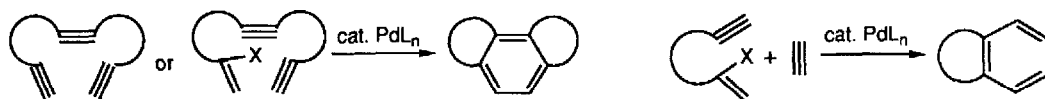


*Tetrahedron Lett.* **1992**, *33*, 3253

**CYCLIC CASCADE CARBOPALLADATION REACTIONS  
AS A ROUTE TO BENZENE AND FULVENE DERIVATIVES**

Ei-ichi Negishi\*, Lori S. Harring, Zbyslaw Owczarczyk, Mohamud M. Mohamud  
and Mehmet Ay, Department of Chemistry, Purdue University, W. Lafayette, IN 47907



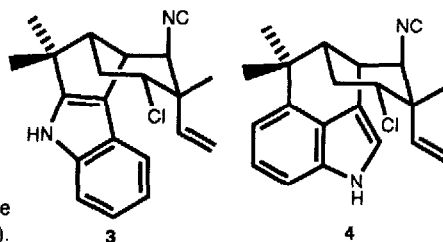
A Pd-catalyzed carbometallation route to benzene and fulvene derivatives has been developed.

*Tetrahedron Lett.* **1992**, *33*, 3257

**Fischerindole L, a New Isonitrile from the Terrestrial  
Blue-Green Alga *Fischerella muscicola***

Aeri Park, Richard E. Moore,\* and Gregory M. L. Patterson  
Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

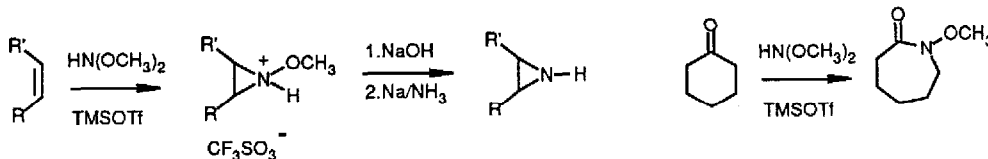
Fischerindole L (3) is a novel 5,6,6a,7,8,9,10,10a-octahydroindeno[2,1-b]indole  
isonitrile that possesses the same relative stereochemistry as hapalindole L (4).



*Tetrahedron Lett.* **1992**, *33*, 3261

**SYNTHESIS OF N-METHOXY AND N-H AZIRIDINES FROM ALKENES**

Edwin Vedejs\* and Hiroshi Sano  
Chemistry Department, University of Wisconsin, Madison, Wis. 53706

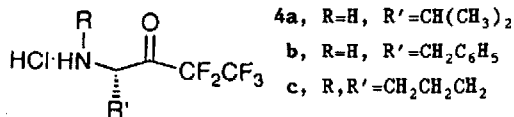


*Tetrahedron Lett.* **1992**, *33*, 3265

**EFFICIENT PREPARATION OF PEPTIDYL PENTAFLUOROETHYL KETONES**

Michael R. Angelastro, Joseph P. Burkhardt, Philippe Bey and Norton P. Peet\*  
Marion Merrell Dow Research Institute, 2110 East Galbraith Road, Cincinnati, OH 45215-6300

An efficient synthesis of pentafluoroethyl ketone  
salts from amino acids is described. These com-  
pounds (4a-c) are useful for the preparation of  
peptidyl pentafluoroethyl ketones.



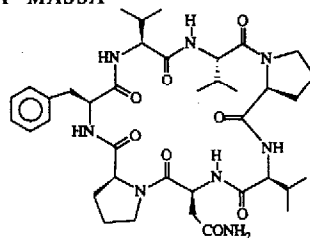
**PSEUDOAXINELLIN, A CYCLIC HEPTAPEPTIDE ISOLATED FROM THE PAPUA NEW GUINEA SPONGE *PSEUDOAXINELLA MASSA***

F. Kong<sup>1</sup>, D. L. Burgoyne<sup>1</sup>, R.J. Andersen<sup>1\*</sup> and T.M. Allen<sup>2</sup>.

<sup>1</sup>Departments of Chemistry and Oceanography, UBC, Vancouver, B.C., CANADA V6T 1Z4.

<sup>2</sup>Department of Pharmacology, University of Alberta, Edmonton, Alberta, CANADA T6G 2H7

The structure of pseudoaxinellin (1) was solved by spectroscopic analysis and chemical degradation. Pseudoaxinellin is the first cyclic heptapeptide from a marine source. It has one cis amide bond.



**A NOVEL CARBONYL YLIDE REARRANGEMENT**

James D. Rodgers\*

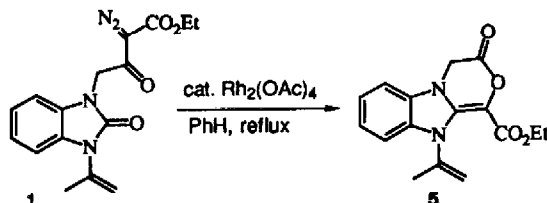
Janssen Research Foundation

Gary W. Caldwell, A. Diane Gauthier

R. W. Johnson Pharmaceutical Research Institute

Welsh & McKean Rd., Spring House PA 19477

Rh<sub>2</sub>(OAc)<sub>4</sub> catalyzed decomposition of 1 gave the novel carbonyl ylide rearrangement product 5.

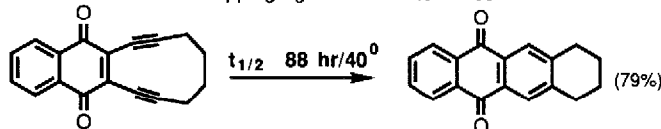


**ARENE 1,4-DIRADICAL FORMATION FROM  $\alpha$ -DIALKYNYLARENES**

M. F. Semmelhack\*, Thomas Neu, and Francisco Foubelo

Department of Chemistry, Princeton University, Princeton, NJ 08544

A series of cyclic  $\alpha$ -dialkynylarenes was prepared, including derivatives of benzene, 1,4-dimethoxynaphthalene, 9/10-dimethoxyanthracene, and the corresponding quinones. The half-time for Bergman rearrangement in the presence of 1,4-cyclohexadiene and other trapping agents was determined.

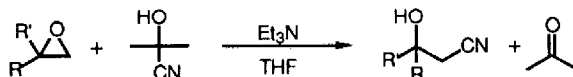


**REGIOSPECIFIC OPENING OF 1,2-EPOXIDES WITH ACETONE CYANOHYDRIN UNDER MILDLY BASIC CONDITIONS**

David Mitchell\* and Thomas M. Koehnig

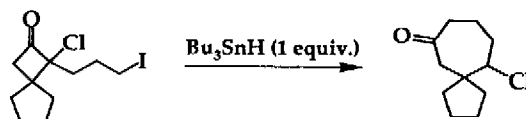
Lilly Research Laboratories, Eli Lilly and Company, Lilly Corporate Center, Indianapolis, Indiana 46285

Acetone cyanohydrin with triethylamine opens epoxides regioselectively to give  $\beta$ -hydroxy nitriles.



### A New Free Radical-Based Method for the Synthesis of Spiroannulated Medium Rings

Wei Zhang and Paul Dowd\*  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, Pennsylvania 15260

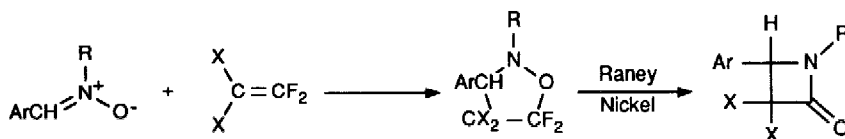


Free radical promoted cyclobutanone ring expansion provides a new entry to a variety of spiroannulated ring systems.

