

*Tetrahedron*, 1993, 49, 7837

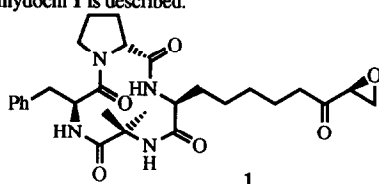
**STEREOSPECIFIC SYNTHESIS OF CHLAMYDOCIN**

Jack E. Baldwin,<sup>a</sup> Robert M. Adlington,<sup>a</sup> Christopher R. A. Godfrey,<sup>b</sup> and Vipulkumar K. Patel<sup>a</sup>

<sup>a</sup>The Dyson Perrins Laboratory and the Oxford Centre for Molecular Sciences, University of Oxford, South Parks Road, Oxford OX1 3QY, U. K.

<sup>b</sup>ICI Agrochemicals, Jealott's Hill Research Centre, Bracknell, Berks., RG12 6EY, U.K.

A new homolytic route to chlamydocin **1** is described.

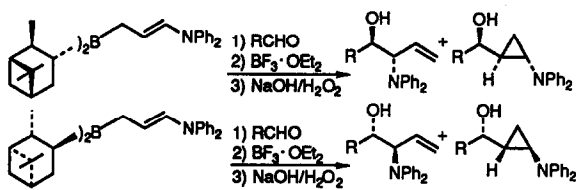


*Tetrahedron*, 1993, 49, 7857

**The Use of *B*-[(*E*)-3-(Diphenylamino)allyl]diisopinocampheylborane as a Reagent for the Stereoselective Synthesis of *anti*-β-Diphenylamino Alcohols and *trans*-1-Diphenylamino-2-(1-hydroxyalkyl)cyclopropanes**

A. G. M. Barrett\* and M. A. Seefeld  
Department of Chemistry  
Imperial College of Science, Technology and Medicine  
London SW7 2AY, U. K.

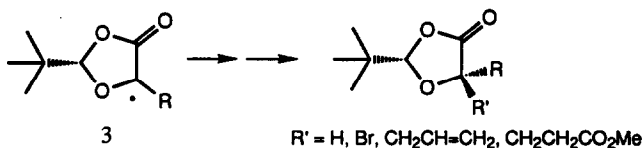
(-) and (+)-*B*-[(*E*)-3-(Diphenylamino)allyl]diisopinocampheylboranes have been utilised in the stereoselective synthesis of *anti*-β-amino alcohols and *trans*-1-amino-2-(hydroxyalkyl)-cyclopropanes in a simple one-pot process.



*Tetrahedron*, 1993, 49, 7871

**Some Diastereoselective Radical Reactions of Substituted 1,3-Dioxolan-4-ones**

Athelstan L.J. Beckwith, and Christina L.L. Chai  
Research School of Chemistry, Australian National University, Canberra, Australia, ACT 2001



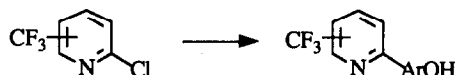
Radicals of the general type **3**, generated by  $\text{S}_\text{N}\text{H}$  or radical addition processes of appropriately substituted dioxolanones, undergo diastereoselective bond formation trans to the *tert*-butyl group

# **S<sub>RN</sub>1 REACTIONS OF CHLOROTRIFLUOROMETHYL PYRIDINES WITH NAPHTHOLATE, PHENOLATE AND MALONATE ANIONS**

René Beugelmans\* and Jacqueline Chastanet

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

2-Chloro-3,4,5 or 6 trifluoromethyl pyridine undergo photostimulated S<sub>RN</sub>1 reactions with 2-naphthol or various phenols to give heterobiaryl derivatives.



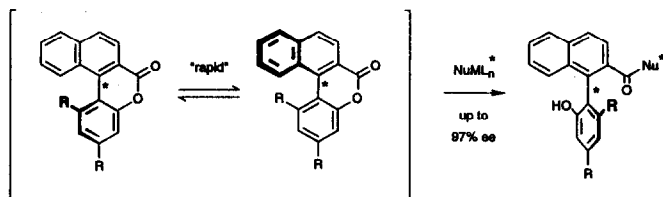
# **Atropo-Enantioselective Biaryl Synthesis by Stereocontrolled Cleavage of Configuratively Labile Lactone-Bridged Precursors using Chiral H-Nucleophiles**

Gerhard Bringmann\* and Thomas Hartung

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

The highly stereocontrolled ring opening of lactone-bridged, configuratively labile biaryl precursors, using chiral *H*-nucleophiles, is described.

