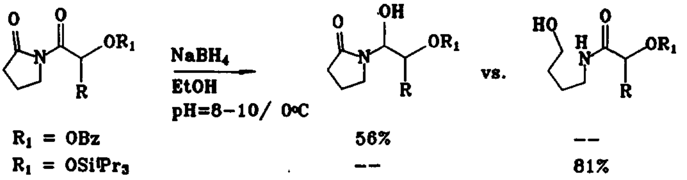
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1992,** *33,* 6041

REDUCTIVE ROUTES TO RIGID PEPTIDE BUILDING BLOCKS: THE DEPENDENCE OF A REGIOSELECTIVE IMIDE REDUCTION ON THE NATURE OF AN α-ALKOXY SUBSTITUENT.

Kevin D. Moeller* and Cathleen E. Hanau, Department of Chemistry, Washington University, St. Louis, MO 63130

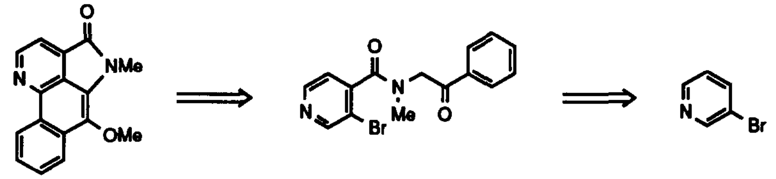
The reduction of several *N*-acylpyrrolidinones has been studied. The regioselectivity of the reductions was found to depend on the nature of the *N*-acyl group.



Tetrahedron Lett. **1992,** *33,* 6045

AN EXCEPTIONALLY BRIEF SYNTHESIS OF EUPOLAURAMINE

R. Richard Goehring
Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204



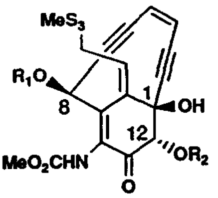
Tetrahedron Lett. **1992,** *33,* 6049

STEREOCHEMICAL STUDIES ON ESPERAMICINS: THE ABSOLUTE CONFIGURATION OF THEIR BICYCLIC AGLYCONE.

Jerzy Golik, Bala Krishnan and Terrence W. Doyle
Bristol-Myers Squibb Research Institute, 5 research Parkway, Wallingford, Connecticut 06492

Gregory VanDuyne and Jon Clardy
Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853

Based on single crystal x-ray and CD data the absolute stereochemistry for [7,3,1] bicyclic aglycone of esperamicins has been assigned as C-1 (S), C-8 (S) and C-12 (S).

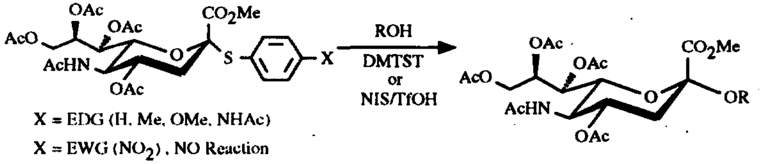


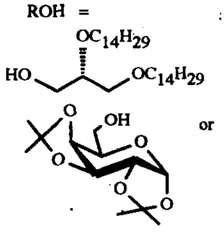
Tetrahedron Lett. **1992,** *33,* 6053

"ACTIVE" and "LATENT" THIOGLYCOSYL DONORS in OLIGOSACCHARIDE SYNTHSESIS. APPLICATION to the SYNTHESIS of α-SIALOSIDES.

René Roy*, Fredrik O. Andersson, Marie Letellier
Department of Chemistry, University of Ottawa, Ottawa, Ont. Canada K1N 6N5

The use of a new "active" and "latent" thioglycosyl donor strategy in glycoside synthesis is described using aryl 2-thio-α-sialosides of modulated reactivities.



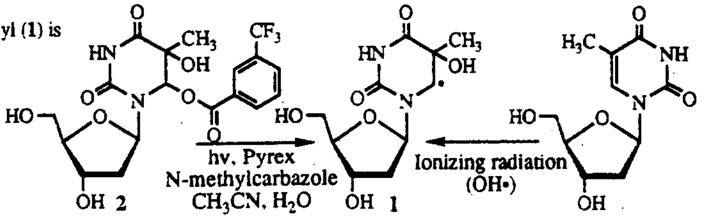


Tetrahedron Lett. **1992**, *33*, 6057

Independent Generation of the Major Adduct of Hydroxyl Radical and Thymidine. Examination of Intramolecular Hydrogen Atom Transfer in Competition With Thiol Trapping.

Mark R. Barvian and Marc M. Greenberg* Department of Chemistry, Colorado State University, Ft. Collins CO 80523

5,6-Dihydro-5-hydroxythymid-6-yl (1) is generated in solution from 2 via photoinduced electron transfer.

