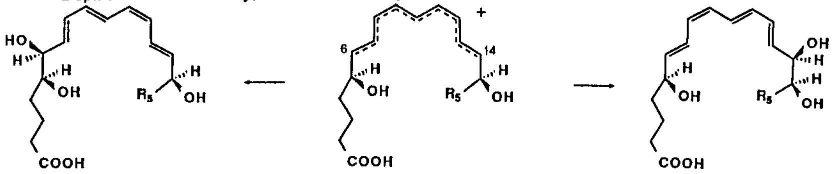
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 27,5173(1986)

A STEREOSELECTIVE AND PRACTICAL SYNTHESIS OF 5,6(*S*,*S*)-EPOXY-15(*S*)-HYDROXY-7(*E*),9(*E*),11(*Z*),13(*E*)-EICOSATETRAENOIC ACID (4), POSSIBLE PRECURSOR OF THE LIPOXINS

E. J. Corey and Mukund M. Mehrotra
Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138



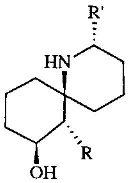
LIPOXIN BIOSYNTHESIS

Tetrahedron Lett. 27,5177(1986)

A STEREOSELECTIVE SYNTHESIS OF THE AZASPIROUNDECANE RING SYSTEM OF (-)-HISTRIONICOTOXIN

Jeffrey D. Winkler*, Paul M. Hershberger and James P. Springer
Department of Chemistry, The University of Chicago,
Chicago, Illinois, 60637

The first stereoselective synthesis of the (-)-histrionicotoxin ring system is described.



Tetrahedron Lett. 27,5181(1986)

REACTIONS OF BrCl WITH ALKYL RADICALS.

P. S. Skell*, H. N. Baxter, III, J. M. Tanko*
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

$$\mathrm{RH + BrCl \Longrightarrow RBr + RCl}$$

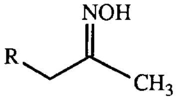
Photoinitiated halogenations of alkanes with BrCl occur readily, forming both alkylbromides and chlorides in ratios of 1-15:1. Depending on the reactivity of RH, both Cl• and Br• H-abstraction selectivities can be observed.

Tetrahedron Lett. 27,5185(1986)

KINETICS OF UNCATALYZED ISOMERIZATION OF ALIPHATIC KETOXIMES, Robert E. Gawley* and Teresa Garcia-Pons,

Department of Chemistry,University of Miami, Coral Gables, Florida 33124

The kinetics of uncatalyzed isomerization of oximes **1a-c** and the activation parameters for **1a** are reported.



1

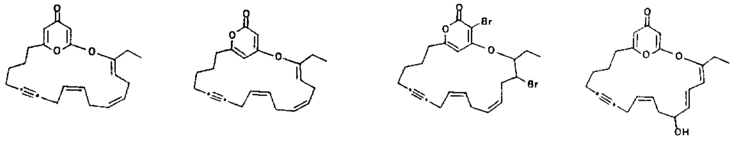
(a) R = $CH_2{=}CHCH_2$
(b) R = $CH_2{=}C[Si(C_2H_5)_3]CH_2$
(c) R = $(CH_3)_2C{=}CHCH_2$

Tetrahedron Lett.27,5189(1986)

NEW MACROCYCLIC ALPHA AND GAMMA-PYRONES FROM THE MARINE RED ALGA PHACELOCARPUS LABILLARDIERI.

J. Shin, V. J. Paul and W. Fenical*, Institute of Marine Resources, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093

The structures of 4 new macrocyclic alpha and gamma-pyrones are described as:

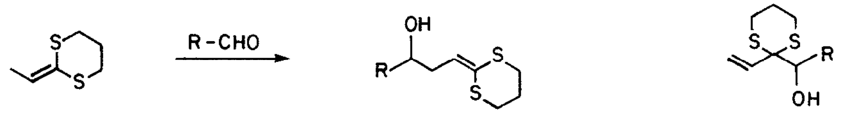


Tetrahedron Lett.27,5193(1986)

REGIOSELECTIVE CONTROL OF ALLYL ANIONS WITH CADMIUM CHLORIDE: α vs. γ CONDENSATION WITH ALDEHYDES.

Lei Bo and Alex G. Fallis*
Department of Chemistry, Memorial University of Newfoundland, St. John's, Nfld., Canada A1B 3X7

The addition of cadmium chloride to lithium allyl anions such as 2-ethylidene-1,3-dithiane resulted in preferential condensation at the γ position.

