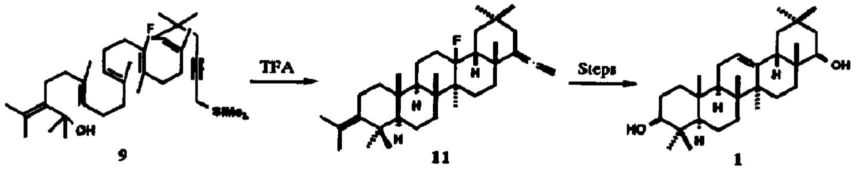
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 1469

The Tetramethylallyl Cation as a Surrogate for the Epoxide Function as an Initiator of Biomimetic Polyene Pentacyclizations. Total Synthesis of Sophoradiol.

Paul V. Fish and William S. Johnson. Department of Chemistry, Stanford University, Stanford, CA 94305, USA



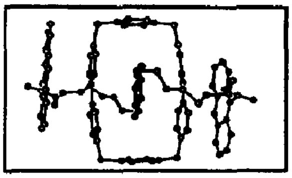
The biomimetic total synthesis of (±)-sophoradiol (1) is reported. The key step of the strategy involved the pentacyclization of tertamethylallyl alcohol 9, a surrogate for the epoxide function, to fluoropentacycle 11.

Tetrahedron Letters, **1994**, *35*, 1473

PHOTOACTIVE [2]ROTAXANES FORMED BY MULTIPLE π-STACKING.

Andrew C. Benniston, Anthony Harriman,* and Vincent M. Lynch, Center for
Fast Kinetics Research and Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA

A novel [2]rotaxane is described for which the polyether thread folds to facilitate π-stacking between the terminal anthracene stoppers and the central N,N'-bipyridinium-derived cyclophane, as seen in the X-ray crystal structure shown here.

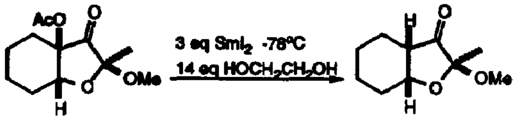


Tetrahedron Letters, **1994**, *35*, 1477

SELECTIVE DEOXYGENATION OF α,α'-DIOXYGENATED 3-(2H)-FURANONES

Russell J. Linderman*, Kevin P. Cusack, and William R. Kwochka
Department of Chemistry, North Carolina State University, Raleigh NC 27695-8204

Regioselective monodeoxygenation of α,α'-dioxygenated 3-(2H)-furanones has been achieved using SmI_2 in the presence of an excess of ethylene glycol.



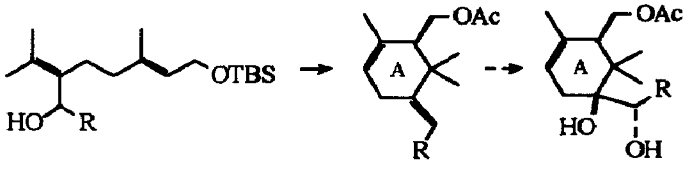
Tetrahedron Letters, **1994**, *35*, 1481

Regiospecificity in the Cyclization of 6-(1-Hydroxyalkyl)geraniol Derivatives. A Simple Route to the Taxol A-Ring System.

Takayuki Doi, Jeremy Robertson, Gilbert Stork*, and A. Yamashita

Department of Chemistry, Columbia University, New York, NY 10027

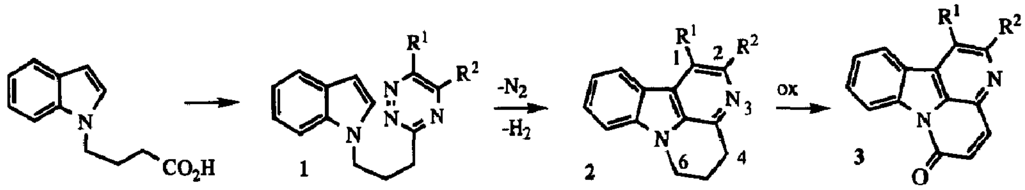
Cationic cyclization of certain hydroxyalkyl derivatives of geraniol leads, regiospecifically, to cyclogeraniols with a substitution pattern suggestive of their potential use in the construction of the ring A of Taxol.