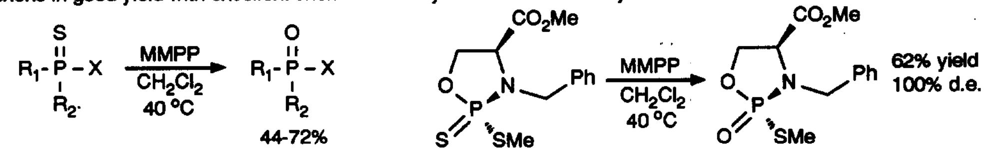


Tetrahedron Lett. **1992**, *33*, 6061

STEREOSELECTIVE AND CHEMOSELECTIVE OXIDATION OF PHOSPHOROTHIONATES USING MMPP

John A. Jackson, Clifford E. Berkman and Charles M. Thompson*
Dept. of Chemistry, Loyola University of Chicago, Chicago IL 60626

MMPP (monoperoxyphthalic acid, magnesium salt) converts phosphorothionates to the corresponding oxons in good yield with excellent chemoselectivity and stereoselectivity.

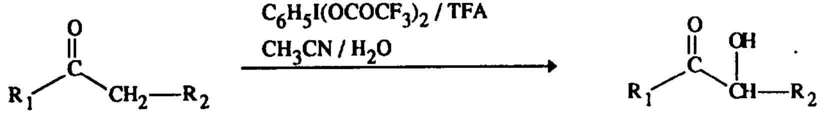


Tetrahedron Lett. **1992**, *33*, 6065

DIRECT α-HYDROXYLATION OF KETONES UNDER ACIDIC CONDITIONS USING [BIS(TRIFLUOROACETOXY)] IODOBENZENE

Robert M. Moriarty*, Bruce A. Berglund, and Raju Penmasta
Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

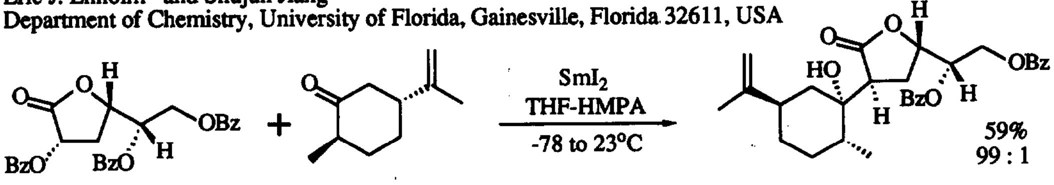
[Bis(trifluoroacetoxy)] iodobenzene and trifluoroacetic acid in CH_3CN/H_2O reacts with aromatic, heteroaromatic, and aliphatic ketones to afford α-hydroxyketones in moderate to good yields.



Tetrahedron Lett. **1992**, *33*, 6069

HIGHLY STEREOSELECTIVE COUPLINGS OF CARBOHYDRATE LACTONES WITH TERPENE KETONES PROMOTED BY SmI_2

Eric J. Enholm* and Shujun Jiang
Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

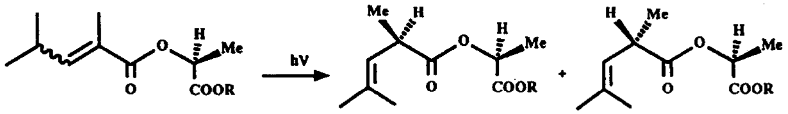


Tetrahedron Lett. **1992**, *33*, 6073

LACTATE AS CHIRAL AUXILIARY IN ASYMMETRIC PHOTODECONJUGATION OF UNSATURATED ESTERS

James L. Charlton and Vinh C. Pham, Department of Chemistry, University of Manitoba, Winnipeg, Canada R3T 2N2
Jean-Pierre Pete, Laboratoire des Réarrangements Thermiques et Photochimiques, Unité Associée au C. N. R. S.
U. F. R. Sciences, Université de Reims-Champagne-Ardenne, 51062 Reims, France.

Solvent dependent diastereoselective photdeconjugation of the following esters is described.

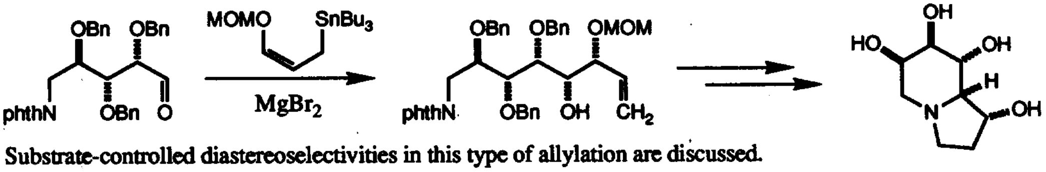


R = Me, H, K$^+$

Tetrahedron Lett. **1992**, *33*, 6077

An Asymmetric Synthesis of D-1,6-Diepicastanospermine

Kevin Burgess* and David A. Chaplin, Chemistry, Texas A & M University, College Station, TX 77843, USA



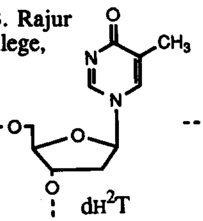
Substrate-controlled diastereoselectivities in this type of allylation are discussed.

Tetrahedron Lett. **1992**, *33*, 6081

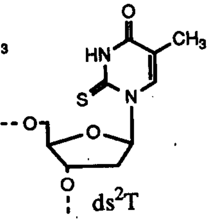
THE SYNTHESIS OF OLIGODEOXYNUCLEOTIDES CONTAINING 2-THIOTHYMINE AND 5-METHYL-4-PYRIMIDINONE BASE ANALOGUES.

