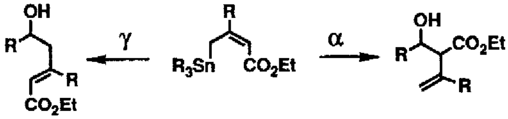
# GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30,5533(1989)

## TIN ANALOGS OF THE VINYLOGOUS REFORMATSKY REACTION. REGIO- AND STEREOCHEMICAL CONSIDERATIONS

R. L. Fan and Tomas Hudlicky*
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

The regioselectivity in the α– vs. γ-additions of reagents **1a** and **1b** to carbonyl compounds under acidic conditions was investigated.



**1a.** R = Me
**1b.** R = OMe

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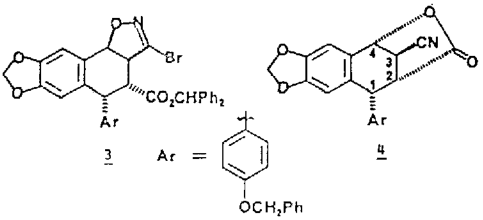
Tetrahedron Lett. 30,5537(1989)

## SYNTHESIS OF A PODOPHYLLOTOXIN ANALOG USING A NOVEL IODOTRIMETHYLSILANE MEDIATED FRAGMENTATION

Arthur Haber
Bristol-Myers Company, PRDD, P.O. Box 4755
Syracuse, NY 13221 (USA)

The bromoisoxazoline functionality of podophyllotoxin analog intermediate 3 was fragmented by TMSI to γ-lactone 4. This lactone was converted to a podophyllotoxin analog.



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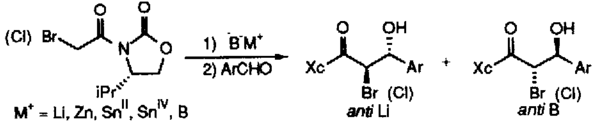
Tetrahedron Lett. 30,5539(1989)

## A PREDOMINATELY *ANTI*-STEREOSELECTIVE CHIRAL METAL DIRECTED ALDOL CONDENSATION WITH AROMATIC ALDEHYDES

Lendon N. Pridgen*, A. Magid, and I. Lantos
Synthetic Chemistry Department, Chemical R&D, Smith Kline & French Laboratories
Post Office Box 1539, King of Prussia, Pennsylvania 19406

Chiral haloacetyl oxazolidinones were reacted with aromatic aldehydes via their kinetically generated Z-enolates to yield predominately anti aldol adducts. The reaction is postulated to proceed through a boat-like transition state. A unique reversal of chirality was observed in using stannous enolates.



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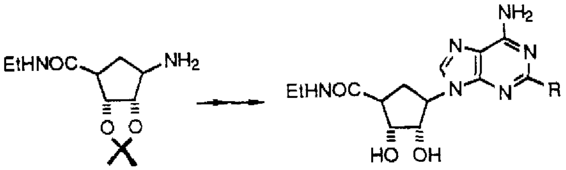
Tetrahedron Lett. 30,5543(1989)

## A NOVEL AND EFFICIENT ROUTE TO CHIRAL 2-SUBSTITUTED CARBOCYCLIC 5'-N-ETHYL-CARBOXAMIDO-ADENOSINE (C-NECA)

Jen Chen*, Michael Grim, Caren Rock and Kenneth Chan
Research Department, Pharmaceutical Division
CIBA-GEIGY Corporation, Summit, N.J. 07901

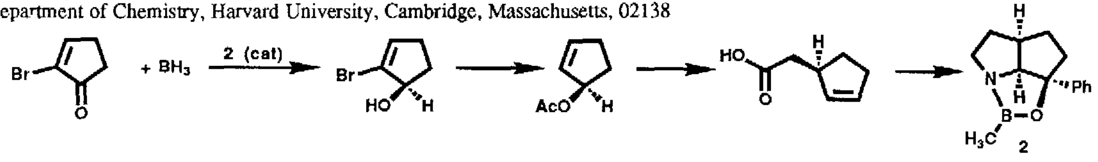
A series of chiral 2-substituted-carbocyclic-NECA analogs was prepared in seven steps with an efficient resolution.



Tetrahedron Lett. 30,5547(1989)

## (+)-1(*S*), 5(*R*), 8(*S*)-8-PHENYL-2-AZABICYCLO[3.3.0]OCTAN-8-OL N,O-METHYLBORONATE (2) AND ITS ENANTIOMER, CHIRAL CHEMZYMES WHICH SERVE AS CATALYSTS FOR THEIR OWN ENANTIOSELECTIVE SYNTHESIS

E. J. Corey, C.-P. Chen, and Gregory A. Reichard
Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138



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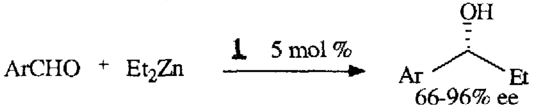
Tetrahedron Lett. 30,5551(1989)

## Chiral Oxazaborolidines as Catalysts for the Enantioselective Addition of Diethylzinc to Aldehydes

N. N. Joshi, M. Srebnik* and Herbert C. Brown*
H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907 USA.

The oxazaborolidine, **1**, conveniently derived from (-)ephedrine and $BH_3{\cdot}SMe_2$ provides an excellent catalyst for the enantioselective addition of diethylzinc to aromatic aldehydes. This is the first example of a chiral boron intermediate for this reaction.



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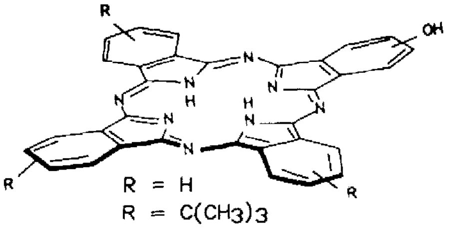
Tetrahedron Lett. 30,5555(1989)

## THE SYNTHESES OF A MONOSUBSTITUTED AND AN UNSYMMETRICAL TETRASUBSTITUTED PHTHALOCYANINE USING BINUCLEAR PHTHALOCYANINES

Clifford C. Leznoff and Shafrira Greenberg
Department of Chemistry, York University,
North York (Toronto),Ontario, Canada M3J 1P3

The syntheses of 2-hydroxyphthalocyanine and 2-hydroxy-9,16,23-tri-*tert*-butylphthalocyanine have been accomplished.



R = H
R = $C(CH_3)_3$

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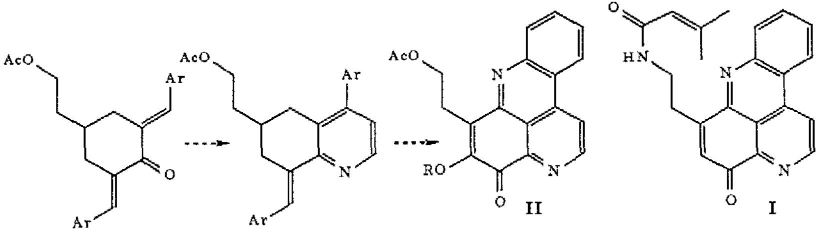
Tetrahedron Lett. 30,5559(1989)

## SYNTHETIC STUDIES TOWARDS CYSTODYTIN A: THE PREPARATION OF NOVEL CYSTODYTIN CONGENERS

Marco A. Ciufolini and Norman E. Byrne
Department of Chemistry, Rice University, P. O. Box 1892, Houston, Texas 77251, U.S.A.

The synthesis of compounds II (R= H, Ac, Me, Tf) is described. These substances exhibit the complete ring system of the cystodytins, e.g. cystodytin A, I.

