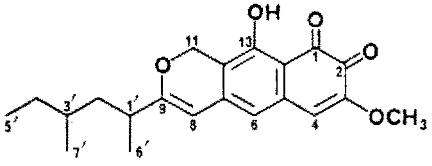
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30,3483(1989)

OBIONIN A: A NEW POLYKETIDE METABOLITE FROM THE MARINE FUNGUS LEPTOSPHAERIA OBIONES

Gregory K. Poch and James B. Gloer*
Department of Chemistry, University of Iowa
Iowa City, Iowa, 52242

Obionin A (1) has been isolated from liquid cultures of the marine fungus Leptosphaeria obiones by chromatography on Sephadex LH-20. Its structure was assigned primarily by selective INEPT and other NMR techniques.



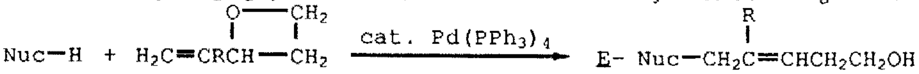
1

Tetrahedron Lett. 30,3487(1989)

HIGHLY STEREOSELECTIVE SYNTHESIS OF DI- AND TRISUBSTITUTED HOMOALLYLIC ALCOHOLS VIA PALLADIUM(O)-CATALYZED NUCLEOPHILIC OPENING OF VINYLIC OXETANES

Richard C. Larock and Sandra K. Stolz-Dunn
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Vinylic oxetanes react in an S_N2' manner with a variety of potential nucleophiles in the presence of catalytic amounts of $Pd(PPh_3)_4$ to afford the corresponding highly functionalized, di- and trisubstituted homoallylic alcohols with high stereoselectivity.



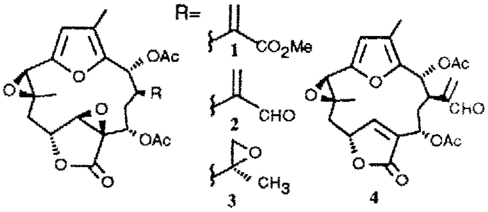
$$\mathrm{Nuc{-}H} + \mathrm{H_2C{=}CR}\overset{\mathrm{O}}{\mathrm{CH}}{-}\overset{\mathrm{CH_2}}{\mathrm{CH_2}} \xrightarrow{\text{cat. Pd(PPh}_3)_4} \mathrm{E\text{-}\ Nuc{-}CH_2}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}CHCH_2CH_2OH}$$

Tetrahedron Lett. 30,3491(1989)

CYTOTOXIC CEMBRANOIDS FROM THE GORGONIAN PSEUDOPTEROGORGIA BIPINNATA

Amy. E. Wright, Neal S. Burres and Gayle K. Schulte
Division of Biomedical Marine Research, HBOI, Ft. Pierce, FL. 34946
Chemical Instrumentation Center, Yale University, New Haven , CT.

Four new cytotoxic cembranoids, 1-4, have been isolated from the gorgonian coral Pseudopterogorgia bipinnata. Their structures have been determined through a combination of spectroscopic and x-ray crystallographic methods.

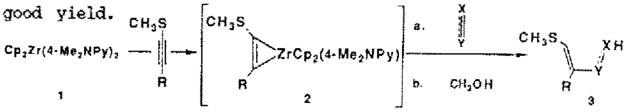


Tetrahedron Lett. 30,3495(1989)

ON THE GENERATION OF STABILIZED LOW-VALENT METALLOCENE DERIVATIVES. THE DIRECT SYNTHESIS AND REDUCTIVE COUPLING REACTIONS OF 1-METHYLTHIOALKYNE-ZIRCONOCENE COMPLEXES.

Bradford C. VanWagenen and Tom Livinghouse*
Department of Chemistry, Montana State University, Bozeman, MT 59717

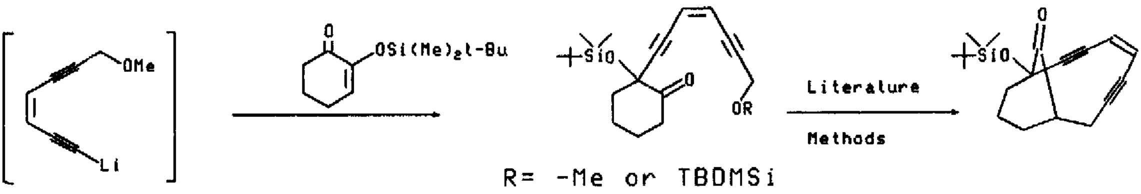
Zirconacyclopropenes derived from 1-methylthioalkynes (e.g., 2a,b) undergo efficient coupling reactions with alkynes, carbonyl compounds, and nitriles to give the corresponding adducts 3 in good yield.