Tetrahedron Letters, **1994**, *35*, 1485

SELECTIVE OXIDATION OF CANTHINES TO CANTHIN-6-ONES WITH TRIETHYLBENZYLAMMONIUM PERMANGANATE

Jia-He Li and John K. Snyder*
Department of Chemistry, Boston University, 590 Commonwealth Ave., Boston, MA 02215

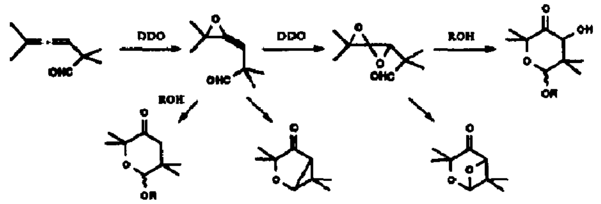


Tetrahedron Letters, **1994**, *35*, 1489

Oxidative Cyclizations of Allenic Aldehydes

Jack K. Crandall and Elisa Rambo
Department of Chemistry, Indiana University, Bloomington, IN 47405

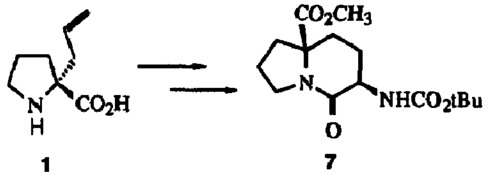
Allenyl aldehydes and ketones are oxidatively cyclized by dimethyldioxirane to provide cyclic acetals and hemiacetals



Tetrahedron Letters, **1994**, *35*, 1493

DESIGN, SYNTHESIS AND EVALUATION OF A NOVEL BICYCLIC LACTAM AS A GLY-PRO TYPE VI BETA-TURN MIMIC

Jean-Philippe Dumas and Juris Paul Germanas* Department of Chemistry, University of Houston, Houston, TX 77204-5641



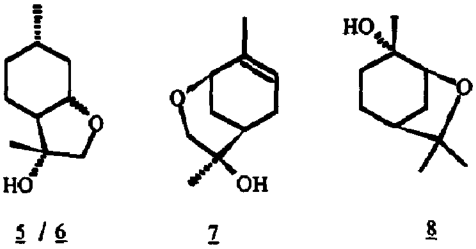
Bicyclic lactam 7, a highly rigid dipeptide mimic for a Gly-Pro type VI turn, has been synthesized from 2-(2'-propenyl)proline (1).

Tetrahedron Letters, **1994**, *35*, 1497

CYCLIZATION OF UNSATURATED MONOTERPENIC ALCOHOLS MEDIATED BY THALLIUM (III) SALTS

Helena M. C. Ferraz*, Carlos M. R. Ribeiro, Mônica V. A. Grazini
Instituto de Química - USP - C.P. 20.780 - S. Paulo - Brazil
Timothy J. Brocksom and Ursula Brocksom
Depto. de Química - UFSCar - C.P. 676
13560 - São Carlos - SP - Brazil

The ethers 5 (α - O -), 6 (β - O -) 7 and 8 were obtained by thallium salt cyclization of isopulegol, neo - isopulegol, cis - carveol and α - terpineol, respectively.

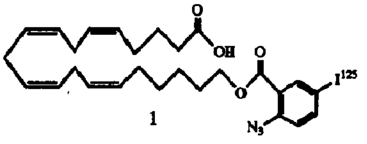


Tetrahedron Letters, **1994**, *35*, 1501

SYNTHESIS OF A RADIOACTIVE PHOTOAFFINITY ARACHIDONIC ACID ANALOG

Hélène Perrier*, Petpiboon Prasit and Zhaoyin Wang
Merck Frosst Centre for Therapeutic Research
P.O. Box 1005, Pointe Claire-Dorval, Québec, Canada H9R 4P8

The synthesis of the novel probe 1, based on arachidonic acid, is described.



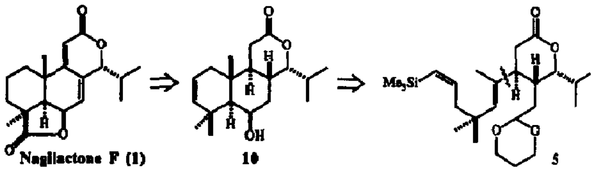
1

Tetrahedron Letters, **1994**, *35*, 1503

Enantioselective Synthesis of Nagilactone F Via Vinylsilane-Terminated Cationic Cyclization

Steven D. Burke,* Michael E. Kort, Sharon M. S. Strickland, Helen M. Organ, Louis A. Silks, III
Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 USA

A convergent enantioselective synthesis of nagilactone F (1) is described. An acetal-initiated vinylsilane-terminated cationic polyene cyclization of 5 and an intramolecular remote functionalization of 10 offer control over stereochemistry and oxidation pattern.

