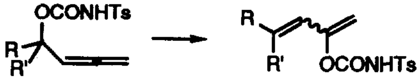
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1992**, *33*, 6715

A NOVEL REARRANGEMENT OF TERTIARY α-ALLENIC ALCOHOL CARBAMATES. PREPARATION OF 2-*O*-CARBAMOYL-4,4-DISUBSTITUTED-1,3-BUTADIENES

Richard W. Friesen,* Aleksandra E. Kolaczewska and Nina Khazanovich
Department of Chemistry, Univeristy of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 1A1

Details of the novel reaction illustrated below are documented.

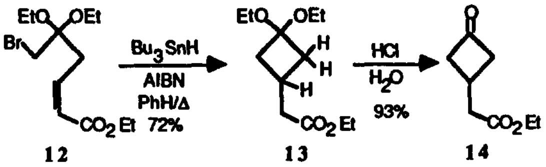


Tetrahedron Lett. **1992**, *33*, 6719

EASY PREPARATION OF A CYCLOBUTANONE KETAL VIA A RADICAL CYCLIZATION. THE GEM-DIALKOXY EFFECT

Michael E. Jung,* Ivan D. Trifunovich, and Nathalie Lensen,
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

A new method for the facile synthesis of cyclobutanones, the key step of which is a radical cyclization to generate the four-membered ring, is reported. Thus reaction of 12 with Bu_3SnH gives in 72% yield 13 which can be hydrolyzed to 14 in excellent yield. In addition, a comparison of the *gem*-dialkyl and *gem*-dialkoxy effects in radical cyclizations to give cyclobutane systems shows that in this system the *gem*-dialkoxy effect is the larger.

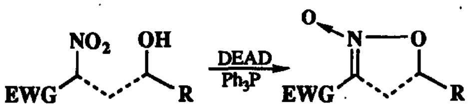


Tetrahedron Lett. **1992**, *33*, 6723

SYNTHESIS OF ALKYL NITRONATES VIA MITSUNOBU CONDENSATION

J.R. Falck and Jurong Yu, Departments of Molecular Genetics and Pharmacology, Univesity of Texas Southwestern Medical Center, Dallas, Texas 75235 U.S.A.*

Nitroalkanes bearing adjacent electron-withdrawing or unsaturated substituents undergo Mitsunobu condensation with alcohols affording alkyl nitronates in 81-98% yields.

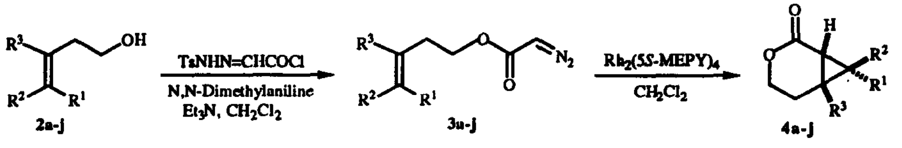


Tetrahedron Lett. **1992**, *33*, 6727

ENANTIOSELECTIVE, RHODIUM CATALYZED INTRAMOLECULAR CYCLOPROPANATIONS OF HOMOALLYLIC DIAZOACETATES.

Stephen F. Martin,* Christopher J. Oalmann, and Spiros Liras
Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712

The homoallylic diazoacetates 3a-j underwent enantioselective intramolecular cyclopropanation with the rhodium catalyst $Rh_2(5S\text{-MEPY})_4$ (1) to give the oxabicyclo[4.1.0]heptanes 4a-j in 71-90% enantiomeric excess and in 55-80% chemical yield.

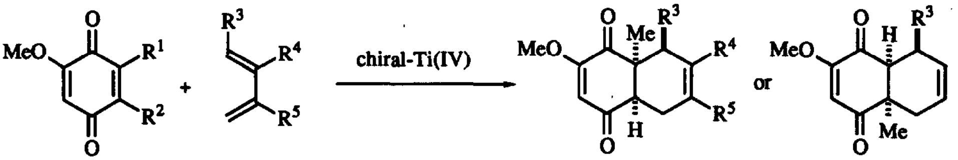


Tetrahedron Lett. **1992**, *33*, 6731

ASYMMETRIC QUINONE-BASED DIELS-ALDER REACTIONS.

Thomas A. Engler,* Michael A. Letavic and Fusao Takusagawa
Department of Chemistry, University of Kansas, Lawrence, KS 66045

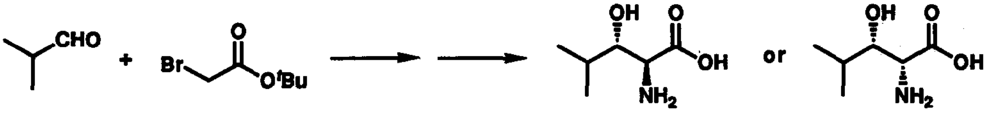
Asymmetric Diels-Alder reactions of 2-methoxy-1,4-benzoquinones with a variety of dienes are reported.