Tetrahedron Lett. 30, 3499 (1989)

CONVERGENT APPROACH TO INTERMEDIATES USED FOR THE SYNTHESIS OF THE ENEDIYNE STRUCTURE OF THE ESPERAMICINS AND CALICHEAMICINS

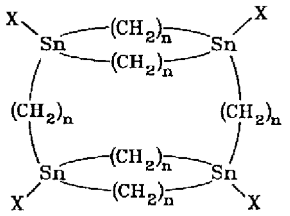
J.F.Kadow*, M.G.Saulnier, M.M.Tun, D.R.Langley, and D.M. Vyas. Bristol-Myers Company, Wallingford, CT. 06492-7660.



Tetrahedron Lett. 30, 3501 (1989)

Macrocycles Containing Tin. Ditopic, Tricyclic, Lewis Acidic Hosts with Four Binding Sites

Michael T. Blanda and Martin Newcomb*, Department of Chemistry, Texas A&M University, College Station, Texas, 77843, USA



Preparation of the title class of anion-binding hosts is described. The ditopic host shown ($n = 5$, X = Cl) binds one, and only one, chloride anion strongly in $CDCl_3$.

Tetrahedron Lett. 30, 3505 (1989)

NUCLEOPHILIC ATTACK ON 4,6-DIMETHOXY-2-PYRONES; DISCOVERY OF A REMARKABLY FACILE REARRANGEMENT OF THE PYRONES

Jin K. Cha*, Thomas M. Harris*, John A. Ray, and Hemalatha Venkataraman
Department of Chemistry, Vanderbilt University, Nashville, TN 37235, U.S.A.

A rapid scrambling reaction has been found between 4,6-dimethoxy-3-methyl-2-pyrone and the corresponding 5-methyl isomer.

Tetrahedron Lett. 30, 3509 (1989)

THE SCOPE AND MECHANISM OF REARRANGEMENT OF 4,6-DIALKOXY-2-PYRONES

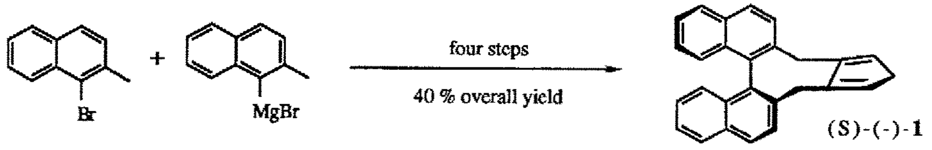
Hemalatha Venkataraman and Jin K. Cha*
Department of Chemistry, Vanderbilt University, Nashville, TN 37235, U.S.A.

The scope and mechanism of a rapid interconversion between 4,6-dialkoxy-3-alkyl-2-pyrones and their corresponding 5-alkyl isomers is described. The preponderance of the latter over the former is rationalized by the stereoelectronic conformational preference of the C-4 alkoxy group.

Tetrahedron Lett. 30,3513(1989)

BINAPHTHYLCYCLOPENTADIENE: A C_2-SYMMETRIC ANNULATED CYCLOPENTADIENYL LIGAND WITH AXIAL CHIRALITY

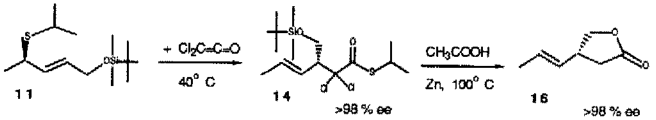
Steven L. Colletti and Ronald L. Halterman*
Department of Chemistry, Metcalf Center for Science and Engineering, Boston University, Boston, MA 02215



Tetrahedron Lett. 30,3517(1989)

STEREOSELECTIVE KETENE-CLAISEN REARRANGEMENT OF CHIRAL ALLYLTHIOETHERS

R. Oehrlein, R. Jeschke, B. Ernst, D. Bellus*
R&D Plant Protection and Central Research Laboratories, CIBA-GEIGY AG, CH-4002 Basel, Switzerland

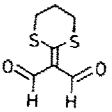


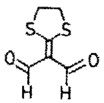
The title reaction, e.g. 11 to 16, proceeds chemo- and stereoselectively (C,S to C,C chirality-transfer).

