Tetrahedron, **1993**, *49*, 8727

ON THE SYNTHESIS OF UNSYMMETRICAL BIS(MACROCYCLIC) LIGANDS

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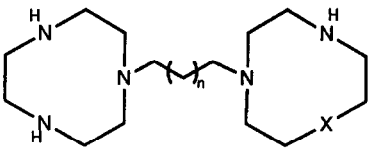
Department of Chemistry and Biochemistry, University of Texas at Austin
Austin, TX 78712, USA

The stepwise syntheses of the three and four carbon-bridged bis(macrocycles) **14**, **15**, **24**, and **25** are described.

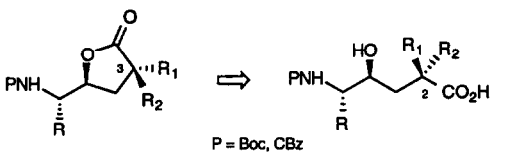


14 n = 1, X = O
15 n = 1, X = CH_2
24 n = 2, X = O
25 n = 2, X = CH_2

Tetrahedron, **1993**, *49*, 8739

Dipeptide Isosteres. 2. Synthesis of Hydroxyethylene Dipeptide Isostere Diastereomers From a Common γ-Lactone Intermediate. Preparation of Renin and HIV-1 Protease Inhibitor Transition State Mimics.§ William R Baker*[1] and John K. Pratt
Pharmaceutical Products Division, Abbott Laboratories, Abbott Park, Illinois 60064.

A general strategy for the synthesis of the hydroxyethylene dipeptide isostere diastereomers **C** or **D** has been developed. The syntheses proceeded through a common γ-lactone intermediate **A** or **B**. The C(3α) γ-lactone diastereomer **A** was prepared from the N-Cbz protected α-amino aldehyde and 2-(2-isopropylpropen-2-yl)trimethylsilane in five steps. The C(3β) γ-lactone diastereomer **B** was obtained by kinetic protonation of the lactone enolate using malonate derivatives.



P = Boc, CBz

A 3α R_1 = alkyl, R_2 = H
B 3β R_1 = H, R_2 = alkyl

C R_1 = alkyl, R_2 = H
D R_1 = H, R_2 = alkyl

Tetrahedron, **1993**, *49*, 8757

BLANCASTEROL, A CYTOTOXIC 9,11-SECOSTEROID ISOLATED FROM THE NORTHEASTERN PACIFIC MARINE SPONGE *PLERAPLYSILLA* SP.

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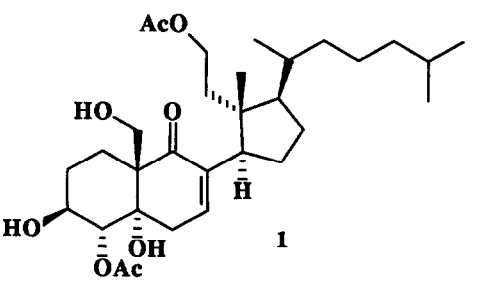
Departments of Chemistry and Oceanography
University of British Columbia
Vancouver, B.C., CANADA V6T 1Z1

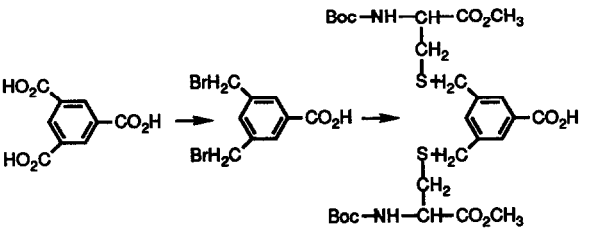
The structure of blancasterol (1), a cytotoxic 9,11-secosteroid isolated from a *Pleraplysilla* sp., has been solved by analysis of spectroscopic data.



1

Tetrahedron, **1993**, *49*, 8761

REGIOSPECIFIC SYNTHESIS OF 3,5-BIS(BROMOMETHYL)BENZOIC ACID, A CYSTEINE CROSSLINKING AGENT. Marisa Engel, Clyde W. Burris, Cheryl A. Slate and Bruce W. Erickson, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599-3290, U.S.A. 3,5-Bis(bromomethyl)benzoic acid was made in 38% yield by a 4-step route from 1,3,5-benzenetricarboxylic acid. Reaction with cysteine methyl ester and then di(*tert*-butyl) dicarbonate gave the 2:1 adduct shown in 60% yield.

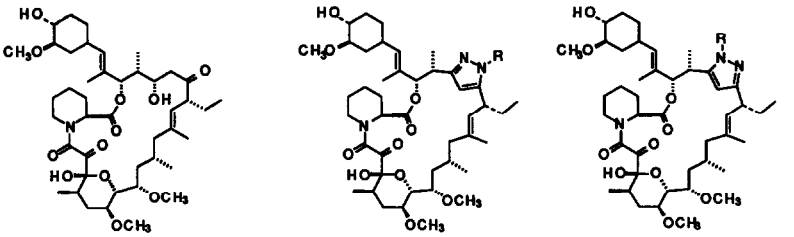


Tetrahedron, **1993**, *49*, 8771

THE CHEMISTRY OF ASCOMYCIN: STRUCTURE DETERMINATION AND SYNTHESIS OF PYRAZOLE ANALOGUES

Yat Sun Or,* Richard F. Clark, Qinghua Xie, James McAlpine, David N. Whittern, Rodger Henry and Jay R. Luly
Abbott Laboratories, Pharmaceutical Products Division,
Abbott Park, Illinois 60064,
USA.

The fermentation and structural determination of ascomycin (1) as well as the synthesis and structure confirmation of pyrazole analogues (3 and 4) from 1 are described.



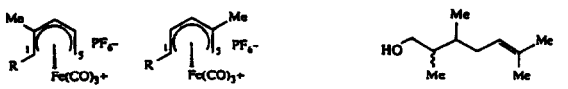
1 **3** **4**

Tetrahedron, **1993**, *49*, 8787

Reactivity of Carbon Nucleophiles with Disubstituted Tricarbonyl(pentadienyl)iron(1+) Cations: Application to the Synthesis of Lasiol and Epi-lasiol

William A. Donaldson*, and Myung-Jong Jin
Department of Chemistry, Marquette University, Milwaukee, WI 53233 USA

The reaction of cations **3a**, **3b**, **4a**, and **4b** with dimethylcuprate and with sodium dimethylmalonate were examined. A short synthesis of **14** used the cation **4a**.



3a, R = Me **4a**, R = Me **14a** *erythro*
3b, R = Ph **4b**, R = Ph **14b** *threo*

Tetrahedron, **1993**, *49*, 8795

ELECTROPHILIC AMINATION OF IMIDAZOLE MOIETIES OF 9-ETHYLGUANINE AND 1-METHYLBENZIMIDAZOLE DERIVATIVES AND REACTIVITIES OF *N*-AMINATED PRODUCTS

Toyo Kaiya, Masahiro Ohta and Kohfuku Kohda*
Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabedori, Mizuho-ku, Nagoya 467, Japan

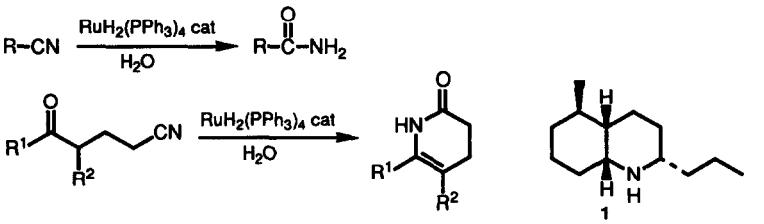
Electrophilic amination of four 9-ethylguanine derivatives and seven 1-methylbenzimidazole derivatives with 2,4-dinitrophenoxyamine was carried out. Reactivity of the imidazole moiety to electrophilic amination and reaction pathways of *N*-aminated compounds with alkaline treatment are discussed.

Tetrahedron, **1993**, *49*, 8805

Ruthenium-Catalyzed Hydration of Nitriles and Transformation of δ-Ketonitriles to Ene-lactams: Total Synthesis of (–)-Pumiliotoxin C

Shun-Ichi Murahashi, Shigehiro Sasao, Eiichiro Saito, and Takeshi Naota
Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan.

Hydration of nitriles and transformation of δ-ketonitriles to ene-lactams in the presence of $RuH_2(PPh_3)_4$ catalyst can be performed efficiently. The effectiveness of the reaction is illustrated by the short-step synthesis of (–)-pumiliotoxin C (1).



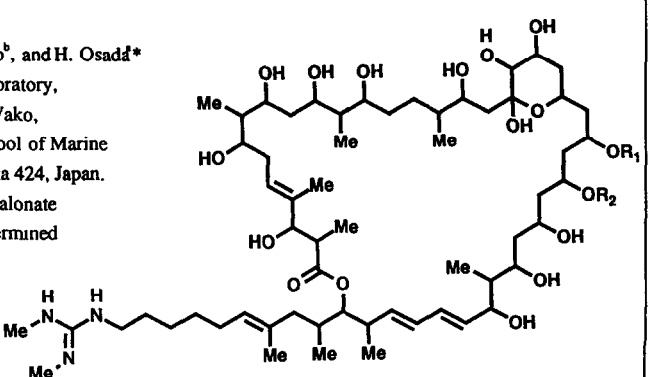
Tetrahedron, **1993**, *49*, 8827

Structure of Malolactomycins A and B, Novel 40-Membered Macrolide Antibiotics

H. Koshino*, K. Kobinata[a], J. Uzawa, M. Uramoto, K. Isono[b], and H. Osada[a]*
Division of Molecular Characterization, and [a]Antibiotics Laboratory,
The Institute of Physical and Chemical Research (RIKEN), Wako,
Saitama 351-01, Japan [b]Department of Marine Science, School of Marine
Science and Technology, Tokai University, Shimizu, Shizuoka 424, Japan.

Malolactomycins A and B are positional isomers of malonate and interconvertible each other. The structures have been determined by spectroscopic analyses, especially NMR.

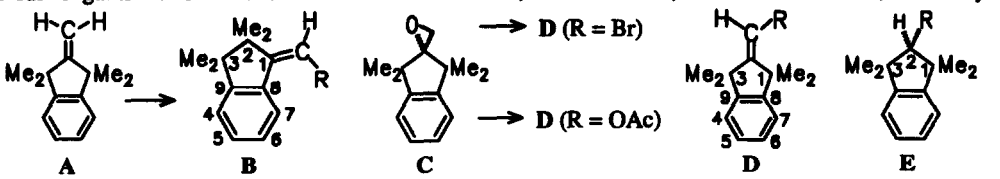
Malolactomycin A R_1=COCH $_2$COOH, R_2=H
Malolactomycin B R_1=H, R_2=COCH $_2$COOH



Tetrahedron, **1993**, *49*, 8837

1,1,3,3-Tetramethyl-2-methyleneindan Derivatives: Syntheses with Imminent Rearrangement

Rudolf Knorr*, Johannes Freudenreich, Therese von Roman, Johann Mehlstäubl and Petra Böhrer
Institut für Organische Chemie der Universität München, Karlstraße 23, D-80333 München, Germany



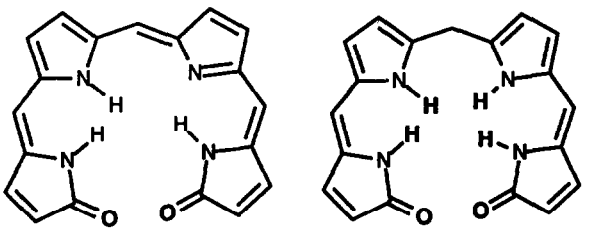
The common methods of olefin functionalization by electrophilic reagents are not applicable to **A** owing to facile methyl migration, as exemplified by the acid-catalyzed formation of **B** (R = H) from **A**. Therefore, *nucleophilic* bromination of the oxirane **C** is a key step for most preparations in the series **D**. Compounds **D** with R = Br, *n*-butyl, OAc, OLi, $OSiMe_3$, OCH_3, SPh and $PhSMe^+$ are described as well as **E** with R = CHO, $CH(OCH_2)_2$ and CO_2H. Characterized examples **B** exist mainly as the *Z* isomers with R = Br, Li, *n*-butyl, CO_2H and acetyl.

Tetrahedron, **1993**, *49*, 8855

INVESTIGATION ON INTERMOLECULAR FORCES BETWEEN BILE PIGMENTS AND POLAR MODEL COMPOUNDS MIMICKING THE CHROMOPHORE - PROTEIN INTERACTIONS IN BILIPROTEINS

Daniel Krois
Institut für Organische Chemie der Universität Wien, Währingerstraße 38, A-1090 Wien, Österreich

The hydrogen bonding sites of helical biliverdins and bilirubins available for heteroassociation are mapped.

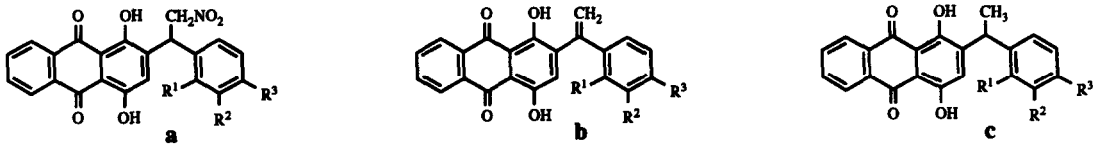


Tetrahedron, **1993**, *49*, 8865

GENERAL SYNTHESES OF NOVEL ANTHRACENE-9,10-DIONE DERIVATIVES: THE 2-(1-ARYL-2-NITROETHYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES, 2-(1-ARYLETHENYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES AND 2-(1-ARYLETHYL)-1,4-DIHYDROXYANTHRACENE-9,10-DIONES

Daniel DAUZONNE* and Stéphane FOURIS
Service de Chimie de l'Institut Curie, Section de Biologie, URA 1387P du CNRS, 26 rue d'Ulm, F-75231 Paris Cedex 05, France

The base-promoted reaction of various (2-chloro-2-nitroethenyl)benzenes with leucoquinizarin leads to the hitherto unknown title anthracene-9,10-diones **a**, **b** or **c** depending on the reaction conditions employed.

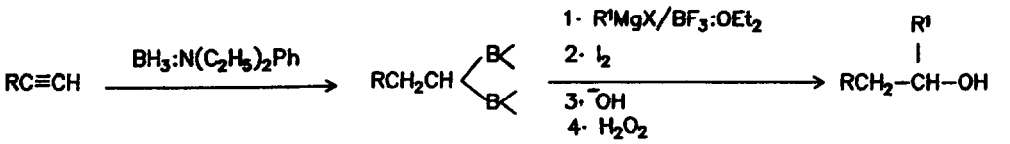


Tetrahedron, **1993**, *49*, 8877

REACTION OF I_2 WITH α-BORAALKYLMAGNESIUM BROMIDE : A NEW SYNTHESIS OF MIXED ALKYL SECONDARY ALCOHOLS

Ch.Kishan Reddy and Mariappan Periasamy*
School of Chemistry, University of Hyderabad, Hyderabad-500 134, India.

Mixed alkyl secondary alcohols are prepared through hydroboration of 1-alkynes with $H_3B{:}N(C_2H_5)_2Ph$ followed by R^1MgX/I_2 treatment and $^-OH/H_2O_2$ oxidation.

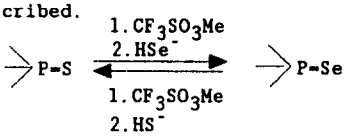


Tetrahedron, **1993**, *49*, 8887

A NEW, STEREOSELECTIVE INTERCONVERSION OF PHOSPHINOTHIO--PHOSPHINOSELENO COMPOUNDS, REDUCTION OF PHOSPHINOSELENO DERIVATIVES AND RETRO PISHCHIMUKA REARRANGEMENT BASED ON METHYLTHIO- AND METHYLSELENOPHOSPHONIUM SALTS CHEMISTRY

J.Omelańczuk
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland

A highly stereoselective interconversion of phosphine sulfides ⇆ phosphine selenides via their methylthiophosphonium salts is described.

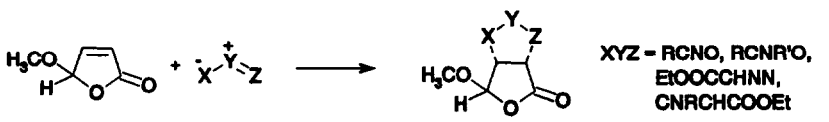


Tetrahedron, **1993**, *49*, 8899

1,3-DIPOLAR CYCLOADDITIONS TO 5-METHOXY-2(5H)-FURANONE

Erik Keller, Ben de Lange, Minze T. Rispens and Ben L. Feringa
Department of Organic and Molecular Inorganic Chemistry, Groningen Center for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

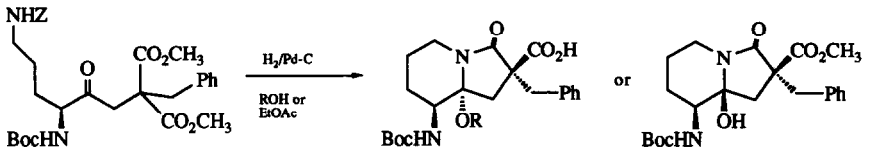
The 1,3-dipolar cycloaddition of several nitrile oxides, nitrones, ethyl diazoacetate and an azomethine ylide to 5-methoxy-2(5H)-furanone were examined.



Tetrahedron, **1993**, *49*, 8911

ONE-POT STEREOSPECIFIC SYNTHESIS OF 8a-HYDROXY- AND 8a-ALKOXY-2,2,8-TRISUBSTITUTED-3-OXOINDOLIZIDINES. MECHANISTIC STUDIES ON THE ELABORATION OF THE 8a-SUBSTITUTED INDOLIZIDINE RING

María José Domínguez, María Teresa García-López and Rosario González-Muñiz,*
Instituto de Química Médica (C.S.I.C.), Juan de la Cierva, 3. 28006 Madrid, Spain



Tetrahedron, **1993**, *49*, 8919

THE FISCHER INDOLISATION REACTION AND THE SYNTHESIS OF INDENOINDOLES

David W. Brown[a], Mary F.Mahon[a], Aleyamma Ninan[a], Malcolm Sainsbury[a], and H.G.Shertzer[b].
[a]School of Chemistry, University of Bath, Bath BA2 7AY;Dept. Environmental Health, University of Cincinnati, Ohio 45267-0056, USA.

Reasons for the failure of Fischer indolisation reactions using phenylhydrazines bearing electron-rich substituents are discussed. New routes to aryl hydrazines are described and methods for the conversion of these compounds into dihydroindenoindoles are disclosed.