GRAPHICAL ABSTRACTS

Tetrahedron Lett.30,6797(1989)

STRAINED OXIRANES FROM CIS-DIOLS

Eduardo Palomino^{1*}, A. Paul Schaap and Mary Jane Heeg Department of Chemistry, Wayne State University, Detroit, MI 48201

Cis-diols of some strained molecules are converted to epoxides without inversion of configuration by the use of the redox system triphenylphosphine:diethylazodicarboxylate, or by treatment of their dimethylaminodioxolane derivatives with trifluoroacetic anhydride as catalyst.



PHOTOOXYGENATION OF STRAINED EPOXIDES

Eduardo Palomino^{1*}, A. Paul Schaap and Mary Jane Heeg Department of Chemistry, Wayne State University, Detroit, MI 48201



Photooxygenation of strained epoxides, type 1, in the presence of DCA or TCA afforded ozonide 2 in different ratios. A mechanism involving trapping of a radical cation by ³O₂ is proposed. Trapping of an ylide



Tetrahedron Lett.30,6805(1989)

Tetrahedron Lett.30,6801(1989)

TRANS-CYCLOHEPTENE: SPECTRAL CHARACTERIZATION AND DYNAMIC BEHAVIOR

intermediate by ¹O₂ is also considered in the DCA-sensitized photooxygenation.

Michael Squillacote*, Adelle Bergman and James De Felippis Department of Chemistry, Auburn University, Auburn University, AL 36849-5312

We have produced trans-cycloheptene via a singlet exciplex of the cis isomer and have obtained NMR and UV spectra of this strained cyclic alkene. This ring system undergoes a pseudorotation process with a barrier of 10.0 kcal/mole. The UV spectrum suggests a substantial twist to the double bond, but interestingly the vinyl H-H coupling constant implies a 180° dihedral angle for the vinyl protons.

A CONCISE ROUTE TO THE OXATHIAZEPINE CONTAINING EUDISTOMIN SKELETON AND SOME CARBA-ANALOGS

Tetrahedron Lett.<u>30</u>,6809(1989)

Michael P Kirkup*, B.B. Shankar, Stuart McCombie, and Ashit K. Ganguly, Schering-Plough Corporation, Bloomfield, NJ 07003

Andrew T. McPhail, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706

The unsubstituted Eudistomin skeleton containing the oxathiazepine D ring was prepared along with a series of unsubstituted and amino substituted carba-analogs, using an intramolecular Pictet-Spengler condensation.

Tetrahedron Lett.30,6813(1989)

Tetrahedron Lett.30,6817(1989)

Tetrahedron Lett.30,6821(1989)

STEREOSELECTIVITY IN THE HOMO DIELS-ALDER REACTION

Mark Lautens*, Louise G. Edwards
Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

Ni(COD)₂/Ph₃P and Ni(acac)₂/Et₃Al/Ph₃P are effective catalysts for the stereospecific homo Diels-Alder reaction. Reaction with methyl vinyl ketone or phenyl vinyl sufoxide gives predominantly the exo isomer 1. Cyclic enones such as cyclopentenone give the cycloadduct 2 with high endo selectivity, i.e. >20:1

EWG

Ni(COD)2/Ph3P or Ni(acac)2/EtaAl/PhaF

RING OPENING REACTIONS OF AN OXABICYCLIC COMPOUND WITH

CUPRATES

Mark Lautens*, Carlo Di Felice and Alexandre Huboux Department of Chemistry, University of Toronto, Toronto, Ontario Canada M5S 1A1

The ring opening reaction of 8-oxabicyclo[3.2.1]oct-6-cn-3-one 1, with cuprates is described. S_N2' attack to give 3 is the predominant pathway giving rise to products isomeric to those derived from opening of vinyl epoxides under similar conditions, e.g. 4.

NORASPERENALS A-D, UNPRECEDENTED TRISNORDITERPENOIDS FROM THE CARIBBEAN GORGONIAN EUNICEA SP.

Jonghoon Shin and William Fenical* Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0228

The structures of four new trisnorditerpenoids, norasperenals A-D (4-7) were determined by spectral methods.

