

## GRAPHICAL ABSTRACTS

*Tetrahedron*, 1993, 49, 319

**STRUCTURES AND BIOACTIVITIES OF NEW ASBESTININ  
DITERPENOIDS FROM THE CARIBBEAN GORGONIAN OCTOCORAL  
BRIAREUM ASBESTINUM.**

Abimael D. Rodriguez\* and Oscar Cobar Pinto, Department of Chemistry, P.O. Box 23346  
University of Puerto Rico, U.P.R. Station, Río Piedras, Puerto Rico 00931-3346

The extraction of several specimens of the Caribbean gorgonian octocoral Briareum asbestinum produced five new diterpenoids possessing the rare asbestinane carbon skeleton. Most of the new compounds exhibited in vitro antitumor activity against a panel of five human tumor cell lines. The complete structural assignments of these new metabolites have been accomplished exclusively from in-depth NMR spectral analyses.

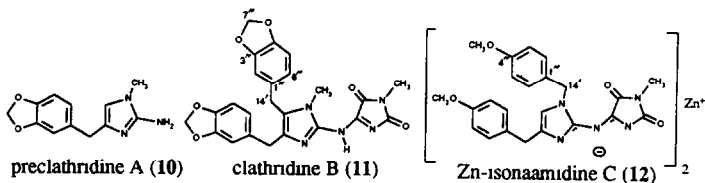
*Tetrahedron*, 1993, 49, 329

**2-AMINOIMIDAZOLES AND THEIR ZINC COMPLEXES FROM INDO-  
PACIFIC LEUCETTA SPONGES AND NOTODORIS NUDIBRANCHS**

K. A. Alvi, Barbara M. Peters, Lisa M. Hunter and Phillip Crews\*

Department of Chemistry and Biochemistry and Institute of Marine Sciences Univ. of Calif., Santa Cruz, Santa Cruz, CA 95064

Known metabolites clathridine (7), and its corresponding Zn complex (8), and the new compounds, preclathridine A (10), clathridine B (11) and Zn-isonaamidine (12), are discussed. This study reports the first instance of an organometallic compound isolated from a nudibranch.



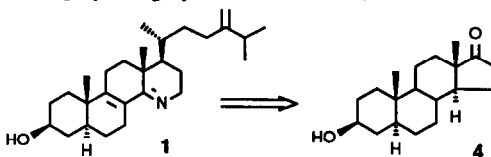
*Tetrahedron*, 1993, 49, 337

**SYNTHESIS OF ANTIBIOTIC A25822 B**

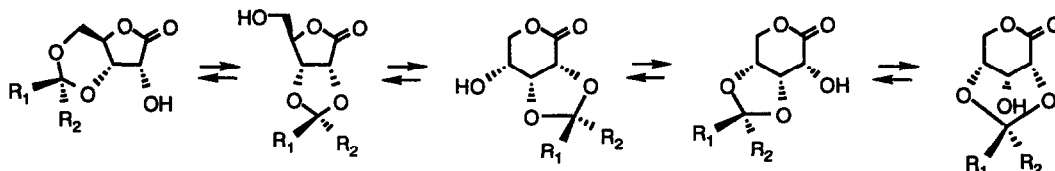
Thomas G. Back\* and Nan-Xing Hu

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

The synthesis of antibiotic A25822 B (1) from epiandrosterone (4) is described.



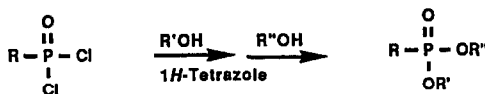
So-Yeop Han, Madeleine M. Joullie\*, Nicos A. Petasis\* Joaquim Bigorra, Jordi Corbera, Josep Font\*, Rosa M. Ortuño.\*  
 Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, and Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain,  
 The reactions of D-ribonolactone, and D-2-deoxyribonolactone with benzaldehyde and acetone in acidic media were investigated. The products obtained were isolated and characterized. The observed ring expansion of D-ribonolactone was found to occur via prior acetal formation. The *endo* preference of benzylidene acetals was explained by the transition state conformation of the reactants and the thermodynamic stability of the products, as calculated with molecular mechanics.



TETRAZOLE CATALYZED SYNTHESIS OF PHOSPHONATE ESTERS

Kang Zhao and Donald W. Landry, Department of Chemistry, New York University, New York, New York 10003

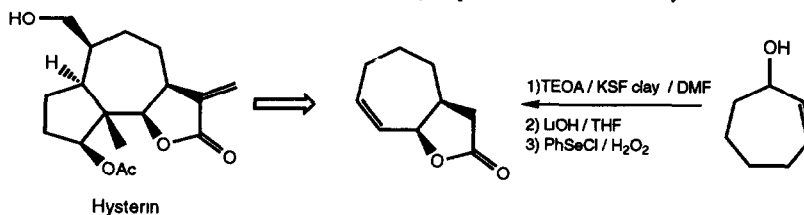
1*H*-tetrazole selectively catalyzed mono addition of alcohols to phosphonic dichlorides providing a means to mixed diesters in high yield.