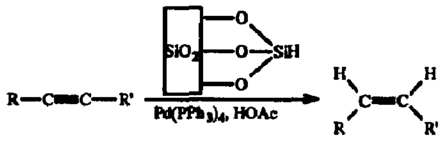


Tetrahedron Letters, **1994**, *35*, 1507

SELECTIVE REDUCTION OF ALKYNES TO Z-ALKENES USING HYDROSILANE FUNCTIONS IMMOBILIZED ON SILICA GEL

Abhay D. Kini, Durgesh V. Nadkarni, and James L. Fry*, Bowman-Oddy Laboratories, Department of Chemistry,
The University of Toledo, Toledo, OH 43606-3390 U.S.A.

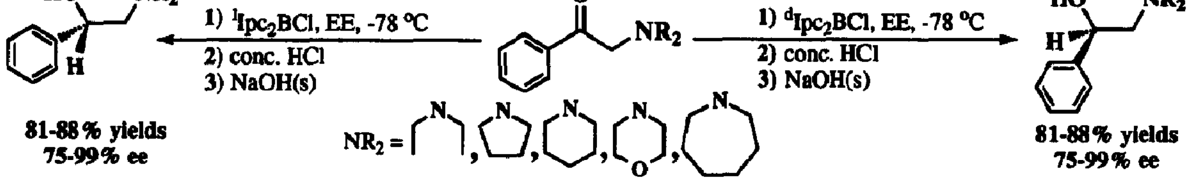
Hydrosilane functions immobilized on the surface of silica gel effect the selective reduction of alkynes to *Z*-olefins when used in conjunction with acetic acid and tetrakis(triphenylphosphine)palladium(0) catalyst.



Tetrahedron Letters, **1994**, *35*, 1511

Boranes In Synthesis. 2. Asymmetric Synthesis of β-Amino Alcohols. A Facile Conversion of 2-Amino Acetophenones to the Corresponding β-Amino Alcohols in High Enantiomeric Purity.

David A. Beardsley, Gary B. Fisher, Christian T. Goralski, Lawrence W. Nicholson, and Bakthan Singaram*
Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, Calif. 95064



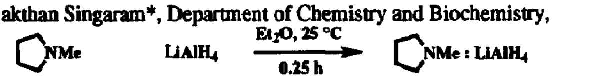
81-88 % yields
75-99 % ee

81-88 % yields
75-99 % ee

Tetrahedron Letters, **1994**, *35*, 1515

Lithium Aluminum Hydride-*N*-Methylpyrrolidine Complex. 1. Synthesis and Reactivity of Lithium Aluminum Hydride-*N*-Methylpyrrolidine Complex. An Air and Thermally Stable Reducing Agent Derived from Lithium Aluminum Hydride.

Joseph C. Fuller, Eric L. Stangeland, Thomas C. Jackson and Bakthan Singaram*, Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, Calif. 95064



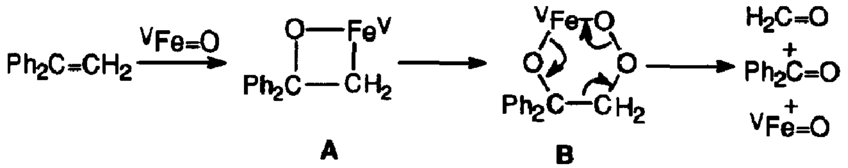
Lithium aluminum hydride-*N*-Methylpyrrolidine complex (LAHNMP), obtained by the reaction of lithium aluminum hydride (LAH) with *N*-methylpyrrolidine, is a powerful reducing agent, comparable to LAH in its reducing properties. LAHNMP reduces esters, lactones, anhydrides, and carboxylic acids to the alcohols. Test reductions show that LAHNMP also reduces a wide range of functional groups, including amides, epoxides, oximes, nitriles, nitro compounds and halides. LAHNMP can be safely transfered in air with the use of a plastic spatula and used in an open container without the need for an inert atmosphere, provided that hydrogen is not evolved during the reduction.

Tetrahedron Letters, **1994**, *35*, 1519

THE OXIDATION OF METHYLENE CARBON-CARBON DOUBLE BONDS UNDER Fe^{III}-TBHP AND Fe^{III}-TBHP-PA CONDITIONS

Derek H. R. Barton* and Tie-Lin Wang
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

The oxidation of 1,1-diphenylethylene under Fe^{III}-TBHP AND Fe^{III}-TBHP-PA conditions followed a pathway *alkene to intermediate* A to *intermediate* B to *ketone*. Intermediate A could be trapped by NaN_3.

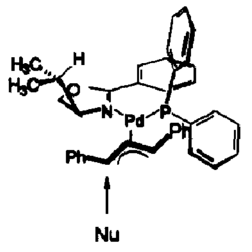


Tetrahedron Letters, **1994**, *35*, 1523

Catalysis of Allylic Substitutions by Pd Complexes of Oxazolines Containing an Additional P, S, or Se Center. X-Ray Crystal Structures and Solution Structures of Chiral π-Allyl Palladium Complexes of Phosphinoaryloxazolines.