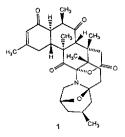
5 OHC CHO

ZOANTHAMINONE, A NEW ALKALOID FROM A MARINE ZOANTHID

Tetrahedron Lett.30,6825(1989)

Atta-ur-Rahman*, K. Ahmed, S. A. Abbas, M. Iqbal Choudhary¹ and J. Clardy^{1*} H. E. J. Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan ¹ Department of Chemistry, Cornell University, Ithaca, New York 14853, U. S. A

An unusual alkaloid, zoanthaminone (1) has been isolated from a marine zoanthid. Its structure has been established by using X-ray crystallographic and spectroscopic techniques.



Tetrahedron Lett.30,6829(1989

Tetrahedron Lett.30,6833(1989)

A NEW APPROACH TO THE PREPARATION OF 2-SUBSTITUTED TETRAHYDROFURANS WITH ALPHA-SYN SELECTIVITY

Keith T. Mead and Hui-Li Yang Department of Chemistry, Mississippi State University, Mississippi State 39762

Lewis acid initiated intramolecular 2-oxetanone ring cleavage has been shown to proceed with inversion of stereochemistry

THE REDUCTION OF N-(PHENYLSULFONYL)INDOLES WITH SODIUM CYANOBOROHYDRIDE IN TRIFLUOROACETIC ACID.

Daniel M. Ketcha* and Brett A. Lieurance

Department of Chemistry, Wright State University, Dayton Ohio 45435

A variety of N-(phenylsulfonyl)indoles can be reduced to the corresponding N-protected indolines using sodium cyanoborohydride in trifluoroacetic acid.

Tetrahedron Lett.30,6837(1989)

SUBSTITUTED HYDRAZULENONES VIA CYCLOPROPANONE ADDITION, CYCLOPROPANOL REARRANGEMENT, AND A RETROALDOL/RE-ALDOL SEQUENCE

Valérie Reydellet and Paul Helquist*, Department of Chemistry and Biochemistry,

University of Notre Dame, Notre Dame, Indiana 46556 U.S.A.

Tetrahedron Lett.30,6841(1989)

ASYMMETRIC SYNTHESIS OF UNUSUAL AMINO ACIDS: SYNTHESIS OF OPTICALLY PURE ISOMERS OF B-METHYLPHENYLALANINE.

Ramalinga Dharanipragada, Ernesto Nicolas, Geza Toth and Victor J. Hruby, Department of Chemistry, University Of Arizona, Tucson, AZ 85721 USA.

Tetrahedron Lett.30,6845(1989

Tetrahedron Lett. 30,6849 (1989)

ASYMMETRIC SYNTHESIS OF UNUSUAL AMINO ACIDS: SYNTHESIS OF OPTICALLY PURE ISOMERS OF β-METHYLTYROSINE.

Ernesto Nicolas, Ramalinga Dharanipragada, Geza Toth and Victor J. Hruby. Department of Chemistry, University Of Arizona, Tucson, AZ 85721 USA.

OH
$$H^{W}$$
 CH_3 $Ar = C_6H_4$ OCH_3

THE PREPARATION OF 9-ALKYLTHIOFLUORENES FROM BIPHENYL-2-CARBOXALDEHYDES

Jack D. Leber and John D. Elliott*, Department of Medicinal Chemistry, Smith Kline and French Laboratories, P.O. Box 1539, King of Prussia, PA 19406-0939

Treatment of the biphenyl 2-carboxaldehyde 3 with BF3.Et2O/EtSH produces 9-alkylthiofluorenes 4a/4b through a thionium ion induced cyclization.

4 b

PHOTOCHEMISTRY OF 1,1,3-TRIPHENYL-2-INDANONE.
SPONTANEOUS AND PHOTOCHEMICAL DECAY OF ortho-XYLYLENES
J. C. Netto-Ferreira, Véronique Wintgens and J. C. Scaiano*

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6 and Ottawa–Carleton Chemistry Institute, University of Ottawa, Ottawa, Canada K1N 6N5.

Xylylene II decays by a competition of two processes ultimately leading to ${\bf V}$ and ${\bf VI}$. Two-photon processes favor the cyclization leading to ${\bf VI}$.

Tetrahedron Lett.30,6855(1989)

Tetrahedron Lett.30,6851(1989)

CHIRALE INDUKTION BEI DER PHOTOCHEMISCHEN UMLAGERUNG VON 3,6-HEXANCOXEPIN-4,5-DICARBONSÄUREESTERN W. Tochtermann*, U. Schlösser und B. Popp Institut für Organische Chemie der Universität Kiel Olshausenstr. 40, D-2300 Kiel, F.R.G. E.-M. Peters, K. Peters und H.G. von Schnering Max-Planck-Institut für Festkörperforschung Heisenbergstr. 1, D-7000 Stuttgart 80, F.R.G. Irradiation of an aqueous suspension of the crystalline diacetone glucose diester 1d affords(+)-(3aS,6R,8aR)-2d in 45% yield with 83% de.