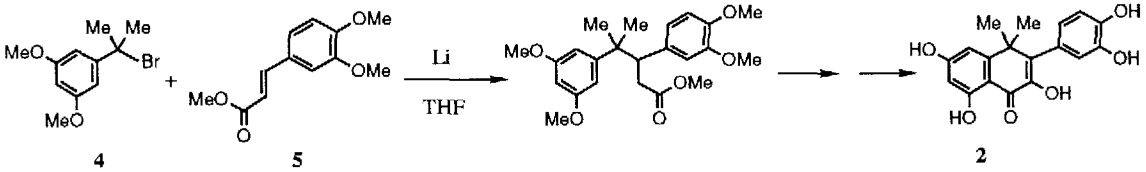


Tetrahedron Lett. 30,5563(1989)

## SYNTHESIS OF A CARBOCYCLIC ANALOG OF QUERCETIN VIA A BARBIER REACTION

Neng-Yang Shih, Pietro Mangiaracina, Michael J. Green, and Ashit K. Ganguly
Schering-Plough Research, Schering-Plough Corporation, 60 Orange Street, Bloomfield, N.J. 07003

The Michael addition of a tertiary bromide **4** to α,β-unsaturated ester **5** by a Barbier reaction is described, which is a key step in the synthesis of a carbocyclic analog of quercetin **2**.



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Tetrahedron Lett. 30,5567(1989)

## DIMETHYLDIOXIRANE: MECHANISM OF BENZALDEHYDE OXIDATION

A.L. Baumstark,* M. Beeson and P.C. Vasquez
Department of Chemistry and LMBS, Georgia State University
*Atlanta, Georgia 30303-3083 U.S.A.*

$$XC_6H_4CHO + 1 \xrightarrow{N_2} XC_6H_4CO_2H$$

Dimethyldioxirane **1**, under $N_2$, converts benzaldehydes solely to the corresponding acids; the reaction is insensitive to electronic effects; yields are limited by the decomposition of 1 to acetol; $O_2$-trapping experiments support a hydrogen-atom abstraction mechanism.

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Tetrahedron Lett. 30,5571(1989)

## PREPARATION OF α-FLUORO-α,β-UNSATURATED ESTERS VIA TWO CARBON HOMOLOGATION OF ESTERS

Alagappan Thenappan and Donald J. Burton
Dept. of Chemistry, The University of Iowa,
Iowa City, IA 52242, USA

In the presence of diisobutyl aluminum hydride, esters react with an anion derived from $(EtO)_2P(O)CFHC(O)OEt$ to give the title compounds in good yields. The scope of this method and the factors which influence the stereochemistry of the products are discussed.

$$RC(O)OR' \xrightarrow[\substack{1)\,DIBAL \\ 2)\,[(EtO)_2P(O)C^{-}FC(O)OEt]\ M^{+}}]{THF/-78^{\circ}\ C} RCH{=}CFCOOEt \quad (E\ and\ Z)$$

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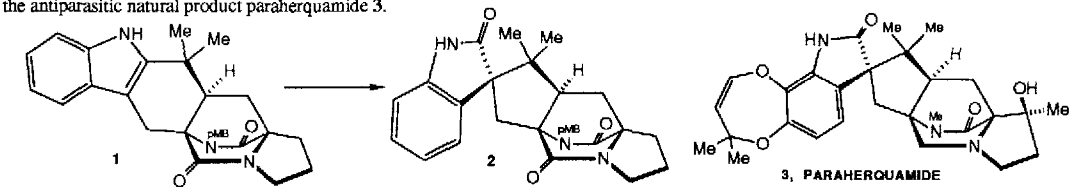
Tetrahedron Lett. 30,5575(1989)

## SYNTHETIC STUDIES ON PARAHERQUAMIDE: REGIOSELECTIVITY OF INDOLE OXIDATION

Robert M. Williams*; Tomasz Glinka and Ewa Kwast
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Regioselective oxidation of the hexacyclic indole 1 provides the spiro-oxindole 2 which serves as a model to construct the antiparasitic natural product paraherquamide 3.