Sharanabasava B. Rajur and Larry W. McLaughlin*, Department of Chemistry, Boston College, 140 Commonwealth Ave., Chestnut Hill, MA 02167

Synthesis of the 2'-deoxynucleosides, the phosphoramidite derivatives and oligodeoxynucleotides containing the base analogues dH^{2}T and ds^{2}T is described.



dH^{2}T



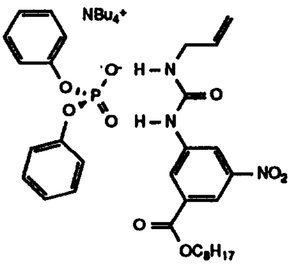
ds^{2}T

Tetrahedron Lett. **1992**, *33*, 6085

ION PAIR BINDING BY A UREA IN CHLOROFORM SOLUTION.

Paul J. Smith, Mark V. Reddington, and Craig S. Wilcox*
Department of Chemistry - University of Pittsburgh
Pittsburgh, PA 15260

A urea has been synthesized which binds very strongly to ion pairs containing sulfonates, phosphates and carboxylates in chloroform. Data suggest complexation is due to hydrogen bond formation between the urea and anion. Application to the design of molecular catalysts is planned.

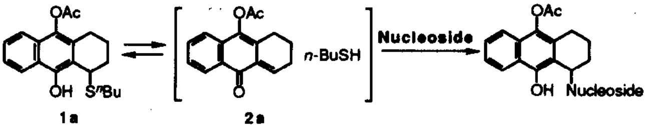


Tetrahedron Lett. **1992,** *33*, 6089

pH-DEPENDENT STABILITY AND REACTIVITY OF A THIOL-QUINONE METHIDE ADDUCT

Steven R. Angle* and Wenjin Yang
Department of Chemistry, University of California , Riverside, California 92521

10-Acetyl-1-(butanethio)-1,2,3,4-tetrahydro-9,10-anthracenediol **2a** has been prepared in 63% yield. The pH-dependent stability and reaction with 2'-deoxyadenosine showed that the nucleoside can be exchanged for the thiol at pH 7

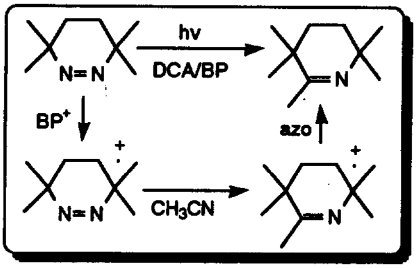


Tetrahedron Lett. **1992,** *33*, 6093

MECHANISTIC STUDIES ON AZOALKANE CATION RADICAL DECOMPOSITION

Thomas A. Zona and Joshua L. Goodman*
Department of Chemistry
University of Rochester
Rochester, New York 14627

The cation radicals of two azoalkane, azo-t-butane and 3,3,6,6-tetramethyl-1,2-diazacyclohex-2-ene decompose at rates $\geq 10^{18}$ times faster than their neutral precursors. This can be attributed to a decrease in the C-N bond dissociation energy of ≥24 kcal/mol upon oxidation.

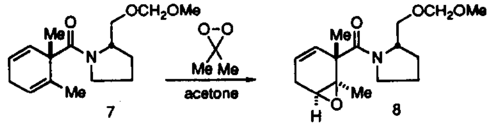


Tetrahedron Lett. **1992,** *33*, 6097

REGIO- AND STEREOSELECTIVE EPOXIDATION OF CHIRAL 1,4-CYCLOHEXADIENES

Arthur G. Schultz*, Roger E. Harrington and Fook S. Tham. Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

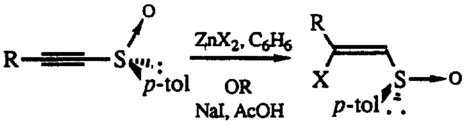
A rationale for high diastereoselectivities for monoepoxidations of diene amides **1b**, **7** and **9** is supported by an X-ray crystallographic structure determination for epoxide **8**.



Tetrahedron Lett. **1992,** *33*, 6101

SYNTHESIS OF ENANTIOMERICALLY PURE (Z)-2-HALOALKENYL SULFOXIDES

Roberto Fernández de la Pradilla[a]*, Miguel Morente[a],
Robert S. Paley[b]*
[a]Instituto de Química Orgánica, C.S.I.C.,
Juan de la Cierva 3, 28006, Madrid, Spain
[b]Swarthmore College, Dept. of Chemistry,
Swarthmore, PA 19081, USA



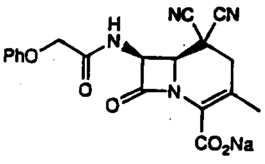
Efficient procedures to prepare enantiomerically pure (Z)-2-haloalkenyl sulfoxides from alkynyl sulfoxides are described.