THE CLAISEN REARRANGEMENT IN SYNTHESIS: ACCELERATION OF THE JOHNSON ORTHOESTER PROTOCOL *EN ROUTE* TO BICYCLIC LACTONES

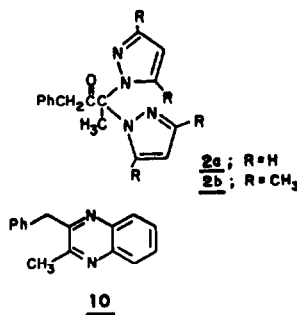
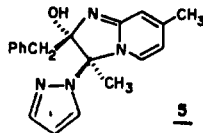
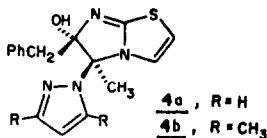
Graham B. Jones \* Robert S. Huber and Sotheyary Chau, Department of Chemistry, Clemson University, Clemson S C 29634

Efficient catalysis of the Claisen orthoester rearrangement derived from combination of triethylorthoacetate and a number of 2-cycloalken-1-ols is achieved using montmorillonite KSF clay coupled with microwave thermolysis.



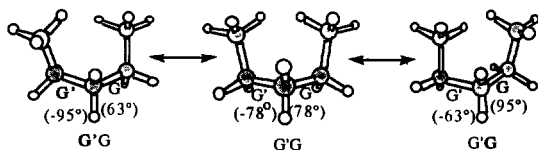
**ALKYL-C VERSUS PHENYL-C REACTIVITY IN UNSYMMETRICAL CYCLOPROPENONES. REACTION OF METHYLPHENYLCYCLOPROPENONE WITH PYRAZOLES.** A. Kascheres, J.C. Filho and S. Cunha - Unicamp, Instituto de Química, CP 6154, 13081, Campinas, SP, Brasil.

Methylphenylcyclopropenone reacts with pyrazoles to afford **2** resulting from initial nucleophilic attack at methyl-C, in agreement with an AM<sub>1</sub> calculation. Other nucleophiles may be incorporated via a dipolar species to produce **4**(2-aminothiazole), **5**(2-amino-4-methylpyridine), or **10**(0-phenylenediamine).



**HOW MANY CONFORMERS ARE THERE FOR SMALL *n*-ALKANES? CONSEQUENCES OF ASYMMETRIC DEFORMATION IN GG' SEGMENT**

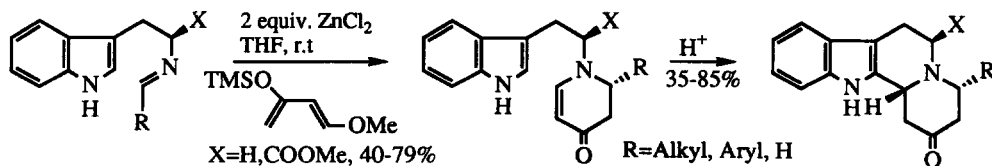
Hitoshi Gotō,<sup>a</sup> Eiji Ōsawa\*<sup>ab</sup> and Masaru Yamato<sup>b</sup>, <sup>a</sup>Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, <sup>b</sup>Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, Japan



Total number of conformers of *n*-heptane is 109, greater than 3<sup>4</sup> (=81), mainly due to GG' part. The significance of this observation is discussed.

**Asymmetric Synthesis of Indolo[2,3-*a*]-quinolizidin-2-ones - Congeners to Yohimbine-Type Alkaloids**

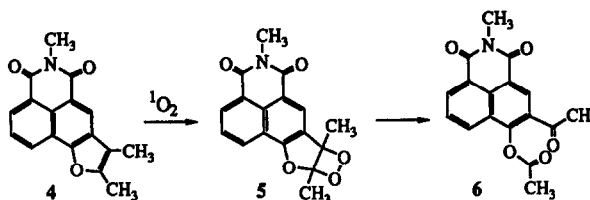
Herbert Waldmann\*, Matthias Braun, Markus Weymann and Markus Gewehr  
Universität Bonn, Inst. f. Organ. Chemie und Biochemie, Gerhard-Domagk-Straße 1, D-5300 Bonn