J. Sprinz, M. Kiefer, G. Helmchen*, G. Huttner, O. Walter and L. Zsolnai, Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg. M. Reggelin, Organisch-chemisches Institut der Universität, Marie-Curie-Str. 11, D-60439 Frankfurt.

Crystal (X-ray) and solution structures (NMR cross relaxation experiments) of palladium π-allyl complexes were determined. Conclusions concerning the mechanism of allylic substitutions are drawn.

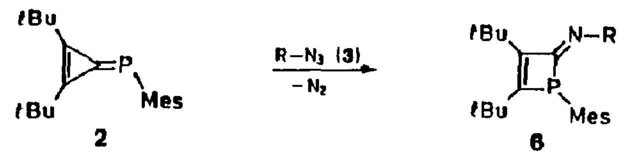


Tetrahedron Letters, **1994**, *35*, 1527

RING ENLARGEMENT OF PHOSPHATRIAFULVENES WITH AZIDES TO 1H-2-IMINOPHOSPHETES

Wolfgang Eisfeld, Michael Slany, Uwe Bergsträßer and Manfred Regitz, Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Federal Republic of Germany

The phosphatriafulvene 2 reacts with azides 3 under the formation of the 1H-2-iminophosphetes 6.

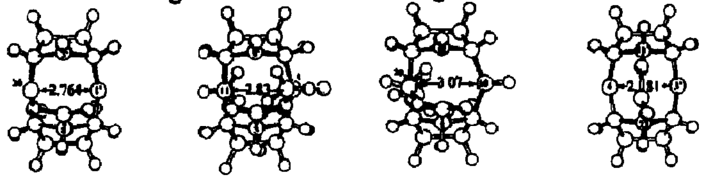


Tetrahedron Letters, **1994**, *35*, 1531

X-RAY CRYSTAL STRUCTURE ANALYSES OF UNSATURATED BISSECO/BISHOMO DODECAHEDRANES

Manfred Keller, Klaus Scheumann, Klaus Weber, Torsten Voss, Horst Prinzbach*, Hermann Irngartinger*,
and Uwe Reifenstahl, Universities of D-79104 Freiburg and D-69120 Heidelberg

X-ray stuctural analyses provide experimental transannular π,π (π,σ) distances in unsaturated bisseco/bishomo dodecahedranes

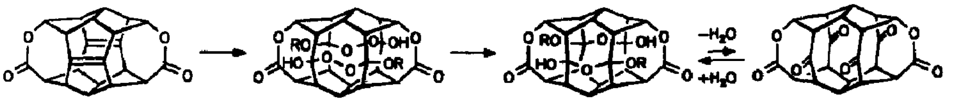


Tetrahedron Letters, **1994**, *35*, 1535

SKELETAL EXPANSIONS of (HOMO) DODECAHEDRANES NOVEL HETEROPOLYCYCLIC CAGE STRUCTURES

Torsten Voss and Horst Prinzbach*, Chemisches Laboratorium der Universität Freiburg

In unsaturated (bisseco)dodecahedranes expansion of the molecular peripheries by dioxa(oxa) linkages is effected through ozonolysis.

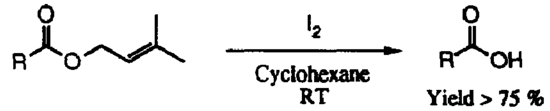


Tetrahedron Letters, **1994**, *35*, 1539

A VERY USEFUL AND MILD METHOD FOR THE PROTECTION AND DEPROTECTION OF CARBOXYLIC ACIDS

Janine Cossy*, Arnaud Alboay, Michael Scheloske, Domingo Gomez Pardo
Laboratoire de Chimie Organique, Associé au CNRS, ESPCI, 10 rue Vauquelin, 75231 PARIS Cedex 05 - France.

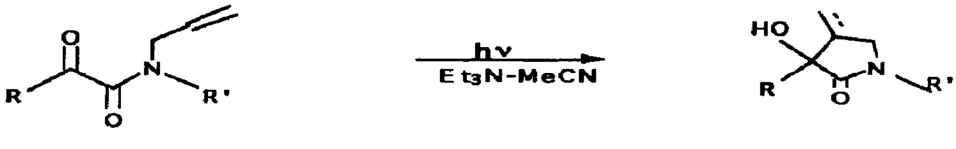
3-Methylbut-2-enyl group is a good protecting group of carboxylic acid that can be removed by using iodine in cyclohexane.



