

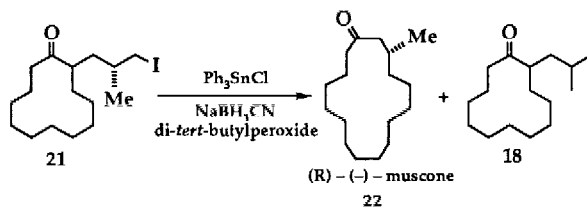
## GRAPHICAL ABSTRACTS

*Tetrahedron Lett.* **1991**, 32, 565

### FREE RADICAL RING EXPANSION AND REARRANGEMENT OF LARGE CARBOCYCLIC RINGS

Paul Dowd\* and Soo-Chang Choi  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260

A free radical-based synthesis of large rings including (R)-(-)-muscone is reported.

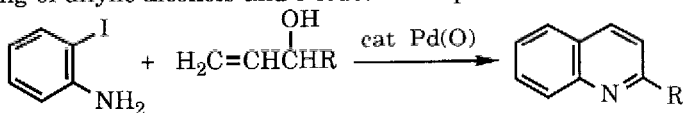


*Tetrahedron Lett.* **1991**, 32, 569

### PALLADIUM-CATALYZED SYNTHESIS OF QUINOLINES FROM ALLYLIC ALCOHOLS AND *o*-IODOANILINE

Richard C. Larock and Mann-Yan Kuo  
Department of Chemistry, Iowa State University, Ames, IA 50011

The palladium-catalyzed coupling of allylic alcohols and *o*-iodoaniline provides a convenient, one-step synthesis of quinolines.

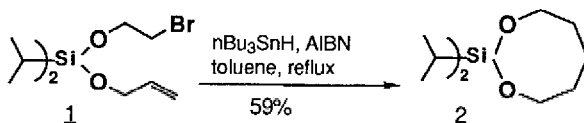


*Tetrahedron Lett.* **1991**, 32, 573

### Silaketals as Tethers in Intramolecular Radical Cyclisations

J.H Hutchinson\*, T.S. Daynard and J.W. Gillard  
Merck Frosst Centre for Therapeutic Research, P.O. Box 1005, Pointe Claire-Dorval  
Quebec, Canada H9R 4P8

Silaketals (eg. 1) are readily prepared and undergo radical cyclisation reactions to give cyclic protected diols which can be deprotected under standard, mild conditions.



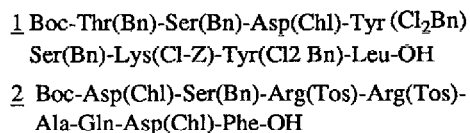
*Tetrahedron Lett.* **1991**, 32, 577

### A NEW SOLID PHASE STRATEGY FOR THE SYNTHESIS OF MAMMELIAN GLUCAGON

N.A. Abraham, G. Fazal, J.M. Ferland, S. Rakhit and J. Gauthier\*

Bio-Mega Inc., 2100 Cunard, Laval (Qc), Canada H7S2G5

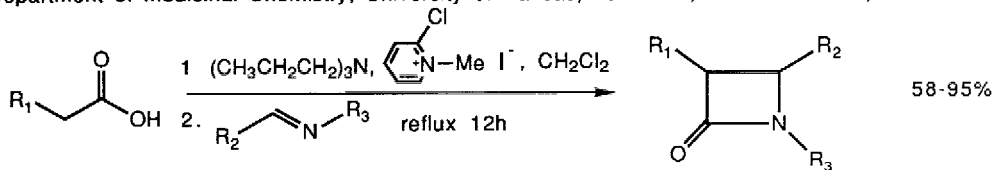
A solid phase convergent strategy of glucagon using peptide segments **1** and **2** is described using a novel side chain attachment of the peptide to a polystyrene resin support.



**An Improved Method for the Stereoselective Synthesis of  $\beta$ -Lactams from Carboxylic Acids and Imines**

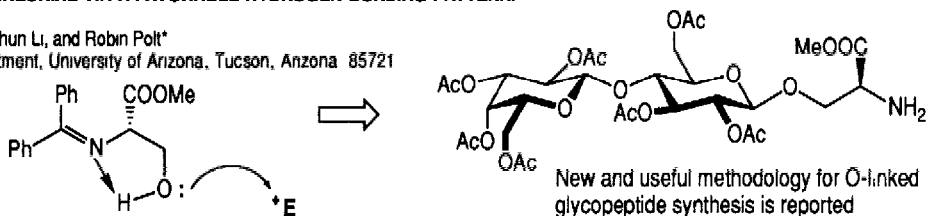
Gunda I. Georg, Peter M. Mashava, and Xiangming Guan.