Tetrahedron Lett. **1992**, *33*, 6103

Synthesis of a Highly Reactive 1,1-Dicyanomethylene-1-dethiacephalosporin

Norma K. Dunlap*, Milana Dezube, Dennis D. Keith and Manfred Weigele
Roche Research Center, Hoffmann-La Roche Inc., Nutley, New Jersey 07110

The novel 1,1-dicyanomethylene-1-dethiacephalosporin **1a** was synthesized in optically pure form.



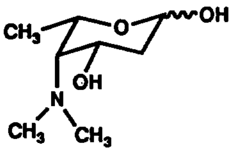
1a

Tetrahedron Lett. **1992**, *33*, 6107

KEDARCIDIN CHROMOPHORE: STRUCTURE ELUCIDATION OF THE AMINO SUGAR KEDAROSAMINE

John E. Leet*[a], Jerzy Golik[a], Sandra J. Hofstead[a], James A. Matson[a], Angela Y. Lee[b], and Jon Clardy[b] a. Bristol-Myers Squibb Pharmaceutical Research Institute, P. O. Box 5100, Wallingford, Connecticut 06492-7660 b. Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853-1301

The structure elucidation of kedarosamine, the amino sugar fragment of the new antitumor agent kedarcidin chromophore, is reported.



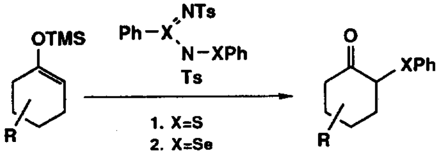
Kedarosamine

Tetrahedron Lett. **1992**, *33*, 6111

New Mild Methodology for the Synthesis of α-Phenylthio and α-Phenylseleno Ketones

Philip Magnus* and Pascal Rigollier
Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712.

Treatment of trimethylsilyl enol ethers with the adduct **1**, derived from chloramine-T and $(PhS)_2$, gave good yields of α-phenylthioketones. The selenium version of this reagent **2** gave α-phenylselenoketones.

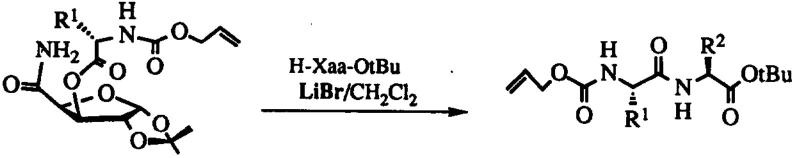


Tetrahedron Lett. **1992**, *33*, 6115

Metal Ion-Promoted Activation of Amino Acid Esters of Carbohydrates in a Biomimetic Synthesis of Peptides

Horst Kunz* and Richard Kullmann,Institut für Organische Chemie, Universität Mainz, Becherweg 18, D- 6500 Mainz, Germany

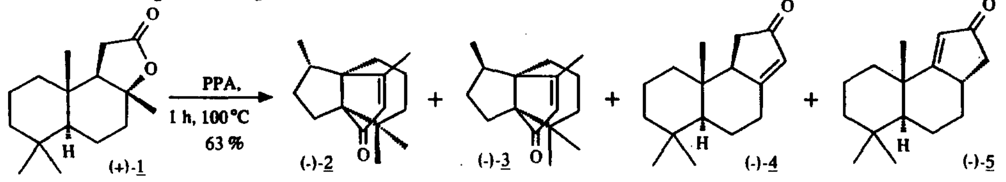
Carbohydrate esters of N-protected amino acids are activated by coordination of metal ions and subjected to aminolysis by amino acid esters to form peptides.



Tetrahedron Lett. **1992**, *33*, 6119

Rearrangement of sclareolide to [4,3,3]-propellanes under strongly acidic conditions.

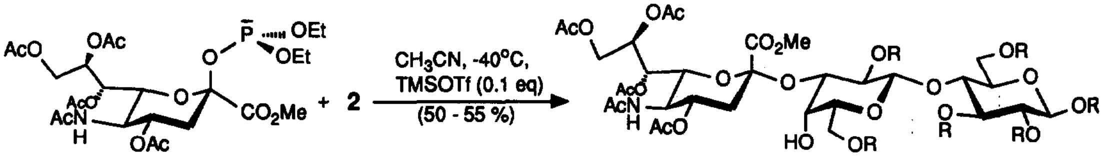
Daniel Helmlinger, Georg Fráter, Givaudan-Roure Research Ltd, CH-8600 Dübendorf/Switzerland



Tetrahedron Lett. **1992**, *33*, 6123

EFFICIENT SIALYLATION WITH PHOSPHITE AS LEAVING GROUP

Thomas J. Martin and Richard R. Schmidt
Fakultät Chemie, Universität Konstanz, D-7750 Konstanz, Germany



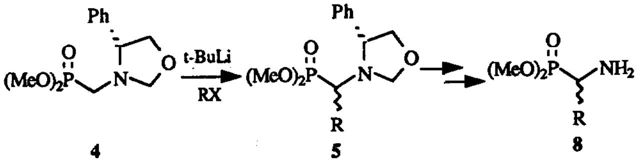
1c **3**

Tetrahedron Lett. **1992**, *33*, 6127

A Simple and General Method for the Asymmetric Synthesis of α-Aminophosphonic Acids

C. Maury, J. Royer and H.-P. Husson
Institut de Chimie des Substances Naturelles du CNRS, 91198 Gif sur Yvette cedex, France.