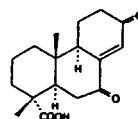
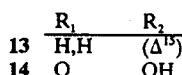
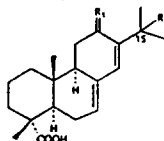
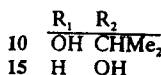
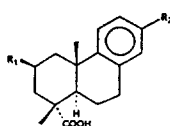
This conceptionally novel methodology offers an efficient route to stereochemically homogeneous hindered biaryl systems.



# **Further Acidic Constituents and Neutral Components of *Pinus Massoniana* Resin**

H.T. Andrew Cheung, Toshio Miyase, Mark P. Lenguyen, and Mary A. Smal  
Department of Pharmacy, University of Sydney, Sydney, NSW 2006, Australia

Of 12 minor components isolated, 15-hydroxy-7,13-abietadien-12-on-18-oic acid (14) and 8(14)-podocarp-7,13-dien-18-oic acid (17) are hitherto unknown, while acids 10, 13 and 15 are new plant products.

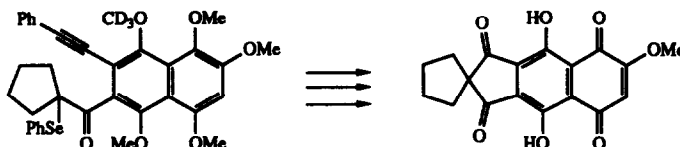


17

### Protecting Group Improvement by Isotopic Substitution: Synthesis of the Quinone System of Fredericamycin A

Derrick L.J. Clive,\* Michel Cantin, Ahmad Khodabocus, Xianglong Kong and Yong Tao  
Chemistry Department, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

Use of a trideuteriomethyl group (instead of a methyl group) for protection of phenolic oxygen serves to suppress an unwanted intramolecular hydrogen transfer during radical cyclization. The technique was used in the preparation of a model for the spirodiketone-quinone system of the antitumor agent, Fredericamycin A.

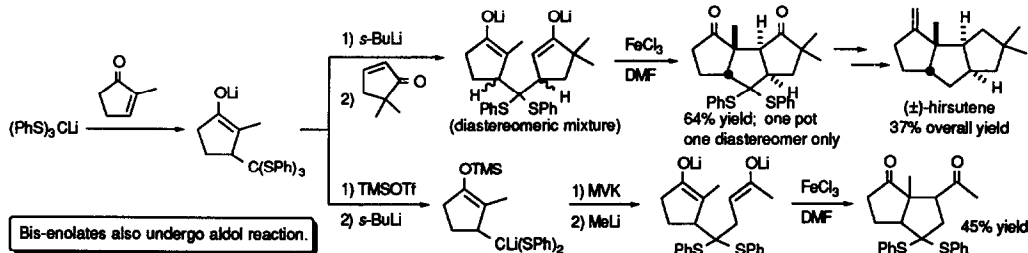


### A NOVEL ONE-FLASK CYCLOPENTANNULATION INVOLVING A DILITHIOMETHANE EQUIVALENT AS A $\beta$ -CONNECTOR OF TWO ENONES. A HIGHLY EFFICIENT TOTAL SYNTHESIS OF ( $\pm$ )-HIRSUTENE

Theodore Cohen,\*<sup>a</sup> Kevin McNamara,<sup>a</sup> Michael A. Kuzemko,<sup>a</sup> Keith Ramig,\*<sup>b</sup> John J. Landi Jr.,<sup>b</sup> Yong Dong<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