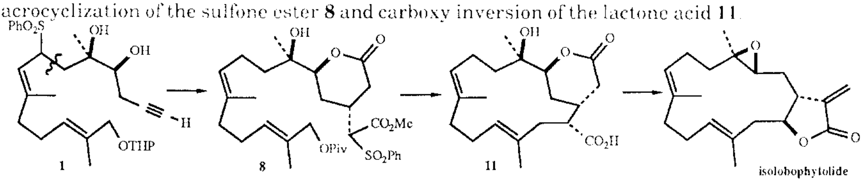


Tetrahedron Lett.27,5197(1986)

STEREOSELECTIVE TOTAL SYNTHESIS OF (±)-ISOLOBOPHYTOLIDE, A MARINE CEMBRANOLIDE NATURAL PRODUCT

James A. Marshall* and Robert C. Andrews
Department of Chemistry, University of South Carolina, Columbia, SC 29208 USA

The synthesis of (±)-isolobophytolide has been achieved from the geraniol-derived coupling product **1**. Key steps include macrocyclization of the sulfone ester **8** and carboxy inversion of the lactone acid **11**.

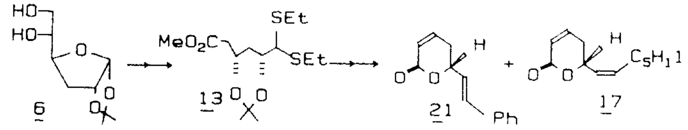


Tetrahedron Lett.27,5201(1986)

SYNTHESES OF ARGENTILACTONE (17) and Goniothalamin (21)

George Just and Brian O'Connor
Department of Chemistry, McGill University, Montreal, Canada H3A 2K6

Syntheses of (-)-(5R)-argentilactone 17 and (+)-(5R)-goniothalamin 21 are described starting from diol 6.

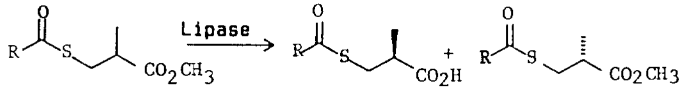


Tetrahedron Lett.27,5203(1986)

BIFUNCTIONAL CHIRAL SYNTHONS VIA BIOCHEMICAL METHODS. VIII. OPTICALLY-ACTIVE 3-ARYLTHIO-2-METHYLPROPIONIC ACIDS.

Qu-Ming Gu, D. R. Reddy and C. J. Sih*
School of Pharmacy, University of Wisconsin, Madison, WI 53706 U.S.A.

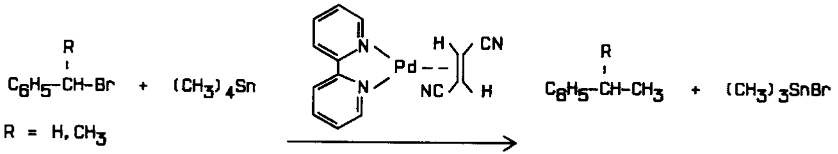
Optically-active 3-arylthio-2-methylpropionic acids have been prepared via lipase-catalyzed enantiospecific hydrolysis of their corresponding esters.



Tetrahedron Lett.27,5207(1986)

Alkylation of Aralkyl Bromides with Tetra Alkyl Tin Compounds in Presence of (2,2'-Bipyridine) Fumaronitrile Palladium(0)

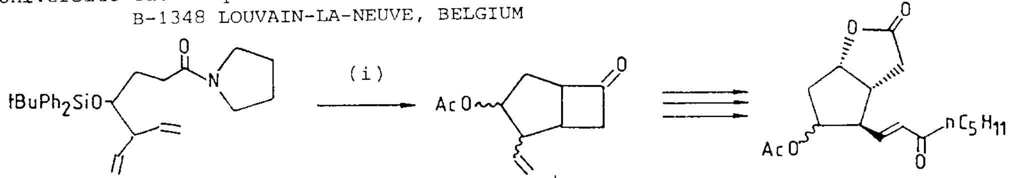
Reiner Sustmann*, Jürgen Lau and Manfred Zipp
Institut für organische Chemie der Universität Essen D-4300 Essen1



Tetrahedron Lett.27,5211(1986)

INTRAMOLECULAR CYCLOADDITIONS OF KETENIMINIUM SALTS. A NOVEL APPROACH TOWARD PROSTAGLANDINS

Léon Ghosez*, Istvan Marko, Anne-Marie Hesbain-Frisque
Laboratoire de Chimie Organique de Synthèse
Université Catholique de Louvain, Place L. Pasteur, 1
B-1348 LOUVAIN-LA-NEUVE, BELGIUM



