

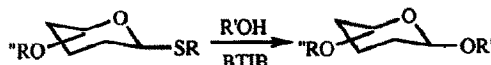
GRAPHICAL ABSTRACTS

Tetrahedron Letters, 1994, 35, 7147

Stabilization of Glycosyl Sulfonium Ions for Stereoselective *O*-Glycosylation

Lihong Sun, Pan Li, and Kang Zhao*
Department of Chemistry, New York University
New York, NY 10003

Bis(trifluoroacetoxy)iodobenzene can be used for studying the stereoselectivity of *O*-glycosylation from thioglycosides and the use of reagent-stabilized sulfonium ions to prohibit the formation of oxonium ions is also discussed.



Tetrahedron Letters, 1994, 35, 7151

Improvements in the Synthesis of Adamantane-2,6-dione and Preparation of the Novel Adamantane-2,6-dione mono-ketal Fred D. Ayres,* Saeed I. Khan, Orville L. Chapman, and Steven N. Kaganove, Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90024-1569 USA

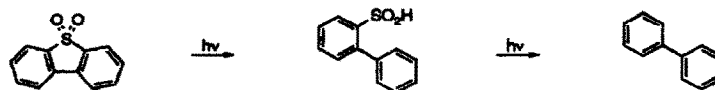


Tetrahedron Letters, 1994, 35, 7155

PHOTOCHEMISTRY OF DIBENZOTHIOPHENE-S,S-DIOXIDE: REACTIONS OF A HIGHLY CONSTRAINED BIRADICAL.

William S. Jenks,* Lisa M. Taylor, Yushen Guo, and Zehong Wan,
Department of Chemistry, Iowa State University, Ames, IA 50011-3111 USA

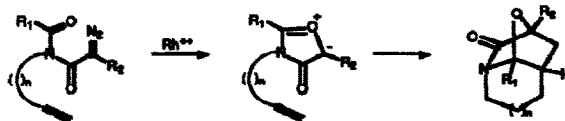
Photolysis of dibenzothiophene sulfone in isopropanol yields biphenyl in quantitative yields. The reaction takes place in two stages.



Tetrahedron Letters, 1994, 35, 7159

SYNTHESIS OF POLYHETEROCYCLIC RING COMPOUNDS BY THE INTRAMOLECULAR CYCLOADDITION OF N-ALKENYL SUBSTITUTED DIAZOIMIDES

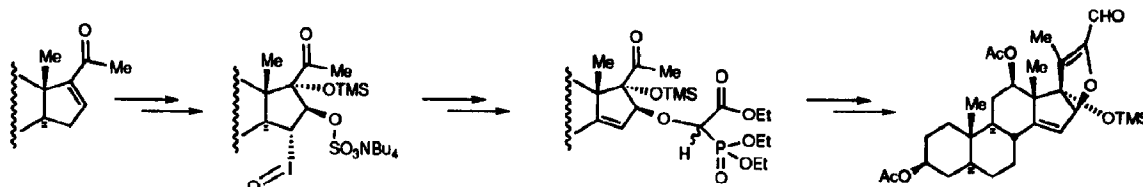
Albert Padwa*, David J. Austin, and Alan T. Price
Department of Chemistry, Emory University Atlanta, GA 30322 USA
Rhodium(II) catalysis of various diazoimides containing tethered π -systems attached to the nitrogen atom results in isomfinchone dipole formation followed by intramolecular dipolar-cycloaddition.



APPLICATION OF THE REICH IODOSO SYN-ELIMINATION FOR THE PREPARATION OF AN INTERMEDIATE APPROPRIATE FOR THE SYNTHESIS OF BOTH HEXACYCLIC STEROIDAL UNITS OF CEPHALOSTATIN 7.

S. Kim, P. L. Fuchs*

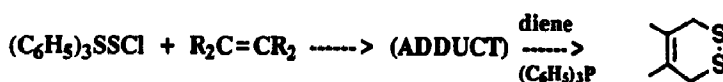
Department of Chemistry, Purdue University, West Lafayette, IN 47907



SULFENYL CHLORIDE CHEMISTRY. PRECURSORS FOR DIATOMIC SULFUR TRANSFER.