Tetrahedron Lett. **1992**, *33*, 6735

AN ENANTIOSELECTIVE SYNTHESIS OF (*2S,3S*)- AND (*2R,3S*)-3-HYDROXYLEUCINE

E. J. Corey, Duck-Hyung Lee, and Soongyu Choi
Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138

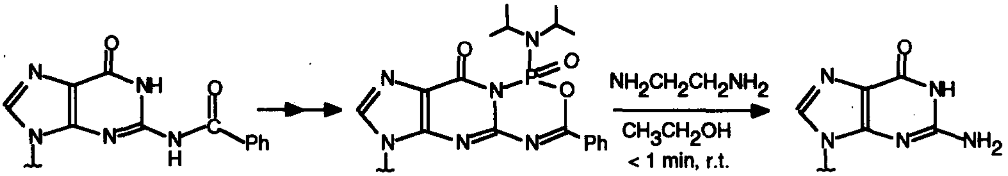


96 : 4 enantioselectivity

Tetrahedron Lett. **1992**, *33*, 6739

TRICYCLIC "OXADIAZAPHOSPHORINOXIDE" GUANOSINES: A NEW STRATEGY TO THE PROTECTION OF GUANINE BASES DURING RNA SYNTHESIS

Masad J. Damha*, Yunkui Guo, Steven V. Zabarylo, Kanjana Ganeshan and Paul A. Giannaris
Department of Chemistry, Erindale College, University of Toronto, Mississauga, Ontario, Canada L5L 1C6

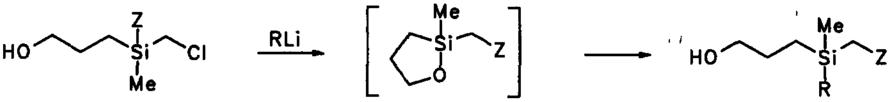


Tetrahedron Lett. **1992**, *33*, 6743

REARRANGEMENTS OF α-HALOSILANES INDUCED BY INTRAMOLECULAR NUCLEOPHILIC ATTACK AT SILICON

Paul F. Hudrlik,* Yousef M. Abdallah, and Anne M. Hudrlik
Department of Chemistry, Howard University, Washington, D. C. 20059

Migrations of organic groups from silicon to carbon are facilitated by intramolecular attack by alkoxide at silicon.

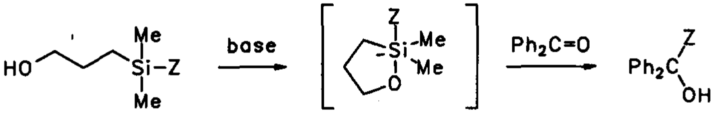


Tetrahedron Lett. **1992**, *33*, 6747

GENERATION OF ANIONIC INTERMEDIATES BY INTRAMOLECULAR NUCLEOPHILIC ATTACK AT SILICON

Paul F. Hudrlik,* Yousef M. Abdallah, and Anne M. Hudrlik
Department of Chemistry, Howard University, Washington, D. C. 20059

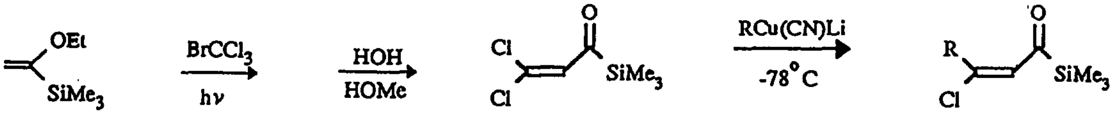
Benzyl and allyl anion equivalents can be generated from benzyl- and allylsilanes by intramolecular alkoxide attack at silicon.



Tetrahedron Lett. **1992**, *33*, 6751

THE PREPARATION OF 3-CHLOROALKENOYLTRIMETHYLSILANES

Robert F. Cunico* and Cui-ping Zhang
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115

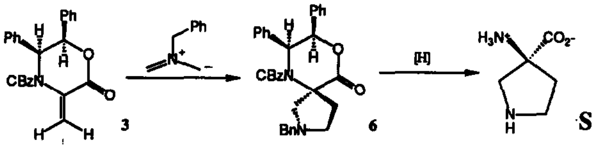


Tetrahedron Lett. **1992**, *33*, 6755

Asymmetric Synthesis of (S)-(-)-Cucurbitine

Robert M. Williams* and Glenn J. Fegley
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

The asymmetric synthesis of (S)-(-)-cucurbitine in greater than 98 % ee is described. The key step of the synthesis involves 1,3-dipolar cycloaddition of azomethine ylide (1) to α,β-dehydrolactone (3) to give pyrrolidine (6) as a single diastereomer.