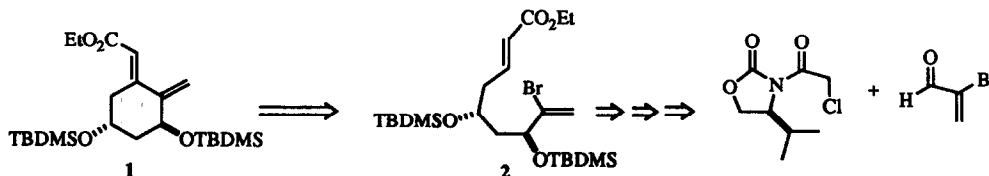
<sup>b</sup>Synthesis Development Department, Hoffmann-La Roche Inc., 340 Kingsland St., Nutley, NJ 07110

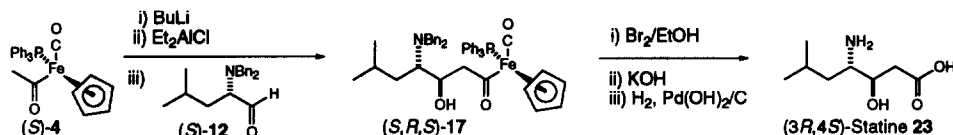


### The Cyclization Route to the Calcitriol A-ring: A Formal Synthesis of (+)-1 $\alpha$ ,25-Dihydroxyvitamin D<sub>3</sub>

Chen Chen and David Crich\* Department of Chemistry, University of Illinois at Chicago (M/C 111), 801 W. Taylor St., Chicago, IL 60607-7061, USA

The diene ester 1 has been synthesized in scalemic form by intramolecular Heck reaction of 2 which in turn is derived from an asymmetric aldol reaction.



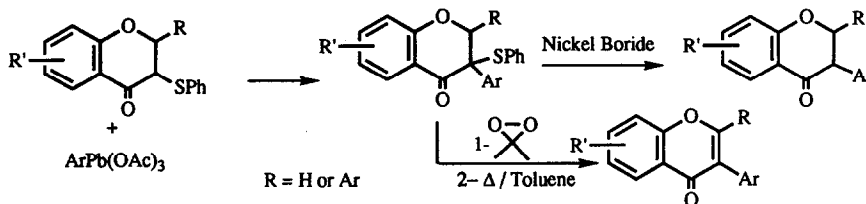
STERESELECTIVE SYNTHESIS OF (3*R*,4*S*)-STATINE UTILISING THE IRONACETYL COMPLEX  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COMe}]$  AS A CHIRAL ACETATE ENOLATE EQUIVALENT.Jason W.B. Cooke<sup>a</sup>, Stephen G. Davies<sup>ab</sup> and Alan Naylor<sup>b</sup>,<sup>a</sup>The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, U.K. <sup>b</sup>Glaxo Group Research, Ware, Herts, SG12 0DJ, U.K.ARYLEAD MEDIATED SYNTHESIS OF ISOFLAVANONE  
AND ISOFLAVONE DERIVATIVES

Dervilla M.X. DONNELLY\*, Brendan M. FITZPATRICK, Bernadette A. O'REILLY,

Department of Chemistry, University College Dublin, Belfield, DUBLIN 4, Ireland

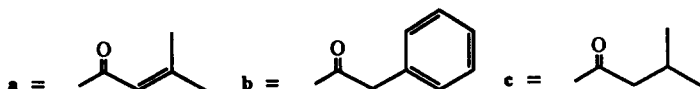
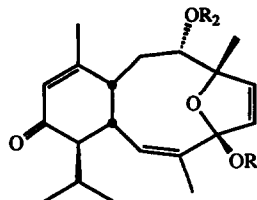
Jean-Pierre FINET\*

Laboratoire SREP, URA-CNRS 1412, Université de Provence, 13397 MARSEILLE Cedex 20, France.

THE VALDIVONES, ANTI-INFLAMMATORY DITERPENE ESTERS  
FROM THE SOUTH AFRICAN SOFT CORAL  
*ALCYONIUM VALDIVAE*

Yongcheng Lin, Carole A. Bewley, and D. John Faulkner

Scripps Institution of Oceanography, UCSD, La Jolla, CA 92093-0212, USA.

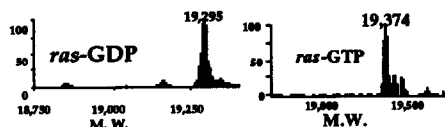
Valdivones A (1) and B (2), the methoxy ketals 3 and 4, and dihydrovaldivone A (5) were isolated from the South African soft coral *Alcyonium valdivae*.

