from ajmaline utilizing a biogenetically patterned synthesis.

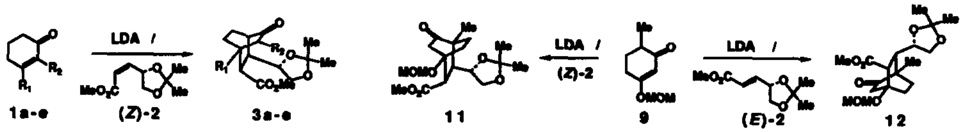


20-Hydroxydihydrorankinidine (1) Ajmaline (2)

Tetrahedron Lett. **1993**, *34*, 4039

SYNTHESIS OF OPTICALLY ACTIVE BICYCLO[2.2.2]OCTANES. SUBSTITUTION EFFECT OF THE CYCLOHEXENONE RING ON THE SEQUENTIAL MICHAEL REACTION.

Hiroto Nagaoka,[a]* Kimiyuki Shibuya,[b] Kaoru Kobayashi,[a] Isao Miura,[a] Michitaka Muramatsu,[a] and Yasuji Yamada[a]*
[a] Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan
[b] Tokyo Research Laboratories Kowa Co. Ltd., 2-17-43 Noguchi-cho, Higashimurayama, Tokyo 189, Japan



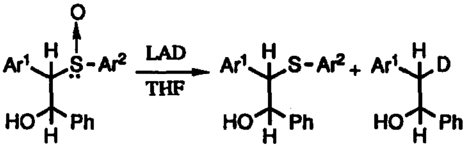
1a-e (Z)-2 3a-e 11 (Z)-2 9 (E)-2 12

Tetrahedron Lett. **1993**, *34*, 4043

Stereochemical Proof for Front Side Deuteride Attack via σ-Sulfurane in the Reductive Desulfinylation of Sulfoxides with Lithium Aluminum Deuteride

Takahiro Sagae, Satoshi Ogawa[#], and Naomichi Furukawa*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan and [#]Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka 020, Japan

Concomitant reduction and desulfinylation of sulfoxide 1 and 2 with lithium aluminum deuteride reveal that the reactions proceed stereospecifically via σ-sulfurane.

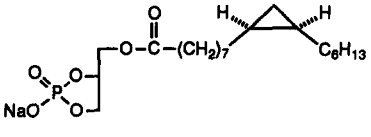


1; Ar^1= 2-Pyridyl, Ar^2= *p*-Tolyl; 2; Ar^1, Ar^2= Phenyl

Tetrahedron Lett. **1993**, *34*, 4047

Synthesis of 1-O-Acylglycerol 2,3-Cyclic Phosphate: Determination of the Absolute Structure of PHYLPA, A Specific Inhibitor of DNA Polymerase α

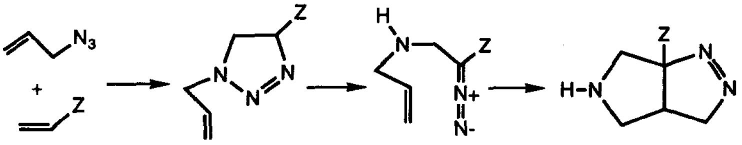
Susumu Kobayashi[b]*, Ryosuke Tokunoh[a], Masakatsu Shibasaki[a], Rumi Shinagawa[b], and Kimiko Murakami-Murofushi[c]
[a] Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan,
[b] Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara 229, Japan,
[c] Faculty of Sciences, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan



Tetrahedron Lett. **1993**, *34*, 4051

ONE POT MULTIPLE-STEPS REACTION OF ALLYL AZIDE AND ALKENES CARRYING ELECTRON-WITHDRAWING GROUPS

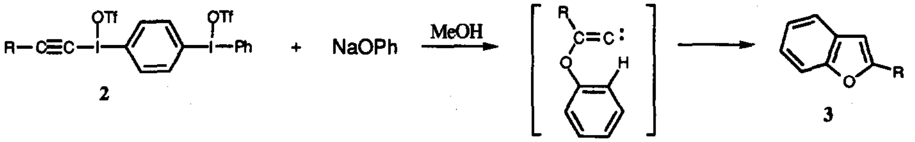
Chia-Hsi Yang* and Huang-Jang Shen,
Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan, R.O.C.