Department of Medicinal Chemistry, University of Kansas, Lawrence, KS 66045-2506, U.S.A.



**O-GLYCOPEPTIDES: A SIMPLE  $\beta$ -STERESELECTIVE GLYCOSIDATION OF SERINE AND THREONINE VIA A FAVORABLE HYDROGEN BONDING PATTERN.**

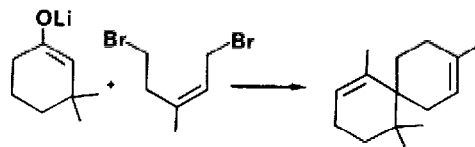
Lajos Szabó, Yushun Li, and Robin Polt\*  
 Chemistry Department, University of Arizona, Tucson, Arizona 85721



**SYNTHESIS OF ( $\pm$ )- $\alpha$ -CHAMIGRENE**

Josée Plamondon and Perséphone Canonne\*.  
 Département de chimie, Université Laval  
 Québec (Québec), Canada G1K 7P4

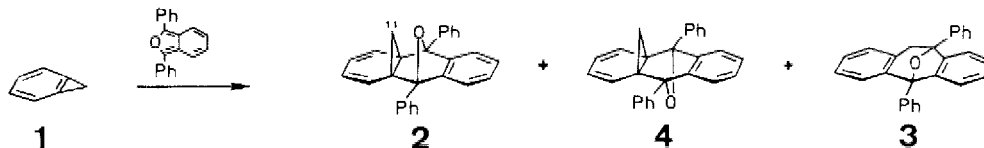
Regiospecific spiroalkylation of the selectively generated enolate arising from the 1,4-addition of lithium dimethylcuprate to 3-methylcyclohex-2-en-1-one allows an efficient preparation of spiroketones, a key intermediate for the synthesis of ( $\pm$ )- $\alpha$ -Chamigrene.



**THE REACTION OF CYCLOPROPABENZENE WITH 1,3-DIPHENYLISOBENZOFURAN: FORMAL  $[4\pi + 2\pi]$  AND  $[4\pi + 2\sigma]$  CYCLOADDITIONS**

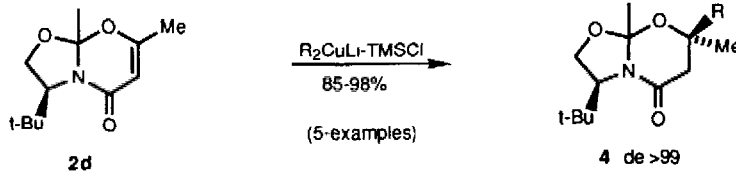
U.H. Brinker\* and H. Wüster

Department of Chemistry, State University of New York, Binghamton, NY 13902-6000, U.S.A.



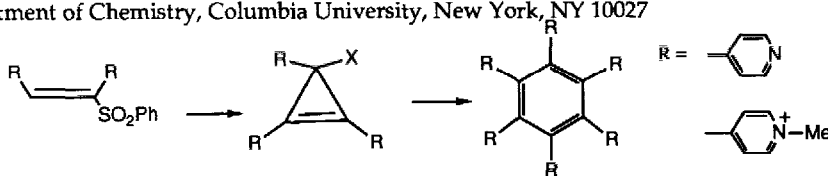
**HIGHLY DIASTEREOSELECTIVE ADDITION TO A NOVEL CHIRAL OXAZINONE. FURTHER APPROACHES TO CHIRAL QUATERNARY CARBON COMPOUNDS.**

A. I. Meyers,\* William R. Leonard, Jr., Jeffrey L. Romine  
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA



**TRIPYRIDYLCYCLOPROPENE DERIVATIVES AND THEIR CONVERSION TO HEXAPYRIDYLBENZENE**

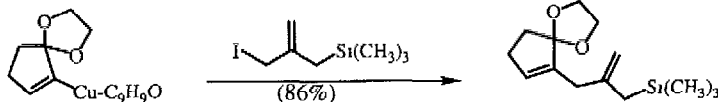
Ronald Breslow and Gerard A. Crispino  
Department of Chemistry, Columbia University, New York, NY 10027