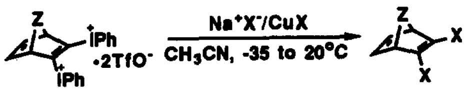
S-(-)-CUCURBITINE

Tetrahedron Lett. **1992**, *33*, 6759

REACTIONS OF BICYCLOALKENYLIODONIUM SALTS WITH NUCLEOPHILES

Peter J. Stang*, Andreas Schwarz, Thorsten Blume, Viktor V. Zhdankin*
Chemistry Department, University of Utah, Salt Lake City, Utah 84112 USA

Bicycloalkenyldiiodonium salts 1 react with a number of anionic nucleophiles ($X^- = I^-, Br^-, CN^-, PhCO_2^-$) in the presence of copper(I) salts to give the corresponding products of the vinylic nucleophilic substitution of the iodobenzene moiety (2).



1 (Z = O, CH_2)

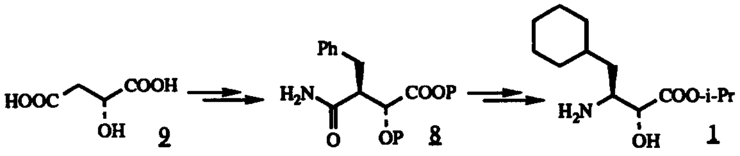
2 (60-80%)

Tetrahedron Lett. **1992**, *33*, 6763

A Novel Synthesis of nor-C-Statine.

Robert W. Dugger*, Janet L. Ralbovsky, Don Bryant,
Jane Commander, Steve S. Massett, Nancy A. Sage and Joe R. Selvidio.
Pfizer Central Research, Process Research and Development Department, Eastern Point Road, Groton, CT 06340

Nor-C-statine has been prepared by benzylation of a malate dianion, differentiation of the two carboxylates and a Hofmann degradation of one of the carboxylates.

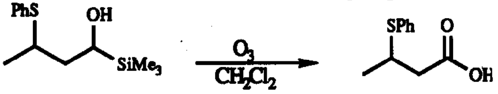


Tetrahedron Lett. **1992**, *33*, 6767

A DIRECT CONVERSION OF (α-HYDROXYALKYL)-SILANES TO CARBOXYLIC ACIDS.

Russell J. Linderman* and Kangyi Chen, Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204.

(α-Hydroxyalkyl)trialkylsilanes are efficiently oxidized to the corresponding carboxylic acid in very good yield. The reaction is tolerant of several functional groups. For example:

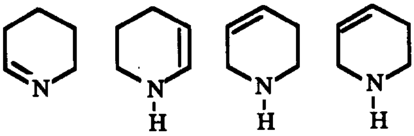


Tetrahedron Lett. **1992**, *33*, 6771

Conformations and Relative Energies of Tetrahydropyridines

Steven M. Bachrach* and Meixiao Liu
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115

Ab inito calculations (MP2/6-31G*) find all tetrahydropyridine isomers are half chairs with relative energies shown below.

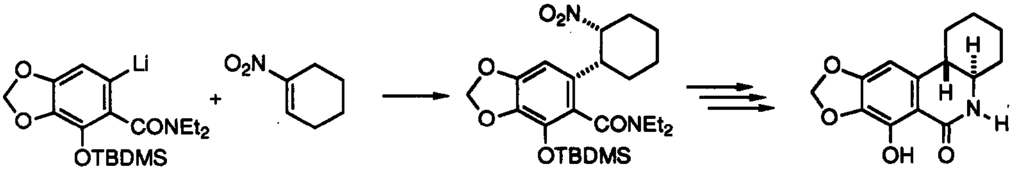


	1	2	3 (ax)	3 (eq)
rel E (kcal/mol)	0.00	6.39	11.90	12.22

Tetrahedron Lett. **1992**, *33*, 6775

Synthesis of Pancratistatin Models

Rosangela S. C. Lopes, Claudio C. Lopes, and Clayton H. Heathcock*
Department of Chemistry, University of California, Berkeley, CA 94720

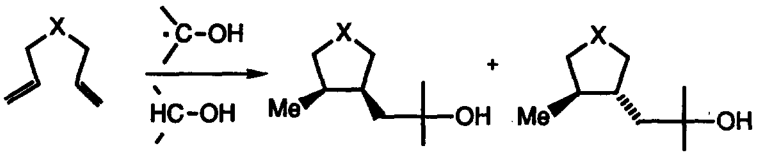


Tetrahedron Lett. **1992**, *33*, 6779

Cyclization of 1,6-Heptadienes by α-Hydroxy Radicals

Abdul Naim, German Mills,* Philip B. Shevlin*
Department of Chemistry, Auburn University, AL 36849, USA