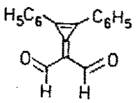
Tetrahedron Lett. 30,3521(1989)

SYNTHESIS AND STRUCTURE OF NOVEL ALKYLIDENEMALONALDEHYDES: 2-(DIFORMYLMETHYLENE)-1,3-DITHIANE AND -1,3-DITHIOLANE AS WELL AS (2,3-DIPHENYLCYCLOPROPEN-1-YLIDENE)-MALONALDEHYDE

C. Reichardt[x], B.-V. Herget, M. Schulz,
W. Massa, S. Peschel, Fachbereich Chemie der
Universität, Hans-Meerwein-Straße, D-3550 Marburg


7

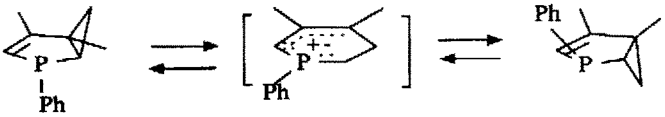

8


4

Tetrahedron Lett. 30,3525(1989)

Reactivity of Cyclopentenyl-Anion Analogous Heterocycles: Synthesis and 1,5-Electrocyclization of Homophosphole.

Dirk Oebels and Frank-Gerrit Klärner* Fakultät für Chemie der Ruhr Universität
Postfach 10 21 48, D-4630 Bochum 1 (FRG)



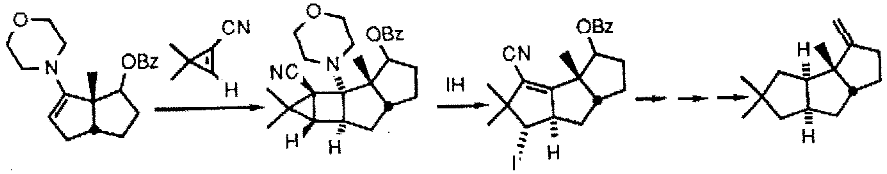
Racemization of optically active homophosphole

CYCLOPROPENIC TOTAL SYNTHESIS OF (±)-HIRSUTENE, A NATURAL LINEAR TRIQUINANE.

Tetrahedron Lett. 30, 3529 (1989)

Michel FRANCK-NEUMANN, Michel MIESCH, Eric LACROIX

Laboratoire de Chimie Organique Synthétique URA CNRS n° DO466, Institut de Chimie,
Université Louis Pasteur, 1, rue Blaise Pascal 67008 - STRASBOURG (France)

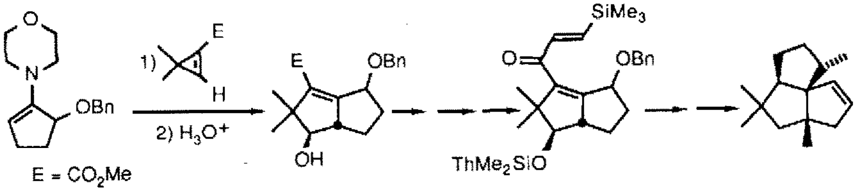


CYCLOPROPENIC TOTAL SYNTHESIS OF (±)-SILPHINENE, A NATURAL ANGULAR TRIQUINANE.

Tetrahedron Lett. 30, 3533 (1989)

Michel FRANCK-NEUMANN, Michel MIESCH, Eric LACROIX

Laboratoire de Chimie Organique Synthétique URA CNRS n° DO466, Institut de Chimie,
Université Louis Pasteur, 1, rue Blaise Pascal 67008 - STRASBOURG (France)