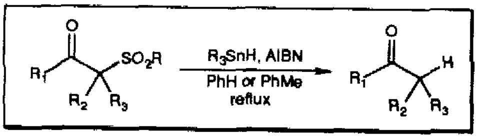


Tetrahedron Lett. 30, 5579 (1989)

## AN EFFICIENT NEW METHOD FOR THE DESULFONYLATION OF β-KETO PHENYLSULFONES

Amos B. Smith, III* Karl J. Hale and John P. McCauley, Jr.
*Department of Chemistry, the Laboratory for Research on the Structure of Matter and the Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, PA 19104, U.S.A.*

β-Keto phenylsulfones can be readily desulfonylated with excess tributyl- or triphenylstannane and AIBN at reflux in toluene, affording the corresponding ketones in good to excellent yields. The reaction proceeds under neutral conditions and is therefore compatible with a wide variety of functionalities.



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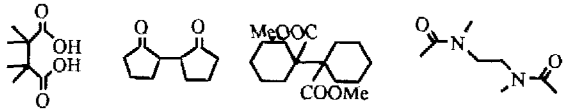
Tetrahedron Lett. 30, 5583 (1989)

## EHYDRODIMERIZATION OF KETONES, CARBOXYLIC CIDS, AMIDES, ESTERS, ALCOHOLS, AND AMINES VIA MERCURY-PHOTOSENSITIZATION

Constantine G. Boojamra, Robert H. Crabtree*, Richard R. Ferguson, and Cesar A. Muedas
Sterling Chemistry Laboratory, Yale University, New Haven, CT 06520, USA

$$R\text{-}H \xrightarrow[254\ \mathrm{nm}]{Hg,\ H_2} R\text{-}R$$

e.g., R-R =



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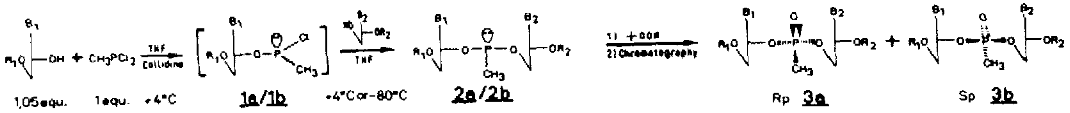
Tetrahedron Lett. 30, 5587 (1989)

## ONE POT $R_P$-DIASTEREOSELECTIVE SYNTHESIS OF DINUCLEOSIDE METHYLPHOSPHONATES USING $CH_3PCl_2$

Thomas Löschner and Joachim Engels, J.W. Goethe-Universität,
Institut für Organische Chemie, Niederurseler Hang, D-6000 Frankfurt/Main 50

Using $CH_3PCl_2$ and suitably protected nucleosides at low temperature remarkable diastereoselectivity is possible in the synthesis of dinucleoside methylphosphonates



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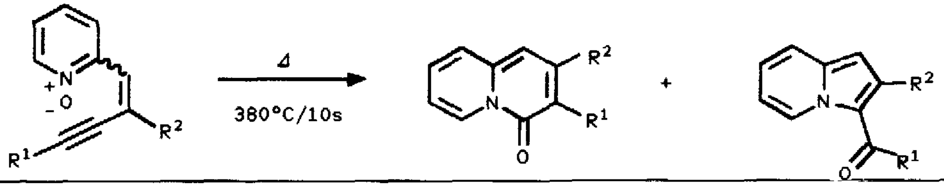
Tetrahedron Lett. 30, 5591 (1989)

## HETEROCYCLIC SYNTHESIS BY ELECTROCYCLIZATION OF EXTENDED DIPOLES: A NOVEL ACCESS TO THE INDOLIZINE AND QUINOLIZINE SYSTEMS

Wolfgang Eberbach* and Wolfram Maier, Institut für Organische Chemie und Biochemie der Universität Albertstrasse 21, D-7800 Freiburg i.Br., West Germany

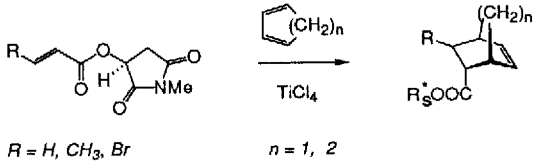


Tetrahedron Lett. 30,5595(1989)