(i) $(CF_3SO_2)_2O$, Collidine, CH_2Cl_2, Δ ; $Bu_4N^+F^-$, 20°C; CH_3COCl, pyridine

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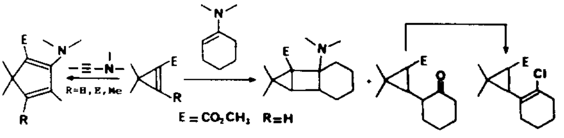
Tetrahedron Lett.27,5215(1986)

REACTIONS OF YNAMINES AND ENAMINES WITH ELECTROPHILIC CYCLOPROPENE ESTERS. BICYCLO (2.1.0) PENTANE ADDUCTS, SYNTHESIS OF HALOPYRETHROIDS.

M. FRANCK-NEUMANN, M. MIESCH, H. KEMPF, UA CNRS n°466, Institut de Chimie de l'Université Louis Pasteur, 1, rue Blaise Pascal 67008 - Strasbourg (France).

Electrophilic cyclopropene esters react with ynamines to cyclopentadiene enaminoesters. In contrast, with enamines they show a different reactivity than cyclopropenones, allowing the synthesis of cyclopropanic derivatives, here for instance halopyrethroids.



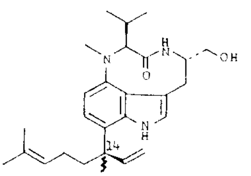
Tetrahedron Lett. 27, 5219 (1986)

ABSOLUTE COFIGURATION OF LYNGBYATOXIN A (TELEOCIDIN A-1) AND TELEOCIDIN A-2

Shin-ichiro Sakai,*,[a] Yukio Hitotsuyanagi,[a] Norio Aimi,[a]
Hirota Fujiki,[b] Masami Suganuma,[b] Takashi Sugimura,[b]
Yasuyuki Endo,[c] Koichi Shudo[c]

Faculty of Pharmaceutical Sciences, Chiba University,[a] 1-33, Yayoi, Chiba 260, Japan, National Cancer Center Research Institute,[b] Chuo, Tokyo 104, Japan and Faculty of Pharmaceutical Sciences, University of Tokyo,[c] Hongo, Bunkyo, Tokyo 113, Japan

The absolute configuration of the titled toxins has been determined by chemical method.



14R: lyngbyatoxin A
14S: teleocidin A-2

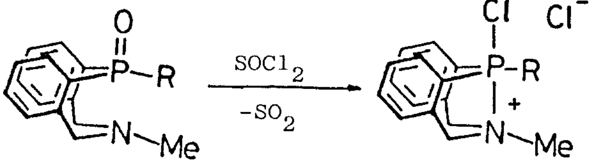
Tetrahedron Lett. 27, 5221 (1986)

FORMATION OF AMMONIOPHOSPHORANES BY TRANSANNULAR INTERACTION IN DIBENZ[c,f][1,5]AZAPHOSPHOCINE SYSTEM

Kin-ya Akiba,* Keiji Okada, and Katsuo Ohkata

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima 730, Japan

Formation of novel bicyclic phosphoranes (1a' and 3') were verified on the basis of the NMR (^1H and ^{31}P) parameters.



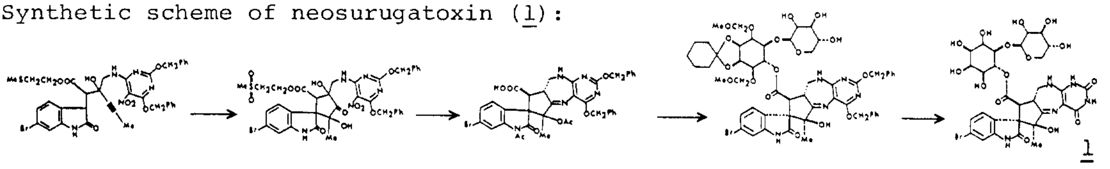
	1a'	3'
R	C_6H_5	Me

Tetrahedron Lett. 27, 5225 (1986)

TOTAL SYNTHESIS OF NEOSURUGATOXIN

Shoji Inoue*, Kunisuke Okada, Hideo Tanino, and Hisae Kakoi
Faculty of Pharmacy, Meijo University, Tenpaku, Nagoya 468, Japan