Addition of α-hydroxy isopropyl radicals, generated by γ irradiation of 2-propanol or photolysis of 2-propanol with acetone, to a variety of 1,6-heptadienes generates a 1-methyl-2-(2-hydroxyethyl)-cyclopentane or its heterocyclic equivalent:

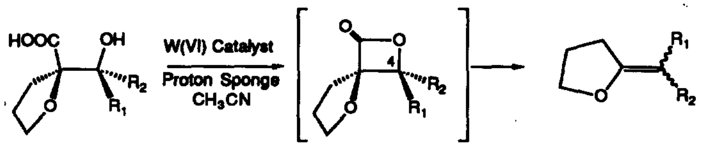


Tetrahedron Lett. **1992**, *33*, 6783

THE PREPARATION OF (α-ALKYLIDENE)TETRAHYDROFURANS BY TUNGSTEN CATALYZED DECARBOXYLATION OF ALDOL PRECURSORS

Tomoya Tanzawa and Jeffrey Schwartz*
Department of Chemistry, Princeton University, Princeton, NJ 08544-1009

Substituted (α-alkylidene)tetrahydrofurans were prepared by tungsten catalysis from substituted hydroxyfuroic acids.

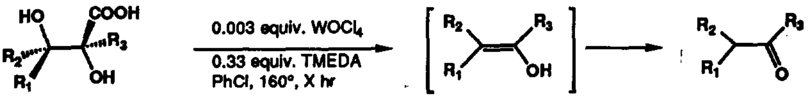


Tetrahedron Lett. **1992**, *33*, 6787

TUNGSTEN COMPLEX CATALYZED DEHYDRATIVE DECARBOXYLATION OF 2,3-DIHYDROXYCARBOXYLIC ACIDS

Hye Kyung Bae Yu and Jeffrey Schwartz*
Department of Chemistry, Princeton University, Princeton NJ 08544-1009 USA

$WOCl_4$ catalyzes dehydrative decarboxylation of 2,3-dihydroxycarboxylic acids to enols, likely via β-lactone intermediates; classical reagents for such conversions fail with these substrates.

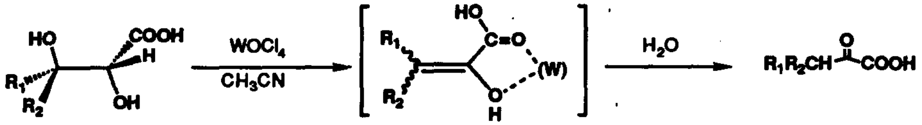


Tetrahedron Lett. **1992**, *33*, 6791

TUNGSTEN COMPLEX INDUCED DEHYDRATION OF 2,3-DIHYDROXYCARBOXYLIC ACIDS TO α-KETO ACIDS

Hye Kyung Bae Yu and Jeffrey Schwartz*
Department of Chemistry, Princeton University, Princeton NJ 08544-1009 USA

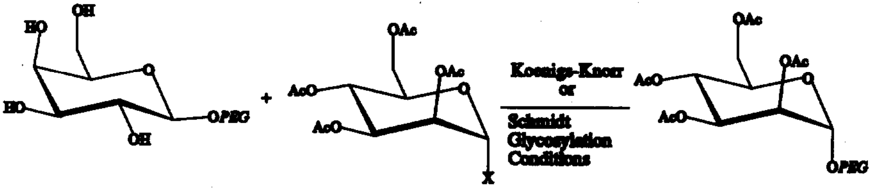
In the absence of added base, $WOCl_4$ induces rapid dehydration of the title compounds to give α-keto acids.



Tetrahedron Lett. 1992, *33*, 6795

METATHESIS OF OLIGOSACCHARIDES. RELATIVE STABILITIES OF ACTIVATED AND DEACTIVATED GLYCOSIDES OF POLYETHYLENE GLYCOL.

Dennis M. Whitfield, Stephen P. Douglas, and Jiri J. Krepinsky* Departments of Molecular and Medical Genetics and Immunology, and Carbohydrate Research Centre, University of Toronto, Toronto, Ontario, Canada M5S 1A8.

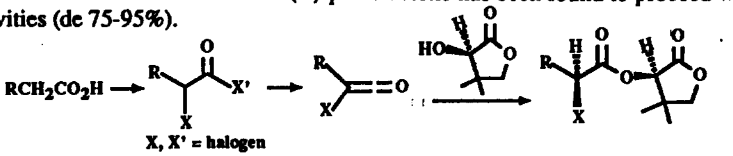


Tetrahedron Lett. 1992, *33*, 6799

Asymmetric Synthesis of alpha-Halo Esters

Tony Durst* **and Kevin Koh**, Ottawa-Carlton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada. K1N 6N5

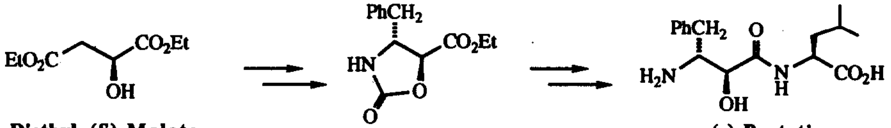
Reaction of α-halogenated ketenes with the chiral alcohol (R)-pantolactone has been found to proceed with good to excellent diastereoselectivities (de 75-95%).