ROOC
$$(CH_2)_6$$
 ROOC $\frac{3}{4}$ ROOC $\frac{1}{4}$ ROOC $\frac{1}{4}$ ROOC $\frac{1}{4}$ ROOC $\frac{1}{4}$ ROOC $\frac{1}{4}$ CHO

Tetrahedron Lett.30,6859(1989)

TERT-BUTYL ESTERS OF N-PROTECTED AMINO ACIDS WITH TERT-BUTYL FLUOROCARBONATE (Boc-F)

A. Loffet a, N. Galeotti b, P. Jouin b* and B. Castro b

^aPROPEPTIDE, B. P. 12, 91710 VERT-LE-PETIT, FRANCE.

^bCentre CNRS-INSERM de Pharmacologie-Endocrinologie rue de la Cardonille, 34094, MONTPELLIER, FRANCE.

tert-Butyl fluorocarbonate (Boc-F) is efficiently used in the presence of triethylamine and 4-dimethylamino-pyridine for the synthesis of tert-butyl esters of N-protected amino acids.

SYNTHESIS OF NEW PHOSPHONATE INHIBITORS OF SERINE PROTEASES

Jacques Fastrez^a, Laurent Jespers^a, Dominique Lison^b, Michel Renard^b, and Etienne Sonveaux^{a*}

^aLaboratoire de Biochimie Physique et des Biopolymères, 1, Place Louis Pasteur, B-1348 Louvain-La-Neuve, Belgium.

^bUnité de Toxicologie Industrielle et de Médecine du Travail, 30, Clos Chapelle-aux-Champs, B-1200, Bruxelles, Belgium, and STFT/CT, B-1800, Vilvoorde, Belgium.

Tetrahedron Lett. 30,6861(1989)

X(andY)=leaving group(s)

Tetrahedron Lett.30,6865(1989)

DIENAMIDES AS VERSATILE PRECURSORS OF POLYCYCLIC PYRIDINES AND ISOQUINOLINES

Axel Couture*, Christophe Bochu and Pierre Grandclaudon

Laboratoire de Chimie Organique Physique (UA CNRS N° 351) Université des Sciences et

Laboratoire de Chimie Organique Physique (UA CNRS N° 351) Université des Sciences Techniques de Lille Flandres-Artois 59655 Villeneuve d'Ascq Cedex, France

Tetrahedron Lett.30,6867(1989)

An unexpected difficulty in the use of MEM as a protective group for phenolic hydroxyl. Joëlle MAYRARGUE, Mustapha ESSAMKAOUI et Henri MOSKOWITZ*

Faculté de Pharmacie, Laboratoire de Chimie Organique, associé au CNRS, 92296 Châtenay-Malabry (France). During the *ortho*lithiation of methoxyethoxymethyl protected phenolic hydroxyl, an unexpected deprotection in the basic medium occurs, leading to the deprotected phenol and an unsaturated ether:

Tetrahedron Lett.30,6869(1989)

PHOSPHORUS DIENIC LIKE SYSTEMS

Anne-Marie Caminade , Christian Roques , Nathalie Dufour, Dominique Colombo , Frédéric Gonce and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination du CNRS, 205, Route de Narbonne, 31077 Toulouse, France

$$X=P-CI$$
 + $Me_3Si-N=Y$ $-Me_3SiCI$ $X=P-N=Y$

 $X = C(SiMe_3)_2$; N-Ar $(Ar = tBu_3C_6H_2)$

Y = CHPh; $C(Me)OSiMe_3$; CPh_2 ; PPh_3 ; $P(NMe_2)_3$

Tetrahedron Lett.30,6873(1989)

COMPOSITE CONSTITUENTS: NEW MIGRATED GAMMACERANE TRITERPENOIDS FROM ROOTS OF *PICRIS HIERACIOIDES* SUBSP. *JAPONICA*

Kenji Shiojima, Kazuo Masuda, Yuko Ooishi, Hideki Suzuki and Hiroyuki Ageta,* Showa College of Pharmaceutical Sciences, 5-1-8 Tsurumaki, Setagaya-ku, Tokyo 154, JAPAN

Pichierenyl acetate (1) and isophichierenyl acetate (2) were isolated and their structures were established as the members of migrated gammaceane series with a $\Delta^{9}(11)$ and a Δ^{8} double bond respectively.