**Synthetic Applications of Gilman Reagents Derived from 2-Bromo-2-cycloalken-1-one Ethylene Ketals**

G. Majetich, A. J. Leigh and S. Condon, The Department of Chemistry,  
The University of Georgia, Athens, Georgia 30602

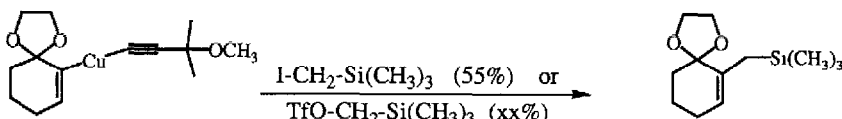
Gilman reagents derived from 2-bromo-2-cycloalken-1-one ethylene ketals react with allylic, propargylic or benzylic halides to produce 1,4-dienes while reaction with Michael acceptors gives 1,4-adducts.



**The Preparation of Allylsilanes From Vinyl Cuprates**

G. Majetich and A. J. Leigh, The Department of Chemistry,  
The University of Georgia, Athens, Georgia 30602

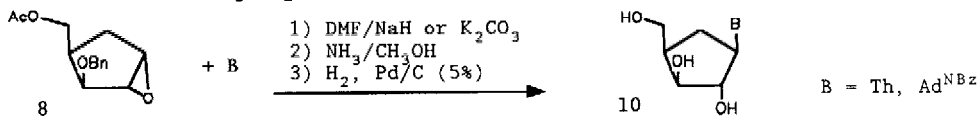
Gilman reagents derived from vinylic nucleophiles react with iodomethyltrimethylsilane or trimethylsilyltri-fluoromethane sulfonate to afford allylsilanes.



**GENERAL SYNTHESIS OF CARBANUCLEOSIDES VIA REGIOSPECIFIC EPOXIDE OPENING BY THE AGLYCON**

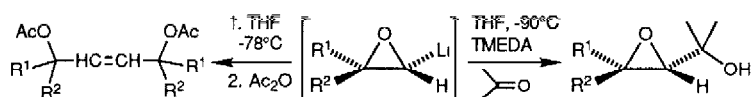
Harald Baumgartner, Christoph Marschner, Rainer Pucher and Herfried Griengl  
 Institute of Organic Chemistry, Graz University of Technology  
 Stremayrgasse 16, A-8010 Graz, Austria

By reaction of 1,2-anhydro-5-O-acetyl-3-O-benzyl- $\alpha$ -D-carboxylofuranose **8** with the aglycone in alkaline medium followed by deprotection carbanucleosides **10** can be obtained.

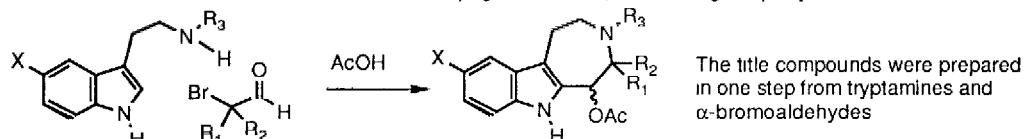

**OXIRANYLLITHIUM REAGENTS: GENERATION FROM ORGANOTIN PRECURSORS, ADDITION TO ALDEHYDES AND KETONES, AND DIMERIZATION TO  $\alpha,\alpha'$ -DIALKOXYOLEFINS**

Peter Lohse, Helena Loner, Pierre Acklin, Francine Sternfeld, and Andreas Pfaltz\*  
 Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zurich, Switzerland

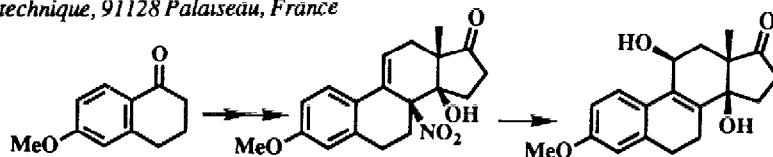
In the presence of TMEDA, oxiranyl-lithium compounds react with aldehydes and ketones to give epoxy alcohols in good yields. In the absence of TMEDA, they dimerize to  $\alpha,\alpha'$ -dialkoxyolefins