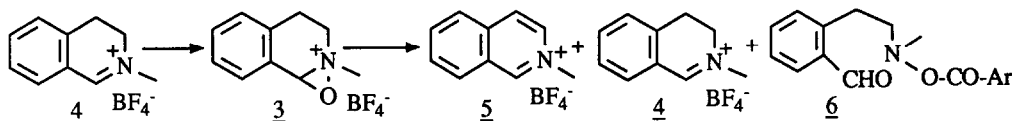
**SYNTHESIS AND PHOTOOXYGENATION OF  
2,3,6-TRIMETHYLFURO[2,3-b][1]NAPHTHO[4a,7a-e,f]PYRIDA-  
5,7-DIONE, A POTENTIAL CHEMILUMINESCENT PROBE FOR SINGLET OXYGEN**

Waldemar Adam\*, Xuhong Qian, Chantu R. Saha-Möller  
Institute of Organic Chemistry, University of Würzburg  
Am Hubland, D-8700 Würzburg, Germany

The novel furonaphthalimide **4** was prepared from 4-chloro-1,8-naphthalic anhydride, its photooxygenation gave the naphthalimide **6** by decomposition of the labile dioxetane **5**. The fluorescence properties of the 1,8-naphthalimide derivatives were determined.



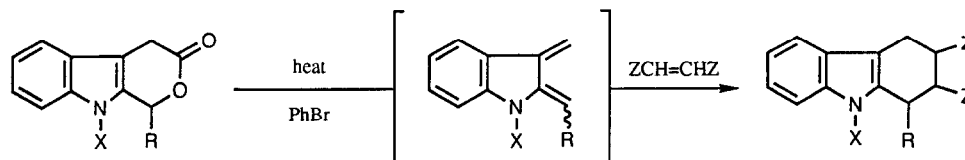
Action de l'acide paranitrobenzoïque sur le tétrafluoroborate de N-méthyl-3,4-dihydroisoquinolinium. Formation d'un sel d'oxaziridinium. G. Hanquet, X. Lusmichi, P. Milhet; Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette, France.



L'action d'un peracide en présence d'une quantité substoechiométrique de base conduit à un sel d'oxaziridinium, lequel en présence d'un équivalent de base conduit ensuite au mélange des sels d'isoquinolinium **5** et d'iminium **4** et à un dérivé ouvert **6**.

**1,4-DIHYDROPYRANO[3,4-b]INDOL-3-ONES AS PRECURSORS TO  
INDOLE-2,3-QUINODIMETHANES**

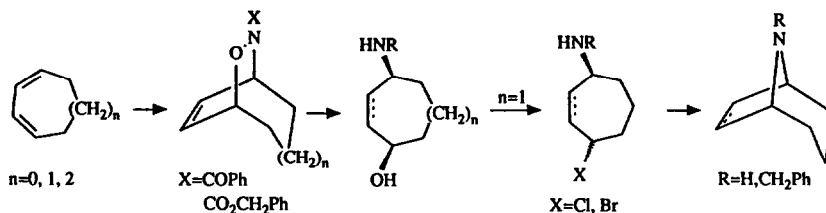
Edward B. Fray,<sup>a</sup> Christopher J. Moody\*<sup>a,b</sup> and Pritom Shah<sup>b</sup> <sup>a</sup>Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, U.K.; <sup>b</sup>Department of Chemistry, Imperial College, London, SW7 2AY, U.K.



The 1,4-dihydropyrano[3,4-b]indolones lose CO<sub>2</sub> on heating to generate the corresponding indole-2,3-quinodimethanes, which can be intercepted in Diels-Alder reactions with a range of dienophiles

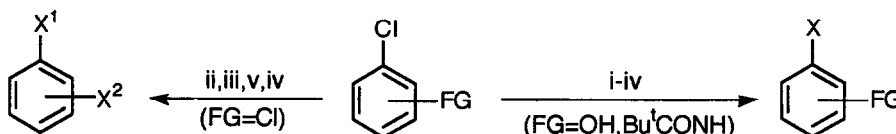
**SYNTHETIC APPROACHES TO NORTROPANES AND NORTROP-6-ENES; INTRAMOLECULAR DISPLACEMENT BY NITROGEN IN 7-MEMBERED RINGS**

Antoinette Naylor (née Bathgate), Nicola Howarth and John R. Malpass\*  
Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK.