Synthetic scheme of neosurugatoxin (1):

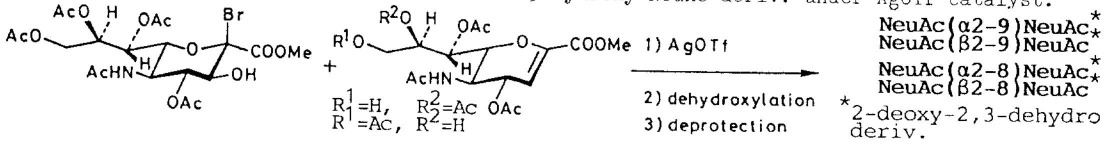


Tetrahedron Lett. 27, 5229 (1986)

SYNTHESES OF (α2-9) AND (α2-8) LINKED NEURAMINYL-NEURAMINIC ACID DERIVATIVES

Kaoru Okamoto, Tadao Kondo,[†*] and Toshio Goto*
Faculty of Agriculture; and [†]Chem. Instrument Center; Nagoya University, Nagoya 464, Japan

NeuAc(α2-9)NeuAc and NeuAc(α2-8)NeuAc derivs. were synthesized via the glycosylation of 2-deoxy-2,3-dehydro-NeuAc deriv. with 2-bromo-3-hydroxy-NeuAc deriv. under AgOTf catalyst.



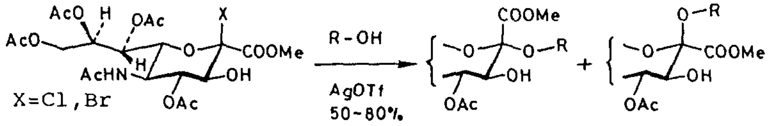
*2-deoxy-2,3-dehydro deriv.

Tetrahedron Lett. 27, 5233 (1986)

AN EFFECTIVE SYNTHESIS OF α-GLYCOSIDES OF N-ACETYLNEURAMINIC ACID BY USE OF 2β-HALO-3β-HYDROXY-4,7,8,9-TETRA-O-ACETYL-N-ACETYLNEURAMINIC ACID METHYL ESTER

Kaoru Okamoto, Tadao Kondo,[†*] and Toshio Goto[*]
Faculty of Agriculture; and [†]Chem. Instrument Center; Nagoya University, Nagoya 464, Japan

Condensation of the protected 2β-halo-3β-hydroxy-NeuAc with 6-unprotected Glc, 3-unprotected Gal, or 3'-unprotected Lac derivs. gave α-glycosides in preference to the β-glycosides.



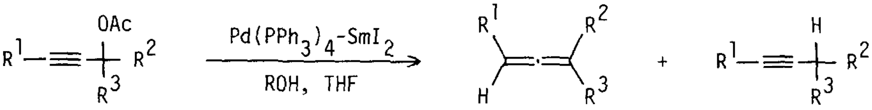
R–OH: benzyl-protected methyl glycosides
2,3,4-triBzl-Glc
2,6-diBzl-Gal
2,3,6,2',6'-pentaBzl-Lac

Tetrahedron Lett. 27, 5237 (1986)

PALLADIUM-CATALYZED REDUCTION OF PROPARGYLIC ACETATES WITH SmI_2. A MILD AND CONVENIENT METHOD FOR THE PREPARATION OF ALLENES

Takanori Tabuchi, Junji Inanaga,[*] and Masaru Yamaguchi
Department of Chemistry, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

A new general method for the preparation of allenes from prapargylic acetates by using Pd(0)-SmI_2 reduction system.

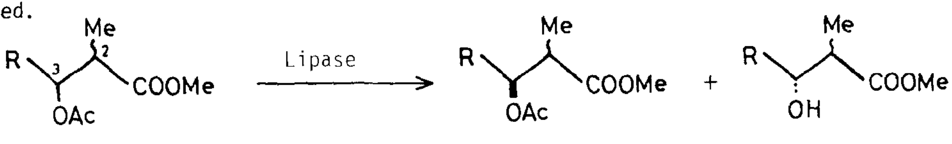


Tetrahedron Lett. 27, 5241 (1986)

LIPASE CATALYZED ENANTIOSELECTIVE HYDROLYSIS OF 2-METHYL 3-ACETOXY ESTERS

Hiroyuki Akita,[*] Hiroko Matsukura and Takeshi Oishi[*]
RIKEN (The Institute of Physical and Chemical Research),
2-1, Hirosawa, Wako-shi, Saitama 351-01, Japan

Highly enantioselective hydrolysis of (±) methyl syn- and anti-2-methyl-3-acetoxy propionate derivatives with lipase "Amano A" and lipase "Amano A-6" isolated from *Aspergillus niger*, are described.

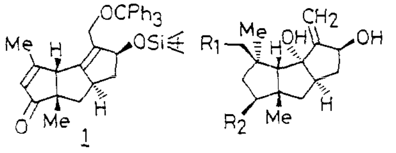


Tetrahedron Lett. 27, 5245 (1986)

SYNTHETIC STUDIES ON CAPNELLOL FAMILY : AN IMPROVED SYNTHESIS OF $\Delta^{9(12)}$-CAPNELLENE-3β,8β,10α-TRIOL AND THE FIRST TOTAL SYNTHESIS OF $\Delta^{9(12)}$-CAPNELLENE-3β,8β,10α,14-TETROL

Toshiaki Mase and Masakatsu Shibasaki[*]
Sagami Chemical Research Center, Nishi-Ohnuma
Sagamihara, Kanagawa 229, Japan

A much improved synthesis of $\Delta^{9(12)}$-capnellene-3β,8β,10α-triol(2) and the first total synthesis of $\Delta^{9(12)}$-capnellene-3β,8β,10α,14-tetrol(3) have been accomplished via the common synthetic intermediate 1.



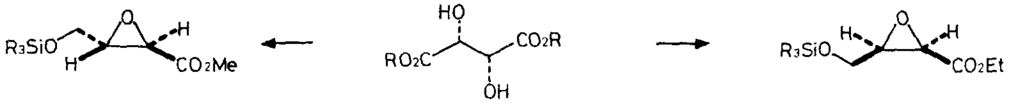
2 R_1=H, R_2=OH
3 R_1=OH, R_2=OH

Tetrahedron Lett. 27, 5249 (1986)

NOVEL APPROACH TO STEREOISOMERICALLY FULL SET OF OPTICALLY PURE 2,3-EPOXYESTERS FROM TARTARIC ACIDS

Seiki Saito, Yuki Nagao, Masahiro Miyazaki, Masami Inaba, and Toshio Moriwake
Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700, Japan

Four possible stereoisomers of 4-(t-butyldimethylsilyloxy)-2,3-epoxybutanoic acid esters are now available with respective absolute configurations from L- or D-tartaric acid.

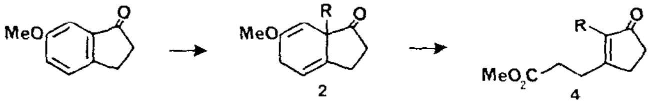


Tetrahedron Lett. 27, 5253 (1986)

A NEW USE OF THE BIRCH REDUCTION. SYNTHESIS OF 2,3-DISUBSTITUTED CYCLOPENT-2-EN-1-ONES FROM 6-METHOXYINDANONE

Christopher J. Moody* and Judy Toczek
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

Reductive alklyation of 6-methoxyindanone gives the dihydroindanones (2), ozonolysis and oxidation of which leads directly to the cyclopentenones (4).



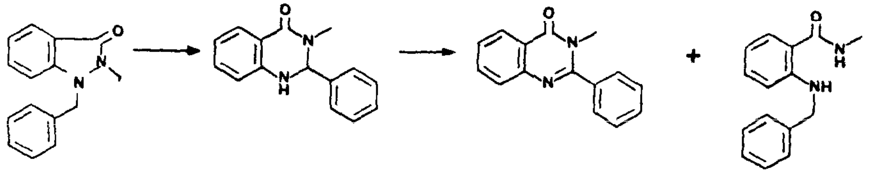
R=Me, Et, $H_2C{=}CH\text{-}CH_2$, $EtC{\equiv}C\text{-}CH_2$, $Me(CH_2)_4C{\equiv}C\text{-}CH_2$, $PhCH_2$, $EtO_2C\text{-}CH_2$.

Tetrahedron Lett. 27, 5255 (1986)

ON THE ISOMERIZATION OF DIALKYL INDAZOLONES TO DIHYDRO-QUINAZOLINONES

Leandro Baiocchi and Giuseppe Picconi
Research Institute Angelini F., Viale Amelia 70 - 00181 ROMA - ITALY

Isomerization of 1,2-dialkyl indazolones to dihydro-quinazolinones and their subsequent dismutation



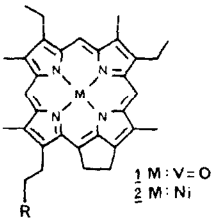
Tetrahedron Lett. 27, 5257 (1986)

IDENTIFICATION OF A NOVEL C_{33} DPEP PETROPORPHYRIN FROM BOSCAN CRUDE OIL : EVIDENCE FOR GEOCHEMICAL REDUCTION OF CARBOXYLIC ACIDS.

J. VERNE-MISMER, R. OCAMPO, H.J. CALLOT* and P. ALBRECHT*
Departement de Chimie, Université Louis Pasteur,
67008 Strasbourg, France.

Isolation of 2 after transmetallation from 1 occurring in Boscan crude oil ; identification of 2 by synthesis and n.O.e. NMR.

$$R = CO_2H \xrightarrow{\text{Geochemical reduction}} R = CH_3$$

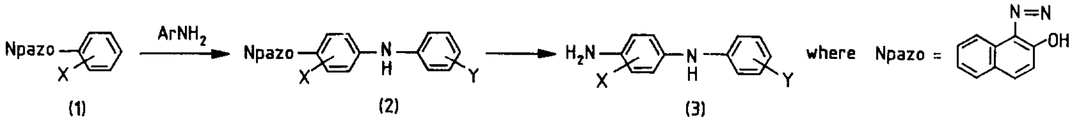


Tetrahedron Lett.27,5261(1986)

ELECTROCHEMICAL OXIDATIVE SUBSTITUTION AND DIMERISATION OF 1-ARYLAZO-2-NAPHTHOLS, LEADING TO A NEW SYNTHESIS OF SOME UNSYMMETRICAL DIARYLAMINES

T. William Bentley, David J. Richards and Michael G. Hutchings
Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP
Imperial Chemical Industries plc, Organics Division, Blackley, Manchester M9 3DA.

Electron-rich 1-arylazo-2-naphthols(1) undergo electrochemical oxidations, leading either to substitution by nucleophilic anilines giving (2) or to oxidative dimerisation. Reduction of the azo bond of (2) provides a new route to unsymmetrical diarylamines (3).

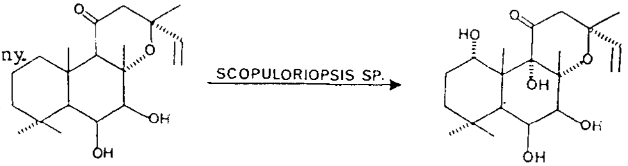


Tetrahedron Lett.27,5265(1986)

MICROBIAL TRANSFORMATION OF 1,9-DIDEOXYFORSKOLIN TO FORSKOLIN

S.R. Nadkarni[a], P.M. Akut[a], B.N. Ganguli[a], Y. Khandelwal*[b], N.J. de Souza, R.H. Rupp[b],
Departments of [a]Microbiology and [b]Chemistry, Hoechst India Limited, Mulund, Bombay 400 080, India,
and H.W. Fehlhaber, Hoechst AG., Pharma Synthese, 6230 Frankfurt(M)-80, W.Germany.

Screening of hydroxylating fungi provided a <u>Scopuloriopsis</u> species which transformed 7-deacetyl-1,9-dideoxy-forskolin to 7-deacetyl-forskolin.

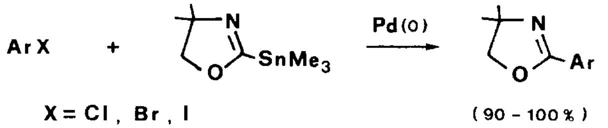


Tetrahedron Lett.27,5269(1986)

Masked Multifunctionalization of Aromatics by Palladium--catalyzed Halogen-Oxazoline Exchange

A. Dondoni* et al. , Dipt. Chimica, Università, Ferrara, Italy

A novel and direct entry to aromatic 2-oxazolines from aryl halides and a stannyloxazoline is described.

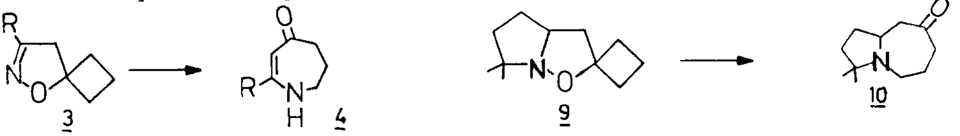


Tetrahedron Lett.27,5271(1986)

NEW SYNTHESIS OF AZEPIN-4-ONES BY FLASH VACUUM THERMOLYSIS OF DIHYDRO AND TETRAHYDROISOXAZOLE-5-SPIROCYCLOBUTANE DERIVATIVES.

A. Goti, A. Brandi*, F. De Sarlo and A.Guarna.
Centro Eterocicli, *CNR*. Dipartimento di Chimica Organica, Università di Firenze, Italy.

Azepin-4-ones are synthesized by FVT of the isoxazolines (3) and of the isoxazolidine (9) .



FURTHER INFORMATION ON THE STERIC COURSE OF THE BAKER'S YEAST REDUCTION OF 4-SUBSTITUTED-3-OXOBUTANOATES

Tetrahedron Lett. 27,5275(1986)

C.Fuganti, P.Grasselli, P.F.Seneci, P.Casati
(Dipartimento di Chimica del Politecnico, 20133 Milano, Italy, and Sclavo, Divisione Biochimica DE.BI., 20060, Cassina de'Pecchi, Italy)

Baker's yeast reduction of (1) gives rise to (3*R*) materials when X= Cl or N_3 and Y= $NHCH_2COOC_2H_5$; to racemic product when X= CF_3CONH and Y is $NHCH_2COOC_2H_5$; to (3*S*) materials when X= CF_3CONH and Y= ethyl or *n*-octyl.

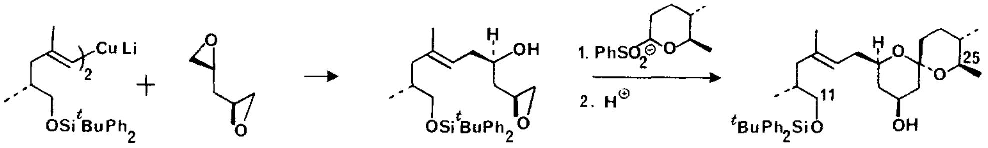
XCH_2COCH_2COY (1)

PREPARATION OF SPIROKETALS BY REACTION OF ANIONS FROM 2-BENZENESULPHONYLTETRAHYDROPYRANS WITH EPOXIDES: SYNTHESIS OF THE C-11 TO C-25 FRAGMENT OF THE MILBEMYCINS

Tetrahedron Lett. 27,5277(1986)

Christine Greck, Peter Grice, Steven V. Ley* and Anne Wonnacott
Department of Chemistry, Imperial College, London SW7 2AY, U.K.

Deprotonation of 2-benzenesulphonyltetrahydropyrans with n-butyllithium affords anions which react with substituted epoxides to give spiroketals upon acidification. Using this approach a highly convergent synthesis of the C-11 to C-25 fragment of the milbemycins was achieved.

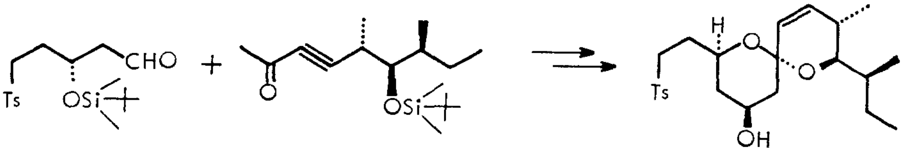


ENANTIOSPECIFIC SYNTHESIS OF THE SPIROACETAL UNIT OF AVERMECTIN B$_{1a}$

Tetrahedron Lett. 27,5281(1986)

Masahiro Hirama,* Takeshi Nakamine and Shô Itô
Department of Chemistry, Tohoku University, Sendai 980, Japan

A concise synthesis of the spiroacetal moiety of avermectin B$_{1a}$ taking advantage of stereo-controlled baker's yeast reduction.

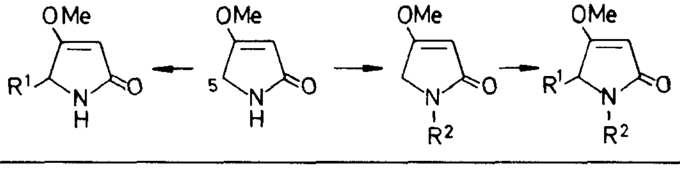


SYNTHESIS OF 5-SUBSTITUTED 4-O-METHYL TETRAMATES

Tetrahedron Lett. 27,5285(1986)

Raymond C.F. Jones* and Andrew D. Bates.
Department of Chemistry, The University, Nottingham, NG7 2RD, England.

The alkylation of 4-methoxy-Δ^3-pyrrolin-2-one at C-5 and/or N-1 is described.