Tetrahedron Lett. 1992, *33*, 6803

A Stereospecific Synthesis of (-)-Bestatin from L-Malic Acid

Bryan H. Norman* and Michelle L. Morris
Monsanto Corporate Research, Chemical Sciences, 800 N. Lindbergh Blvd., St. Louis, MO 63167

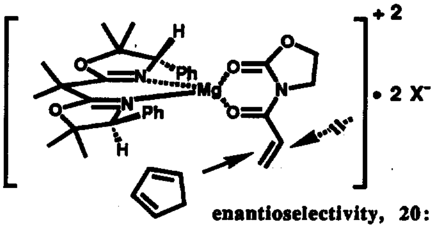


Diethyl (*S*)-Malate **(-)-Bestatin**

Tetrahedron Lett. 1992, *33*, 6807

HIGHLY ENANTIOSELECTIVE CATALYTIC DIELS-ALDER ADDITION PROMOTED BY A CHIRAL BIS(OXAZOLINE)-MAGNESIUM COMPLEX

E. J. Corey and Kazuaki Ishihara
Department of Chemistry, Harvard University
Cambridge, MA 02138



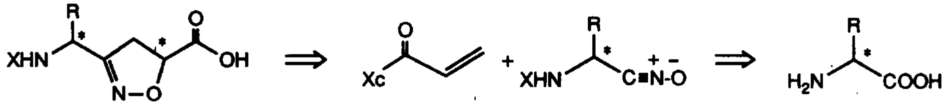
enantioselectivity, 20 : 1

Tetrahedron Lett. **1992**, *33*, 6811

A NEW PEPTIDE BOND SURROGATE : 2-ISOXAZOLINE IN PSEUDODIPEPTIDE CHEMISTRY

Byeang Hyean Kim*, Yong Jun Chung, Gyochang Keum, Jaheon Kim and Kimoon Kim
Department of Chemistry, Center for Biofunctional Molecules,
Pohang Institute of Science and Technology, Pohang, 790-600, Korea

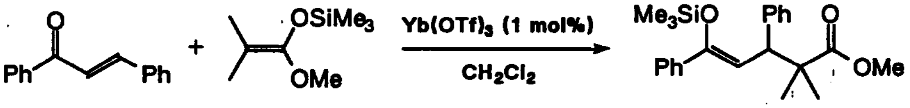
The 2-isoxazoline ring has been incorporated as a new peptide bond surrogate into pseudodipeptide.



Tetrahedron Lett. **1992**, *33*, 6815

Lanthanide Trifluoromethanesulfonates as Reusable Catalysts. Michael and Diels-Alder Reactions

Shū KOBAYASHI,* Iwao HACHIYA, Takeshi TAKAHORI, Mitsuharu ARAKI, and Haruro ISHITANI
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo (SUT), Kagurazaka,
Shinjuku-ku, Tokyo 162



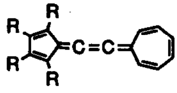
The catalyst can be easily recovered and reused. *89% yield*

Tetrahedron Lett. **1992**, *33*, 6819

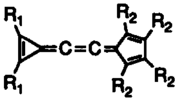
Dipole Moments of 1-Cyclopentadienylidene-2-cycloheptatrienylidene-ethylene and its Related Compounds

Shigeyoshi Katagiri, Susumu Sudoh*, Toshiharu Ozaki, Takashi Toda
and Norihiko Shimazaki
Department of Chemistry, Faculty of Science, Hirosaki University Hirosaki 036, Japan

The dipole moments 1a, 2a and its related compounds are calculated by ab initio and MNDO molecular orbital methods. The calculated dipole momonts are compared with the experimental values.