- 1 R<sub>1</sub> = H R<sub>2</sub> = a  
 2 R<sub>1</sub> = H R<sub>2</sub> = b  
 3 R<sub>1</sub> = Me R<sub>2</sub> = a  
 4 R<sub>1</sub> = Me R<sub>2</sub> = b  
 5 R<sub>1</sub> = H R<sub>2</sub> = c

# STUDIES OF THE RAS-GDP AND RAS-GTP NONCOVALENT COMPLEXES BY ELECTROSPRAY MASS SPECTROMETRY

Ashit K. Ganguly\*, Birendra N. Pramanik\*, Eric C. Huang, Anthony Tsarbopoulos, and Viyyoor M. Girijavallabhan, Schering-Plough Research Institute, Kenilworth, NJ 07033; Stephen Liberles, Department of Chemistry, Harvard University, Cambridge, MA 02138.

A MS-based methodology employing electrospray ionization is described for the detection of the noncovalent interaction between the *ras* protein and the nucleotide ligands GDP and GTP. The observed average molecular weights of 19295 and 19374 Da confirmed the presence of *ras*-GDP and *ras*-GTP, respectively.



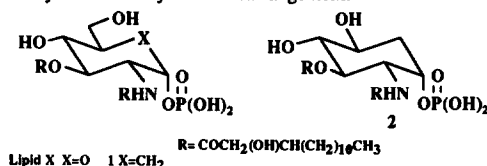
# SYNTHESIS OF CARBOCYCLIC ANALOGUES OF LIPID X

Augy-Dorey<sup>a</sup>, S., Dalko<sup>a</sup>, P., Géro<sup>a</sup>, S. D., Quiclet-Sire<sup>\*a</sup>, B.Eustache<sup>b</sup>, J and Stütt<sup>b</sup>, P.

<sup>a</sup>Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette Cedex, France.

<sup>b</sup>Sandoz Forschungsinstitut, Gesellschaft M.B.H., Brunnerstrasse 59, A-1230 Vienna, Austria

Carbocyclic analogues of lipid X and nor-lipid X (1 and 2) are synthesized from amino-inososes readily prepared from the corresponding exocyclic olefins by Ferrier rearrangement.

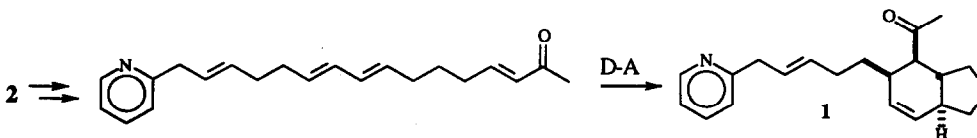


Lipid X X=O 1 X=CH<sub>2</sub>

# SEMPREPARATIVE SYNTHESIS, <sup>13</sup>C- AND 2D-NMR OF PULO'UPONE

Jorma Matikainen, Seppo Kaltia and Tapio Hase\* (Division of Organic Chemistry, Department of Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki, Finland), Ilkka Kilpeläinen (Institute of Biotechnology, University of Helsinki, Valimotie 7, SF-00380 Helsinki, Finland), Torbjörn Drakenberg and Arto Annala (Technical Research Centre of Finland, Chemical Laboratory, BOX 204, SF-02151 Espoo, Finland).

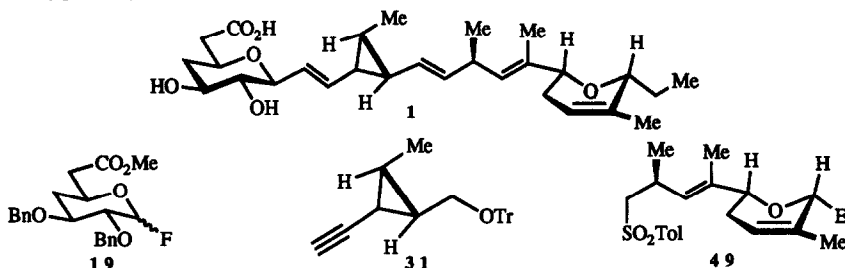
(±)-Pulo'upone (1) is synthesized from 4-pentyn-1-ol (2) (9 steps, 3.8 % overall). A complete <sup>1</sup>H and <sup>13</sup>C NMR signal assignment for (1) is presented.