## N-SUBSTITUTED HYDROXYSUCCINIMIDES FROM (S)-MALIC ACID AS NEW REAGENTS FOR ASYMMETRIC DIELS-ALDER ADDITIONS TO ENOATES

Thomas Poll, A. F. Abdel Hady, Reinhard Karge,
Günter Linz, John Weetman and Günter Helmchen*

Organisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, D-6900 Heidelberg



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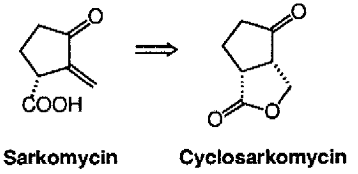
Tetrahedron Lett. 30,5599(1989)

## ASYMMETRIC DIELS-ALDER REACTIONS: EPC-SYNTHESIS OF A STABLE SARKOMYCIN PRECURSOR

Günter Linz, John Weetman, A.F. Abdel Hady and Günter Helmchen*
Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg

The first synthesis of enantiomerically pure cyclosarkomycin, a stable, crystalline precursor of the antitumor agent sarkomycin is reported. Key steps are an asymmetric Diels-Alder reaction of the (E)-3-bromoacrylate of (R)-pantolactone and introduction of oxygen functionality via elimination/ß-addition.



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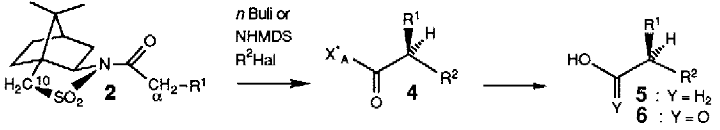
Tetrahedron Lett. 30,5603(1989)

## ASYMMETRIC ALKYLATION OF N-ACYLSULTAMS. A GENERAL ROUTE TO ENANTIOMERICALLY PURE CRYSTALLINE $C(\alpha,\alpha)$-DISUBSTITUTED CARBOXYLIC ACID DERIVATIVES

Wolfgang Oppolzer, Robert Moretti and Silvia Thomi
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Switzerland



Alkylation of acylsultams 2 with primary alkyl halides gave pure 4 which was cleaved to enantiomerically pure alcohols (5) or carboxylic acids (6).

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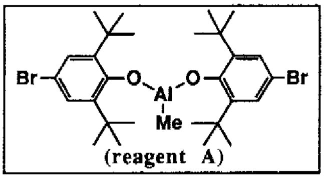
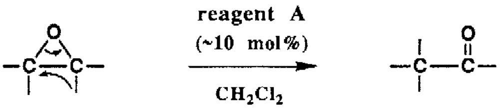
Tetrahedron Lett. 30,5607(1989)

## An Efficient, Catalytic Procedure for Epoxide Rearrangement

Keiji Maruoka, Shigeru Nagahara, Takashi Ooi, and Hisashi Yamamoto*
*Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464-01, Japan*



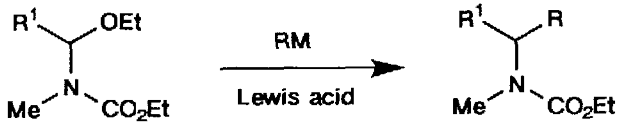


Tetrahedron Lett. 30,5611(1989)

## THE ALKYLATION OF α-ETHOXYCARBAMATES WITH ORGANO-LEAD, -ZINC, AND -COPPER REAGENTS

Jun-ichi Yamada, Hisashi Satô, and Yoshinori Yamamoto*
Department of Chemistry, Faculty of Science,
Tohoku University, Sendai 980, Japan

The alkylation of α-ethoxycarbamates is accomplished with organo-lead, -zinc, and -copper reagents in the presence of Lewis acids.