1a R=H

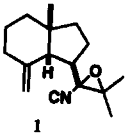


2a R1=H, R2=H

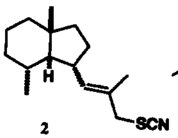
Tetrahedron Lett. **1992**, *33*, 6823

Two Sesquiterpene Isocyanides and a Sesquiterpene Thiocyanate from the Marine Sponge *Acanthella* cf. *cavernosa* and the Nudibranch *Phyllidia ocellata*[1]

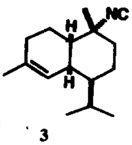
Nobuhiro Fusetani,* Heather J. Wolstenholme,
Katsumi Shinoda, Naoki Asai, and Shigeki Matsunaga
Laboratory of Marine Biochemistry, Faculty of Agriculture
Hiroyuki Onuki and Hiroshi Hirota
Department of Chemistry, Faculty of Science
The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan



1



2



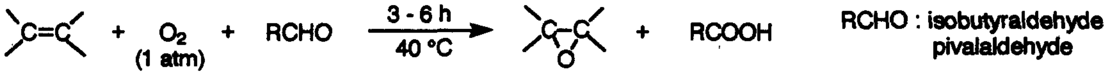
3

A CONVENIENT SYNTHESIS OF EPOXIDES FROM OLEFINS USING MOLECULAR OXYGEN IN THE ABSENCE OF METAL CATALYSTS

Tetrahedron Lett. **1992**, *33*, 6827

Kiyotomi Kaneda,[a]* Shigeru Haruna,[a] Toshinobu Imanaka,[a] Masatoshi Hamamoto,[b] Yutaka Nishiyama,[b] and Yasutaka Ishii[b]
[a] Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan
[b] Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

The system consisting of molecular oxygen and aldehydes oxidizes various olefins except for styrenes and allylic alcohols to give epoxides in high yields.

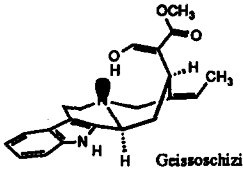


Geissoschizine Revisited - Definite Proof of Its Stereostructure.

Tetrahedron Lett. **1992**, *33*, 6831

Hiromitsu Takayama,[a] Toshiyuki Watanabe,[a] Hiroko Seki,[b] Norio Aimi,[a] and Shin-ichiro Sakai,[a]*
Faculty of Pharmaceutical Sciences[a] and Chemical Analysis Center,[b]
Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba, 263 Japan

The stereostructure of geissoschizine was revised to the conformer **1c** which included the *trans*-quinolizidine configuration, twist boat *D*-ring, and intramolecular hydrogen bonding.

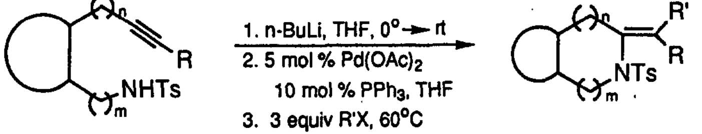


Geissoschizine **1c**

INTRAMOLECULAR AMINOPALLADATION AND CROSS COUPLING OF ACETYLENIC AMINES

Tetrahedron Lett. **1992**, *33*, 6835

Fen-Tair Luo,* Ren-Tzong Wang
Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, ROC

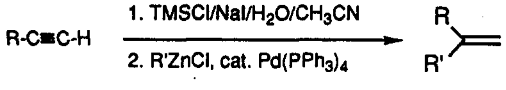


n = 1, 2. m = 0,1. R = H, Me. R' = phenyl, heteroaryl, alkenyl.

One-Pot Conversion of Terminal Alkynes into *gem*-Disubstituted-Alkenes

Tetrahedron Lett. **1992**, *33*, 6839

Fen-Tair Luo,*[a] Shiang-Long Fwu,[b] Wen-Shu Huang[b]
[a] Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, ROC
[b] Department of Chemistry, National Sun Yet-Sen University, Kaoshiung, Taiwan, ROC



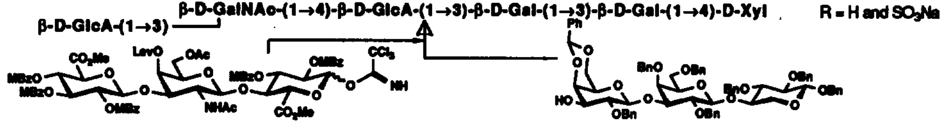
R = n-C_6H_{13}, Ph. R' = alkyl, alkenyl, alkynyl, phenyl, heteroaryl.

Tetrahedron Lett. **1992**, *33*, 6841

SYNTHESIS OF SULFATED GLYCOHEXAOSE OF LINKAGE REGION OF CHONDROITIN 4-SULFATE: β-D-GlcA-(1→3){(SO3Na→4)}-β-D-GalNAc-(1→4)-β-D-GlcA-(1→3)-β-D-Gal-(1→3)-β-D-Gal-(1→4)-D-Xyl

Fumitaka Goto[a] and Tomoya Ogawa*[a,b]
a) The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama, 351-01 Japan
b) Faculty of Agriculture, University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113 Japan

A synthesis of two glycohexaoses that represent a linkage region of chondroitin 4-sulfate to a core protein is achieved.