### $\beta$ -LACTAMS FROM 5,5-DIFLUOROISOXAZOLIDINES.

Suzanne T. Purrington\* and Kuen-Wang Sheu  
Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

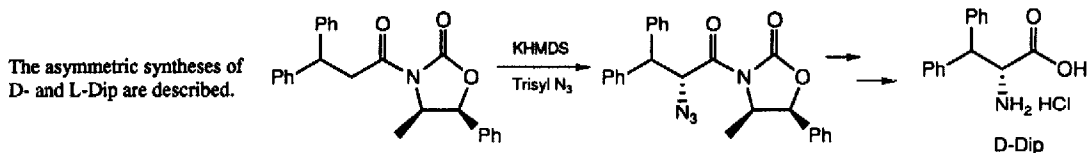
1,3-Dipolar cycloaddition of nitrones to 1,1-difluoroolefins give rise to fluorinated isoxazolidines in 85% yield; Raney nickel reduction of the adducts produces  $\beta$ -lactams.



### Chiral Synthesis of D- and L-3,3-Diphenylalanine (Dip), Unusual $\alpha$ -Amino Acids for Peptides of Biological Interest

Huai G. Chen, V. G. Beylin, M. Marlatt, B. Leja and O. P. Goel\*

Parke-Davis Pharmaceutical Research Division/Warner-Lambert Company, 2800 Plymouth Road, Ann Arbor, MI, 48105 USA

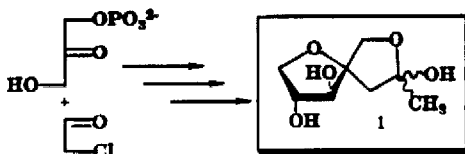


### CHEMO-ENZYMATIC SYNTHESIS OF NATURAL PRODUCTS: SYNTHESIS OF SPHYDROFURAN

Balu P. Malickal and Walther Schmid\*

Institut für Organische Chemie der Universität Wien, Währingerstraße 38, A-1090 Vienna, AUSTRIA

A novel synthesis of sphydrofuran **1** starting from achiral precursors has been developed. The stereocenters were introduced via a short chemo-enzymatic reaction sequence.





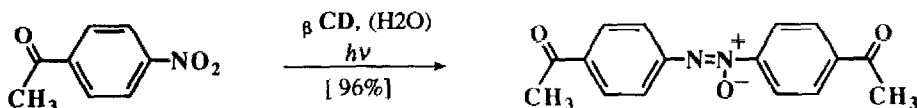
**PHOTOCHEMICAL REACTION BETWEEN  $\beta$ -CYCLODEXTRIN AND p-NITROACETOPHENONE IN AN INCLUSION COMPLEX IN WATER SOLUTION**

Y.L. Chow<sup>a</sup>, J. Michon<sup>b</sup>, P. Michon<sup>b</sup>, C. Morat<sup>b</sup>, A. Rassat<sup>\*c</sup>

<sup>a</sup> Simon Fraser University, Burnaby, B.C. Canada V5A 1S6

<sup>b</sup> L.E.D.S.S., Université Joseph Fourier, BP 53X, 38041 Grenoble Cedex, France

<sup>c</sup> Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France

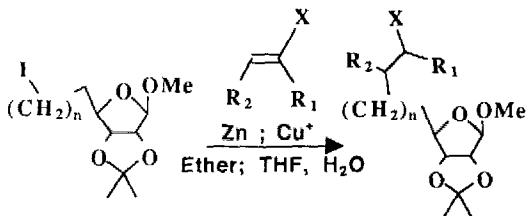


**A Conjugate Addition of Primary Alkyl Iodide Derived Species to Electron Deficient Olefins**

P. Blanchard, M. S. El Kortbi, J.-L. Fourrey\* and M. Robert-Gero

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

Simple reaction conditions for the addition of species generated by the Zn/Cu couple in the carbohydrate and amino acid series to electron deficient olefins have been defined.