Tetrahedron Lett. **1993**, *34*, 4055

Novel Cyclization to Benzofurans in the Reaction of Alkynyl-(*p*-phenylene)bisiodonium Ditriflates with Phenoxide Anion

Tsugio Kitamura,* Lei Zheng, Hiroshi Taniguchi,* Makoto Sakurai, and Ryuichi Tanaka; Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Fukuoka 812, Japan and Department of Chemical Engineering, Faculty of Engineering, Fukuoka University, Fukuoka 814-01, Japan

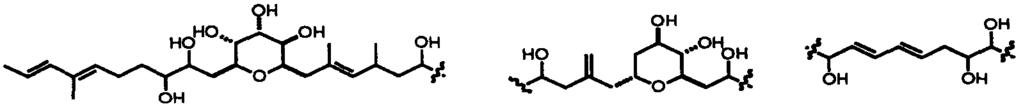


Tetrahedron Lett. **1993,** *34,* 4059

STRUCTURES OF PERIODATE OXIDATION PRODUCTS WITH A CONJUGATED DIENE OR AN EXOMETHYLENE FROM ZOOXANTHELLATOXIN-A

Tohru Asari, Hideshi Nakamura,* and Akio Murai, Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.
Yukiko Kan, Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770, Japan.

The following partial structures of zooxanthellatoxin-A were established on the basis of spectroscopic analyses of degradation products prepared by periodate oxidation followed by reduction with $NaBH_4$.

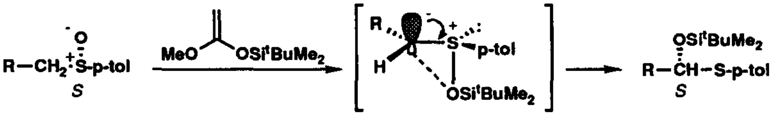


Tetrahedron Lett. **1993,** *34,* 4063

THE FIRST HIGHLY ASYMMETRIC PUMMERER-TYPE REACTION IN CHIRAL ACYCLIC SULFOXIDES: CHEMISTRY OF *O*-SILYLATED KETENE ACETALS

Yasuyuki Kita,* Norio Shibata, and Naoki Yoshida
Faculty of Pharmaceutical Sciences, Osaka University 1-6, Yamada-oka, Suita, Osaka 565, Japan

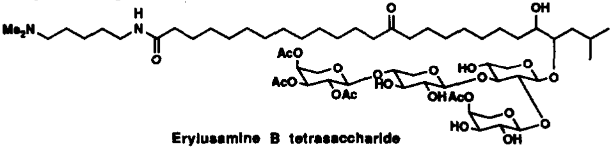
The chiral sulfoxides were reacted with *O*-silylated ketene acetal in acetonitrile to give the corresponding α-siloxysulfides in high degree of stereochemistry and high yields.



Tetrahedron Lett. **1993,** *34,* 4067

ISOLATION AND STRUCTURE ELUCIDATION OF ERYLUSAMINE B, A NEW CLASS OF MARINE NATURAL PRODUCTS, WHICH BLOCKED AN IL-6 RECEPTOR, FROM THE MARINE SPONGE *ERYLUS PLACENTA* THIELE.

Nobuhiro Fusetani,* Noriko Sata, Naoki Asai, and Shigeki Matsunaga, Laboratory of Marine Biochemistry, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

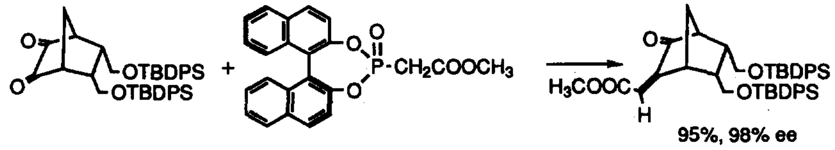


Erylusamine B tetrasaccharide

Tetrahedron Lett. **1993,** *34,* 4071

Differentiation of Enantiotopic Carbonyl Groups by the Horner-Wadsworth-Emmons Reaction

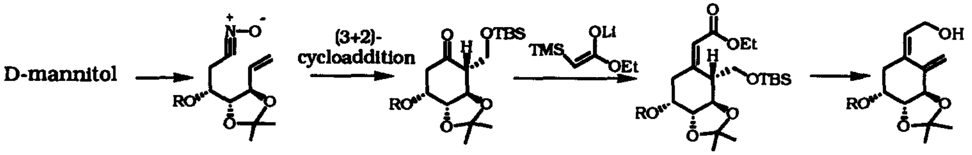
Kiyoshi Tanaka,[1] Yoshihisa Ohta,[1] Kaoru Fuji,*[1] and Tooru Taga[2]
[1]*Institute for Chemical Research, Kyoto University, Uji 611, Japan.* [2]*Faculty of Pharmaceutical Sciences,
Kyoto University, Sakyo-ku,
Kyoto 606, Japan*



Tetrahedron Lett. **1993**, *34*, 4075

A (3+2)-Cycloaddition Approach to 1α, 2β, 25-Trihydroxyvitamin D_3 A Ring Synthon

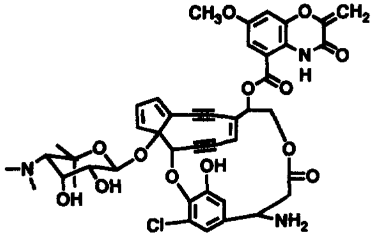
T. Takahashi,* M. Nakazawa, Y. Sakamoto, K. N. Houk
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan;
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, U.S.A.



Tetrahedron Lett. **1993**, *34*, 4079

SYNTHESIS AND ABSOLUTE STEREOCHEMISTRY OF THE AMINOSUGAR MOIETY OF ANTIBIOTIC C-1027 CHROMOPHORE

Kyo-ichiro Iida, Takaaki Ishii, and Masahiro Hirama*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai, 980. Japan
Toshio Otani, Yoshinori Minami, and Ken-ichiro Yoshida
Tokushima Research Center, Taiho Pharmaceutical Co., Ltd., Kawauchi-cho, Tokushima 771-01, Japan



Tetrahedron Lett. **1993**, *34*, 4083

The Isolation and Absolute Configuration of (1*S*,2*S*,3*R*)-4-Hydroxymethyl-cyclopent-4-ene-1,2,3-triol: A Putative Intermediate in the Biosynthesis of Aristeromycin by *Streptomyces citricolor*.

Stanley M. Roberts[a], Andrew J. Thorpe[a], Nicholas J. Turner*[a], W. Michael Blows[b], Antony D. Buss*[b], Michael J. Dawson[b], David Noble[b], Brian A.M. Rudd[b], Phillip J. Sidebottom[c], and Wilfred F. Wall[b], [a]Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, U.K. [b]Department of Natural Products Discovery and [c]Structural Chemistry, Glaxo Group Research, Greenford Road, Greenford, Middlesex UB6 OHE, U.K.

Tetrol 5 has been isolated from cultures of *Streptomyces citricolor* and implicated as a likely precursor of aristeromycin 1.

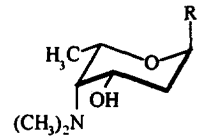
5

1

Tetrahedron Lett. **1993**, *34*, 4087

DEFINITIVE SYNTHESIS OF METHYL α-KEDAROSAMINIDE, A SUGAR COMPONENT OF THE ANTITUMOR ANTIBIOTIC KEDARCIDIN.

Miklós Hornyák, István F. Pelyvás and Ferenc J. Sztaricskai*
Research Group for Antibiotics of the Hungarian Academy of Sciences,
P.O.Box 70, Debrecen H-4010 Hungary



1 R=OH
2 R=OMe

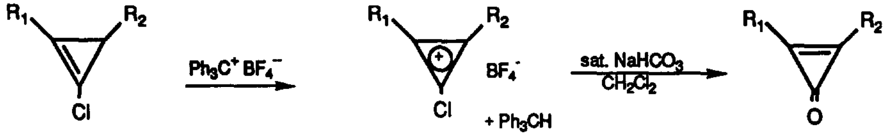
The first definitive synthesis and physical data of the α-methyl glycoside (methyl α-kedarosaminide 2) of kedarosamine (1), the aminodeoxy sugar component of the antibiotic kedarcidin is presented.