Tetrahedron Letters, **1994**, *35*, 1541

Photoreduction of α-Ketoamides; Cyclization of Unsaturated Captodative Radicals

Janine Cossy, Abdelaziz Madaci and Jean-Pierre Pete
Unité des Réarrangements Thermiques et Photochimiques, Associée au CNRS, U.F.R. Sciences, B.P. 347, 51062 REIMS, France



R– CH_3 , C_2H_5 , C_6H_5
R– CH_3 , allyl

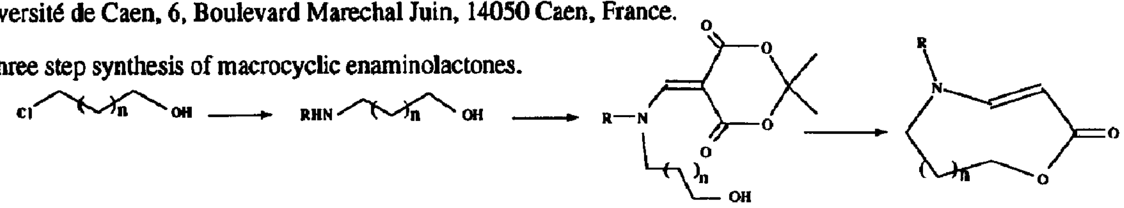
Captodative radicals, generated by photochemical reduction, add intramolecularly to ethylenic or acetylenic bonds.

Tetrahedron Letters, **1994**, *35*, 1545

A NEW SYNTHETIC ROUTE TO MACROCYCLES: SYNTHESIS OF LARGE RING ENAMINOLACTONES

F. Jourdain and J. C. Pommelet.* Laboratoire des composés Thioorganiques, associé au CNRS, ISMRA, Université de Caen, 6, Boulevard Marechal Juin, 14050 Caen, France.

A three step synthesis of macrocyclic enaminolactones.

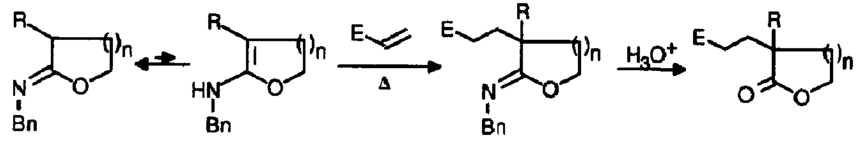


Tetrahedron Letters, **1994**, *35*, 1549

Iminoether - Enaminoether Tautomerism. Elaboration of Quaternary Carbon Centers by a New Michael-type Reaction

Michel Pfau, Anasse Felk, and Gilbert Revial
Laboratoire de Recherches Organiques, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France.

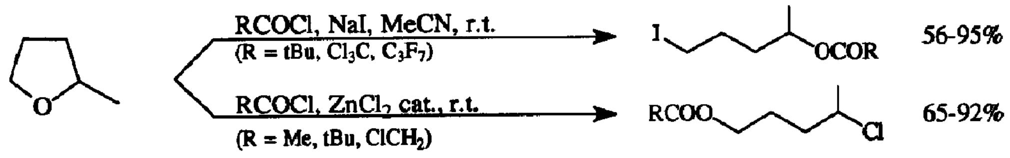
Iminoethers are in tautomeric equilibrium with the corresponding enaminoethers which can be *C*-alkylated with electrophilic olefins, leading to the α,α-disubstituted iminoethers and yielding new functionalized lactones upon hydrolysis.



Tetrahedron Letters, **1994**, *35*, 1553

REGIOCONTROLLED RING OPENING OF 2-METHYLTETRAHYDROFURAN WITH ACID CHLORIDES AND IODIDES

P. Mimero, C. Saluzzo, R. Amouroux
Laboratoire de Chimie Organique Physique et Synthétique, CNRS URA 463
Université Claude Bernard, 43 Boulevard du 11 Novembre 1918, 69 622 VILLEURBANNE Cedex, FRANCE

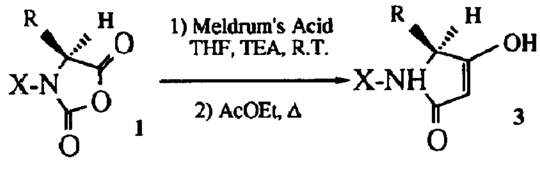


Tetrahedron Letters, **1994**, *35*, 1557

Synthesis of Chiral Urethane N-Alkoxycarbonyl Tetramic Acids from Urethane N-Carboxyanhydrides (UNCAs)

Jean-Alain Fehrentz[1], Elisabeth Bourdel[1], Jean-Christophe Califano[1], Olivier Chaloin[1], Chantal Devin[1], Patrick Garrouste[1], Ana-Christina Lima-Leite[1], Muriel Llinares[1], François Rieunier[1], Jean Vizavonna[1], François Winternitz[1], Albert Loffet[2] & Jean Martinez[1]*. [1] Chimie et Pharmacologie de Molécules d'Intérêt Biologique, CNRS, Faculté de Pharmacie, 15 av. C. Flahault, 34060 Montpellier, France. [2] Propeptide, 91710 Vert-le-Petit, France.