Imad A. Abu-Yousef and David N. Harpp*
Department of Chemistry
McGill University
Montreal, Quebec, Canada, H3A 2K6

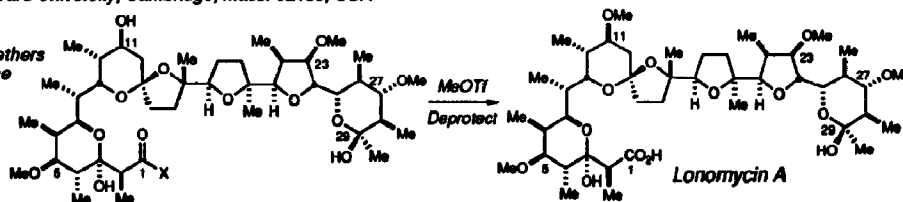
When triphenylmethanethiosulfonyl chloride (as well as its dithio homolog) is treated with various alkenes, 1,2 addition reactions take place. When these adducts are warmed with 1,3-dienes, diatomic sulfur is delivered in good, overall yield.



Mild Alcohol Methylation Procedures for the Synthesis of Polyoxygenated Natural Products. Applications to the Synthesis of Lonomycin A

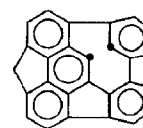
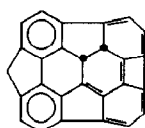
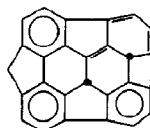
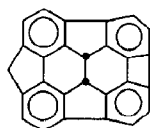
David A. Evans*, Andrew M. Ratz, Bret E. Huff, and George S. Sheppard
Department of Chemistry, Harvard University, Cambridge, Mass. 02138, USA

Selective formation of methyl ethers in four key intermediates for the asymmetric total synthesis of lonomycin A is described.



C₆₀ DIHYDRIDES AND FULLERENE AROMATICITY. INSIGHTS FROM CALCULATIONS ON MODEL COMPOUNDS. Philip M. Warner,
Department of Chemistry, Northeastern University, Boston, MA 02115 USA

AM1 calculations on fullerene model compounds (e.g., 15, 16, 24) reveal that C₆₀ is quite aromatic, with each C having a resonance energy of about 3.33 kcal/mol. Also, ring-opened fullerene dihydrides (e.g., 25) (fulleroids) are discussed.

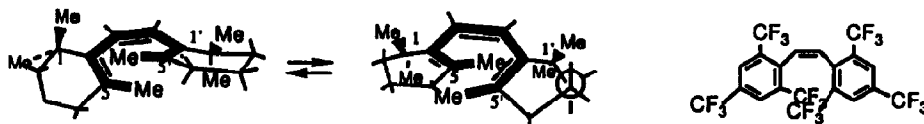


Tetrahedron Letters, 1994, 35, 7177

Spiral Hexatrienes. The Hindered cis Isomer of Mini-carotene-3 and Hexakis-(2,2',4,4',6,6'-

trifluoromethyl)stilbene. Rongliang Chen, Leticia U. Colmenares, J. R. Thiel & Robert S. H. Liu*,
Department of Chemistry, University of Hawaii, Honolulu, HI 96822, U. S. A.

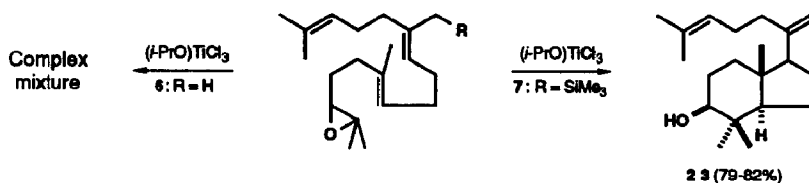
Spectroscopic (UV-VIS and NMR) and chemical properties of the cis isomers of the titled compounds are reported.



