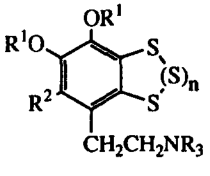
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 12785

PENTATHIEPINS AND TRITHIANES FROM TWO *LISSOCLINUM* SPECIES AND A *EUDISTOMA* SP.:INHIBITORS OF PROTEIN KINASE C.

Rienaldo S. Compagnone, D. John Faulkner, Brad K. Carte, George Chan, Alan Freyer, Mark E. Hemling, Glenn A. Hoffmann, and Michael R. Mattern.
Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093-0212, and Department of Biomolecular Discovery, SmithKline Beecham Pharmaceuticals, King of Prussia, PA 19406.



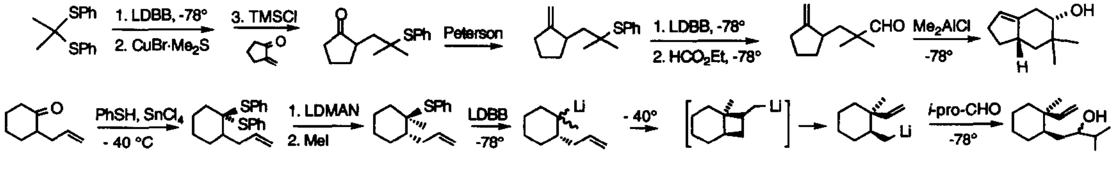
Three benzopentathiapins (n = 3; R = R^1 = Me, R^2 = SMe: R = H, R^1 = Me, R^2 = SMe: R = R^1 =R^2 = H) and two benzotrithianes (n = 1; R = R^1 = Me, R^2 = SMe: R = H, R^1 = Me, R^2 = SMe) were isolated from three tunicates. The pentathiepins and trithianes selectively inhibit PKC.

Tetrahedron, **1994**, *50*, 12793

Generation, Rearrangements and Some Synthetic Uses of Bishomoallyllithiums

Fangping Chen, Boguslaw Mudryk and Theodore Cohen*
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA

II° and III° bishomoallyllithiums (γ-lithioalkenes), from reductive lithiation of readily available bishomoallyl phenyl sulfides, are capable of rearrangement to I° bishomoallyllithiums via cyclobutylcarbinyllithiums and of formylation to precursors of intramolecular ene reactions.

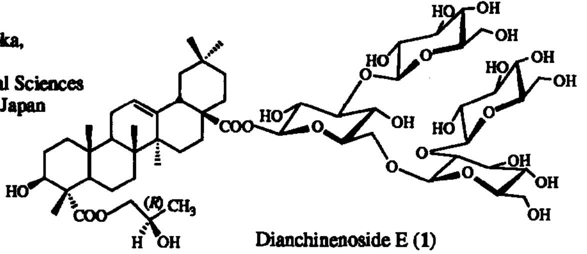


Tetrahedron, **1994**, *50*, 12811

Triterpenoid Saponins from *Dianthus chinensis*

Kazuo Koike, Hongyu Li, Zhonghua Jia, Hitomi Muraoka, Satoko Fukui, Masako Inoue, and Taichi Ohmoto*
Department of Pharmacognosy, School of Pharmaceutical Sciences
Toho University 2-2-1 Miyama, Funabashi, Chiba 274, Japan

Four novel triterpenoid saponins, dianchinenosides E, F, G and H were isolated from the aerial parts of *Dianthus chinensis* L. Their structures including the absolute configuration of the 1,2-propanediol fragments were established by spectral and chemical evidence as well as chiral HPLC analysis.

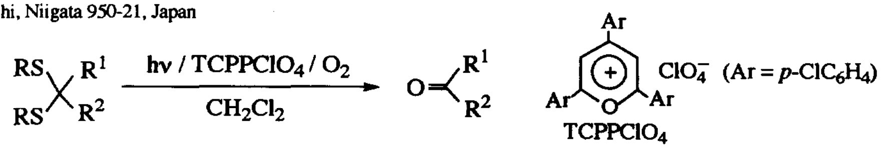


Dianchinenoside E (1)

Tetrahedron, **1994**, *50*, 12821

Pyrylium Salt Sensitized Photochemical Deprotections of Dithioacetals and Ketals

Masaki Kamata,*[a] Yukiko Murakami,[a] Yasuko Tamagawa,[a] Mitsuaki Kato,[a] and Eietsu Hasegawa*[b]
[a]Department of Chemistry, Faculty of Education and [b]Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21, Japan