ACO
$$\frac{11}{23}$$
 $\frac{27}{28}$ $\frac{28}{11}$ $\frac{27}{29}$ $\frac{28}{29}$ $\frac{1}{2}$ $\frac{\Delta^{9(11)}}{2}$ $\frac{\Delta^{9(11)}}{2}$

Tetrahedron Lett.30,6875(1989)

PREPARATION AND CHARACTERIZATION OF IMINOQUINONE AND AMINOPHENOL DERIVATIVES OF COENZYME PQQ

Minae Mure, Shinobu Itoh, and Yoshiki Ohshiro* Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

5-Iminoquinone derivative of PQQ was easily prepared by treatment with ammonia. Reduction of the iminoquinone with MeNHNH2 gave the aminophenol.

Iminoquinone

retrahedron Lett.<u>30</u>,6879(1989)

Aminophenol

Cp₂ZrCl₂-AgBF₄ in Benzene: A New Reagent System for Rapid and Highly Selective α-Mannoside Synthesis from Tetra-O-benzyl-D-mannosyl Fluoride Keisuke Suzuki* Hideki Maeta Toshiyuki Suzuki and Takashi Matsumoto

Keisuke Suzuki*, Hideki Maeta, Toshiyuki Suzuki, and Takashi Matsumoto Department of Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan

> BnO OBn BnO BnO

Cp₂ZrCl₂ - AgBF₄ ➤

ROH, MS 4A / Benzene, 20 min.

PQQ

BnO OBn BnO OBn

Tetrahedron Lett.30,6883(1989

Interaction between Cofacially Oriented Metalloporphyrins in Aqueous Media. Unusual Acidolytic Properties of an

Amphiphilic Iron Porphyrin µ-Oxo Dimer Carrying Poly(oxyethylene) Side Chains.

Takuzo Aida, Akihiko Takemura, and Shohei Inoue*

Department of Synthetic Chemistry, Faculty of Engineering University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

The acid titration of the amphiphilic iron porphyrin µ-oxo dimer carrying poly(oxyethylene) side chains demonstrates the pronounced dependence of the acidolytic property of the internal μ-oxo bridge on the length of the watersoluble polyether side chains.

Tetrahedron Lett.30,6887(1989)

Tetrahedron Lett.30,6891(1989)

RHODIUM(I)-CATALYZED ISOMERIZATION OF SILOXYCYCLOPROPANES LEADING TO ENOL SILYL ETHERS AND ALLYL SILYL ETHERS

Kiyoshi Ikura, Ilhyong Ryu,* Akiya Ogawa, Nobuaki Kambe, and Noboru Sonoda*

Department of Applied Chemistry,

Faculty of Engineering,

Osaka University, Suita, Osaka 565, Japan

HALICLAMINES A AND B, CYTOTOXIC MACROCYCLIC ALKALOIDS FROM A SPONGE OF THE GENUS HALICLONA

N. Fusetani, * K. Yasumuro, S. Matsunaga Laboratory of Marine Biochemistry, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo (Japan)

Department of Chemistry, Faculty of Science,

The University of Tokyo, Bunkyo-ku, Tokyo (Japan)

Two cytotoxic alkaloids, haliclamines A and B, have been isolated from a sponge Haliclona sp.

Tetrahedron Lett.30,6895(1989)

FROM CAGES TO WEDGES AND CLEFTS: DESIGN OF SOME NOVEL HOSTS BASED ON cis, syn, cis-TRIQUINANE FRAMEWORK

Mehta*, C. Prabhakar, School of Chemistry, University of Hyderabad, lerabad - 500 134, India, N. Padmaja, S. Ramakumar and M.A. Viswamitra*, Department of Physics and ICMR Centre on Genetics and Cell Biology, Institute of Science, Bangalore-560 012, India.

Summary: Annulation of aromatic rings on the folded cis, syn, cis-triquinane backbone has led to the design of potential host systems 4 and 6.