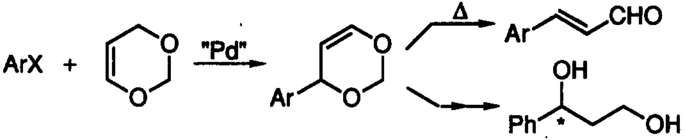


Tetrahedron Lett. **1992**, *33*, 6845

THE PALLADIUM-CATALYZED ARYLATION of 4*H*-1,3-DIOXIN

Takao Sakamoto, Yoshinori Kondo, and Hiroshi Yamanaka*

Pharmaceutical Institute, Tohoku University
Aobayama, Aoba-ku, Sendai 980, Japan

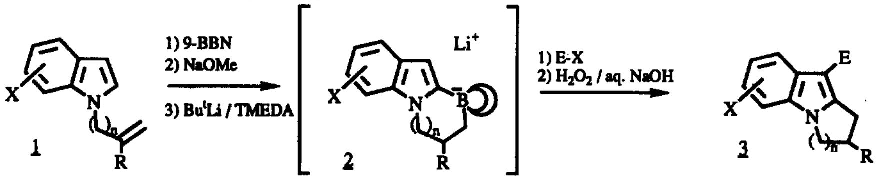


Ar: Ph, p-MeOC$_6$H$_4$, p-EtOOCC$_6$H$_4$, p-O$_2$NC$_6$H$_4$

Tetrahedron Lett. **1992**, *33*, 6849

A NOVEL SYNTHETIC USE OF TRIALKYL(INDOL-2-YL)BORATE FOR A "ONE-POT" SYNTHESIS OF [*a*]-ANNELATED INDOLES

Minoru Ishikura and Masanao Terashima*
Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02, Japan

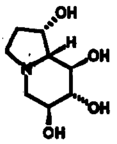


Tetrahedron Lett. **1992**, *33*, 6853

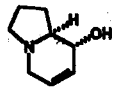
ENANTIOSPECIFIC SYNTHESIS OF FUNCTIONALIZED INDOLIZIDINES.SYNTHESIS OF (8*S*, 8a*R*)-6,7-DEHYDRO-8-HYDROXYINDOLIZIDINE.

Ari M.P. Koskinen*,[1] and Jane M. Paul
[1]Department of Chemistry, University of Oulu, Linnanmaa, SF-90570 Oulu, Finland and Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.

A stereocontrolled route for the title compound *2* has been realised using L-proline as starting material. The route is amenable to modifications to provide a variety of stereoisomers of glycosidase inhibitors, *e.g.* those of castanospermine *1*.



1



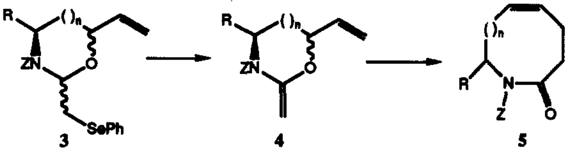
2

SYNTHESIS OF MONOCYCLIC MEDIUM RING LACTAMS

Tetrahedron Lett. **1992**, *33*, 6857

P. Andrew Evans and Andrew B. Holmes*
University Chemical Laboratory, Lensfield Road, CAMBRIDGE CB2 1EW, UK.
Keith Russell
I.C.I. Pharmaceuticals, Mereside, Alderley Park, MACCLESFIELD SK10 4TG, UK.

Selenoxide elimination of the aminals 3 afforded the ketene aminals 4 which underwent *in situ* Claisen rearrangement to the lactams 5.

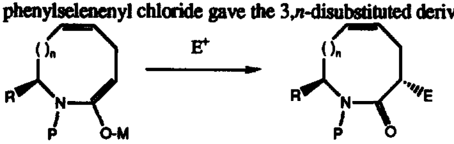


REGIO- AND STEREOSELECTIVE FUNCTIONALISATION OF MONOCYCLIC MEDIUM RING LACTAMS

Tetrahedron Lett. **1992**, *33*, 6859

P. Andrew Evans, Ian Collins, Peter Hamley, Andrew B. Holmes*, and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, CAMBRIDGE CB2 1EW, UK.
Keith Russell
I.C.I. Pharmaceuticals, Mereside, Alderley Park, MACCLESFIELD SK10 4TG, UK.

Treatment of the potassium enolates of a series of racemic 7-, 8-, and 9-membered unsaturated lactams with trisyl azide and phenylselenenyl chloride gave the 3,*n*-disubstituted derivatives with good selectivities.

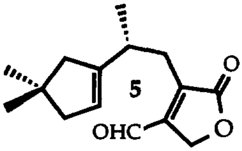


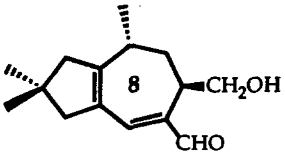
THE ISOLATION OF NEW SESQUITERPENE ALDEHYDES FROM INJURED FRUIT BODIES OF *LACTARIUS SCROBICULATUS*.