Tetrahedron Letters, 1994, 35, 7181

Selective Termination of a Polyene Cyclization by an Internally Situated Allylsilane Group

Paul V. Fish, Department of Chemistry, Stanford University, Stanford, CA 94305, USA



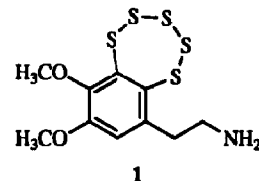
The cyclization of epoxides 6 and 7, incorporating the internally situated propenyl and allylsilane terminator groups respectively, has demonstrated that the allylsilane function is the far superior group for terminating the cyclization process.

Tetrahedron Letters, 1994, 35, 7185

CHIRALITY IN UNSYMMETRICALLY SUBSTITUTED BENZOPENTATHIEPINS: THE RESULT OF A HIGH BARRIER TO RING INVERSION

Bradley S. Davidson,* Paul W. Ford, and Magnus Wahlman
Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

Evidence obtained using NMR and molecular mechanics calculations indicates that unsymmetrically substituted benzopentathiepins, such as the ascidian metabolite varacin (1), are asymmetric molecules as a result of a high energy barrier to inversion of the low energy chair conformations of the polysulfide ring. Derivatization of varacin with a chiral auxiliary provides a mixture of diastereomeric products which can be separated by fractional recrystallization.



Tetrahedron Letters, 1994, 35, 7189

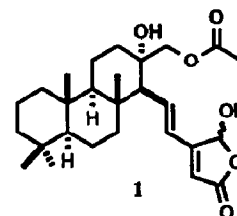
NEW CYTOTOXIC SESTERTERPENES FROM THE MARINE SPONGE SPONGIA SP.

Haiyin He[†], Palaniappan Kulanthaivel[†] and Bill J. Baker[‡]

[†]Sphinx Pharmaceuticals Corporation, 4 University Place, Durham, NC 27717, USA

[‡]Department of Chemistry, Florida Institute of Technology, Melbourne, FL 32901, USA

Six new cytotoxic sesterterpene lactones, spongianolides A-F (1-6) were isolated from the extracts of the marine sponge *Spongia* sp. The structures were determined by the interpretation of spectral data.

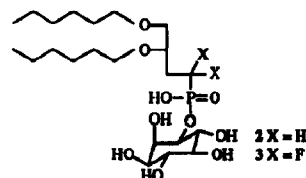


Tetrahedron Letters, 1994, 35, 7193

**SYNTHESIS OF ISOSTERIC AND ISOPOLAR PHOSPHONATE
SUBSTRATE ANALOGUES DESIGNED AS INHIBITORS FOR
PHOSPHATIDYLINOSITOL-SPECIFIC PHOSPHOLIPASE C**

FROM *BACILLUS CEREUS*. Thottumkara K. Vinod, O. Hayes Griffith* and John F. W. Keana,* Department of Chemistry and
The Institute of Molecular Biology, University of Oregon, Eugene, OR 97403 USA

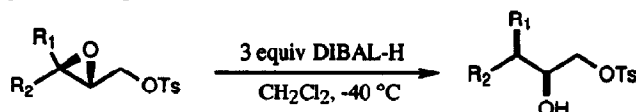
The synthesis of substrate analogues 2 and 3 designed as inhibitors for phosphatidylinositol-specific phospholipase C from *Bacillus cereus* is described.



Tetrahedron Letters, 1994, 35, 7197

**CHEMOSELECTIVE REDUCTION OF 2,3-EPOXY
TOSYLATES WITH DIBAL-H AS A GENERAL ROUTE
TO ENANTIOMERICALLY-ENRICHED 1-TOSYLOXY-2-ALKANOLS**

J. Michael Chong* and James Johannsen, Guelph-Waterloo Centre for Graduate Work in Chemistry
Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1



2,3-Epoxy tosylates may be reduced with DIBAL-H in CH₂Cl₂ or ether at -40 °C to 1-tosyloxy-2-alkanols in high (94-98%) yields.