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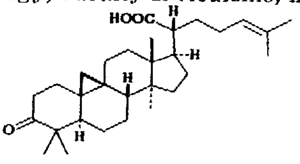
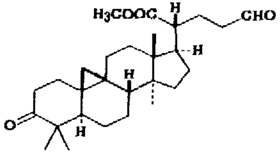
Tetrahedron Lett. 30,5615(1989)

## ISOLATION OF A NEW CYCLOARTANOID TRITERPENE FROM LEAVES OF *LANSIUM DOMESTICUM*, NOVEL SKIN-TUMOR PROMOTION INHIBITORS

Mugio NISHIZAWA,* Makoto EMURA, Hidetoshi YAMADA, Motoo SHIRO,† CHAIRUL,†† Yuji HAYASHI,†† and Harukuni TOKUDA††† *Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-Cho, Tokushima 770, Japan; †Shionogi Research Laboratories, Shionogi & Co. Ltd., Fukushimaku, Osaka 553, Japan; ††Faculty of Science, Osaka City University, Sumiyoshiku, Osaka 558, Japan, †††Department of Microbiology, Faculty of Medicine, Kyoto University, Sakyoku, Kyoto 606, Japan*





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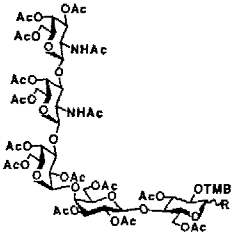
Tetrahedron Lett. 30,5619(1989)

## A TOTAL SYNTHESIS OF PARA-FORSSMAN GLYCOLIPID ISOLATED FROM HUMAN ERYTHROCYTE MEMBRANE

Shigeki Nunomura, Masato Mori, Yukishige Ito, and Tomoya Ogawa*
RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01 Japan

A total synthesis of Para-Forssman glycolipid, GalNAcβ1→ 3GalNAcβ1→ 3Galα1 →4Galβ1→ 4Glcβ1→ 1Cer was achieved in a stereo-controlled manner by use of the key glycopentaosyl fluoride and trichloroacetimidate (R = F and OC=NHCCl$_3$) which carry 2, 4, 6-trimethylbenzoyl (TMB) group at 2-Oa as a stereocontrolling auxiliary.



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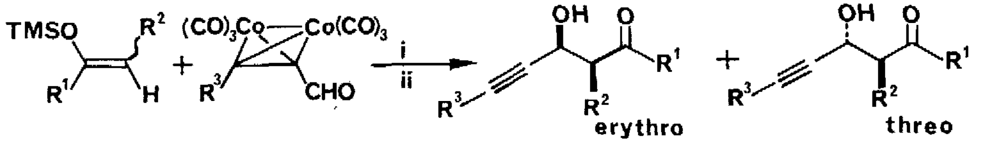
Tetrahedron Lett. 30,5623(1989)

## Dicobalt Hexacarbonyl-Complex of Propynals in Organic Synthesis: Erythro-Selective Aldol Reaction of Cobalt-Complexed Propynals with Silyl Enol Ethers

Chisato Mukai, Kazuyoshi Nagami, and Miyoji Hanaoka*
Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa 920, Japan

Highly erythro-selective aldol reaction of propynals was developed.

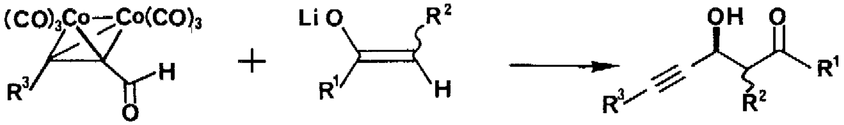


Tetrahedron Lett. 30,5627(1989)

## Dicobalt Hexacarbonyl-Complex of Propynals in Organic Synthesis: Strong E-Enolate:Threo/Z-Enolate:Erythro Correlation in the Aldol Reaction of Cobalt-Complexed Propynals

Chisato Mukai, Kazuyoshi Nagami, and Miyoji Hanaoka*
Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa 920, Japan

Stereoselective reaction of propynals with lithium enolates was described.