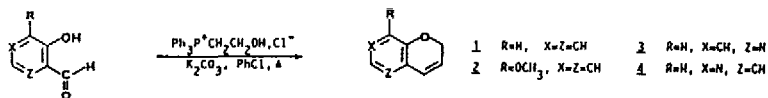

**"HOMO-PICLET-SPENGLER" CYCLIZATION OF TRYPTAMINES  
 AN EASY ACCESS TO THE HEXAHYDROAZEPINO[4,5-b]INDOLE RING SYSTEM**

Jean-Yves Laronze\*, Christine Gauvin- Hussenet and Jean Levy  
 Laboratoire de Transformations et Synthèse de Substances Naturelles, associé au CNRS,  
 Faculté de Pharmacie, Université de Reims Champagne- Ardenne, 51, rue Cognacq- Jay, F 51096 REIMS FRANCE


**AN EXPEDIENT TOTAL SYNTHESIS OF ( $\pm$ )-ESTRONE DERIVATIVES**

Bernard Barlaam, Jean Boivin, Laurent El Kaim, and Samir Z. Zard\*  
 Laboratoire de Synthèse Organique associé au CNRS,  
 Ecole Polytechnique, 91128 Palaiseau, France

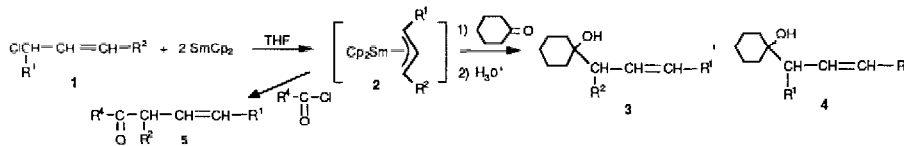


SYNTHESIS OF FUNDAMENTAL HETEROCYCLES C<sub>5</sub>O-C<sub>5</sub>N :  
ZH-PYRANO [3,2-b] PYRIDINE AND ZH-PYRANO [2,3-c] PYRIDINE.D. Billeret, D. Blondeau and H. Sliwa\*  
Laboratoire de Chimie Organique, Université des Sciences et Techniques  
de Lille Flandres Artois, 59655 Villeneuve d'Ascq Cedex, F-France.

## SYNTHESIS AND REACTIVITY OF ALLYL SAMARIUM COMPLEXES

J. Collin, C. Bied, H. B. Kagan\*.

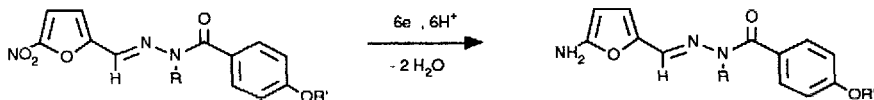
Laboratoire de Synthèse Asymétrique Associé au CNRS, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, 91405 Orsay, France

*Reaction of allyl chlorides on SmCp<sub>2</sub> followed by addition of ketones or acid chlorides leads respectively to alcohols or ketones. The intermediate species is presumably an η<sup>3</sup>-allyl samarium complex.*

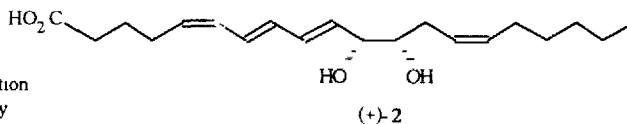
## ELECTROCHEMICAL SYNTHESIS OF 2-SUBSTITUTED 5-AMINOFURANS.

Martine LARGERON and Maurice-Bernard FLEURY\*, laboratoire de Chimie Analytique et Electrochimie, Centre associé au CNRS, Faculté de Pharmacie, 4, avenue de l'Observatoire, 75270 Paris cedex 06 (France).

Electrochemical reduction of 2-substituted 5-nitrofurans in neutral hydroalcoholic media leads to the corresponding 5-aminofurans which have been isolated as the major products.