N-protected (Fmoc, Boc, Z) chiral tetramic acid derivatives which are important precursors of β-hydroxy-γ-amino acids can be easily obtained in high yields from N-urethane-N-carboxyanhydrides and Meldrum's acid. The reaction proceeds smoothly in mild conditions.

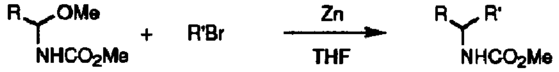


Tetrahedron Letters, **1994**, *35*, 1561

Reaction of *N*-Acyl-α-methoxyamines with Organozinc Reagents. A Convenient Method for the Synthesis of Homoallylamines and β-Amino Esters.

Naoki Kise,* Hiroki Yamazaki, Toshirou Mabuchi, and Tatsuya Shono
Division of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto, Japan

The reaction of *N*-acyl-α-methoxyamines with allyl-, propargyl-, and benzylzinc bromides and Reformatsky reagents proceeds in THF at room temperature. Homoallyl- and homopropargylamines and β-amino esters are synthesized in good yields.



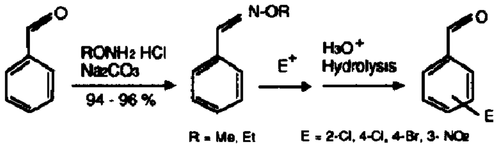
R=H, Me, i-Pr, PhCH$_2$, Ph
R'=allyl, propargyl, benzyl, CH$_2$CO$_2$R"

Tetrahedron Letters, **1994**, *35*, 1565

Change of Orientation in Electrophilic Substitution of Benzaldehydes by *O*-Alkyloximation Derivatives

Hiroshi Goda[a], Makoto Sato[b], Hirotaka Ihara[a], Chuichi Hirayama[a]
[a] Department of Applied Chemistry, Kumamoto University, Kumamoto 860, Japan
[b]Research Laboratory-I, Sumitomo Seika Chemical Co. Ltd., Hyogo 675-01, Japan

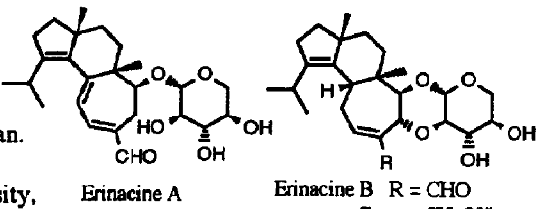
By the introduction of O-alkyloxyimino group, orientation in electrophilic substitution of benzaldehyde can be selectively controlled.



Tetrahedron Letters, **1994**, *35*, 1569

ERINACINES A, B, AND C, STRONG STIMULATORS OF NERVE GROWTH FACTOR (NGF)-SYNTHESIS, FROM THE MYCELIA OF *HERICIUM ERINACEUM*

Hirokazu Kawagishi [a], Atsushi Shimada [a], Ryoko Shirai [a], Kenji Okamoto,[b] Fumihiro Ojima [b], Hideki Sakamoto [b], Yukio Ishiguro [b], and Shoei Furukawa [c]*
[a] Department of Applied Biological Chemistry, Faculty of Agriculture, Shizuoka University, 836 Ohya, Shizuoka 422, Japan.
[b] Research Institute, Kagome Co., Ltd., Tochigi 329-27, Japan
[c] Department of Molecular Biology, Gifu Pharmaceutical University, Japan



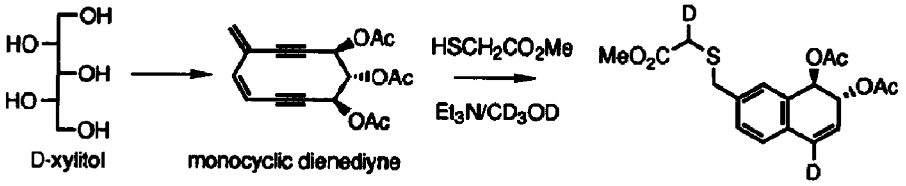
Erinacine A

Erinacine B R = CHO
C CH$_2$OH

Tetrahedron Letters, **1994**, *35*, 1573

A NOVEL MONOCYCLIC DIENEDIYNE SYSTEM: SYNTHESIS AND MODE OF AROMATIZATION

Kazunobu Toshima*, Koji Yanagawa, Kazumi Ohta, Takaaki Kano and Masaya Nakata
Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-Ku, Yokohama 223, Japan