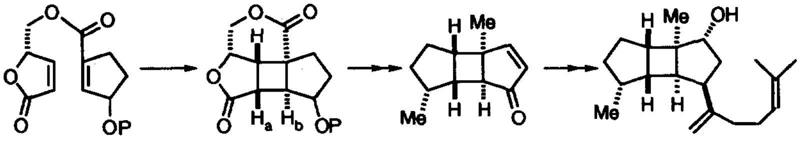


TCPPClO$_4$

Enantioselective Total Synthesis of (+)-Stoechospermol *Via* Stereoselective Intramolecular (2+2) Photocycloaddition of the Chiral Butenolide

Tetrahedron, **1994**, *50*, 12829

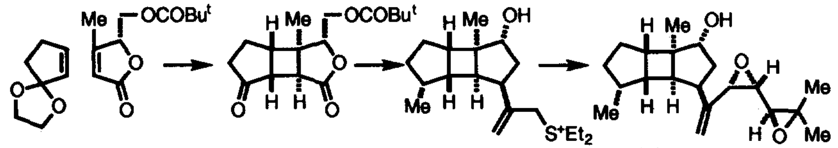
Masahide Tanaka, Kiyoshi Tomioka,[†] and Kenji Koga*
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113,
[†]Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan



Total Synthesis of Natural (+)-Spatol. Confirmation of The Absolute Stereostructure

Tetrahedron, **1994**, *50*, 12843

Masahide Tanaka, Kiyoshi Tomioka,[†] and Kenji Koga*
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113,
[†]Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan



(+)-spatol

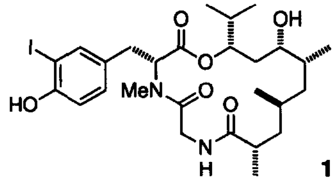
Enantioselective Total Synthesis of Doliculide, a Potent Cytotoxic Cyclodepsipeptide of Marine Origin and Structure-Cytotoxicity Relationships of Synthetic Doliculide Congeners

Tetrahedron, **1994**, *50*, 12853

Hiroyuki Ishiwata, Hiroki Sone, Hideo Kigoshi, and Kiyoyuki Yamada*

Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa, Nagoya, 464, Japan

The enantioselective total synthesis of doliculide (1) has been accomplished efficiently and the structure-cytotoxicity relationships of 1 and its artificial congeners were examined.



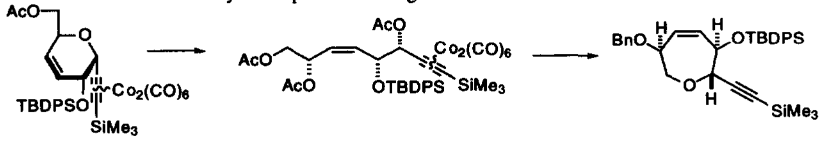
1

Ring Opening of Alkynyl Sugars by Nicholas Reaction-----Application to Enantioselective Synthesis of Oxepane Subunits of Marine trans-fused Polyether Toxins

Tetrahedron, **1994**, *50*, 12883

S. Tanaka, N. Tatsuta, O. Yamashita, M. Isobe, Nagoya Univ. Chikusa, Nagoya 464-01; Kao Co. 1334 Minato, Wakayama 640, Japan

Pyranose ring of cobalt-complexed alkynyl sugars was diasteroselectively cleaved by Nicholas reaction. The resulting linear cobalt complex was modified and converted into dehydrooxepane unit of ciguatoxin.

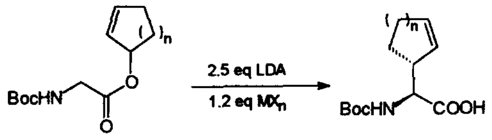


Stereoselective Synthesis of 2-(2'-Cycloalkenyl) Glycinates via [3,3] Sigmatropic Rearrangement of Chelated Ester-Enolates

Tetrahedron, **1994**, *50*, 12895

Uli Kazmaier
Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Ester-enolate Claisen rearrangement of chelated *N*-protected cycloalkenyl glycinates results in the formation of cyclic γ,δ-unsaturated amino acids in good yields and in a highly diastereoselective fashion.

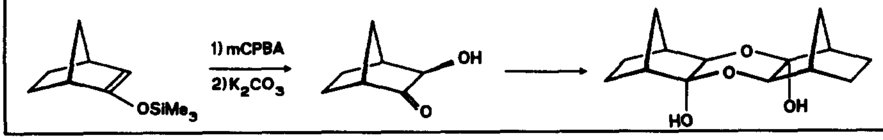


Stereochemistry of the Rubottom Oxidation with Bicyclic Silyl Enol Ethers; Synthesis and Dimerization Reactions of Bicyclic α-Hydroxy Ketones

Tetrahedron, **1994**, *50*, 12903

Johann Jauch, Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

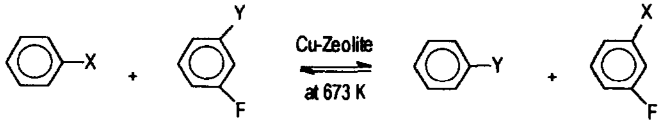
A modified and improved procedure for the Rubottom oxidation of bicyclic silyl enol ethers is described. The stereochemical outcome of this reaction is studied.



Exchange of Halogens Between Aromatic Compounds in the Presence of Cu-HZSM-5 Zeolite

Tetrahedron, **1994**, *50*, 12913

S. Imhaoulène, L. Vivier, M. Guisnet and G. Pérot, URA CNRS 350, Catalyse en Chimie Organique
40, avenue du Recteur Pineau 86022 Poitiers Cedex, France.
M. Gubelmann, Rhône-Poulenc Recherches, Centre d'Aubervilliers 93308 Aubervilliers Cedex, France.



(X, Y = Cl, Br)

Halogen exchange reaction between aromatics was carried out in the presence of Cu-HZSM-5 zeolite at 673 K.

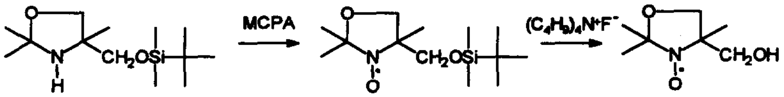
NITROXIDES: SYNTHESIS AND PARAMAGNETIC PROPERTIES OF AN α-HYDROXYMETHYL DERIVATIVE OF DOXYL

Tetrahedron, **1994**, *50*, 12923

Aziz Chaouni-Benabdallah, Guy Subra, Pierre A. Bonnet*, Jean P. Fernandez, Jean P. Chapat, Patrick Vallet, Robert N. Muller

URA CNRS 1111, Fac. Pharmacie, 34060 Montpellier, France
Département de Chimie Organique et Laboratoire de RMN, Université de Mons, B-7000 Mons, Belgique

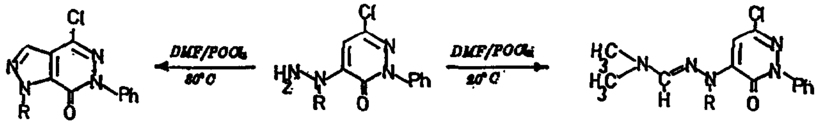
The synthesis of new α-(hydroxymethyl)oxazolidin-3-oxyls was achieved after protection by silylation of the hydroxyl groups. Relaxivity studies of (*R,S*)-4-(hydroxymethyl)-2,2,4-trimethyloxazolidin-3-oxyl show no beneficial effect of the presence of an hydroxymethyl in α of the N-O group.



Tetrahedron, **1994**, *50*, 12933

Reactivity of 6-Chloro-4- and 5-Hydrazino-2-phenyl-3(2*H*)-pyridazinones with Vilsmeier Reagent

Anna Katrusiak, Andrzej Katrusiak * and Sylwester Bałoniak
Department of Organic Chemistry, School of Medicine, 60780 Poznań, Poland
* Faculty of Chemistry, Adam Mickiewicz University, 60780 Poznań, Poland

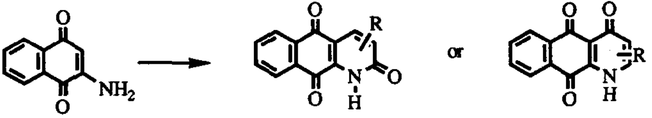


Tetrahedron, **1994**, *50*, 12941

SYNTHESIS OF 2- AND 4-OXO-1*H*-1-AZAANTHRACENE-9,10-DIONES FROM 2-AMINO-1,4-NAPHTHOQUINONE.

Alicia Marcos, Carmen Pedregal and Carmen Avendaño
Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad Complutense, 28040-Madrid, Spain

2-Amino-1,4-naphthoquinone reacts with β-dielectrophiles to give either 2-oxo- or 4-oxo-1-*H*-1-azaanthracene-9,10-diones.

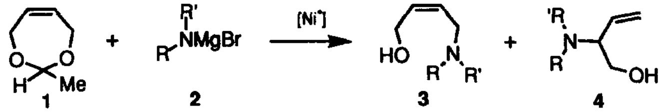


Tetrahedron, **1994**, *50*, 12953

CATALYZED REACTION OF 2-METHYL-1,3-DIOXEP-4-ENE AND HALOGEN MAGNESIUM SALTS OF SECONDARY AMINES. A NEW APPROACH TO ALLYLAMINOALCOHOLS.

Luciano Lardicci, Corrado Malanga,* Federica Balzano, Rita Menicagli.
Dipartimento di Chimica e Chimica Industriale and Centro di Studi del CNR per le Macromolecole Stereordinate ed Otticamente Attive
Via Risorgimento 35, 56126 Pisa - Italy

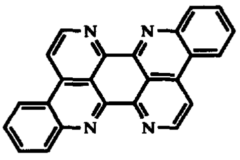
Ni° catalyzed reaction of 2-methyl-1,3-dioxep-4-ene (1) with 2 gives mixtures of 3 and 4 in good yield.

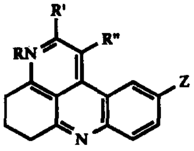


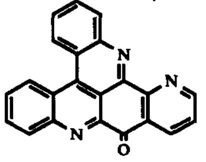
Tetrahedron, **1994**, *50*, 12959

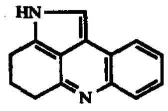
THE BIOMIMETIC SYNTHESIS OF MARINE ALKALOID RELATED PYRIDO- AND PYRROLO[2,3,4-*kl*]ACRIDINES

Gari Gellerman, Amira Rudi and Yoel Kashman*
School of Chemistry Tel Aviv University, Ramat Aviv 69978, ISRAEL







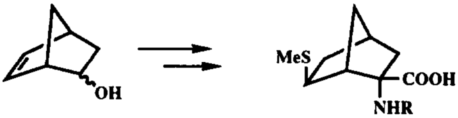


Tetrahedron, **1994**, *50*, 12973

CONFORMATIONALLY CONSTRAINED AMINO ACIDS: A CONCISE ROUTE TO A METHIONINE ANALOGUE

G. Fantin, M. Fogagnolo, R. Guerrini, M. Marastoni, A. Medici, P. Pedrini, Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy ; Dipartimento di Scienze Farmaceutiche, Università di Ferrara, Ferrara, Italy

A facile and concise synthesis of (±)-2-*endo*-amino-6-*exo*-(methylthio)bicyclo[2.2.1]heptane-2-*exo*-carboxylic acid starting from 5-norbornen-2-ol is described.



Tetrahedron, **1994**, *50*, 12979

SELECTIVITY IN SODIUM BOROHYDRIDE REDUCTION OF COUMARIN ENCAPSULATED IN ß-CYCLODEXTRIN

Kasi Pitchumani*[a], Ponnusamy Velusamy and Chockalingam Srinivasan*
Department of Materials Science, Madurai Kamaraj University, Madurai-625021 India and [a] School of Chemistry, Madurai Kamaraj University, Madurai

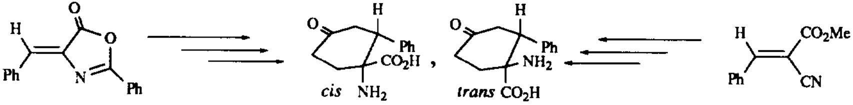
The sodium borohydride reduction of solid ß-cyclodextrin complex of coumarin selectivity leads to the *cis*-o-hydroxycinnamyl alcohol.

Tetrahedron, **1994**, *50*, 12989

A NEW EFFICIENT SYNTHESIS OF 2-PHENYL-4-OXO-1-AMINO-CYCLOHEXANECARBOXYLIC ACIDS.

Carlos Cativiela*. Dº of Organic Chemistry. ICMA. Universidad de Zaragoza-CSIC. 50009 Zaragoza. Spain. Alberto Avenoza, Héctor Busto and Jesús M. Peregrina. Dº of Chemistry (Organic Chemistry). Ciencias. Universidad de La Rioja. 26001 Logroño. Spain.

The present report describes the synthesis of both the *cis*- and *trans*-2-phenyl-4-oxo-1-aminocyclohexanecarboxylic acids starting from (Z)-2-phenyl-4-benzylidene-5(4H)-oxazolone and methyl (E)-2-cyanocinnamate respectively, where the key steps are the Diels-Alder cycloadditions of these dienophiles with Danishefsky's diene in the first case and with 2-methoxy-1,3-butadiene in the second case.

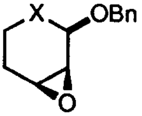


Tetrahedron, **1994**, *50*, 12999

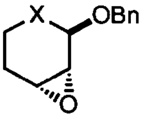
REGIOCHEMICAL CONTROL OF THE RING OPENING OF 1,2-EPOXIDES BY MEANS OF CHELATING PROCESSES. 8. SYNTHESIS AND RING OPENING REACTIONS OF cis- AND trans-OXIDES DERIVED FROM 3-BENZYLOXYCYCLOHEXENE AND 2-BENZYLOXY-5,6-DIHYDRO-2*H*-PYRAN

Federico Calvani, Paolo Crotti,* Cristina Gardelli, and Mauro Pineschi
Dipartimento di Chimica Bioorganica, Università di Pisa, Via Bonanno 33, 56126 Pisa, Italy

The regiochemical outcome of the ring opening of 1,2-epoxides bearing polar remote functionalization through chelation processes assisted by metal ions, was verified in cyclic oxirane systems (epoxides 5-8) having the polar functionality in an allylic position to the oxirane ring.



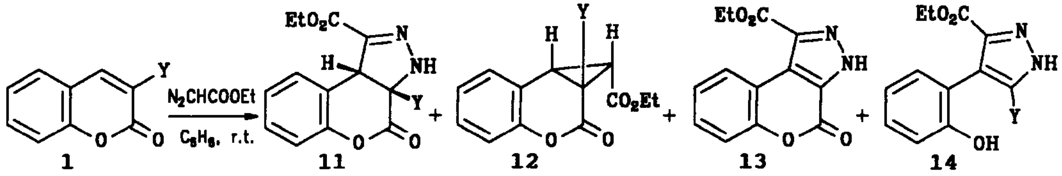
5 $X=CH_2$ **6**
7 $X=O$ **8**



Tetrahedron, **1994**, *50*, 13023

REGIO- AND STEREO-SELECTIVE 1,3-DIPOLAR CYCLOADDITION REACTIONS OF ETHYL DIAZOACETATE TO 3-SUBSTITUTED 2*H*-1-BENZOPYRAN-2-ONES.

A. Bojilova, I. Videnova and C. Ivanov, University of Sofia, Bulgaria, **N. A. Rodios***, University of Thessaloniki, Greece;
A. Terzis and C. P. Raptopoulou, NCR Demokritos, Athens, Greece

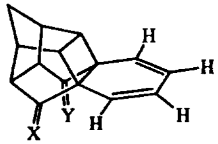


1 11 12 13 14

Tetrahedron, **1994**, *50*, 13037

DIASTEREOFACIAL SELECTIVITY IN DIELS-ALDER CYCLOADDITIONS OF METHYL ACRYLATE TO FACIALLY DIFFERENTIATED UNSYMMETRICAL CYCLOHEXA-1,3-DIENES

James M. Coxon*, Siew Tai Fong, Karen Lundie, D. Quentin McDonald, and Peter J. Steel**University of Canterbury, NZ,* Alan P. Marchand*, Florencio Zaragoza, Umesh R. Zope, D. Rajagopal and Simon G. Bott* *University of North Texas,* William H. Watson* and Ram P. Kashyap *Texas Christian University.*



1b: $X = H_2$, $Y = OCH_2CH_2O$ **1d:** $X = O$, $Y = H_2$
1c: $X = O$, $Y = OCH_2CH_2O$ **1e:** $X =$ *endo*-OH $Y = H_2$ **1f:** $X =$ *endo*-OH, $Y = OCH_2CH_2O$

The Diels Alder reactions of **1b-f** with methyl acrylate occurred with a high degree of facial selectivity and a moderate degree of regioselectivity. Fixed model transition state calculations establish the controlling factors.