Tetrahedron Letters, 1994, 35, 7201

A Novel One-Pot Conversion of Methyl Sulfones to Sulfonamides

Hong-Chih Huang,* Emily J. Reinhard and David B. Reitz

G. D. Searle, Department of Medicinal Chemistry, 700 North Chesterfield Parkway
St. Louis, Missouri 63198

A one-pot synthesis of sulfonamides from methyl sulfones has been developed. Treatment of methyl sulfones with base and trialkylboranes gave the corresponding rearranged sulfinic acid salts which were converted to sulfonamides during oxidative-amination workup.



Tetrahedron Letters, 1994, 35, 7205

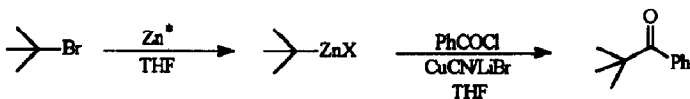
Direct Formation of Secondary and Tertiary Alkylzinc

Bromides. Mark V. Hanson, Jeff D. Brown, and Reuben D. Rieke,*

Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304.

Q. Jason Niu, Rieke Metals, Inc., 6133 Heide Lane, Lincoln, Nebraska 68512

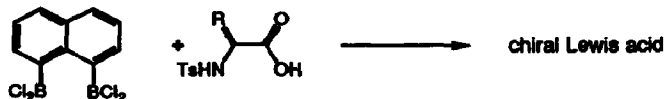
The direct formation of secondary and tertiary alkylzinc bromides.



CHIRAL LEWIS ACIDS DERIVED FROM 1, 8-NAPHTHALENEDIYLBIS-(DICHLOROBORANE). Michael Reilly and Taeboem Oh*, Department of Chemistry, State University of New York, Binghamton, NY 13902-6000

Tetrahedron Letters, 1994, 35, 7209

1, 8-Naphthalenediylbis(dichloroborane) was modified with chiral ligands derived from amino acids and diols. These Lewis acids were examined in the context of asymmetric Diels-Alder reactions.



Extrusion Reactions of Carbon Dioxide from Orthoesters and Derivatives: An *ab initio* Study of Some Cyclic Carbenes.

Tetrahedron Letters, 1994, 35, 7213

Ronald R. Sauer, Department of Chemistry, Rutgers, The State University, New Brunswick, NJ 08903, USA

Loss of carbon dioxide from dioxocarbene 1 can proceed via a concerted process with activation energy: $\Delta G^\ddagger = \text{ca. } 7.1 \text{ kcal/mol}$ (MP2/6-31G**). The unsaturated analog 2 is calculated to be more stable: $\Delta G^\ddagger = \text{ca. } 2.5 \text{ kcal/mol}$.



Fragmentation-Cyclization Reactions by Photoinduced Electron Transfer.

Tetrahedron Letters, 1994, 35, 7217

Thorsten Kirschberg, Jochen Mattay*, Organisch-Chemisches Institut der Universität Münster, Orleansring 23, D-48149 Münster, Germany.

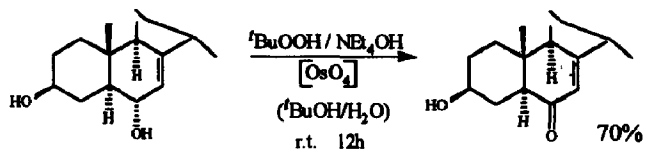
By PET induced formation of V spirocyclic and ring annelated compounds are accessible.



A Novel and Selective Oxidation of Steroidal Allylic Alcohols to the Corresponding Ketones

Tetrahedron Letters, 1994, 35, 7221

Christian Beck and Karlheinz Seifert*, Lehrstuhl für Organische Chemie I/2, NWII, Universität Bayreuth, D-95440 Bayreuth; The oxidation of steroidal allylic alcohols with ^tBuOOH and catalytic amounts of OsO₄ yielded the corresponding α,β -unsaturated ketones in good yields.



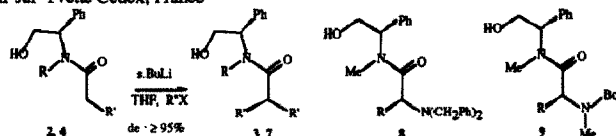
ASYMMETRIC SYNTHESIS. XXXIII. DIASTEREOSELECTIVE ALKYLATION OF N,N-SUBSTITUTED AMIDES.

Tetrahedron Letters, 1994, 35, 7223

Laurent Micouin^a, Vincent Schanen^b, Claude Riche^b, Angèle Chiaroni^b, Jean-Charles Quirion^{a*} and Henri-Philippe Husson^a.

a) Laboratoire de Chimie Thérapeutique associé au CNRS, Faculté des Sciences Pharmaceutiques et Biologiques, Université R. Descartes, 4, Av. de l'Observatoire, 75270 Paris Cedex 06, FRANCE.
b) Institut de Chimie des Substances Naturelles du CNRS, 91198 Gif-sur-Yvette Cedex, France

A series of substituted amides **3** and **7** has been synthesized in enantiomerically pure form from amides **2** and **4** by a stereospecific alkylation. This strategy has been applied to the asymmetric synthesis of diamine derivatives **8** and **9**.



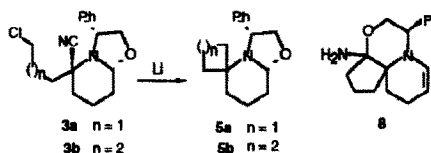
ASYMMETRIC SYNTHESIS. XXXIV. SYNTHESIS OF SPIRO-PIPERIDINE DERIVATIVES VIA THE CN(R,S) METHOD.

Tetrahedron Letters, 1994, 35, 7227

Carlos M. R. Ribeiro, Sebastião J. de Melo, Martine Bonin, Jean-Charles Quirion*, Henri-Philippe Husson*.

Laboratoire de Chimie Thérapeutique associé au CNRS, Université René Descartes, Faculté des Sciences Pharmaceutiques et Biologiques, 4, Av. de l'Observatoire, 75270, Paris Cedex 06, France.

5-Aza-spiro-[3,5] nonane **5a**, 6-aza-spiro-[4,5] decane **5b** and tricyclic enamine **8** were prepared from **3a** and **3b** under dissolving metal conditions.



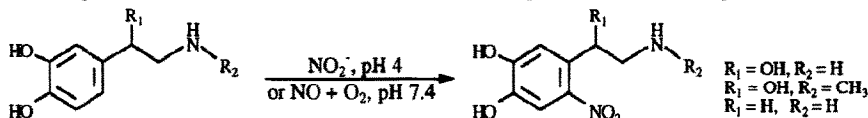
NITRATION OF CATECHOLAMINES WITH NITROGEN OXIDES IN MILD CONDITIONS : A HYPOTHESIS FOR THE REACTIVITY OF NO IN PHYSIOLOGICAL SYSTEMS

Tetrahedron Letters, 1994, 35, 7231

Marie-Laure de la Bretèche, Claudine Servy, Maryse Lenfant and Claire Ducrocq*

Institut de Chimie des Substances Naturelles, avenue de la Terrasse, C.N.R.S. F-91198 Gif-sur-Yvette France

Catecholamines react at pH 3-6 with sodium nitrite or in non-deaerated buffer (pH 7.4) with NO leading to the 6-nitro derivatives.

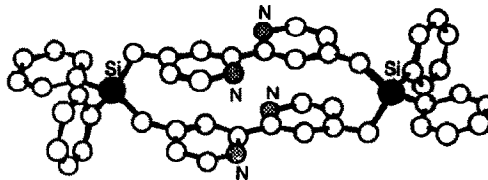


EXODITOPIC RECEPTORS II: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF A DISILAMACROCYCLE BEARING TWO BIPYRIDINE UNITS

Tetrahedron Letters, 1994, 35, 7233

Christian Kaes, Mir Wais Hosseini*, Romain Ruppert, André De Cian and Jean Fischer, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France

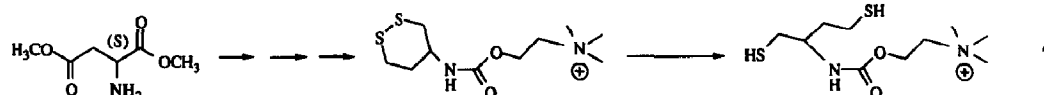
The synthesis of a macrocyclic compound composed of two 2,2'-bipyridines interconnected by two $-\text{CH}_2\text{SiCH}_2-$ fragments was achieved and its structure was established.



DESIGN AND SYNTHESIS OF A NOVEL SITE-DIRECTED REDUCING AGENT FOR THE DISULFIDE BOND INVOLVED IN THE ACETYLCHOLINE BINDING SITE OF THE AChOR.

Pascal Kessler*, Denis Servent and Christian Hirth†
CEA, Département d'Ingénierie et d'Etudes des Protéines (DIEP), C.E. Saclay, 91191 Gif-sur-Yvette, France.

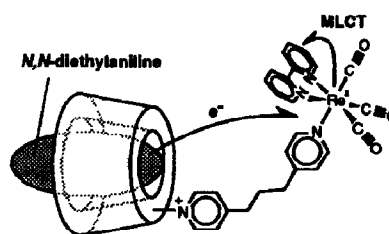
Compound 7 was shown to selectively reduce a disulfide bond in the vicinity of the acetylcholine binding site of the AChOR.



SYNTHESIS OF A RHENIUM COMPLEX APPENDING

A CYCLODEXTRIN UNIT ON A LIGAND. Asao Nakamura, Satoshi Okutsu, Yuji Oda, Akihiko Ueno and Fujio Toda; Department of Bioengineering, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan.

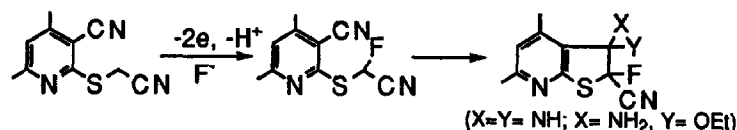
A rhenium complex with a hydrophobic binding pocket capable of catching electron donor molecules has been designed for studying photoinduced long-range electron transfer through non-covalent bonding.



Electrolytic Partial Fluorination of Organic Compounds. 13.

Selective Anodic α -Fluorination of Nitrogen-Containing Heterocyclic Sulfides and Its Application to the Synthesis of Fluorinated Fused Heterocycles

Ayman W. Erian, Akinori Konno, and Toshio Fuchigami,*
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

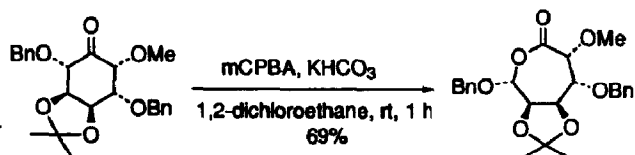


Regioselective Baeyer-Villiger Reaction of Polyhydroxycyclohexanone Derivatives

Noritaka Chida, Takahiko Tobe, and Seiichiro Ogawa

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan

The regioselectivity observed in Baeyer-Villiger reaction of polyhydroxycyclohexanone derivatives possessing various substituents at adjacent carbons to the carbonyl are reported.

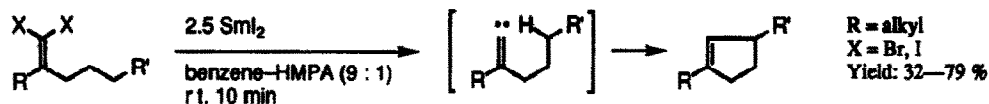
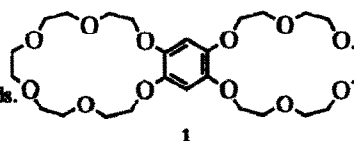


ALKYLIDENECARBENES FROM 1,1-DIHALOGENOALKENES WITH SAMARIUM DIODIDE: MILD AND EFFICIENT METHOD FOR THE SYNTHESIS OF CYCLOPENTENES

Munetaka Kunishima, Kazuhito Hiki, Shohei Tani,* and Akira Kato†

Faculty of Pharmaceutical Sciences, Kobe Gakuin University, Nishi-ku, Kobe 651-21, Japan

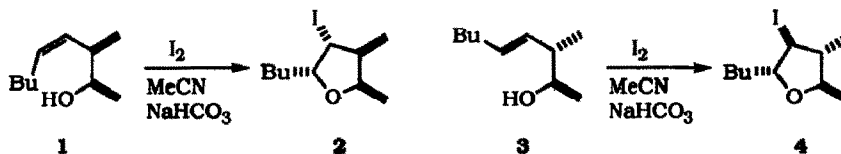
†Niigata College of Pharmacy, Kamishin'ei-cho, Niigata 950-21, Japan

A new mild method for construction of cyclopentenes via 1,5-C—H insertion of alkylidenecarbenes by the reaction of 2,2-dialkyl-1,1-dihaloalkenes with SmI_2 in benzene—HMPA was developed.
1,2,4,5-BIS-(1,4,7,10,13,16-HEXAOXAHEXADECAMETHYLENE)
BENZENE: BENZO-BIS-(18-CROWN-6).
J.J.H. Schlotter,^a I.J.A. Mertens,^a A.M.A. van Wageningen,^a F.P.J.Mulders,^a J.W. Zwikker,^a H.-J. Buschmann^b and L.W. Jenneskens.^a^aDebye Institute, Dept. of Phys. Org. Chem., Utrecht University, The Netherlands.^bDeutsches Textilforschungszentrum Nord-West e.V., Krefeld, Germany.

Alkali metal cation complexation of 1,2,4,5-Bis-(1,4,7,10,13,16 hexaoxahexadecamethylene)benzene (1) shows that the second ligand site only moderately affects 1:1 and 1:2 complex formation.

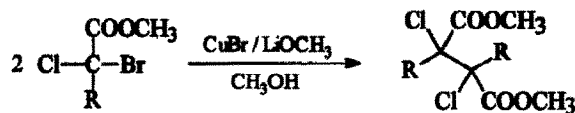
PREDICTIVE MODELS FOR THE OVERALL 5-ENDO-TRIG IODOCYCLISATION OF HOMOALLYLIC ALCOHOLS

J. M. Barks, D. W. Knight,* C. J. Seaman and G. G. Weingarten, Chemistry Department, University Park, Nottingham, NG7 2RD and Glaxo Research and Development, Ltd., Greenford, Middlesex, UB6 0HE, UK.

Iodocyclisations of the homoallylic alcohols 1 and 3 lead to iodoTHFs 2 and 4, by *anti*-addition
REDUCTIVE COUPLING OF
METHYL α -BROMO- α -CHLOROCARBOXYLATES.

Monica Boni, Franco Ghelfi*, Ugo M. Pagnoni and Claudia Zucchi

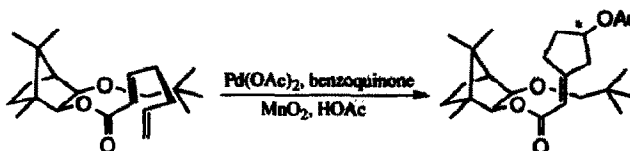
Dipartimento di Chimica dell'Università, via Campi 183, I-41100, Modena (Italy).

 $\text{CuBr}\cdot\text{LiOCH}_3$ in methanol efficiently promotes the reductive coupling of methyl α -bromo- α -chlorocarboxylates to dimethyl α,α' -dichloro-succinates.

**REMOTE ASYMMETRIC INDUCTION IN PALLADIUM-CATALYZED
OXIDATIVE CYCLIZATION OF 2,6-HEPTADIENOATES**

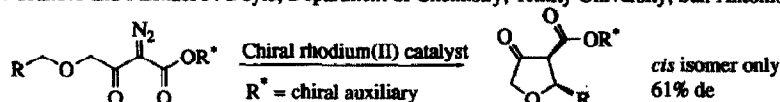
Kerstin Nordström and Christina Moberg*, Department of Chemistry, Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)

1,8-Asymmetric induction (up to 35% de) was observed in the palladium-catalyzed oxidative cyclization of esters of 2,6-octadienoic acid derived from chiral alcohols.

**Stereoselective Synthesis of Disubstituted 3(2H)-Furanones via Catalytic Intramolecular
C-H Insertion Reactions of α -Diazo- β -Keto Esters Including Asymmetric Induction**

Tao Ye and M. Anthony McKervy*, School of Chemistry, The Queen's University, Belfast BT9 5AG, N. Ireland, U.K.

Bridget D. Brandes and Michael P. Doyle, Department of Chemistry, Trinity University, San Antonio, Texas 78212, U.S.A.

**SYNTHESIS OF THE FIRST [1,3]BENZOXAZINO[3,2-b][1,2]
BENZOXAZINE AND ITS TANDEM RETRO-DIELS-ALDER - DIELS-ALDER**

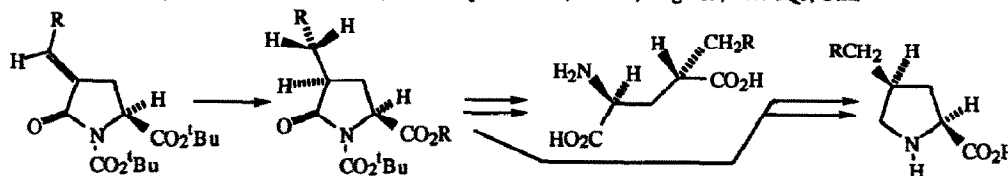
REARRANGEMENT TO A NOVEL [1,3]BENZOXAZINO[2,3-b][1,3]BENZOXAZINE. Zeev Goldschmidt*

Shlomo Levinger and Hugo E. Gottlieb, Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Thermolysis of 3-methyl-4*H*-1,2-benzoxazine gave 12*a*-methyl-7*H*,12*aH*,13*H*-[1,3]benzoxazino[3,2-*b*][1,2]benzoxazine, which rearranged to 5*a*-methyl-5*aH*,11*H*,13*H*-[1,3]benzoxazino[2,3-*b*][1,3]benzoxazine via 2-methyl-4*H*-1,3-benzoxazine and *o*-quinone methide.**STEREOSPECIFIC SYNTHESIS OF 4-ALKYLGLUTAMATES
AND 4-ALKYLPROLINES**

Claire M. Moody and Douglas W. Young*

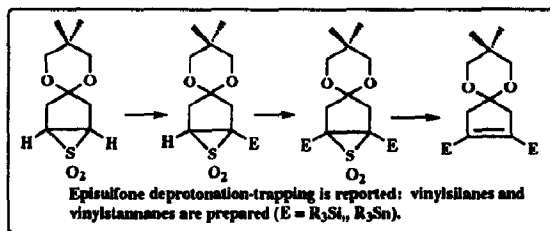
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**Episulfone α -Anions:
Preparation and Synthetic Utility**

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Tetrahedron Letters, 1994, 35, 7281



**SPATIAL ORIENTATION EFFECTS ON THE σ -ASSISTANCE IN THE
SOLVOLYSIS OF METHYL SUBSTITUTED 1-NORBORNYL TRIFLATES.**

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The σ -participation of the C_2-C_3 bond in the solvolysis of methyl substituted 1-norbornyl triflates is dependent on the spatial orientation of the methyl groups.



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