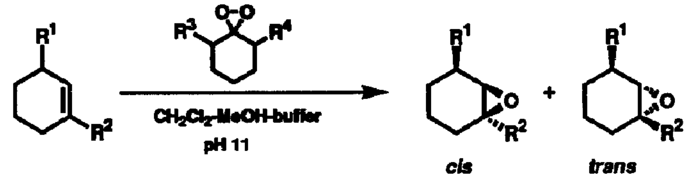


Tetrahedron Letters, **1994**, *35*, 1577

Stereoselective Epoxidation with Dioxiranes Generated from Ketones.

Masaaki Kurihara, Sachiko Ito, Nozomi Tsutsumi, and Naoki Miyata
Division of Organic Chemistry, National Institute of Health Sciences,
Kamiyoga, Setagaya-ku, Tokyo 158

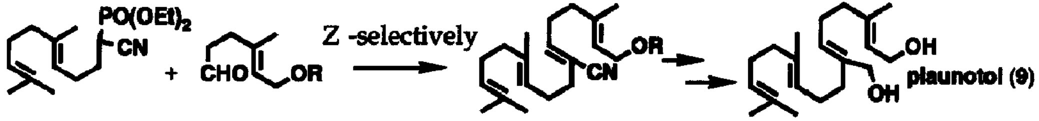
Dioxiranes generated in situ from potassium monoperoxysulfate and cyclohexanones stereoselectively oxidized cyclohexene derivatives to afford epoxides.



Tetrahedron Letters, **1994**, *35*, 1581

Z-selective Formation of Trisubstituted α,β-Unsaturated Nitrile by the Horner-Emmons Reaction

Hisao Takayanagi, Pharmaceuticals Laboratory, Research Center,
Mitsubishi Kasei Corporation, 1000, Kamoshida-cho, Midori-ku, Yokohama 227,Japan

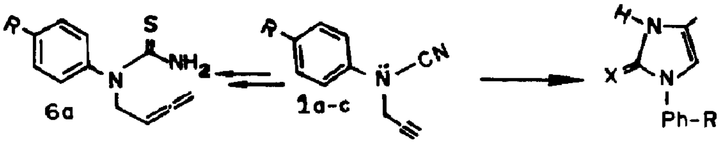


Conditions which allow the Horner-Emmons reaction of phosphononitrile to proceed Z-selectively were clarified.

Tetrahedron Letters, **1994**, *35*, 1585

SYNTHESIS OF 2(3H)-IMIDAZOLETHIONES AND 2(3H)-IMIDAZOLONES FROM β,γ - ALKYNYL CARBANILIDES.

Balachari Devan and Krishnamoorthy Rajagopalan*
Department of Organic Chemistry, University of Madras, Guindy Campus, Madras-600025, INDIA.



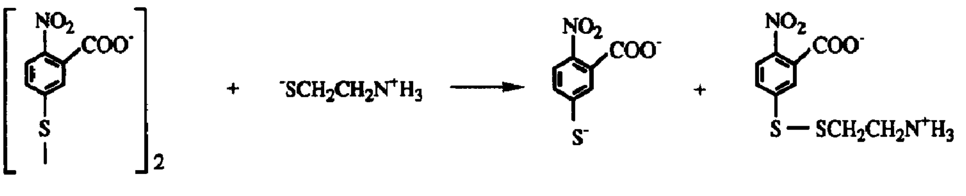
X = S ; 4a-c
X = O ; 7a-c

Tetrahedron Letters, **1994**, *35*, 1587

REACTIVITY OF PROTEIN SULFHYDRYL GROUPS WITH DISULFIDES.

Helen H. Petach*, Department of Biological Sciences,
University of Waikato, Hamilton, New Zealand

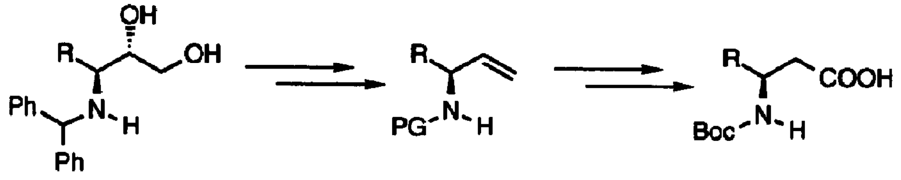
Protein -SH groups react with RSSR to produce freely mobile sulfhydryls which react with colorimetric reagents such as DTNB.