A simple and general method for the asymmetric synthesis of α-aminophosphonic acids is described. A chiral phosphonate 4 prepared in one step from R-(-)-phenylglycinol was alkylated with good diastereoselectivity using different electrophiles.

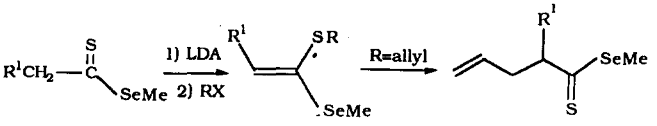


Tetrahedron Lett. **1992**, *33*, 6131

Syntheses of Ketene Thioselenoacetals and of γ-Unsaturated Se-Alkyl Carboxylic Thionoselenoesters

Margareth Lemarié, Yannick Vallée* and Mark Worrell
Laboratoire de Chimie des Composés Thio-organiques, URA CNRS 480, ISMRA, 14050 Caen, France

E-ketene thioselenoacetals were obtained from Se-alkyl carboxylic thionoselenoesters. When the alkylation was conducted with an allylic halide a thio-Claisen rearrangement was observed.



Tetrahedron Lett. **1992**, *33*, 6135

RHODIUM CATALYSED DECARBONYLATION OF OPTICALLY ACTIVE CAMPHOLENAL ANALOGUES

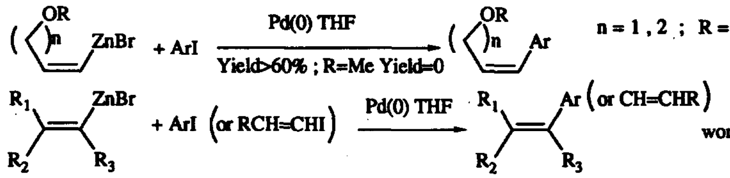
C. Chapuis*, B. Winter and K. H. Schulte-Elte
Firmenich SA, Research Laboratories, P.O.B. 239, 1211 Geneva 8, Switzerland.

Abstract: Campholenal analogues (+)-**1a-d** were decarbonylated with a catalytic amount of Rh/Al_2O_3 with only slight racemization. Experiments with other catalysts showed that racemization increases with the ability of the metal to form a π-allyl complex and to catalyse the hydrogenation of the β-elimination side product. $(Ph_3P)_3RhCl$ gave the best results.

Tetrahedron Lett. **1992**, *33*, 6139

COUPLING BETWEEN VINYL OR ARYL IODIDES AND VINYL ZINC BROMIDES (EITHER BEARING AN ALKOXY MOIETY OR TRISUBSTITUTED) UNDER Pd(0) CATALYSIS.

Lydie Labaudinière and Jean-F. Normant*. Laboratoire de Chimie des Organoéléments, associé au C.N.R.S., Tour 44-45. Université Pierre et Marie Curie, 4 Place Jussieu, F-75252 Paris Cédex 05.



n = 1 , 2 ; R = t-Bu, Me, $SiMe_2$thex

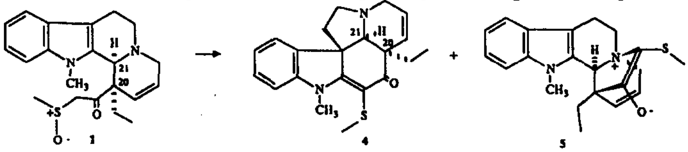
works only if DMA and CuBr present

Tetrahedron Lett. **1992**, *33*, 6143

β-Oxo-Sulfoxide Rearrangements under Sila-Pummerer Reactions Contitions

Martial Dardaine, Angèle Chiaroni, Claude Riche, Nicole Langlois*
Institut de Chimie des Substances Naturelles, C.N.R.S., F91198 Gif-sur-Yvette

Under Sila-Pummerer reaction conditions, the β-oxo-sulfoxide **1** gave rise to a new pentacyclic compound **5** together with the known aspidospermane derivative **4**.

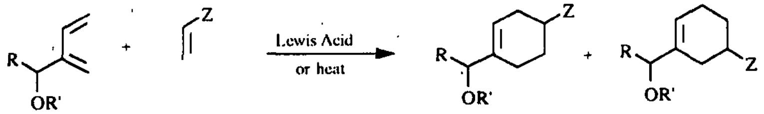


Tetrahedron Lett. **1992**, *33*, 6147

Diastereofacial Selectivity in Diels-Alder Reactions of Chiral 2-substituted-1,3-dienes.

Robert Bloch* and Nathalie Chaptal-Gradoz.