# TOTAL SYNTHESIS OF NATURAL (+)-AMBRUTICIN

Andrew S. Kende,\* José S. Mendoza, and Yasuhiro Fujii  
Department of Chemistry, University of Rochester, Rochester, New York 14627

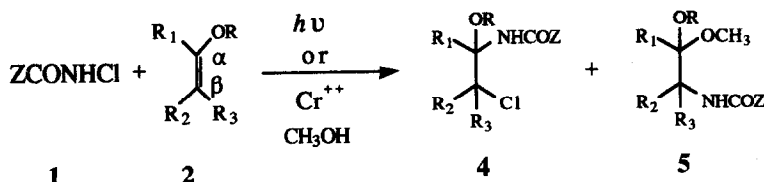
The total synthesis of (+)-ambruticin (**1**) has been achieved for the first time. The strategy involved the independent preparation of the enantiomerically pure fragments **19**, **31**, and **49**.



# The Regiochemistry of the Radical Addition of N-Chloroamides to Enol Ethers

Gilles Caron and Jean Lessard

Département de chimie, Université de Sherbrooke, Sherbrooke (Québec) Canada J1K 2R1



The orientation of the radical addition of N-chloroamides to enol ethers was studied as a function of Z and the enol ether structure.

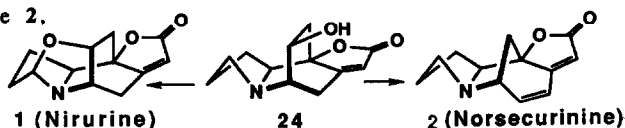
# Synthesis of the *Securinega* Alkaloids (±)-Norsecurinine and (±)-Nirurine from 3-Hydroxypyridine.

Philip Magnus\*, Julian Rodríguez-López, Keith Mulholland and  
Ian Matthews†.

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712.

†Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

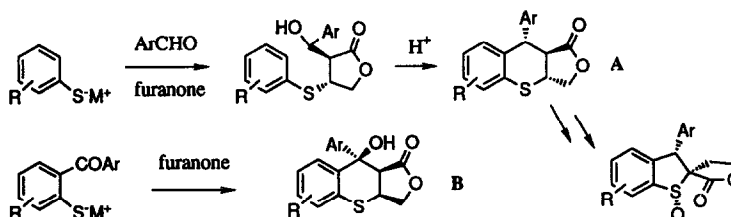
Mesylation of the alcohol **24** gave norsecurinine **2**,  
whereas an oxidation reduction sequence gave  
nirurine **1**, albeit as a minor product.



**Synthesis and Chemistry of Thia-analogs of the Anti-mitotic *Podophyllum* Lignans.**

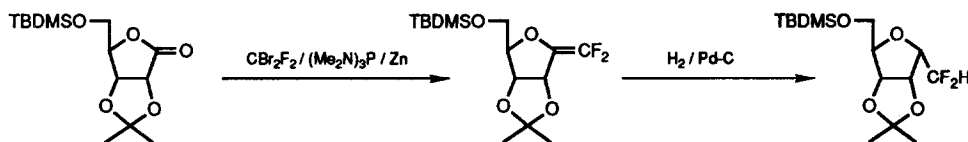
S. W. McCombie\*, J. R. Tagat, W. A. Metz, D. Nazareno and M. S. Puar. Schering-Plough Research Institute, 2015 Galloping Hill Road, Kenilworth, NJ 07033-0539, U.S.A.

Tricyclic compounds A, B are prepared via Michael-aldol-cyclisation and Michael-intramolecular aldol protocols. Isomerisations and sulfoxide rearrangements of these systems are described.



**A CONVENIENT STRATEGY FOR REPLACEMENT OF THE ANOMERIC HYDROXYL GROUP BY DIFLUOROMETHYL FUNCTIONALITY IN CARBOHYDRATE DERIVATIVES**

J. Sarah Houlton, William B. Motherwell,\* Barry C. Ross, Matthew J. Tozer, David J. Williams and Alexandra M.Z. Slawin  
Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, UK.