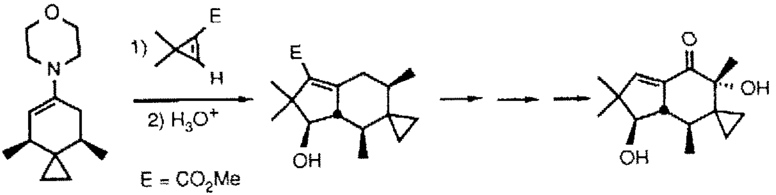


CYCLOPROPENIC SYNTHESIS OF ILLUDINE M DERIVATIVES

Tetrahedron Lett. 30, 3537 (1989)

Michel FRANCK-NEUMANN, Michel MIESCH, Francis BARTH

Laboratoire de Chimie Organique Synthétique URA CNRS n° DO466, Institut de Chimie,
Université Louis Pasteur, 1, rue Blaise Pascal 67008 - STRASBOURG (France)



2,3 - dihydro
illudine M

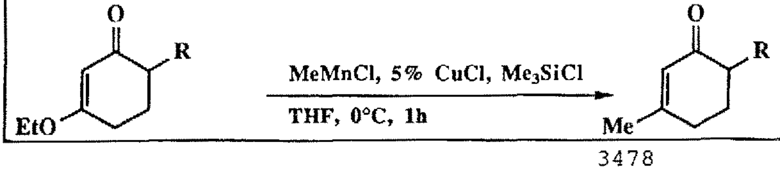
ORGANOMANGANESE (II) REAGENTS XVI : COPPER-CATALYZED 1,4-ADDITION OF ORGANOMANGANESE CHLORIDES TO CONJUGATED ENONES

Tetrahedron Lett. 30, 3541 (1989)

Gérard CAHIEZ * and Mouad ALAMI

Laboratoire de Chimie des Organoéléments, tour 44-45; Université P. & M. Curie, 4 Place Jussieu F-75252 PARIS Cédex 05

Copper-catalyzed conjugate addition of organomanganese chlorides to conjugated enones in THF, at 0°C, leads to the 1,4 addition products in high yields. The scope of the reaction is very large and the results are generally better than those obtained from organomagnesium compounds in the presence of a copper salt as well as from organocopper or cuprate reagents. Furthermore organomanganese chlorides are indisputably cheaper and more stable than these latter.



R= H : 80%
R= CH_2=$CHCH_2$: 88%
(e.g., for R= H,
only 31% from Me_2CuLi-Me_3SiCl)

Tetrahedron Lett. 30, 3545 (1989)

ORGANOMANGANESE (II) REAGENTS XVII . PREPARATION OF ORGANOMANGANESE BROMIDE COMPOUNDS IN ETHER : AN EFFICIENT AND ECONOMIC ALTERNATIVE TO ORGANOMANGANESE IODIDE COMPOUNDS FOR SYNTHETIC APPLICATIONS

Gérard CAHIEZ * and Blandine LABOUE
Laboratoire de Chimie des Organoéléments, tour 44-45; Université P. & M. Curie, 4 Place Jussieu F-75252 PARIS Cédex 05

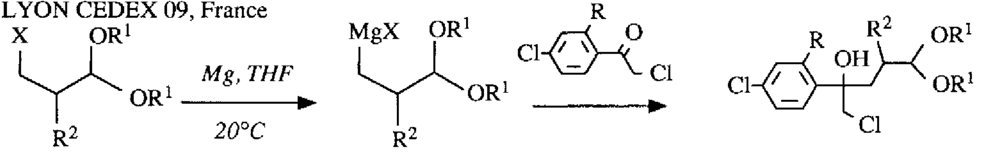
Organomanganese bromide reagents have been quantitatively prepared in ether from organomagnesium (or organolithium) compounds and manganese bromide. The preparation must be performed in the presence of lithium bromide which allows to dissolve the manganese bromide in ether. Organomanganese bromide reagents react quite similarly to their iodide analogous. For synthetic applications they are equivalent or sometimes more efficient than these latter and above all they are cheaper.

$$\mathrm{RMgBr} \xrightarrow[\text{Ether, 20°C}]{\text{1/ LiBr 2/ MnBr}_2} \mathrm{RMnBr} \xrightarrow[\text{0°C to 20°C, 1h 30}]{\text{R'COCl}} \mathrm{RCOR'} \quad \text{80 to 98\%}$$

Tetrahedron Lett. 30, 3547 (1989)

EXTENDED SCOPE OF THE GRIGNARD REACTION OF β-HALOACETALS. USE OF ACYCLIC ACETALS.

A. GREINER
Rhône Poulenc Agrochimie, Centre de Recherches de la Dargoire, BP 9163
69263-LYON CEDEX 09, France



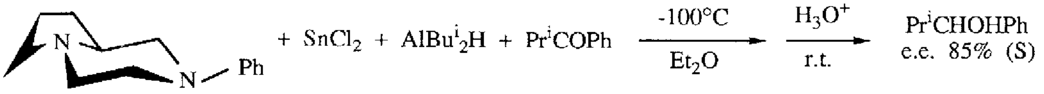
R^1:cyclic or acyclic, X:Bromine or Chlorine, R^2:H or Alkyl

Tetrahedron Lett. 30, 3551 (1989)

CHIRAL LIGANDS CONTAINING HETEROATOMS. III. ENANTIOSELECTIVE KETONE REDUCTIONS USING TIN(II) ORGANOMETALLIC SYSTEMS FROM CHIRAL PIPERAZINES.

Massimo Falorni*, Luciano Lardicci, Giampaolo Giacomelli*, and Mauro Marchetti - *Dipartimento di Chimica e Chim. Ind. dell'Università, I-56100 Pisa, Dipartimento di Chimica dell'Università, I-07100 Sassari* ***(Italy).***

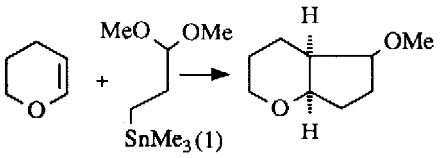
Asymmetric reductions of ketones *via* an hydride tin(II) system, complexed with new chiral diamines.



Tetrahedron Lett. 30, 3555 (1989)

THE REACTION OF BIFUNCTIONAL ANNULATING REAGENTS WITH CYCLIC ENOL ETHERS: A NEW ROUTE TO FUSED CYCLIC ETHERS.

Thomas V.Lee* and Karen L.Ellis
(School of Chemistry, The University, Bristol, England)



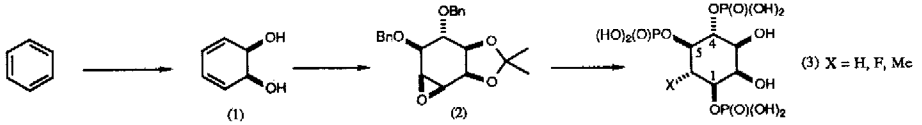
The stannane (1) reacts with cyclic ethers to give a novel synthesis of fused cyclic ethers.

Tetrahedron Lett. 30, 3557 (1989)

Microbial Oxidation in Synthesis: Preparation of 6-Deoxy Cyclitol Analogues of *myo*-Inositol 1,4,5-Trisphosphate from Benzene

Steven V. Ley*, Margarita Parra, Alison J. Redgrave, Francine Sternfeld and Angel Vidal.
Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK.

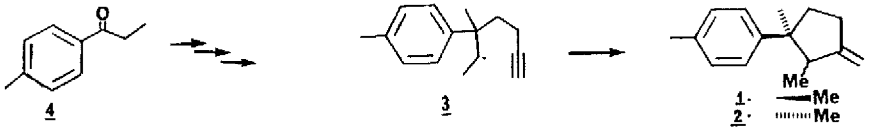
The novel 6-deoxy, 6-deoxy-6-fluoro and 6-deoxy-6-methyl myo-inositol 1,4,5-trisphosphate derivatives (3, X = H, F, Me) were derived from benzene via microbial oxidation to cis-1,2-dihydroxycyclohexa-3,5-diene (1) and conversion through a key epoxyacetonide (2).



Tetrahedron Lett. 30, 3561 (1989)

TOTAL SYNTHESIS OF (±)-LAURENE AND EPILAURENE BY RADICAL CYCLISATION REACTION

A. Srikrishna and G. Sunderbabu
Department of Organic Chemistry, Indian Institue of Science
Bangalore - 560 012 INDIA.

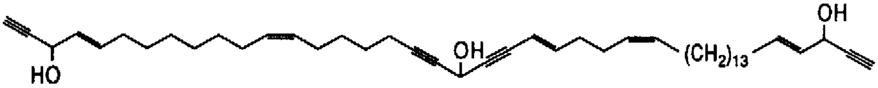


Tetrahedron Lett. 30, 3563 (1989)

HIGH MOLECULAR WEIGHT POLYACETYLENES FROM *PETROSIA FICIFORMIS*: FURTHER STRUCTURAL ANALYSIS AND BIOLOGICAL ACTIVITY

G. Cimino, A. De Giulio, S. De Rosa and V. Di Marzo*
Istituto per la Chimica di Molecole di Interesse Biologico, CNR, via Toiano 6, 80072, Arco Felice, Napoli, Italy

Four linear C-46 polyacetylenes, petroformynes 1-4 (1-4), previously only partially characterized from the marine sponge *Petrosia ficiformis*, have been studied with the aim of obtaining further structural details and of gaining preliminary biological activities.



Petroformyne-1 (1)

Tetrahedron Lett. 30, 3567 (1989)

ULTRASOUND - PROMOTED COUPLING OF HETEROARYL HALIDES IN THE PRESENCE OF LITHIUM WIRE. NOVEL FORMATION OF ISOMERIC BIPYRIDINES IN A WURTZ - TYPE REACTION

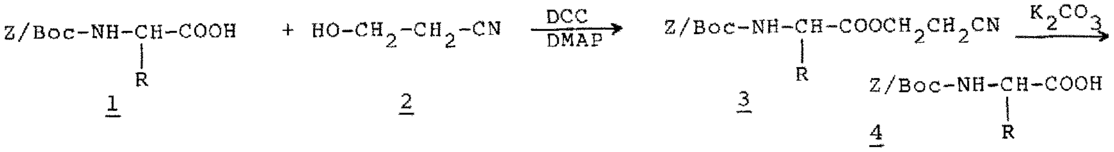
Alan G. Osborne*, Kathryn J. Glass and Miriam L. Staley
Department of Chemistry, City University, London EC1V OHB

Ultrasonic irradiations of bromopyridines in THF solution in the presence of Li wire are described. The products have been identified by ^{13}C NMR.

Tetrahedron Lett. 30,3569(1989)

3-HYDROXYPROPIONITRILE: A NEW REAGENT FOR CARBOXYL PROTECTION IN PEPTIDE SYNTHESIS

P.K.Misra, S.A.N.Hashmi, W.Haq and S.B.Katti*
Division of Biopolymers, Central Drug Research Institute, Lucknow 226001, India.



$$\underset{\underline{1}}{\text{Z/Boc-NH-}\underset{\substack{|\\ \text{R}}}{\text{CH}}\text{-COOH}} + \underset{\underline{2}}{\text{HO-CH}_2\text{-CH}_2\text{-CN}} \xrightarrow[\text{DMAP}]{\text{DCC}} \underset{\underline{3}}{\text{Z/Boc-NH-}\underset{\substack{|\\ \text{R}}}{\text{CH}}\text{-COOCH}_2\text{CH}_2\text{CN}} \xrightarrow{K_2CO_3} \underset{\underline{4}}{\text{Z/Boc-NH-}\underset{\substack{|\\ \text{R}}}{\text{CH}}\text{-COOH}}$$

Tetrahedron Lett. 30,3573(1989)

CARBON SILICON BOND CLEAVAGE IN THE OXIDATION OF BENZYLIC SILANES BY CERIUM(IV) AMMONIUM NITRATE

E. Baciocchi[a*], T. Del Giacco[b], C. Rol[b], and G.V. Sebastiani[b], Dip. di Chimica, Universitâ di Roma[a] and Perugia[b], Italy

Benzyltrimethylsilanes react with cerium(IV) ammonium nitrate in AcOH to give products of C-Si bond cleavage (benzyl nitrate and acetate), under very mild conditions and in quantitative yields. The reaction rate is very sensitive to the nature of the ring substituents ($\rho = 5.4$), which clearly suggests the operation of an one electron transfer mechanism.