Laboratoire des Carbocycles, associé au CNRS, Institut de Chimie Moléculaire d'Orsay, Bât. 420
Université de Paris-Sud, 91405 Orsay (France)



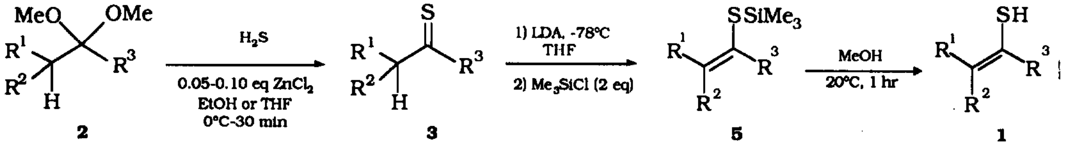
R' = TMS, TBDMS, Me   Z = COMe, CHO

In the catalytic process, a total "para" regioselectivity as well as an excellent stereoselectivity are observed.

Tetrahedron Lett. 1992, 33, 6151

Selective Synthesis of Enethiols

Anne-Marie Le Nocher and Patrick Metzner*
Laboratoire de Chimie des Composés Thio-organiques (Associé au CNRS), ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen, France.



Tautomerically pure aliphatic thioketones **3** have been prepared by treatment of dimethyl acetals **2** with hydrogen sulfide in the presence of zinc chloride. Deprotonation with LDA leads to Z enethiolates **4** which were S-silylated with trimethylsilyl chloride to give silyl vinyl sulfides **5**. Methanolysis of **5** quantitatively affords enethiols **1**, devoid of the isomeric thioketones **3**.

Tetrahedron Lett. 1992, 33, 6155

BASE MEDIATED REACTIONS IN SOLID-LIQUID MEDIA. A 1,3-DIPOLAR CYCLOADDITION ROUTE TO PYRROLINES AND PYRROLES FROM IMINO CHLOROSULFIDES

Fabienne Berrée, Evelyne Marchand and Georges Morel*. Laboratoire de Physicochimie Structurale associé au CNRS, Campus de Beaulieu, 35042 Rennes, France.

Nitrile ylides, generated in basic conditions from imino chlorosulfides 1, undergo 1,3-dipolar cycloadditions with electron-deficient dipolarophiles to produce pyrrolines and pyrroles. The best conditions are found with KF/Al_2O_3 and KOH/Al_2O_3 mixtures as solid supports.

$RSC(Cl){=}NCH_2X$

1

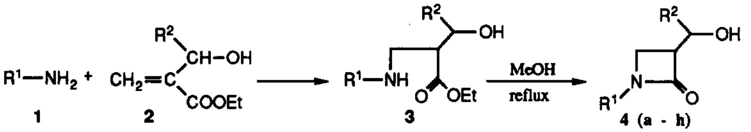
X = Tos, $PO(OEt)_2$, CO_2 Et

Tetrahedron Lett. 1992, 33, 6159

Nouvelle synthèse d'α-(1-hydroxy)alkyl-β-lactames.

H. Amri*, M.M. El Gaied*, T. Ben Ayed* and J. Villiéras**

*Laboratoire de Chimie organique, Faculté des Sciences de Tunis - 1060 Tunisie
**Laboratoire de Synthèse Organique associé au CNRS, Faculté des Sciences et des Techniques, F44072 Nantes Cedex 03-France

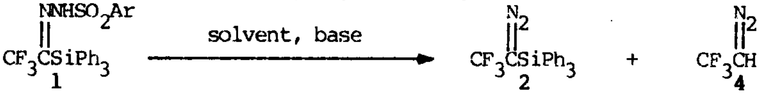


R^1 = n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, c-C_6H_{11}, Ph-CH_2, R^2 = H ; Rdt 44-89%.
R^1 = c-C_6H_{11}, R^2 = CH_3 ; Rdt 41%.

Tetrahedron Lett. 1992, 33, 6161

Facile Conversion of Trifluoroacetyltriphenylsilane 2,4,6-Triisopropylbenzenesulfonylhydrazone to 2,2,2-Trifluorodiazoethane. An Unusual Example of the Bamford-Stevens Reaction

Fuqiang Jin, Yuanyao Xu* and Yiling Ma
Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China



$$\underset{\mathbf{1}}{CF_3\overset{NNHSO_2Ar}{\overset{\|}{C}}SiPh_3} \xrightarrow{\text{solvent, base}} \underset{\mathbf{2}}{CF_3\overset{N_2}{\overset{\|}{C}}SiPh_3} + \underset{\mathbf{4}}{CF_3\overset{N_2}{\overset{\|}{C}}H}$$

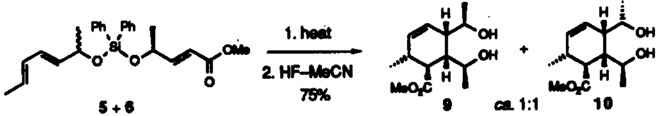
(Ar = Triisopropylphenyl)

The ratio of **2** to **4** is dependent upon the solvent and the base used.

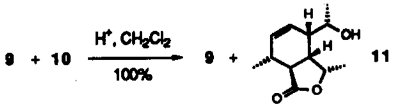
Tetrahedron Lett. **1992**, *33*, 6165

INTRAMOLECULAR DIELS-ALDER REACTIONS OF SILYL ACETAL TRIENES. DIENOPHILE-CONTROLLED CYCLOADDITIONS OF 'MATCHED' AND 'UNMATCHED' DIMETHYLATED SUBSTRATES

Donald Craig* and John C. Reader
Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.