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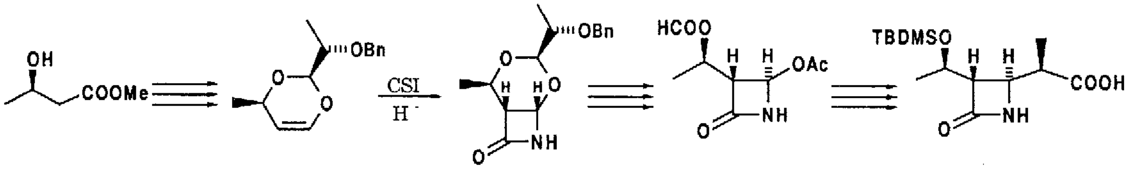
Tetrahedron Lett. 30,5631(1989)

## A NOVEL SYNTHESIS OF THE 1β-METHYLCARBAPENEM KEY INTERMEDIATE EMPLOYING THE [2+2]-CYCLOADDITION REACTION OF CHLOROSULFONYL ISOCYANATE WITH A *4H*-1,3-DIOXIN DERIVATIVE

Yoshio Ito, Yuko Kobayashi, and Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan



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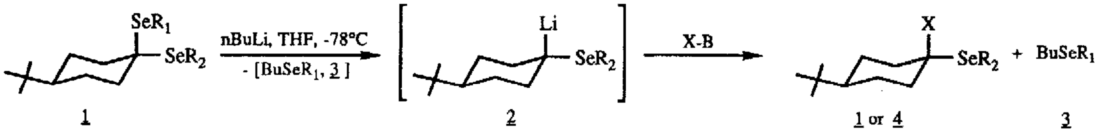
Tetrahedron Lett. 30,5635(1989)

## Stereoselective Synthesis and Reactions of 1-Seleno-4-tert-Butyl Cyclohexyllithiums

A. Krief*, G. Evrard*, E. Badaoui, V. De Beys and R. Dieden
Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles,
B-5000 Namur (BELGIUM)

The axial C-Se bond of seleno- and mixed selenoacetals derived from 4-tert-butyl cyclohexanones exhibit a high tendency to be cleaved by n-butyllithium. The resulting 1-seleno-4-tert-butyl cyclohexyllithiums are selectively protonated or selenylated via axial attack.



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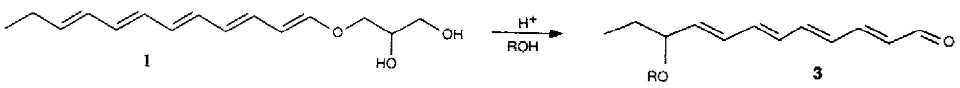
Tetrahedron Lett. 30,5639(1989)

## ANOMALOUS SOLVOLYSIS OF A POLYENOL ETHER OF GLYCEROL.

L.B.J. VERTEGAAL*, M. VAN DER STEEG AND A. VAN DER GEN.
Gorlaeus Laboratories, Department of Organic Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.



Fecapentaene-12 **1** displays an unexpected reactivity when treated with hydrochloric acid in aqueous solvents. The 10-substituted aldehydes **3** (R=H,$CH_3$) are formed as the sole reaction products.

Tetrahedron Lett. 30, 5643 (1989)

## HINDERED ORGANOBORON GROUPS IN ORGANIC SYNTHESIS. 13. THE DIRECT PRODUCTION OF KETONES FROM ALIPHATIC ALDEHYDES BY A UNIQUE VARIANT OF THE BORON-WITTIG REACTION

Andrew Pelter, Keith Smith, Said Elgendy and Martin Rowlands
Department of Chemistry, University College of Swansea, Swansea SA2 8PP, U.K.

$$\mathrm{Mes_2BCHLiR^1 + R^2CHO \xrightarrow[-120^\circ C \rightarrow r.t.]{TFAA\ or\ NCS} R^1CH_2COR^2}$$

$R^1$ = *prim*-alkyl; $R^1 \neq H$

$R^2$ = *prim*-alkyl, *sec*-alkyl, *tert*-alkyl, benzyl.