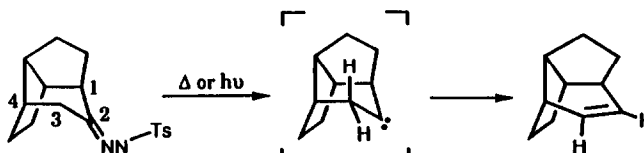
The preparation and reduction of carbohydrate difluoroenol ethers is described.

**Hydrogen Migrations in a Constrained Cyclohexylidene.**

**$H_{ax}/H_{eq}$  Shift Ratios in Thermal and Photic Bamford-Stevens Reactions**

Alfred G. Stern, Martin C. Ilao, and Alex Nickon  
Department of Chemistry, The Johns Hopkins University, Baltimore MD, 21218-2685 USA

Homobrexyl systems labeled at C-3 with  $^{13}C$  and D were used to determine  $H_{ax}/H_{eq}$  migration ratios, which were ca. 1.7 in thermolysis and ca. 1.2 in photolysis. These experimental ratios are free of chair-boat ambiguities.

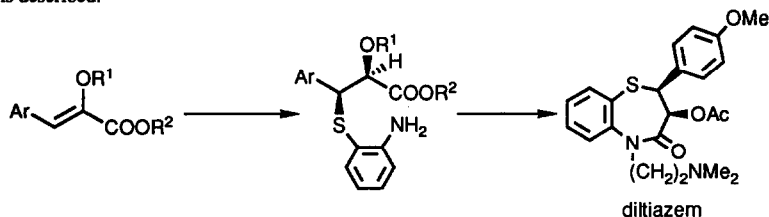


**Stereoselective Addition of 2-Aminothiophenol to  $\alpha$ -Alkoxybenzoic Acid Derivatives---Alternative Synthesis of ( $\pm$ )-Diltiazem---**

Okiko Miyata, Tetsuro Shinada, Takeaki Naito and Ichiya Ninomiya\*

Kobe Women's College of Pharmacy, Motoyamakita, Higashinada, Kobe 658, Japan. Tadamasu Date and Kimio Okamura  
Organic Chemistry Research Laboratory, Tanabe Seiyaku Co., Ltd., Kawagishi, Toda, Saitama 335, Japan

A stereocontrolled synthesis of ( $\pm$ )-diltiazem by applying the nucleophilic addition of 2-aminothiophenol to  $\alpha$ -alkoxybenzoic acid derivatives is described.



**ARYL FLUORIDE SYNTHESIS INVOLVING REACTION OF ARYLEAD TRIACETATES WITH BORON TRIFLUORIDE-DIETHYL ETHER COMPLEX**

Giuseppe De Melo, Jacqueline Morgan and John T. Pinhey\*

Department of Organic Chemistry, University of Sydney, Sydney 2006 Australia



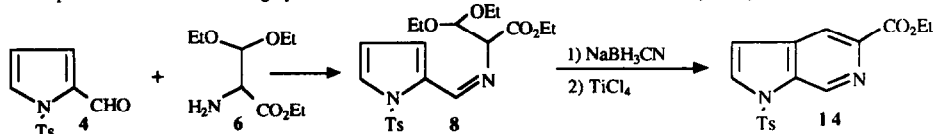
This aryl fluoride synthesis has been adapted to the *in situ* generation of arylead triacetates from the reaction of aryltrimethylsilanes, triarylboroxines and arenes with a  $\text{Pb(OAc)}_4\text{-BF}_3 \cdot \text{Et}_2\text{O}$  mixture.

**A PRACTICAL SYNTHESIS OF 1H-PYRROLO[2,3-c]PYRIDINE-5-CARBOXYLIC ACID DERIVATIVES FROM PYRROLE-2-CARBOXALDEHYDES**

Mouloud Dekhane, Pierre Potier and Robert H. Dodd\*

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

The title compounds were obtained in high yields after reduction and titanium (IV) chloride catalyzed cyclization



of imine **8**, itself obtained by condensation of pyrrole-2-carboxaldehyde **4** and the  $\alpha$ -formylglycine equivalent **6**.