Thermal IMDA reaction of a 1:1 mixture of trienes 5 and 6 gave 9 and 10 upon desilylation. Diol 10 was selectively converted *via* acid catalysis into lactone 11.

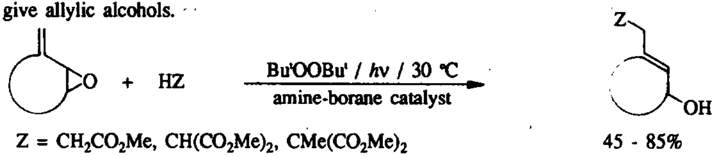


Tetrahedron Lett. **1992**, *33*, 6169

RADICAL CHAIN ADDITION TO VINYL EPOXIDES CATALYSED BY AMINE-BORANES: SYNTHESIS OF ALLYLIC ALCOHOLS

Hai-Shan Dang and Brian P. Roberts*, Christopher Ingold Laboratories, Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, U.K.

In the presence of an amine-borane polarity reversal catalyst, vinyl epoxides react by a radical chain mechanism at the α-C-H group of an ester to give allylic alcohols.

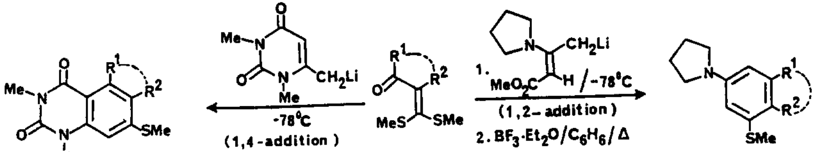


Z = CH_2CO_2Me, $CH(CO_2Me)_2$, $CMe(CO_2Me)_2$

Tetrahedron Lett. **1992**, *33*, 6173

CYCLOAROMATIZATION OF α-OXOKETENE DITHIOACETALS WITH ENAMINONE DERIVED CARBANIONS

J. Satyanarayana, K.R. Reddy, H. Ila* and H.Junjappa*
Deptt. of Chemistry, North Eastern Hill University, Shillong, India



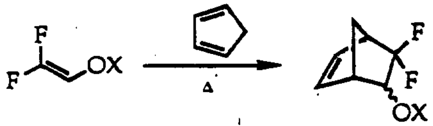
$R^1 = C_6H_5$, 2-furyl, Me, $R^2 = H$; $R^1 = R^2 = -(CH_2)_4-$

Tetrahedron Lett. **1992**, *33*, 6177

DIELS-ALDER REACTIONS OF OXYGEN-SUBSTITUTED DIFLUOROALKENES

Jonathan M. Percy* and Michael H. Rock
Department of Chemistry, Keele University, Keele, Staffordshire, ST5 5BG.

Difluoroalkenes 1 and 2 undergo thermal [4+2] cycloadditions with cyclopentadiene in good yield.



1; X = OMEM
2; X = OCONEt$_2$

3; X = OMEM
4; X = OCONEt$_2$

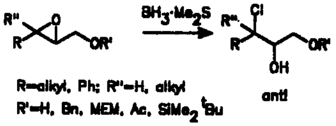
Tetrahedron Lett. **1992**, *33*, 6181

Regio and diastereoselective oxygen assisted opening by monochloroborane-dimethylsulfide of epoxides to chlorohydrins *anti*.

P. Bovicelli[a], E. Mincione[b], P. Lupattelli[a], M.T. Bersani[a]*

[a]Centro C.N.R. di Studio per la Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro, 5 - 00174 Roma, Italy. [b]D.A.B.A.C., Università della Tuscia, V. S.Camillo De Lellis, 01100 Viterbo, Italy.

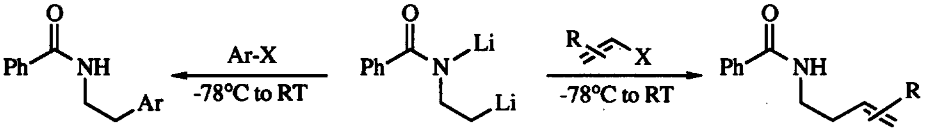
The opening reaction of epoxides by monochloroborane-dimethylsulfide proceeds by oxygen anchimeric assistance in a regio- and diastereoselective manner to give the corresponding *anti* chlorohydrins.



Tetrahedron Lett. **1992**, *33*, 6183

DIRECT COUPLING BETWEEN β-FUNCTIONALIZED ORGANOLITHIUM COMPOUNDS AND ARYL AND VINYL HALIDES

José Barluenga*, Javier M. Montserrat, Josefa Flórez
Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo. Spain

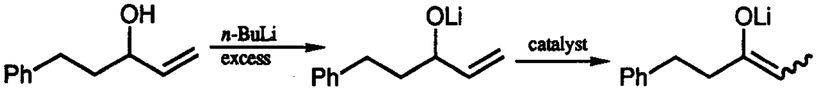


Tetrahedron Lett. **1992**, *33*, 6187

OBSERVATIONS ON A NICKEL-CATALYZED ISOMERIZATION OF ALLYLIC LITHIUM ALKOXIDES.