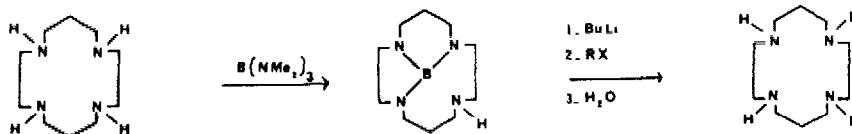


## TOTAL SYNTHESIS OF (1R,12S)-DIHETE

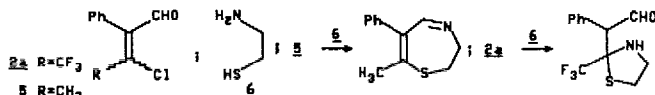
Agnès GIGOU<sup>a</sup>, Jean-Pierre BEAUCOURT<sup>a</sup>, Jean-Paul LELLOUCHE<sup>a\*</sup>,  
René GRÉE<sup>b\*</sup>.<sup>a</sup> CEN Saclay, Service des Molécules Marquées, Bât 547, 91191 Gif-sur-Yvette, France.<sup>b</sup> Laboratoire de Chimie Organique Biologique, associé au CNRS, ENSCR, Avenue du  
Général Leclerc, 35700 Rennes-Beaulieu, FranceThe first total synthesis of (1R,12S)-DIHETE is reported.  
The key step is the highly chemo- and stereoselective osmylation  
of a double bond in a triene system selectively complexed by  
an Fe(CO)<sub>5</sub> group

## GENERAL ROUTE FOR THE SYNTHESIS OF MONO N-ALKYLATED DERIVATIVES OF TETRAAZAMACROCYCLES

H. Barnard, J.J. Yaouanc, J.C. Clément, H. des Abbayes and H. Handel  
 Laboratoire de Chimie, Electrochimie et Photochimie Moléculaires, associé au CNRS,  
 Faculté des Sciences et Techniques, 6, avenue le Gorgeu, 29287 BREST FRANCE.

SYNTHESIS OF  $\beta$ -CHLORO(TRIFLUOROMETHYL)ACROLEINS AND A SPECIFIC REACTION TOWARDS  $\beta$ -AMINOTHIOLS

G. ALVERNHE, B. LANGLOIS, A. LAURENT, I. LE DREAN and A. SELMI  
 UCB-LYON I, lab de Chimie Orga. 3, URA CNRS,43, Bd du 11 11 1918 69622 VILLEURBANNE Cedex (France)  
 M. WEISSENFELS, University of Leipzig, Department of Chemistry, LEIPZIG 7010 (Germany)

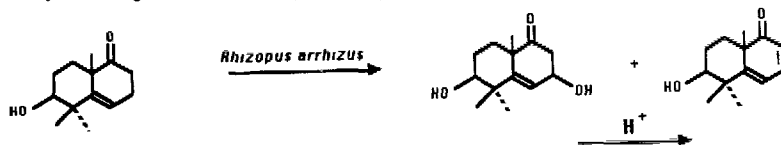


**5** and 2-aminothiophenol produce a benzothiazepine. But **2a** and 2-aminothiophenol give benzothiazole and an unstable benzothiazepine which is transformed into a quinoline.

## Microbial Allylic Hydroxylation of some Octalone Derivatives

J.Ouazzani, S.Arseniyadis\*, R Alvarez-Mazaneda, E Cabrera  
 and G.Ouissou  
 ICSN, CNRS - 91198 - Gif-sur-Yvette, France.

*Rhizopus arrhizus* oxidizes unsaturated substrates in the allylic position with high regio- and stereoselectivity and respects ketals or hydroxyl groups.

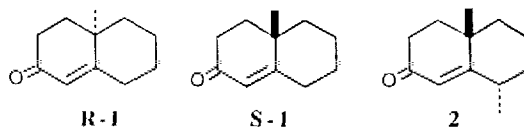


## MICROBIAL HYDROXYLATION AND FUNCTIONALIZATION OF SYNTHETIC BICYCLIC ENONES

A Hammoumi <sup>a</sup>, G.Revial <sup>b</sup>, J.D'Angelo <sup>b</sup> J P Girault <sup>a</sup> and R Azerad <sup>a\*</sup>

<sup>a</sup> Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, URA 400 CNRS, Univ. René Descartes, 45 rue des Saints-Peres, 75270-Paris Cedex 06, France; <sup>b</sup> Laboratoire de Chimie de l'École Supérieure de Physique et Chimie Industrielle, URA 476 CNRS, 10 rue Vauquelin, 75005 - Paris, France

The regio- and stereoselective hydroxylation of substituted octalones **1** or **2** by various fungal strains has been evaluated. Several hydroxylated derivatives have been obtained and the potential of this method for the preparation of useful chiral synthons is discussed.

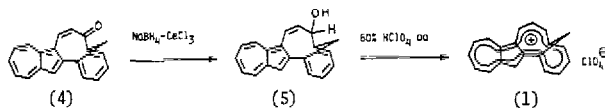


AZULENO[2,1-b]-4,9-METHANO[11]ANNULENIUM PERCHLORATE:  
A PERIPHERAL 18- $\pi$  ELECTRON DIATROPIC SYSTEM

Shigeyasu Kuroda,\* Kazuo Yamazaki, Sunao Maeda, Takeshi Sakaguchi, Hiroyuki Iwaki,  
Masaki Yamada, Ichiro Shimao, and Masafumi Yasunami.†

Department of Materials Science and Engineering, Faculty of Engineering, Toyama University, Gofuku 3190,  
Toyama 930, Japan, †Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan.

The synthesis of parent cation of azuleno-  
[2,1-b]-4,9-methano[11]annuleniium per-  
chlorate (1) as a stable peripheral 18- $\pi$   
electron diatropic compound is described.



### STRUCTURE OF VIRIDENOMYCIN

MASAYA NAKAGAWA

Pharmaceutical Laboratory, Kirin Brewery Co. Ltd.,  
Miyahara, Takasaki, Gunma 370-12, Japan

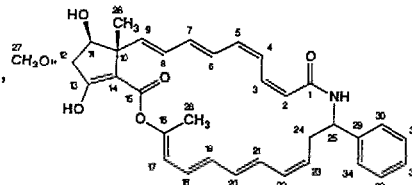
KAZUO FURIHATA

Department of Agricultural Chemistry, The University of Tokyo,  
YOICHI HAYAKAWA and HARUO SETO

Institute of Applied Microbiology, The University of Tokyo,  
Bunkyo-ku, Tokyo 113, Japan

The structure of viridenomycin was determined by NMR spectral  
analysis including a variety of two-dimensional techniques.

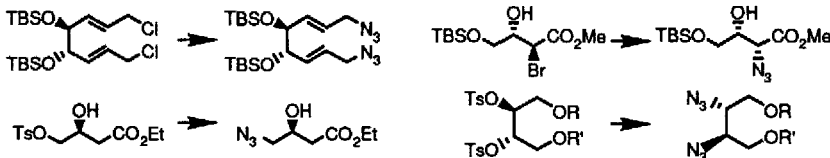
Viridenomycin is a novel 24-membered macrocyclic polyene antibiotic.



### HYDROGEN AZIDE-AMINE SYSTEMS AS AN AZIDE NUCLEOPHILE FOR SUBSTITUTIONS OF SULFONATES, HALIDES, AND VICINAL DISULFONATES

S. Saito,\* H. Yokoyama, T. Ishikawa, N. Niwa, and T. Moriwake\*

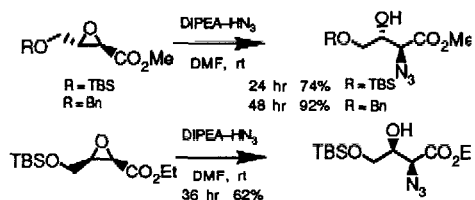
Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama, Japan 700



### SELECTIVE C-2 OPENING OF 2,3-EPOXYESTERS WITH HN3-AMINE SYSTEM: A VIABLE ROUTE TO $\beta$ - HYDROXY- $\alpha$ -AMINO ACIDS

S. Saito,\* N. Takahashi, T. Ishikawa,  
and T. Moriwake\*

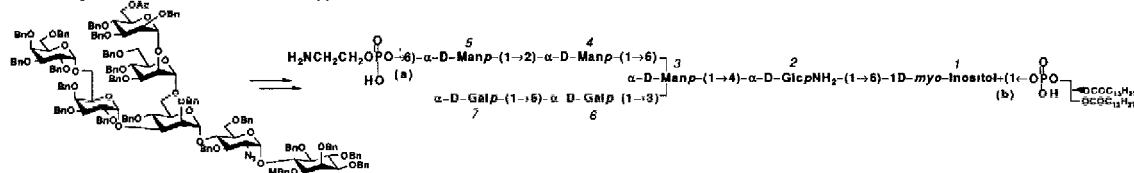
Department of Applied Chemistry, Faculty of  
Engineering, Okayama University, Tsushima,  
Okayama, Japan 700



A TOTAL SYNTHESIS OF GPI ANCHOR OF *TRYPANOSOMA BRUCEI*

Chikara Murakata and Tomoya Ogawa

RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01 Japan

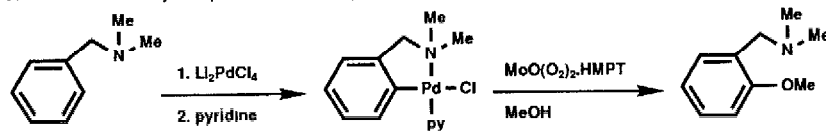
A total synthesis of GPI anchor of *Trypanosoma brucei* was achieved by employing H-phosphonate strategy.