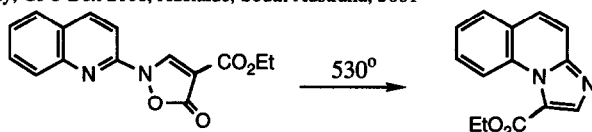
# **The Chemistry of 5-Oxodihydroisoxazoles VII**

## **Conversion of Heterocyclisoxazol-5(2H)-ones to Imidazoles by Flash Vacuum Pyrolysis**

Rolf H. Prager\* and Yogendra Singh

School of Physical Sciences, Flinders University, GPO Box 2100, Adelaide, South Australia, 5001

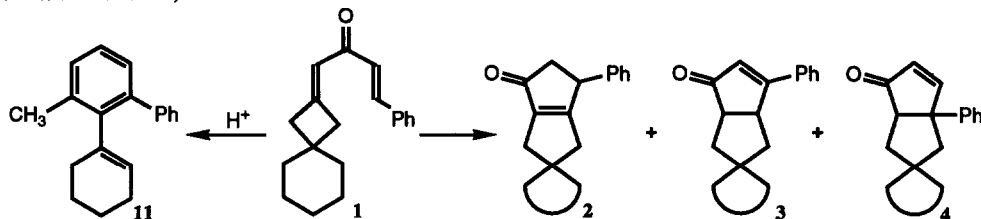
5-Oxo-2,5-dihydroisoxazoles, substituted on nitrogen with nitrogen heterocycles, give annelated imidazoles in excellent yield by flash vacuum pyrolysis



## **Acid-Catalyzed Reactions of a Strained Ring Nazarov Substrate**

April Gu Gruhn and William Reusch\* Department of Chemistry, Michigan State University, E. Lansing, MI 48824

The synthesis of dienone 1 and its reactions with Bronsted and Lewis acids is described. With tin (IV) chloride conversion of 1 to a mixture of 2, 3 and 4 was observed.

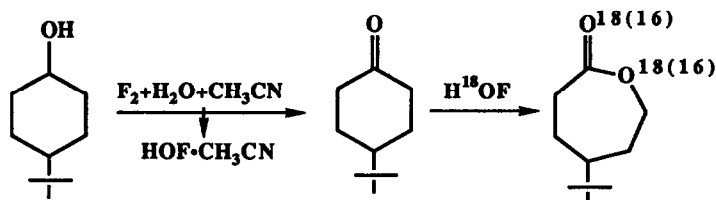


## **HOF·CH<sub>3</sub>CN, MADE DIRECTLY FROM F<sub>2</sub> AND WATER, AS AN ECOLOGICALLY FRIENDLY OXIDIZING REAGENT**

Shlomo Rozen,\* Yifat Bareket and Moshe Kol

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel.

The complex HOF·CH<sub>3</sub>CN, made directly from water, fluorine and acetonitrile, oxidizes secondary alcohols to the corresponding ketones. These could be further oxidized to esters under mild conditions.



### STERIC ACCELERATION OF INTRAMOLECULAR CYCLOADDITION REACTIONS

B. S. Orlek<sup>a</sup>, P. G. Sammes<sup>b</sup> and D. J. Weller<sup>b</sup>

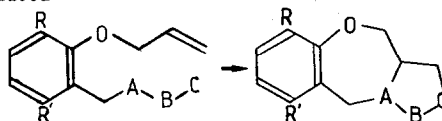
<sup>a</sup> SmithKline Beecham Pharmaceuticals, Coldharbour Lane, The Pinnacles, Harlow, CM19 5AD, U.K.

<sup>b</sup> Molecular Probes Unit, Department of Chemistry, Brunel University, Uxbridge, UB8 3PH, U.K.

A study on the use of conformational constraints, induced

by different *ortho*-substituents in 1-allyloxy-

2-(substituted)methylbenzenes is used to accelerate intramolecular 1,3-dipolar cycloaddition reactions. In this manner cycloadditions that do not otherwise proceed will react.