Tetrahedron Lett. **1992**, *33*, 6863

Zijie Pang, Fabienne Bocchio and Olov Sterner*, University of Lund, P.O.B. 124, Sweden.

The two aldehydes 5 and 8 were isolated as conversion products of stearoylvelutinal in injured fruit bodies of *Lactarius scrobiculatus*.



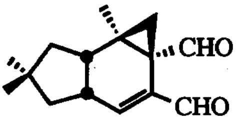


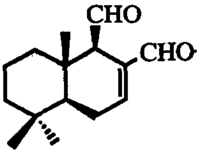
THE INHIBITORY EFFECT OF SESQUITERPENOID UNSATURATED DIALDEHYDES ON THE DOPAMINE D1 RECEPTOR, A QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS STUDY.

Tetrahedron Lett. **1992**, *33*, 6867

F. Bocchio[1], S. Kalf-Hansen[2], K. Dekermendjian[2], O. Sterner[1,*] and R. Witt[2], [1]University of Lund, S-221 00 Lund (Sweden) and [2]Sct. Hans Hospital, DK-4000 Roskilde (Denmark).

The inhibitory effect of 8 sesquiterpenes containing an unsaturated dialdehyde functionality (e.g. isovelleral and polygodial) on the dopamine D1 receptor has been correlated with 22 chemical and molecular descriptors by the multivariate PLS method.



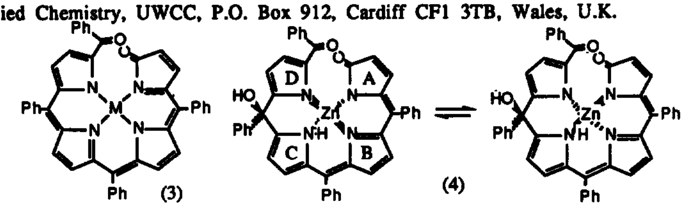


Tetrahedron Lett. **1992**, *33*, 6871

STRUCTURES OF THE ZINC COMPLEXES OF THE BILINONES FORMED BY PHOTO-OXIDATIONS OF *MESO*-TETRAPHENYLPORPHYRINS

José A.S. Cavaleiro,[a] Michael J.E. Hewlins,[b]* the late Anthony H. Jackson[b] and Maria G.P.M.S. Neves[a]
a Departamento de Quimica, Universidade de Aveiro, 3800 Aveiro, Portugal.
b School of Chemistry and Applied Chemistry, UWCC, P.O. Box 912, Cardiff CF1 3TB, Wales, U.K.

The photo-oxidation products from *meso*-tetraphenylporphyrins form yellow-brown (3,M=Zn) and blue(4) zinc complexes.

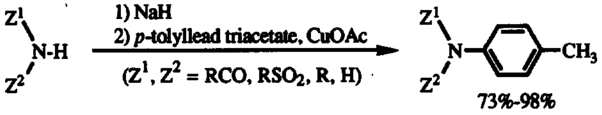


Tetrahedron Lett. **1992**, *33*, 6875

AMIDE N-ARYLATION WITH *p*-TOLYLLEAD TRIACETATE.

Pilar López-Alvarado, Carmen Avendaño and J. Carlos Menéndez. Departamento de Química Orgánica y Farmacéutica. Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain.

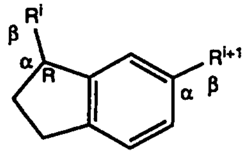
A variety of amidic substrates are efficiently N-arylated by *p*-tolyllead triacetate in the presence of copper II.



Tetrahedron Lett. **1992**, *33*, 6879

THE SYNTHESIS OF 1,6-DISUBSTITUTED INDANES WHICH MIMIC THE ORIENTATION OF AMINO ACID SIDE-CHAINS IN A PROTEIN ALPHA-HELIX MOTIF.

William P. Nolan, Giles S. Ratcliffe and David C. Rees*
Parke-Davis Neuroscience Research Centre,
Addenbrookes Hospital Site, Hills Road, Cambridge, CB2 2QB, U.K.



α-helix template

Tetrahedron Lett. **1992**, *33*, 6883

AN INTRAMOLECULAR ARYNE CYCLOADDITION APPROACH TO PHENANTHRENE ALKALOIDS

Juan C. Estévez, Ramón J. Estévez and Luis Castedo*.
Departamento de Química Orgánica de la Universidad de Santiago and Sección de Alcaloides (C.S.I.C.), 15706 Santiago de Compostela, SPAIN.

A new synthesis of phenanthrene alkaloids which is based on the intramolecular Diels-Alder reaction between a styrene and an aryne is described.