THE FIRST PARTIAL SYNTHESIS OF 14-HYDROXYGIBBERELLIN ESTERS. A TITANIUM (IV)-AMIDE CATALYSED REARRANGEMENT OF EPOXIDES.

Tetrahedron Lett. 30,6899 (1989)

Braulio M. Fraga^a, James R. Hanson^b, Melchor G. Hernández^a and Fernando G. Tellado^a. ^aInstituto Productos Naturales Orgánicos, CSIC, La Laguna, Tenerife, Spain.

bSchool of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK.

GA₃ methyl ester (1) has been efficiently transformed into 14 β -OH GA₇ methyl ester (9) <u>via</u> a titanium (IV)-amide catalysed rearrangement of epoxide (6).

Tetrahedron Lett.30,6903(1989)

REACTIONS OF TRIAZOLINEDIONES WITH CIS-ALKE-NES. A HIGHLY REGIOSELECTIVE ENE REACTION

Yiannis Elemes, Manolis Stratakis and Michael Orfanopoulos*

Department of Chemistry, University of Crete, 71110 Iraklion, Crete, Greece

Tetrahedron Lett.30,6907(1989)

INTRAMOLECULAR CONDENSATION OF STEROIDAL 17α -FORMYL- 17β -ACETATES: SYNTHESIS OF 14-HYDROXYMETHYL-3-OXO-19-NOR- 17α -PREGN-4-ENE-21,17-CARBOLACTONE

James R. Bull* and Lynne M. Steer Department of Chemistry,

University of Cape Town, Rondebosch 7700.

South Africa

R=O or OH, H, etc

UNSYMMETRICAL BIARYLS FROM ARYLOXIDE ANIONS AND ARYLAZO PHENYL SULFIDES IN DMSO.

Tetrahedron Lett.30,6911(1989)

Giovanni Petrillo,* Marino Novi, and Carlo Dell'Erba

Istituto di Chimica Organica dell'Università, C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Corso Europa 26, I-16132 Genova, Italy.

Hydroxybiaryls can be conveniently obtained in DMSO at room temperature by reaction of arylazo phenyl sulfides and aryloxide anions:

Tetrahedron Lett.30,6913(1989)

α-Sulfonyl Radical Initiated Intramolecular Tandem Radical Cyclication V. Reutrakul*, C. Poolsanong and M. Pohmakotr, Department of Chemistry, Mahidol University, Rama VI Rd., Bangkok 10400. Thailand.

STEREOSELECTIVE PAPAIN-CATALYZED SYNTHESIS OF ALAFOSFALIN

Tetrahedron Lett.30,6917(1989)

V.A.Solodenko, V.P.Kukhar

Institute of Bioorganic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str., 5, Kiev 252660, USSR

$$Z-Ala-OH + \sum_{NH_2} P(O)(OPr^i)_2 \xrightarrow{papain} \sum_{NH_2} CO-NH + PO_3H_2$$
(L) (L,D) (L)

Tetrahedron Lett.30,6919(1989)

Stereoselective Conjugate Additions of Benzyl Sulphoxides to α,β-Unsaturated Esters

M. Casey,* A.C. Manage, and R.S. Gairns

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT

The reaction of lithiated benzyl t-butyl sulphoxides with α.β-unsaturated esters gives conjugate addition products in good yield, with high stereoselectivity.

Fetrahedron Lett.30,6923(1989)

CYCLOADDITION REACTIONS OF HETEROAZADIENES:

[4+2] CYCLOADDITION OF 1-THIA-3-AZABUTADIENES WITH ELECTRON-POOR DIENOPHILES.

José Barluenga*, Miguel Tomás, Alfredo Ballesteros, and Luis A. López

Dpto. de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

1-Thia-3-azabutadienes (1) react at 25-60°C with dimethyl acetylenedicarboxylate, N-phenylmaleimide, methyl propiolate, and diethyl azodicarboxylate, to give cycloadducts (2) in high yield.

Tetrahedron Lett.30,6927(1989) A NEW SYNTHESIS OF 10,11-DIHYDRODIBENZ(b,f)OXEPIN-10-ONES: KEY INTERMEDIATES TO CULARINE ALKALOIDS Carlos Lamas, Alberto García, Luis Castedo* and Domingo Domínguez Dpto. de Química Orgánica. Facultad de Química y Sección de Alcaloides del C.S.I.C. Santiago de Compostela. Spain A new synthesis of dihydrodibenzoxepinones is described: