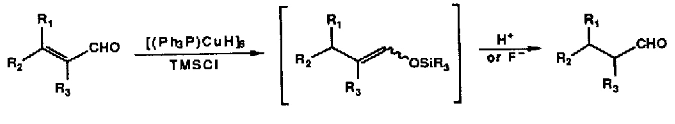
GRAPHICAL ABSTRACTS

Tetrahedron Lett.30,5677(1989)

REGIOSELECTIVE CONJUGATE REDUCTION AND REDUCTIVE SILYLATION OF α,β-UNSATURATED ALDEHYDES USING $[(Ph_3P)CuH]_6$

Donna M. Brestensky and Jeffrey M. Stryker*
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Regioselective conjugate reduction and reductive silylation of α,β-unsaturated aldehydes is reported, using the stable copper(I) hydride. Complete 1,4- and 1,2-reduction can be obtained in some cases.

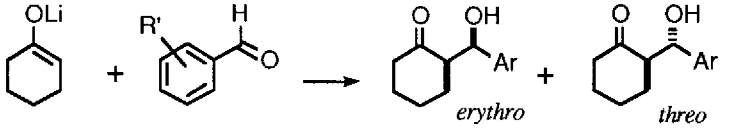


Tetrahedron Lett.30,5681(1989)

DIASTEREOSELECTIVE ALDOL REACTIONS OF CYCLOHEXANONE LITHIUM ENOLATE.

Marek Majewski* and D. Mark Gleave
Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., Canada S7N 0W0

Cyclohexanone lithium enolate reacts with aromatic aldehydes to produce *threo* aldols predominantly

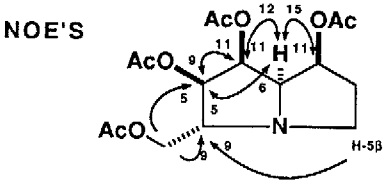


Tetrahedron Lett.30,5685(1989)

1-EPIAUSTRALINE, A NEW PYRROLIZIDINE ALKALOID FROM *CASTANOSPERMUM AUSTRALE*

C. M. HARRIS,[a]* T. M. HARRIS,[a]* R. J. MOLYNEUX,[b] J. E. TROPEA,[c] AND A. D. ELBEIN[c]
a) Chemistry Dept., Vanderbilt Univ., Nashville, TN 37235; b)Western Regional Research Center, ARS-USDA, Berkeley, CA 94710; c) Biochemistry Dept., Univ. of Texas Health Science Center, San Antonio, TX 78284

A new pyrrolizidine alkaloid [1] has been isolated from the legume *Castanospermum australe* A. Cunn. (Leguminosae) and identified as (1*S*,2*R*,3*R*,7*S*,7a*R*)-3-hydroxymethyl-1,2,7-trihydroxypyrrolizidine on the basis of ¹H NMR nuclear Overhauser effects and other spectroscopic studies.



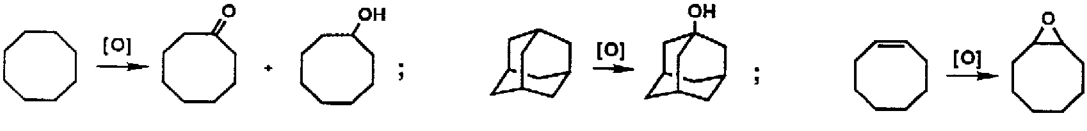
1

Tetrahedron Lett.30,5689(1989)

Oxidation of Hydrocarbons Catalyzed by Manganese Carboxylate Complexes

by Kingsley L. Taft, Robert J. Kulawiec Joseph E. Sarneski¶ and Robert H. Crabtree*
Department of Chemistry, Yale University, New Haven, Connecticut 06511

High-valent manganese carboxylate complexes catalyze the hydroxylation of alkanes and the epoxidation of cyclooctene under mild conditions. Up to 21 turnovers of alkane oxidation in 3 hours are observed.

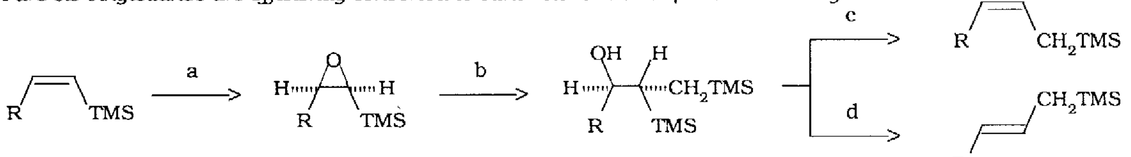


Tetrahedron Lett. <u>30</u>,5693(1989)

THE STEREOSELECTIVE CONVERSION OF VINYLSILANES TO γ-SUBSTITUTED ALLYLSILANES *VIA* HIGHER ORDER CUPRATES

John A. Soderquist* and Braulio Santiago
Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931

Pure cis-vinylsilanes are efficiently converted to either cis- or trans-γ-substituted allylsilanes.



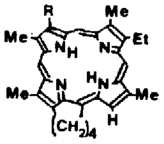
a: *m*-CPBA; b: $Li_2Cu(CN)(CH_2TMS)_2$; c: KH or NaH; d: 1/3 BF_3

Tetrahedron Lett. <u>30</u>,5697(1989)

TOTAL SYNTHESIS OF THE C_{31} AND C_{32} 15,17-BUTANO-PORPHYRINS FROM OIL SHALES

Timothy D. Lash and Marty C. Johnson
Department of Chemistry, Illinois State University, Normal, Illinois 61761, U.S.A.

The total synthesis of two porphyrin geomarkers, <u>1a</u> and <u>1b</u>, by the tripyrrene-a,c-biladiene route is described.

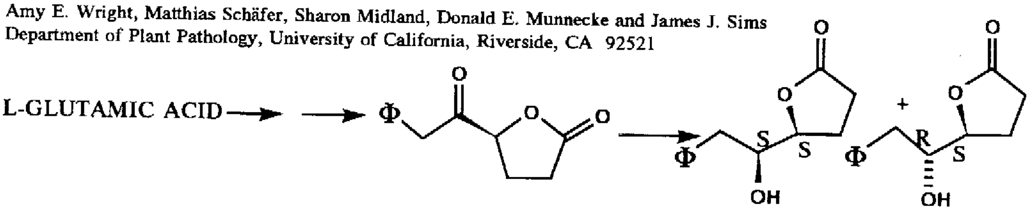


<u>1a</u> R = Et
<u>1b</u> R = Me

Tetrahedron Lett. <u>30</u>,5699(1989)

LATERAL ROOT INDUCING COMPOUNDS FROM THE BACTERIUM *ERWINIA QUERCINA* : ISOLATION, STRUCTURE AND SYNTHESIS

Amy E. Wright, Matthias Schäfer, Sharon Midland, Donald E. Munnecke and James J. Sims
Department of Plant Pathology, University of California, Riverside, CA 92521

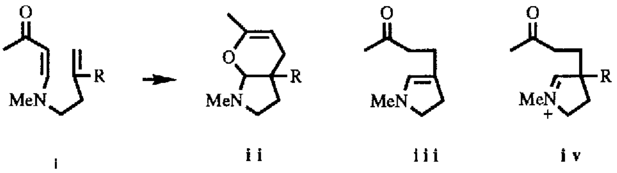


Tetrahedron Lett. <u>30</u>,5703(1989)

INTRAMOLECULAR PHOTOCYCLOADDITION AND RETRO-MANNICH FRAGMENTATION OF ACYLCIC TERTIARY VINYLOGOUS AMIDES

Jeffrey D. Winkler*, Nizar Haddad and Ronald J. Ogilvie
Searle Chemical Laboratories, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

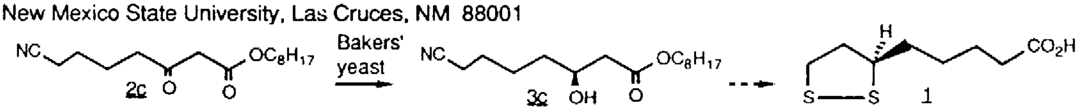
Intramolecular photocycloaddition/retro-Mannich fragmentation of tertiary vinylogous amides, i, and the selective conversion of the derived zwitterionic intermediate to either aminal, ii, ketoenamine, iii, or ketoiminium products, iv, is described.



Tetrahedron Lett. 30, 5705 (1989)

STEREOCHEMICAL CONTROL OF YEAST REDUCTIONS: SYNTHESIS OF R-(+)-α-LIPOIC ACID

Aravamudan S. Gopalan and Hollie K. Jacobs
Department of Chemistry/Plant Genetic Engineering Lab
New Mexico State University, Las Cruces, NM 88001



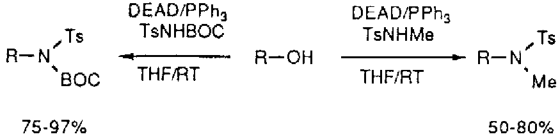
The chiral alcohol, 3c, obtained from bakers' yeast reduction of 2c, was used to synthesize R-(+)-α-lipoic acid(1).

Tetrahedron Lett. 30, 5709 (1989)

MITSUNOBU REACTIONS OF N-ALKYL AND N-ACYL SULFONAMIDES-AN EFFICIENT ROUTE TO PROTECTED AMINES

James R. Henry, Lawrence R. Marcin, Matthias C. McIntosh, Paul M. Scola, G. Davis Harris, Jr. and Steven M. Weinreb*, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

N-Methyl p-toluenesulfonamide and N-BOC p-toluenesulfonamide can be directly coupled with primary and secondary alcohols under Mitsunobu conditions to afford various sulfonamide-protected amines.

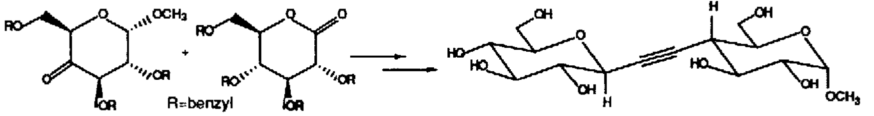


Tetrahedron Lett. 30, 5713 (1989)

STEREOSELECTIVE SYNTHESIS OF "LINEAR" C-DISACCHARIDES

*Sharon M. Daly and Robert W. Armstrong**
Department of Chemistry and Biochemistry,
University of California at Los Angeles, Los Angeles, CA 90024-1569

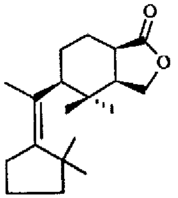
A 1,4'-C-disaccharide containing an acetylenic linkage was synthesized from D-glucose via a homologation of a 4-ulose derivative followed by condensation with 2,3,4,6-tetrabenzyl pyranolactone. Subsequent reduction afforded isomerically pure β-C-disaccharide in good overall yield.



Tetrahedron Lett. 30, 5717 (1989)

GLACIOLIDE, A DEGRADED DITERPENOID WITH A NEW CARBON SKELETON FROM THE NUDIBRANCH *CADLINA LUTEOMARGINATA* AND THE SPONGE *APLYSILLA GLACIALIS*

Mark Tischler and Raymond J. Andersen*
Departments of Chemistry and Oceanography
University of British Columbia
Vancouver, B.C.
CANADA V6T 1W5

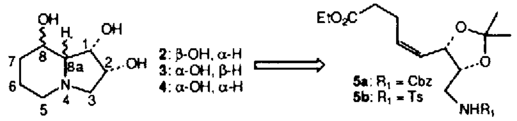


Tetrahedron Lett. 30, 5721 (1989)

DIVERGENT SYNTHESES OF STEREOISOMERS OF SWAINSONINE: (-)-8-*epi*, (-)-8a-*epi* and (-)-8,8a-di*epi*-SWAINSONINE.

Young Gyu Kim and Jin K. Cha*
Department of Chemistry, Vanderbilt University, Nashville, TN 37235, U.S.A.

Divergent stereoselective syntheses of three stereoisomers **2-4** of swainsonine (**1**) starting from the readily available common intermediates **5a,b** are described.

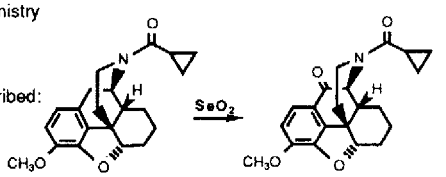


Tetrahedron Lett. 30, 5725 (1989)

10 KETO OPIATES

R. T. Uyeda*, M. A. Wuonola and J. M. Read, Jr.
E. I. du Pont de Nemours and Co., Medical Products Department
Pharmaceuticals and Biotechnology R&D Division, Medicinal Chemistry
Experimental Station, Wilmington, DE 19880-0353

The following transformation with ^1H and ^{13}C NMR spectra is described:



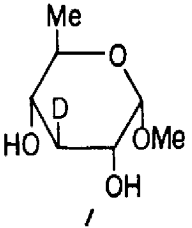
Tetrahedron Lett. 30, 5729 (1989)

SYNTHESIS OF STEREOSPECIFICALLY LABELED CARBOHYDRATES III
PREPARATION OF (3*S*)- AND (3*R*)-[3-$^2H_1$]PARATOSE

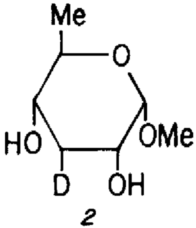
Raymond N. Russell and Hung-wen Liu*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455-0431 USA

Two forms of paratose, a 3,6-dideoxy-D-*ribo*-hexose, stereospecifically labeled with deuterium at 3*S* and 3*R* positions (compounds *1* and *2*), respectively, were synthesized.



1



2

Tetrahedron Lett. 30, 5733 (1989)

STRUCTURES OF THE TRANSITION STATES OF SOME INTERMOLECULAR HYDRIDE TRANSFER REACTIONS

Gerasimos J. Karabatsos* and Michael Tornaritis
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

The large k_H/k_D isotope effects, 7-9, obtained in the hydride transfer reactions of triarylmethanes with triarylmethyl cations support linear(I) rather than nonlinear(II) transition states.

$$\left[Ar_3C\text{---}H\text{---}CAr_3 \right]^+$$

I

$$Ar_3C\overset{\overset{H}{\wedge}}{\text{---}}CAr_3 \quad (+)$$

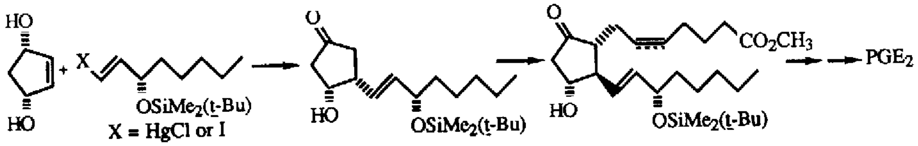
II

Tetrahedron Lett. 30, 5737 (1989)

ORGANOPALLADIUM APPROACHES TO PROSTAGLANDINS. 10. AN EFFICIENT SYNTHESIS OF PROSTAGLANDIN E_2 VIA VINYLPALLADATION OF 4-CYCLOPENTENE-1,3-DIOL

Richard C. Larock,* Fumihiko Kondo, Kris Narayanan, Leiv K. Sydnes, and Min-Fu H. Hsu
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Prostaglandin E_2 is efficiently synthesized by a sequence involving vinylpalladation and subsequent tin enolate alkylation.

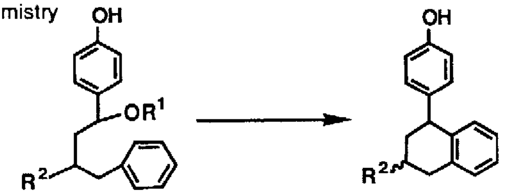


Tetrahedron Lett. 30, 5741 (1989)

CATIONIC CYCLIZATION REACTIONS INITIATED BY STABILIZED BENZYL CATIONS

Steven R. Angle* and Michael S. Louie Department of Chemistry
University of California, Riverside, California 92521

The *in situ* generation of stabilized benzyl cations and their subsequent use in cyclization reactions with a monosubstituted benzene, a furan and a β-keto ester terminators is described.

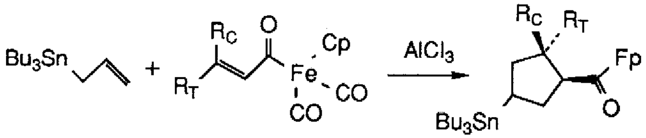


Tetrahedron Lett. 30, 5745 (1989)

STEREOSELECTIVITY IN THE REACTION OF ACYLIRON COMPLEXES WITH ALLYLSTANNANES

James W. Herndon* and Chao Wu; Department of Chemistry & Biochemistry;
University of Maryland; College Park, Maryland 20742

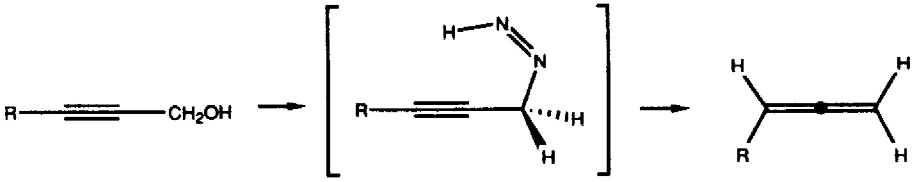
The reaction between acyliron complexes and allylstannanes was found to proceed with retention of stereochemistry about the double bond of the acyliron complex



Tetrahedron Lett. 30, 5747 (1989)

ALLENE SYNTHESIS FROM 2-ALKYN-1-OLS

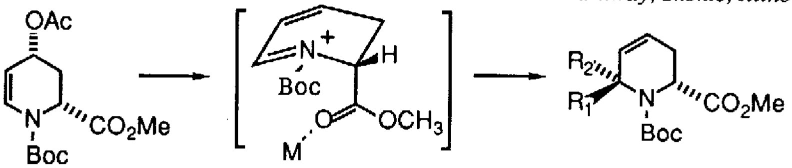
Andrew G. Myers,* Nathaniel S. Finney and Elaine Y. Kuo, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125



Tetrahedron Lett. 30,5751(1989)

Stereoselective Δ^4-Pipecolic Acid Synthesis *via* Alkylation of a Vinyl *N*-Boc-iminium Ion Derived from Baikiain

Gunnar J. Hanson and Mark A. Russell *G.D. Searle & Co. 4901 Searle Parkway, Skokie, Illinois 60077*



Tetrahedron Lett. 30, 5755 (1989)

ALKYLFLUOROLIPOPEPTIDES : UNE NOUVELLE CLASSE DE MOLECULES AMPHIPHILES NON IONIQUES

Claude SELVE*, Faouzia HAMDOUNE
Laboratoire d'Etudes des Solutions Organiques et Colloïdales Associé au CNRS.
UNIVERSITE DE NANCY I - Campus Scientifique Victor GRIGNARD.
B.P. 239 - 54506 - VANDOEUVRE-LES-NANCY - FRANCE

A synthesis of new alkylfluorolipopeptides type I (With R^F= C_6F_{13}, C_8F_{17} and A2= Ala, Sar) is described. The surfactant properties were shown by measurement of the lowering of surface tension of their aqueous solutions.

$$I = R^F\text{-}C_2H_4\text{-}C(O)\text{-Gly-A2-Gly-}NH_2$$

Tetrahedron Lett. 30, 5759 (1989)

UNUSUAL, LINEAR REGIOSELECTIVE HYDROFORMYLATION ON PtL_2Cl_2-IRON OR TIN CATALYSTS

Sylvain Mutez, Eric Paumard, André Mortreux and Francis Petit
Laboratoire de Chimie Organique Appliquée, UA CNRS 402, ENSC Lille
UST Lille Flandres Artois, BP 108, 59652 Villeneuve d'Ascq -France-

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{Sn or Fe anode}]{PtL_2Cl_2\ e^-} RCH_2CH_2CHO(n) + RCH(Me)CHO\ (b)$$

L_2 = DIOP or DPPB

n/b = 9 (R=Ph) and >50 (R = nC_4H_9)

Tetrahedron Lett. 30, 5763 (1989)

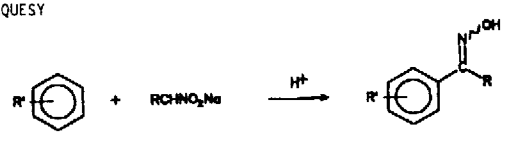
NITRONATE ANIONS AS PRECURSORS OF HYDROXYNITRILIUM IONS EQUIVALENTS IN ELECTROPHILIC AROMATIC SUBSTITUTION

A NOVEL ROUTE TO OXIMES

C. BERRIER, R. BRAHMI, H. CARREYRE, J.M. COUSTARD, J.C. JACQUESY

Laboratoire de Chimie XII, associé au CNRS
40, Avenue du Recteur Pineau - 86022 POITIERS
Cedex (France)

Oximes 3 are prepared from aromatics and nitronate salts in acidic conditions in moderate to fair yields.



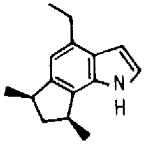
3

R': H, CH_3, OH, OCH_3
R : H, CH_3

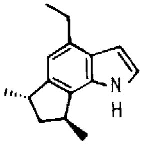
Tetrahedron Lett. 30, 5771 (1989)

DETERMINATION OF THE ABSOLUTE STRUCTURES OF CIS-TRIKENTRIN A AND TRANS-TRIKENTRIN A BY SYNTHESIS OF THEIR ENANTIOMERS

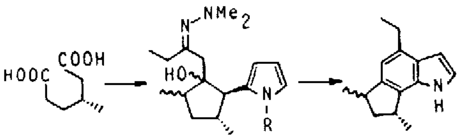
Hideaki Muratake and Mitsutaka Natsume*, Research Foundation Itsuu Laboratory
2-28-10 Tamagawa, Setagaya-ku, Tokyo 158, Japan



cis-trikentrin A



trans-trikentrin A

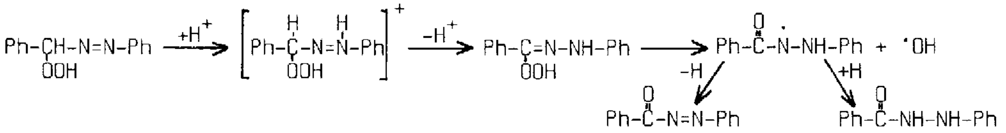


Tetrahedron Lett. 30, 5773 (1989)

ON THE STABILITY AND DECOMPOSITION OF PHENYL(PHENYLAZO)-METHYL HYDROPEROXIDE

Júlia Vágó and Júlia Paál-Lukács
Central Research Institute for Chemistry, P.O.Box 17, H-1025 Budapest, Hungary

The decomposition mechanism of the title compound in the presence of protons is completed by the following pathway:



$$\text{Ph-}\underset{\text{OOH}}{\text{CH}}\text{-N=N-Ph} \xrightarrow{+H^+} \left[\text{Ph-}\underset{\text{OOH}}{\overset{\text{H}}{\text{C}}}\text{-N=}\overset{\text{H}}{\text{N}}\text{-Ph}\right]^+ \xrightarrow{-H^+} \text{Ph-}\underset{\text{OOH}}{\text{C}}\text{=N-NH-Ph} \longrightarrow \text{Ph-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\dot{\text{N}}\text{-NH-Ph} + {}^{\cdot}\text{OH}$$

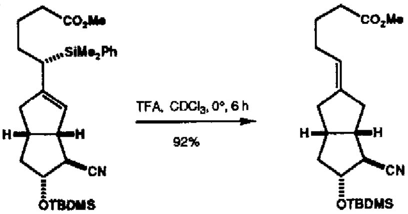
$$\xrightarrow{-H} \text{Ph-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-N=N-Ph} \qquad \xrightarrow{+H} \text{Ph-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-NH-Ph}$$

Tetrahedron Lett. 30, 5777 (1989)

THE STEREOSPECIFIC SYNTHESIS OF A CARBACYLIN ANALOGUE USING THE PROTODESILYLATION OF AN ALLYLSILANE

Ian Fleming* and Dick Higgins
(University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England)

Protodesilylation of the allylsilane **15** gives the E-carbacyclin **16**, with excellent (>96:4) control of the geometry of the double bond exocyclic to the ring.



15 **16**

Tetrahedron Lett. 30, 5781 (1989)

CYCLOPHOSPHAZENIC POLYPODANDS: A NEW CLASS OF POWERFUL METAL CATION COMPLEXING AGENTS AND PHASE-TRANSFER CATALYSTS

D.Landini[a], A. Maia [a]*, L. Corda[b], A.Maccioni and G. Podda[b]*

[a] Centro CNR and Dip. Chim. Org. Ind.le, Università, 20133 Milano, Italy; [b] Ist. Chim. Farm. Tossicolog. e Applicata, Università, 09100 Cagliari, Italy.

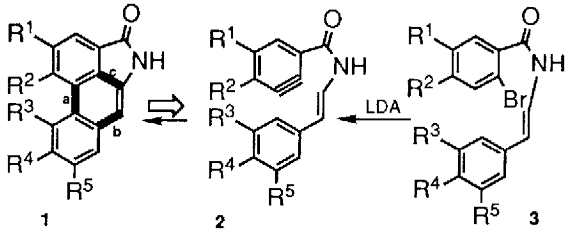
$\{NP[-OCH_2(CH_2OCH_2)_n-CH_2OR]_2\}_3$ **1a** $n = 2$ $R = -C_4H_9$

1b $n = 3$ $R = -C_{12}H_{25}$; **1c** $n = 4$ $R = -C_6H_4-C_8H_{17}$-p

Tetrahedron Lett. 30, 5785 (1989)

INTRAMOLECULAR ARYNE CYCLOADDITION APPROACH TO ARISTOLACTAMS.

J.C. Estévez, R.J. Estévez, E. Guitián, M.C. Villaverde and L. Castedo.



A new procedure for the total synthesis of aristolactams, based on the intramolecular Diels-Alder reaction betwen the styrene and aryne components, is described

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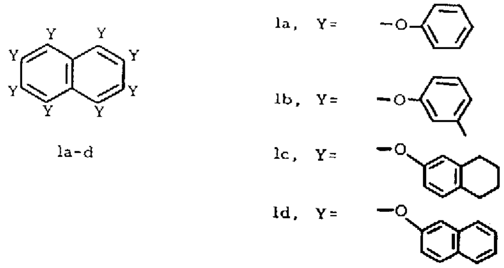
Tetrahedron Lett. 30, 5787 (1989)

OCTAKIS(ARYLOXY)NAPHTHALENES: A NEW CLASS OF HOST MOLECULE.

By Andrew A. Freer, David D. MacNicol, Paul R. Mallinson, and Colin D. Robertson.*
Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland.

The first octakis(aryloxy)naphthalenes, 1a-d, have been synthesised, and X-ray analyses of 1b and the acetone inclusion compound of 1d are described.

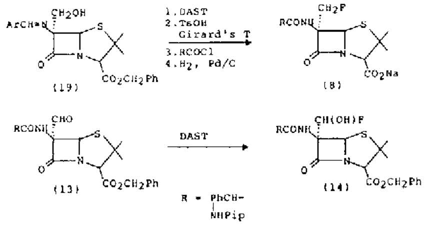


Tetrahedron Lett. 30, 5791 (1989)

6α-(Fluoroalkyl) Penicillins

Angela W. Guest*, Peter H. Milner and Robert Southgate
Beecham Pharmaceuticals, Research Division, Brockham Park, Betchworth, Surrey, RH3 7AJ, England.

Fluorination of the protected 6α-(hydroxymethyl) amine (19), deprotection and acylation afforded the fluoromethyl penicillin (8). Similar reaction with the 6α-formyl penam (13) proceeded only to the intermediate fluorohydrin (14).

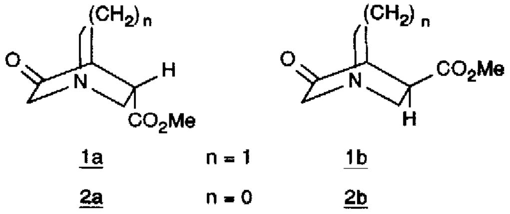


Tetrahedron Lett. 30, 5795 (1989)

SYNTHESIS OF 3,5-DISUBSTITUTED-1--AZABICYCLIC SYSTEMS: INTERMEDIATES FOR NOVEL MUSCARINIC LIGANDS.

Roger J. Snow and Leslie J. Street
Merck Sharp and Dohme Research Laboratories,
Terlings Park, Eastwick Road, Harlow, Essex,
CM20 2QR.

Stereoselective synthesis of each diastereoisomer of the novel 3,5,-disubstituted-1-azabicyclics (1) and (2), useful for the preparation of muscarinic ligands, are reported.

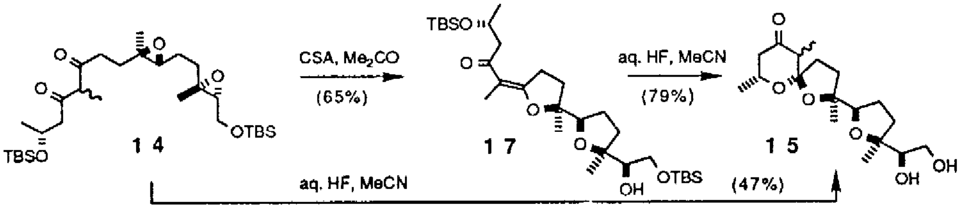


Tetrahedron Lett. 30, 5799 (1989)

STUDIES IN POLYETHER SYNTHESIS: CONTROLLED BISEPOXIDE CYCLISATION USING A β-DIKETONE GROUP.

Ian Paterson* and Peter A. Craw, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

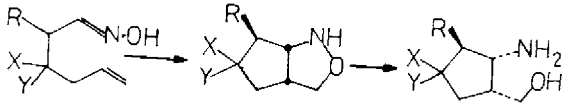
Cyclisation of bisepoxide **14** with participation of the β-diketone group gives the tricyclic polyether segment **15**.



Tetrahedron Lett. 30, 5803 (1989)

STEREOSPECIFIC SYNTHESIS OF FUNCTIONALIZED CYCLOPENTANES.

Alfred Hassner*, Rakesh Maurya
Department of Chemistry
Bar-Ilan University
Ramat-Gan 52100 Israel

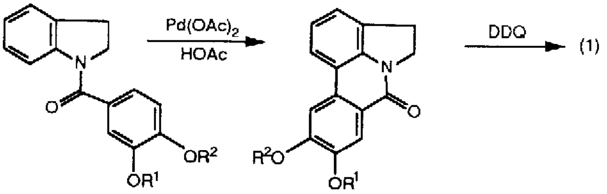


Thermal intramolecular oxime olefin cycloadditions (IOOC) lead stereoselectively to 5-or 6-membered carbocycles fused to an isoxazolidine ring, providing a useful entry in particular to stereospecifically functionalized cyclopentanes.

Tetrahedron Lett. 30, 5807 (1989)

A DIRECT SYNTHESIS OF PYRROLOPHENANTHRIDONE ALKALOIDS

David St C. Black,* P.A. Keller, N. Kumar
School of Chemistry, The University of New South Wales, Kensington, NSW. 2033. Australia



Pyrrolophenanthridone alkaloids were easily synthesized by palladium acetate catalyzed arylation of N-acylindolines (5a-c) followed by dehydrogenation.