## DIRECT ALKOXYLATION OF ORGANOPALLADIUM COMPOUNDS BASED ON A NEW TYPE OF C-O COUPLING MEDIATED BY MOLYBDENUM PEROXIDES.

Paul L. Alsters, Jaap Boersma and Gerard van Koten\*

Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8,

3584 CH Utrecht, The Netherlands

The molybdenum peroxide  $\text{MoO}(\text{O}_2)_2$  HMPT reacts with organopalladium compounds in alcoholic solvents to form alkoxyated products instead of products derived from oxygen insertion in the C-Pd bond

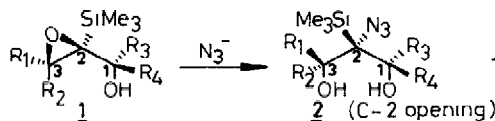
Several examples of this alkylation for other (cyclopalladated) aryl- or alkyl-complexes are given

## STUDIES DIRECTED TOWARDS THE SELECTIVE C-2 OPENING OF 2,3-EPOXY ALCOHOLS WITH AZIDE ION

T K Chakraborty\* and G V Reddy

Indian Institute of Chemical Technology, Hyderabad 500 007, India

The generally observed preference for C-3 opening of simple 2,3-epoxyalcohols was reversed when a silyl group was introduced at 2-position.



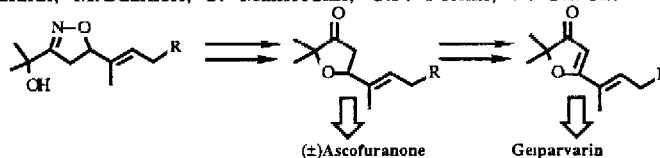
Other regioisomer 3

Only C-2 opening with  $\text{R}_1, \text{R}_3, \text{R}_4 = \text{H}$  and  $\text{R}_2 = \text{alkyl}$ 

## A [3+2] NITRILE OXIDE INTERMOLECULAR CYCLOADDITION APPROACH TO 4,5-DIHYDRO-3(2H)-FURANONE AND 3(2H)-FURANONE RING SYSTEMS: APPLICATION TO THE FORMAL SYNTHESIS OF (±)-ASCOFURANONE AND GEIPARVARIN.

M. Aghazade Tabrizi, P.G.Baraldi, M.Guarneri, S. Manfredini, G.P. Pollini, D. Simoni\*

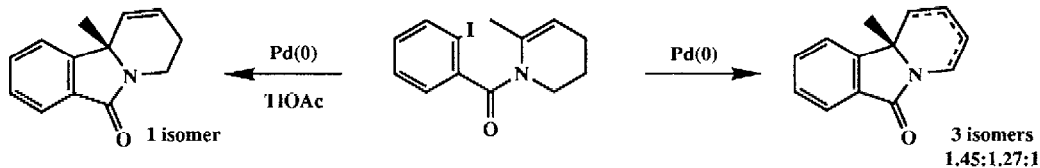
Dipartimento di Scienze Farmaceutiche, Università di Ferrara, 1-44100 FERRARA.





**SUPPRESSION OF ALKENE ISOMERISATION IN PRODUCTS FROM INTRAMOLECULAR HECK REACTIONS BY ADDITION OF Ti(IV) SALTS.**

Ronald Grigg,\* Vani Loganathan, Vijayaratnam Santhakumar, Visuvanathar Sridharan and Andrew Teasdale.  
Chemistry Department, Leeds University, Leeds LS2 9JT.



**REGIOSELECTIVE AND ENANTIOSPECIFIC SYNTHESIS OF 6-SUBSTITUTED AND 5,6-DISUBSTITUTED HEXAHYDROPYRIMIDINES.**

Peter J Garratt, Simon N Thorn and Roger Wrigglesworth  
Department of Chemistry, University College London, Gordon Street, London WC1H 0AJ, U K and Sandoz Institute for Medical Research, Gower Place, London WC1E 6BN, U.K.