Tetrahedron Lett. **1993**, *34*, 4091

The Use of Chlorosubstituted Cyclopropenium Cations for the Synthesis of Substituted Cyclopropenones.

Jonathan M White* and Mark K Bromley, School of Chemistry, University of Melbourne, Parkville VIC 3052, Australia

2-Chlorocyclopropenyl cations are converted to cyclopropenones in high yield upon treatment with aqueous sodium bicarbonate.

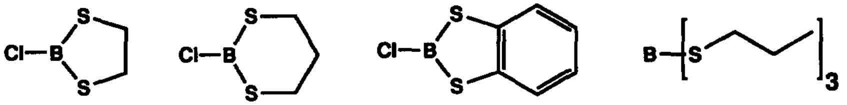


Tetrahedron Lett. **1993**, *34*, 4095

LEWIS ACIDS BASED ON SULFUR CONTAINING BORON HETEROCYCLES AND TRIALKYLTHIOBORANES.

Joshua Howarth, Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K. Gunter Helmchen and Mattias Kiefer, Universität Heidelberg, Im Neuenheimer Feld 270, D-6900, Heidelberg, Germany.

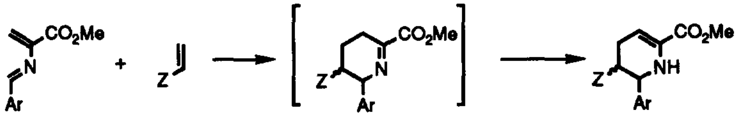
The use of trialkyl- and aryl- thioboranes, along with 2-substituted 1,3,2-dithioborolans as Lewis acids has not been explored. Reactions of such compounds in the Lewis acid catalysed Diels-Alder reactions between cyclopentadiene and four α,β-unsaturated carbonyl compounds are described.



Tetrahedron Lett. **1993**, *34*, 4097

DIELS-ALDER REACTIONS OF 2-AZADIENES DERIVED FROM CYSTEINE METHYL ESTER

Thomas L. Gilchrist, Chemistry Department, University of Liverpool, Liverpool L69 3BX, U.K., António M. d'A. Rocha Gonsalves and Teresa M. V. D. Pinho e Melo, Departamento de Química, Universidade de Coimbra, Coimbra, Portugal

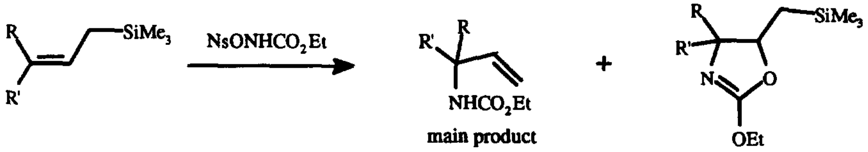


The 2-azadienes shown undergo Diels-Alder reactions both with electron rich dienophiles (enamines) and with electron deficient dienophiles (activated alkenes).

Tetrahedron Lett. **1993**, *34*, 4101

A NOVEL ROUTE TO *N*-SUBSTITUTED ALLYLAMINES BY THE REACTION OF ALLYLSILANES WITH (ETHOXYCARBONYL)-NITRENE.

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



Tetrahedron Lett. **1993**, *34*, 4105

SYNTHESIS OF (+)-8-DEOXYVERNOLEPIN

Rosendo Hernández[a], María S. Rodríguez[b], Silvia M. Velázquez,[a] Ernesto Suárez*[a]

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A short and efficient synthesis of (+)-8-deoxyvernolepin from 6β-tetrahydrosantonin is described. The key steps are: the functionalization of the angular methyl group at C-10 and the 1,4-oxidative fragmentation of the C_2-C_3 bond.