Tetrahedron Letters, **1994**, *35*, 1589

A CONCISE ENANTIOSELECTIVE SYNTHESIS OF ALLYLAMINES AND *N*-BOC-β-AMINO ACIDS

Montserrat Alcón, Marc Canas, Marta Poch, Albert Moyano, Miquel A. Pericàs*, Antoni Riera*
Dep. de Química Orgànica, Universitat de Barcelona, C/ Martí i Franquès, 1-11. 08028-Barcelona, Spain



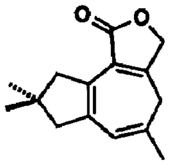
R= CH_3, n-C_3H_7, Ph, $(CH_2)_2Ph$

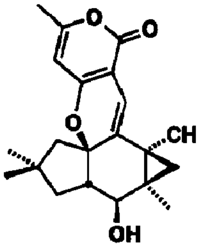
Tetrahedron Letters, **1994**, *35*, 1593

NEW COMPOUNDS ISOLATED FROM THE CULTURE FILTRATE OF THE FUNGUS MERULIUS TREMELLOSUS

M. Jonassohn, H. Anke, O. Sterner and C. Svensson
Universities of Lund (Sweden) and Kaiserslautern (Germany).

A sesquiterpene lactone with a novel skeleton and a pentacyclic aldehyde were isolated from extracts of the culture filtrate of the fungus *Merulius tremellosus*. The stuctures of the compounds were determined by mass and NMR spectroscopy and by X-ray structural analysis.



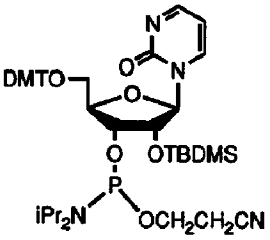


Tetrahedron Letters, **1994**, *35*, 1597

INCORPORATION OF A FLUORESCENT NUCLEOTIDE INTO OLIGORIBONUCLEOTIDES.

Chris J. Adams*,
James B. Murray, John R. P. Arnold and Peter G. Stockley, Department of Genetics, University of Leeds, Leeds LS2 9JT, UK.

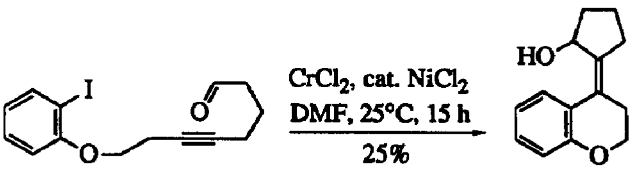
Fluorescent 2-pyrimidinone-1-β-D-riboside has been incorporated into oligoribonucleotides using standard phosphoramidite methodology.



Tetrahedron Letters, **1994**, *35*, 1601

Chromium(II)-Mediated Nickel(II)-Catalysed Cyclisations of (Iodoaryl)-Substituted Alkynes and Alkynals

David M. Hodgson* and Christopher Wells
Department of Chemistry, University of Reading,
Whiteknights, PO Box 224, Reading RG6 2AD, U.K.



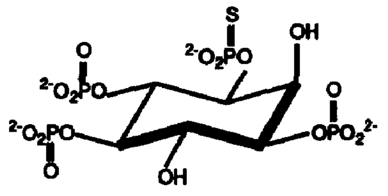
$CrCl_2$, cat. $NiCl_2$
DMF, 25°C, 15 h
25%

Tetrahedron Letters, **1994**, *35*, 1605

SYNTHESIS OF *MYO*-INOSITOL 1,4,5-TRISPHOSPHATE 3-PHOSPHOROTHIOATE AS AN INHIBITOR OF *MYO*-INOSITOL 1,3,4,5-TETRAKISPHOSPHATE 3-PHOSPHATASE

Changsheng Liu and Barry V L Potter*
Department of Medicinal Chemistry, School of Pharmacy and Pharmacology, University of Bath, Claverton Down, Bath BA2 7AY, UK.

Racemic *myo*-inositol 1,4,5-trisphosphate 3-phosphorothioate has been synthesised by stepwise phosphorylation of 1-*O*-cis(prop-1-enyl)-2,4-di-*O*-benzyl-*myo*-inositol.



Tetrahedron Letters, **1994**, *35*, 1609

THE REGIOCHEMISTRY OF CYCLOPROPYLCARBINYLSTANNANE RING FISSION.

Andrew J. Lucke and David J. Young*, Faculty of Science and Technology, Griffith University, Nathan 4111, Brisbane, Q. Australia.

The mode of electrophilic cleavage of 2-methylcyclopropylcarbinyltrimethylstannane is solvent dependent but proceeds predominantly with attack at the unsubstituted metylene in chloroform.