Tetrahedron Lett. 30,3577(1989)

SYNTHESIS OF 2,8-DIDEHYDRO-9-NORADAMANTANONE

M. Šindler-Kulyk, Z. Majerski, D. Pavlović and K. Mlinarić-Majerski*
Ruđer Bošković Institute, Zagreb, Yugoslavia

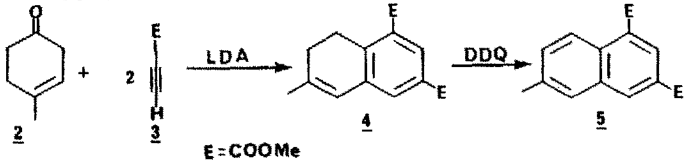
3 4

2,8-Didehydro-9-noradamantanone (4) has been synthesized involving oxa-di-π-methane photo-rearrangement as a key step.

Tetrahedron Lett. 30,3579(1989)

A SIMPLE, ONE POT, REGIOSPECIFIC-1,3-DICARBOXY BENZANNULATION OF ACTIVE ACYL SYSTEMS.

A. Srikrishna* and G. Veera Raghava Sharma
Department of Organic Chemistry, Indian Institute of Science
Bangalore - 560 012 INDIA.

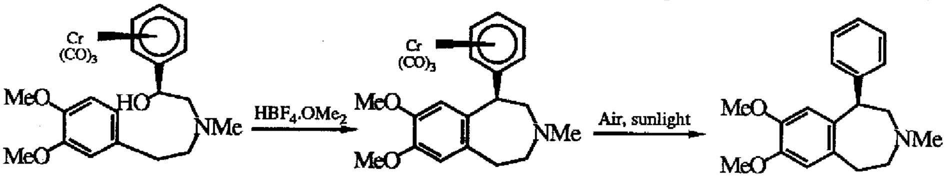


E=COOMe

Tetrahedron Lett. 30, 3581 (1989)

ENANTIOSPECIFIC SYNTHESIS OF (+)-(R)-1-PHENYL-3-METHYL-1,2,4,5-TETRAHYDROBENZ[d]AZEPINE FROM (+)-(S)-N-METHYL-1-PHENYL ETHANOLAMINE.

Steven J. Coote[a], Stephen G.Davies[*a], David Middlemiss[b] and Alan Naylor[b]
[a]The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, UK; [b]Glaxo Group Research, Ware, Herts SG12 0DJ, UK.

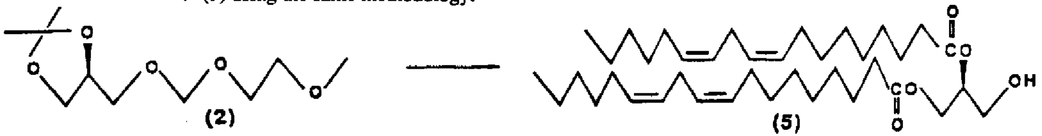


Tetrahedron Lett. 30, 3585 (1989)

SYNTHESIS OF OPTICALLY ACTIVE POLYUNSATURATED DIACYLGLYCEROLS

Andrzej A. Duralski, Paul J.R. Spooner and Anthony Watts*.
Department of Biochemistry, University of Oxford, South Parks Road, Oxford,OX1 3QU, UK.

A stereospecific procedure for the synthesis of optically active polyunsaturated diacylglycerols such as 1,2-dilinoleoyl-*sn*-glycerol (5) from 1,2-isopropylidene-3-methoxyethoxymethyl-sn-glycerol (2) is reported. 1-Methoxyethoxymethyl-2,3-isopropylidene-*sn*-glycerol is converted into the enantiomer of (5) using the same methodology.



(2) (5)

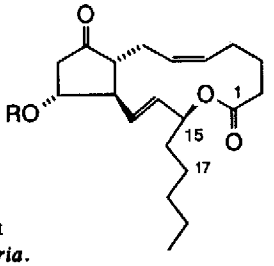
Tetrahedron Lett. 30, 3589 (1989)

NATURALLY OCCURRING PROSTAGLANDIN-1,15-LACTONES

G. Cimino^, A. Spinella^ and G. Sodano°

^Istituto per la Chimica di Molecole di Interesse Biologico, CNR
Via Toiano, 6 - 80072 Arco Felice (NA) - Italy
°Istituto di Chimica, Università della Basilicata
Via N. Sauro 85, 85100 Potenza - Italy

Prostaglandin-1,15-lactones (1-3) have been isolated for the first time from a natural source, the nudibranch mollusc *Tethys fimbria*.



1 ; R = Ac , Δ^{17} *Z*
2 ; R = H
3 ; R = H , Δ^{17} *Z*