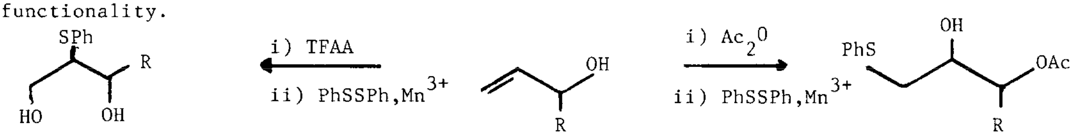


Tetrahedron Lett. 27, 5289 (1986)

REGIOSELECTIVE HYDROXYSULPHENYLATION OF DERIVATIVES OF ALLYLIC ALCOHOLS AND AMINES

Zakaria K M Abd El Samii, Mohamed I Al Ashmawy and John M Mellor*
Department of Chemistry, The University, Southampton S09 5NH

The regiochemistry of hydroxy sulphenylation is controlled by the nature of the ester functionality.

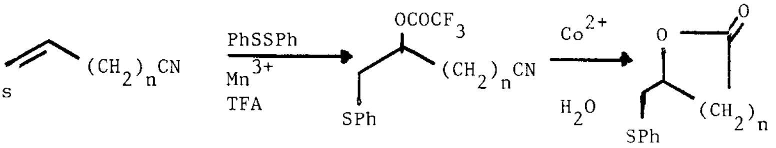


Tetrahedron Lett. 27, 5293 (1986)

TRIFLUOROACETOXYSULPHENYLATION OF UNSATURATED NITRILES AS A ROUTE TO LACTONES

Zakaria K M Abd El Samii, Mohamed I Al Ashmawy and
John M Mellor*, Department of Chemistry, The University, Southampton S09 5NH

A new route to thiophenyl substituted lactones is based on hydroxysulphenylation of unsaturated nitriles and subsequent hydrolysis.

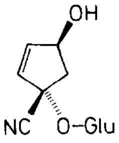


Tetrahedron Lett. 27, 5297 (1986)

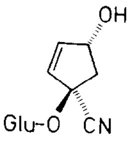
NATURAL GLYCOSIDES OF CYCLOPENTENONE CYANOHYDRINS: REVISED STRUCTURE OF SO-CALLED EPITETRAPHYLLIN B

Jerzy W. Jaroszewski and Elin S. Olafsdóttir
Department of Chemistry BC, Royal Danish School of Pharmacy,
Universitetsparken 2, DK-2100 Copenhagen, Denmark

Volkenin, natural cyclopentenoid glucoside co-occurring with 1 in Adenia volkensii (Passifloraceae), was identified as 2 by means of NMR and CD. The glucosides represent a pair of natural products formed by a partially non stereospecific biosynthetic pathway.



1



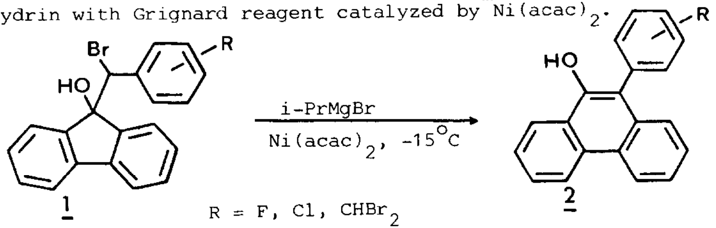
2

Tetrahedron Lett. 27, 5301 (1986)

AN EFFICIENT SYNTHESIS OF 9-PHENANTHROLS

Amnard Tantivanich* and Doungrudee Supatimusro
Department of Chemistry, Kasetsart University
Pholyotin Road, Bangkok 10900, Thailand

Syntheses of certain 10-phenyl-9-phenanthrols via the reaction of bromohydrin with Grignard reagent catalyzed by Ni(acac)$_2$.



R = F, Cl, CHBr$_2$

REDUCTIVE METHYLATION OF α-NAPHTHYL KETONES STEREOCONTROLLED SYNTHESIS OF TRANS-OCTAHYDROPHENANTHRENES RELATED TO DITERPENES

Tetrahedron Lett. 27, 5303 (1986)

Sukanta Bhattacharyya, Tapan K. Karpha, Basudeb Basu and Debabrata Mukherjee*
Department of Organic Chemistry, Indian Association for the Cultivation of Science
Jadavpur, Calcutta - 700 032, India.

Stereocontrolled synthesis of 4 from 1 involving reductive methylation of 2 as the key step.