William B. Motherwell* and David A. Sandham,
Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.

Use of the complex $(Cy_3P)_2NiCl_2$ as catalyst results in regioselective preparation of the first-formed enolate *via* isomerization of the corresponding lithium alkoxide.



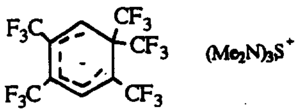
15 : 1
selectivity

Tetrahedron Lett. **1992**, *33*, 6191

TRIS(DIMETHYLAMINO)SULFONIUM 1,1,2,4,5-PENTAKIS(TRIFLUOROMETHYL)- 2,5-CYCLOHEXADIENIDE - A NEW STABLE FLUORINATED CARBANION SALT PREPARED BY ANIONIC TRIFLUOROMETHYLATION OF 1,2,4,5-TETRAKIS(TRIFLUOROMETHYL)BENZENE

Alexander A. Kolomeitsev, Valerie N. Movchun, Yurii L. Yagupolskii*
Institute of Organic Chemistry, Academy of Sciences of Ukraine, 253660,
Kiev-94, Ukraine.

Jacek Porwisiak and Wojciech Dmowski
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224,
Warsaw 44, Poland.

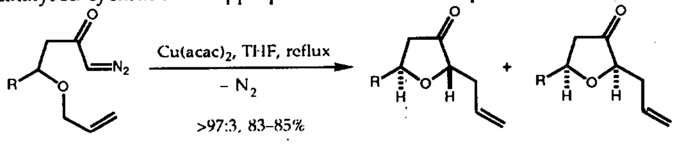


Tetrahedron Lett. **1992**, *33*, 6193

DIASTEREOSELECTIVE SYNTHESIS OF 2,5-DIALKYL TETRAHYDROFURAN-3-ONES BY A COPPER-CATALYSED TANDEM CARBENOID INSERTION AND YLIDE REARRANGEMENT REACTION

J. Stephen Clark, Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, U.K.

The diastereoselective synthesis of *trans*-2,5-dialkyl tetrahydrofuran-3-ones can be accomplished by the Cu(acac)$_2$-catalysed cyclisation of appropriate α-diazo ketone precursors.

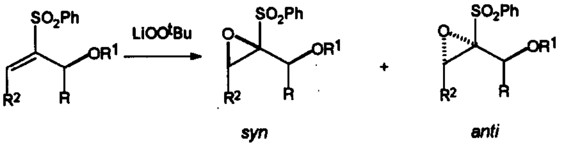


Tetrahedron Lett. **1992**, *33*, 6197

STEREOCONTROL IN THE NUCLEOPHILIC EPOXIDATION OF α-(1-HYDROXYALKYL)-α,β-UNSATURATED SULFONES.

Richard F.W. Jackson,* Stephen P. Standen, William Clegg and Andrew McCamley
Department of Chemistry, Bedson Building, The University, Newcastle upon Tyne, NE1 7RU, UK

Epoxidation of the title compounds with lithium *t*-butylperoxide can be controlled to give good diastereoselectivity.

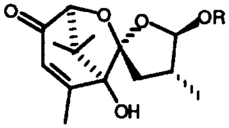


Tetrahedron Lett. **1992**, *33*, 6201

ISOLATION AND STRUCTURAL CHARACTERISATION OF KAMAHINE C: AN UNUSUAL SPIROKETAL FOUND IN A NATIVE NEW ZEALAND HONEY.

Susan J. Broom, Alistair L. Wilkins, Richard M. Ede* and Yinrong Lu,
Department of Chemistry, The University of Waikato, Private Bag 3105, Hamilton, New Zealand.

The structure of the title compound (**1a**) was determined by an NMR and X-ray crystallographic study of its acetate (**1b**).



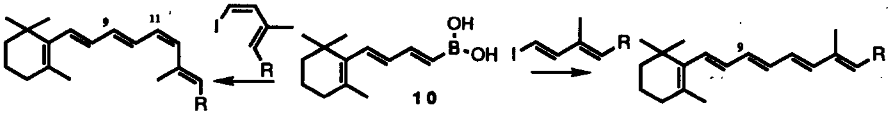
1a R = H
1b R = Ac

Tetrahedron Lett. **1992**, *33*, 6205

STEREOSPECIFIC SYNTHESIS OF 9-DEMETHYLRETINOIDS VIA PALLADIUM-CATALYZED VINYLBORONIC ACID-VINYL IODIDE CROSS COUPLING.

Angel R. de Lera,* Alicia Torrado, Beatriz Iglesias and Susana López.
Departamento de Química Orgánica. Universidade de Santiago de Compostela. 15706 Santiago de Compostela. SPAIN.

9-Demethylretinoids with either *trans* or 11-*cis* geometries are stereospecifically prepared by the thallium-accelerated palladium-catalyzed cross coupling reactions of vinylboronic acid **10** and either (E)- or (Z)-vinyl iodides.



R= -CO$_2$Et
R= -CH$_2$OTBDMS
R= -CH$_2$OH