**NAPHTHALENE-CATALYSED LITHIATION OF FUNCTIONALIZED CHLOROARENES: REGIOSELECTIVE PREPARATION AND REACTIVITY OF FUNCTIONALIZED LITHIOARENES**

Albert Guijarro, Diego J Ramón and Miguel Yus\*  
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, 03080 Alicante, Spain



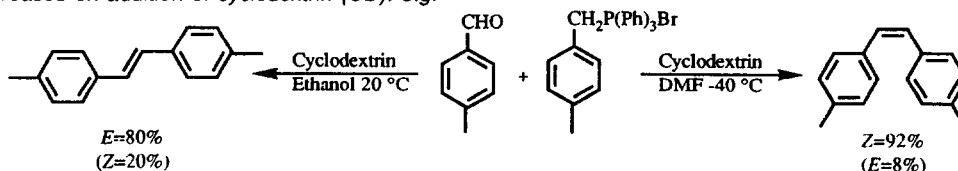
(Reagents: i,  $\text{Bu}^n\text{Li}$ ; ii,  $\text{Li}$ ,  $\text{C}_{10}\text{H}_8$  cat.; iii,  $\text{Et}^1$ ; iv,  $\text{H}_2\text{O}$ ; v,  $\text{Et}^2$ )

**ON THE EFFECT OF CYCLODEXTRIN ON THE Z/E-SELECTIVITY OF WITTIG REACTIONS WITH SEMISTABILIZED YLIDES.**

Gunnar Westman, Olof Wennerström\* and Ilona Raston

Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden.

For Wittig reactions between semistabilized ylides and aromatic aldehydes the Z/E-selectivity increases on addition of cyclodextrin (CD). e.g.



**Water Induced  $\beta$ -Turn Modification in a Chemotactic Tetrapeptide. Synthesis, Crystal Conformation, and Activity of HCO-Met-Leu- $\Delta^2$ Phe-Phe-OMe**

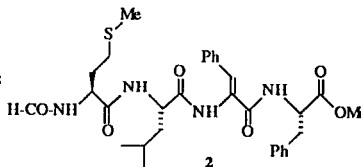
I. Torrini,<sup>a</sup> G.P. Zecchini,<sup>a</sup> M.P. Paradisi,<sup>a</sup> G. Lucente,<sup>a,\*</sup> E. Gavuzzo,<sup>b</sup> F. Mazza,<sup>b</sup> G. Pochetti,<sup>b</sup> and S. Spisani<sup>c</sup>

<sup>a</sup>Dipartimento di Studi Farmaceutici and Centro di Studio per la Chimica del Farmaco del CNR, Università "La Sapienza"

00185 Roma, Italy; <sup>b</sup>Istituto di Strutturistica Chimica "G. Giacomello" CNR, Monterotondo Stazione, Roma, Italy;

<sup>c</sup>Istituto di Chimica Biologica, Università di Ferrara, Ferrara, Italy

The title compound **2** adopts an "open-turn" conformation stabilized by three peptide-water H-bonds. The formyl group does not participate to the turn. **2** is active toward human neutrophils stimulating directed migration, superoxide anion production and lysozyme release.



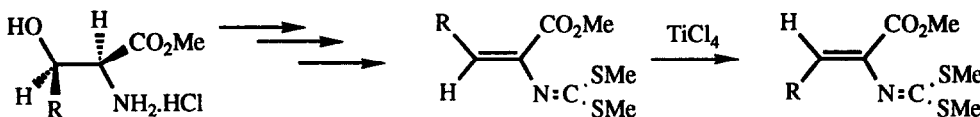
**STEREOSPECIFIC SYNTHESIS OF N-[BIS(METHYLTHIO)METHYLENE]**

**$\alpha,\beta$ -DIDEHYDROAMINO ACID METHYL ESTERS, NEW SYNTHONS IN THE SYNTHESIS OF  $\alpha$ -AMINO ACIDS**

Carlos Cativiela\*, Maria D. Diaz de Villegas

Instituto de Ciencia de Materiales de Aragón. Departamento de Química Orgánica, Universidad de Zaragoza-CSIC, Zaragoza, Spain.

Stereospecific syntheses of (E) and (Z)-N-[bis(methylthio)methylene]- $\alpha,\beta$ -didehydroamino acid methyl esters are described.



**FACILE AERIAL OXIDATION OF A PORPHYRIN. PART 13.**

**GENERATION OF  $\pi$ -CATION RADICALS via ACID ADDITION TO MESOTETRAKIS(3,5-DI-t-BUTYL-4-HYDROXYPHENYL)PORPHYRIN AND ITS TWO-ELECTRON OXIDATION PRODUCT.**

L.R. Milgrom<sup>a,\*</sup> and W.D. Flitter<sup>b,†</sup>; <sup>a</sup>Departments of Chemistry, and

<sup>b</sup>Biochemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH., U.K.

Acid addition to the oxidised porphyrin **2** produces the  $\pi$ -cation radical **3**: the long-lived radical produced by aerial oxidation of porphyrin **1** in acid is shown to be a  $\pi$ -cation radical dimer **4**.