### SYNTHESIS OF OXA ANALOGS OF PORPHOBILINOGEN (PBG) AS PROBES FOR MECHANISTIC STUDIES OF PBG DEAMINASE

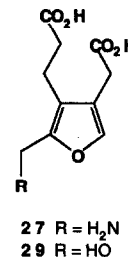
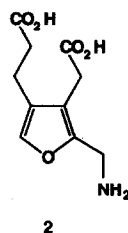
R. E. Danso-Danquah, A. I. Scott\*

Center for Biological NMR, Department of Chemistry,  
Texas A&M University, College Station, Texas 77843, USA

D. Becker

Department of Chemistry, Technion, Israel Institute of  
Technology, Haifa, Israel 32000

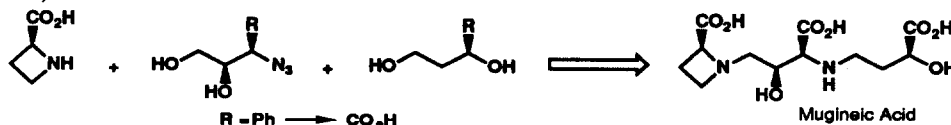
Three oxa analogs of porphobilinogen (PBG) **2**, **27**, and **29** were synthesized from 3-hydroxymethylfuran.



### Total Synthesis of Mugineic Acid. Efficient Use of the Phenyl Group as the Carboxyl Synthone

Fumiyoishi Matsuura, Yasumasa Hamada,\* and Takayuki Shioiri\*

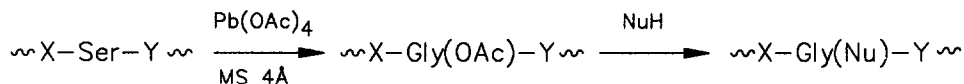
Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya  
467, JAPAN



Stereoselective total synthesis of mugineic acid, a unique phytosiderophore from roots of barley, has been achieved from (2S,3S)- and (2R,3R)-2,3-epoxycinnamyl alcohols employing the phenyl group as the carboxyl synthone.

GENERATION OF  $\alpha$ -ACETOXYGLYCINE RESIDUES WITHIN  
PEPTIDE CHAINS: A NEW STRATEGY FOR THE MODIFICATION OF OLIGOPEPTIDES

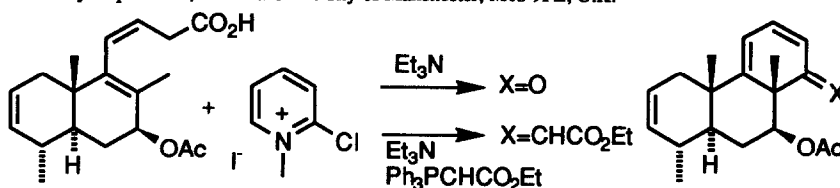
G. Apitz, M. Jäger, S. Jaroch, M. Kratzel, L. Schäffeler and W. Steglich\*,  
Institut für Organische Chemie, Universität München, Germany



NuH = Thiols, carbohydrates, amino acid esters, enamines

The Synthesis of Diterpenoid Intermediates.

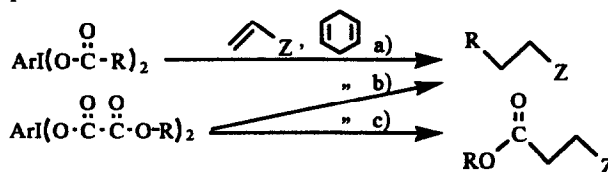
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Reductive Addition to Electron-deficient Olefins with  
Trivalent Iodine Compounds

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(Diacyloxyiodo)arenes and  
[Bis(alkoxyoxalyloxy)iodo]arenes  
were treated with electron-  
deficient olefins in the presence  
of a hydrogen donor to give the  
reductive addition Products.



a) Hg-hv, CH<sub>2</sub>Cl<sub>2</sub>, 30°C; b) Hg-hv, Toluene 100-105°C; c) Hg-hv, CH<sub>2</sub>Cl<sub>2</sub>, 0-5°C

**XANTHIC ANHYDRIDES: A NOVEL AND CONVENIENT SOURCE OF  
ALKOXYTHIOCARBONYL AND ALKYL RADICALS.**

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Upon irradiation with visible light, xanthic anhydrides undergo a chain reaction involving alkoxythiocarbonyl radicals and leading to the corresponding xanthates.