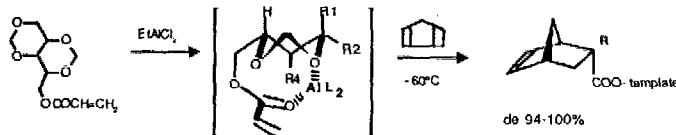


**LIGAND ASSISTED ASYMMETRIC SYNTHESIS. II. DIASTEREOSELECTIVE DIELS-ALDER ADDITIONS WITH LEWIS ACID ATTRACTING AUXILIARIES DERIVED FROM PENTITOLS.**

Jean-Louis Gras\*, Annie Poncet and Robert Nouguièr

Laboratoire de Synthèse Organique, CNRS URA 1411, Faculté des Sciences St-Jérôme D12, 13397 - Marseille Cedex 13 - France

The promoted Diels-Alder addition of acrylates linked to a dimethylene pentitol or to methylene butanetriol results in total  $\pi$ -face stereodifferentiation, via a layered chelate-complex.



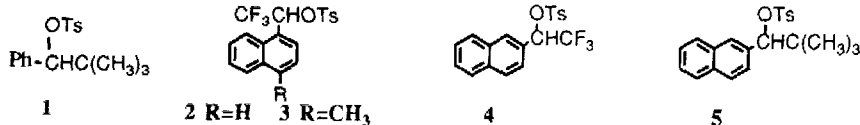
**Solvolyses of Substituted Naphthylmethyl Tosylates.**

**Importance of the Extent of Solvation in the Delocalized Cationic Transition States on the Correlation of Solvolytic Reactivities**

Kwang-Ting Liu, Hung-Yun Hsu, and Jye-Shane Yang

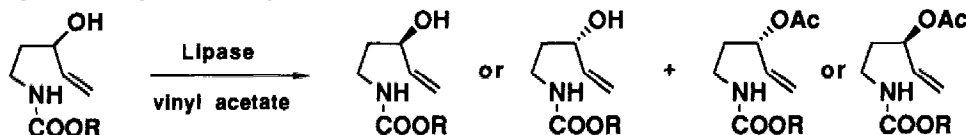
Department of Chemistry, National Taiwan University, Taipei, Taiwan 107, Republic of China

From the solvolysis of tosylates 1-5 the conclusion described in the title is reached.



**TRANSESTERIFICATION-BASED ENZYMIC RESOLUTIONS OF RACEMIC 3-HYDROXY-4-PENTENYLURETHANES IN ORGANIC SOLVENTS**

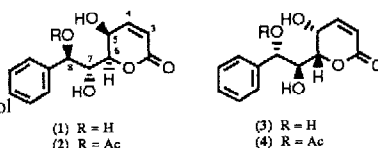
Hiroki Takahata,\* Yasuhiro Uchida, and Takefumi Momose\*  
Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University,  
Sugitani 2630, Toyama 930-01, Japan



**GONIOTRIOL AND 8-ACETYLGONIOTRIOL: SYNTHESSES AND ABSOLUTE CONFIGURATIONS**

Tony K. M. Shing\* and Zhao-hui Zhou  
Department of Chemistry, The Chinese University of Hong Kong,  
Shatin, Hong Kong

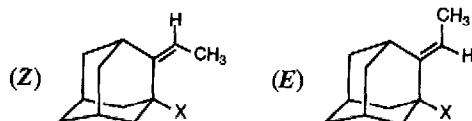
The absolute configurations of natural goniotriol and 8-acetylgoniotriol are shown to be **1** and **2** respectively by unambiguous syntheses of their enantiomers **3** and **4** from *D*-glycero-*D*-gulo-heptono- $\gamma$ -lactone.



**QUANTITATIVE TREATMENT OF RATE ENHANCEMENT DUE TO F-STRAIN IN THE SOLVOLYSIS OF (Z)-2-ETHYLIDENE-1-ADAMANTYL MESYLATE AND HALIDES**

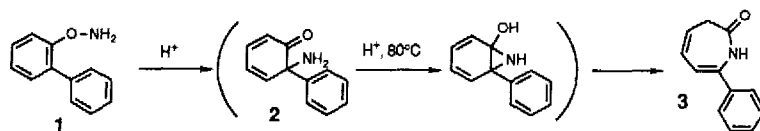
Ken'ichi Takeuchi,\* Yasushi Ohga, Motohiro Munakata, Toshikazu Kitagawa, and Tomomi Kinoshita  
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The *Z*:*E* rate ratios for the trifluoroethanolysis at 25 °C of the title mesylate, chloride, bromide, and iodide are 126, 1020, 2230, and 9680, respectively.



**ACID-CATALYZED REARRANGEMENT OF O-(2-ARYLPHENYL)HYDROXYLAMINES TO ARYLDIHYDROAZEPINONES.**

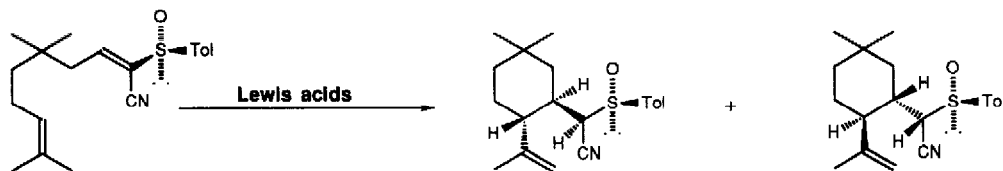
Yasuyuki Endo\*, Ken-ichiro Kataoka, Naoki Haga and Koichi Shudo  
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan



Acid-catalyzed rearrangement of *O*-(2-arylphenyl)hydroxylamines (**1**) to 2-amino-2-phenyl-3,5-cyclohexadienone (**2**) followed by ring enlargement affords 7-aryl-1,3-dihydro-1*H*-azepin-2-ones (**3**). The intermediate **2** was trapped as the *N*-trifluoroacetamide.

## LEWIS ACID-CATALYZED INTRAMOLECULAR ASYMMETRIC ENE REACTIONS OF CHIRAL VINYL SULFOXIDES

Kunio Hirōi\* and Masayuki Umemura  
 Department of Synthetic Organic Chemistry, Tohoku College of Pharmacy,  
 4-4-1 Komatsushima, Aoba-Ku, Sendai, Miyagi 981, Japan

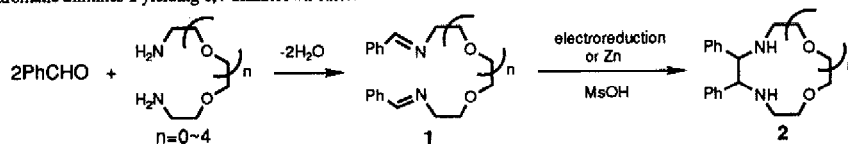


## NOVEL SYNTHESIS OF 1,4-DIAZACROWN ETHERS BY REDUCTIVE COUPLING OF AROMATIC DIIMINES

Tatsuya Shono,\* Naoki Kise, and Eiichi Okazaki

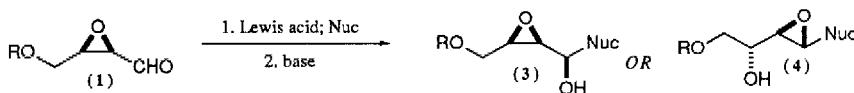
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-01, Japan

The electroreduction or chemical reduction with zinc powder has been found to be effective to intramolecular coupling of aromatic diimines **1** yielding 1,4-diazacrown ethers **2**.

Stereoselective Reactions of  $\alpha,\beta$ -Epoxy-aldehydes; The Formation of "Chelation Controlled" Products

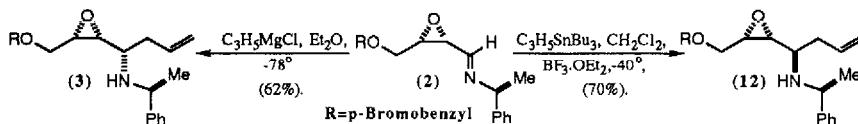
S. Wang, G.P. Howe, R.S. Mahal, and G. Procter, Department of Chemistry, University of Salford, Salford, M5 4WT, Great Britain.

Epoxy-aldehyde (**1**) can be converted into either (**3**) or (**4**) with stereoselectivity of >95:5 by choice of conditions.

Asymmetric Synthesis via Nucleophilic Addition to  $\alpha,\beta$ -Epoxyimines

K.J.M. Beresford, G.P. Howe, and G. Procter, Department of Chemistry, University of Salford, Salford, M5 4WT, Great Britain.

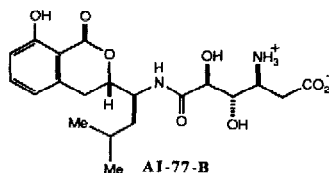
Highly diastereoselective stereocontrolled addition to an  $\alpha,\beta$ -epoxyimine has been carried out.



**A Total Synthesis of AI-77-B**

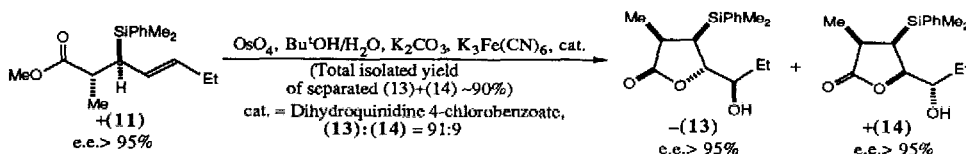
R.A. Ward and G. Procter, Department of Chemistry, University of Salford, Salford, M5 4WT, Great Britain.

A total synthesis of the natural enantiomer of the gastroprotective natural product AI-77-B has been carried out.

**Allyl Silanes in Organic Synthesis; Double Asymmetric Induction in the Dihydroxylation of a Chiral Allylsilane**

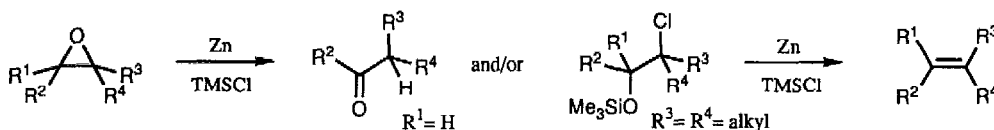
R.A. Ward and G. Procter, Department of Chemistry, University of Salford, Salford, M5 4WT, Great Britain.

Sharpless asymmetric dihydroxylation of two chiral allylsilanes have been investigated.

**OBSERVATIONS ON THE SELECTIVE DEOXYGENATION OF EPOXIDES TO OLEFINS WITH CHLOROTRIMETHYLSILANE AND ZINC.**

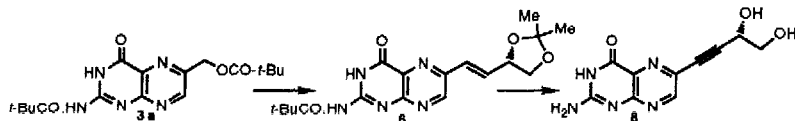
Carlos A. M. Afonso, William B. Motherwell\* and Lee R. Roberts,

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.

Deoxygenation of epoxides to olefins using zinc and chlorotrimethylsilane proceeds *via* two distinct mechanisms.**Model Studies Related to the Cofactor of the Oxomolybdoenzymes Part 5. Synthesis of 6-Alkenyl- and 6-Alkynylpterins**

James R. Russell, C. David Garner, and John A. Joule\*

Chemistry Department, University of Manchester, Manchester M13 9PL, U. K.

6-Alkenylpterin (6) was prepared from pteridine (3a) and (*R*)-glyceraldehyde acetone *via* a Wittig condensation, then converted into the corresponding alkyne (8).





NEW SYNTHETIC STRATEGY FOR THE CONSTRUCTION  
OF TRANS FUSED MEDIUM SIZED CYCLIC ETHERS:  
SYNTHESIS OF THE IJK FRAMEWORK OF THE POLYETHER CIGUATOXIN.

*Tetrahedron Lett.* 1992, 33, 3389

J.L. Ravelo, A. Regueiro and J.D. Martín. Centro de Productos Naturales  
Orgánicos Antonio González, Universidad de La Laguna - CSIC; Carretera  
de La Esperanza 2, 38206 La Laguna, Tenerife, Spain.