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Tetrahedron Lett. 30, 5647 (1989)

## HINDERED ORGANOBORON GROUPS IN ORGANIC SYNTHESIS. 14. STEREOSELECTIVE SYNTHESIS OF ALKENES BY THE BORON-WITTIG REACTION USING ALIPHATIC ALDEHYDES.

Andrew Pelter, Keith Smith, Said Elgendy and Martin Rowlands
Department of Chemistry, University College of Swansea, Swansea SA2 8PP, U.K.

$$\mathrm{Mes_2\,BCHLiR^1 + R^2CHO \xrightarrow[-120^\circ C \rightarrow r.t.]{XH} R^2CH=CHR^1}$$

$R^1$ = H, *prim*-alkyl; $R^2$ = *prim*-alkyl, *sec*-alkyl, *tert*-alkyl; benzyl

XH = $CH_3CO_2H$, $CF_3CO_2H$, $CF_3SO_3H$, HCl

When XH = $CF_3SO_3H$ or HCl products *in all cases* are primarily *E*-alkenes

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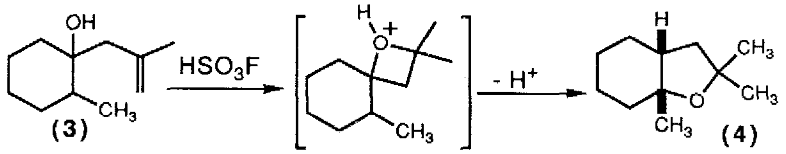
Tetrahedron Lett. 30, 5651 (1989)

## HSO3F INDUCED CYCLISATION OF A METHALLYL CARBINOL INVOLVING AN OXYGEN MIGRATION

Steven T. Bright, James M. Coxon* and Peter J. Steel*
*Chemistry Department, University of Canterbury, Christchurch, New Zealand.*

The methallyl carbinol **3** reacts with $HSO_3F$ to give the ether **4** via a protonated oxetane.



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Tetrahedron Lett. 30, 5653 (1989)

## PREPARATION OF METHYL-2-(W-IODOALKYL)PROPENOATES AND A FACILE ROUTE TO 2-CARBOMETHOXY-1,3-BUTADIENE

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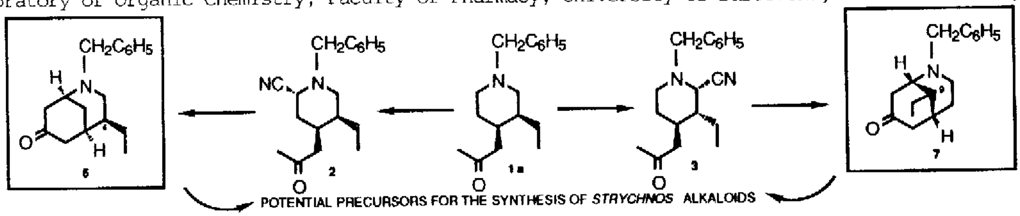
α-Methylene-γ-and-δ-lactones undergo facile ring opening with trimethylsilyl iodide to yield 2-(iodoethyl) propenoic and 2-(iodopropyl)propenoic acids respectively which are methylated to afford the corresponding esters. Treatment of methyl-2-(iodoethyl)propenoate with base generates 2-carbomethoxy-1,3-butadiene which undergoes dimerisation or can be trapped in-situ.

Tetrahedron Lett. 30, 5655 (1989)

## STEREOCONTROLLED SYNTHESIS OF 4- AND 9-ETHYL-2-AZABICYCLO[3.3.1]NONAN-7-ONES VIA 2-CYANOPIPERIDINES

Josep Bonjoch*, Núria Casamitjana, Jordi Gràcia, and Joan Bosch*
Laboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, 08028-Barcelona, Spain



POTENTIAL PRECURSORS FOR THE SYNTHESIS OF *STRYCHNOS* ALKALOIDS

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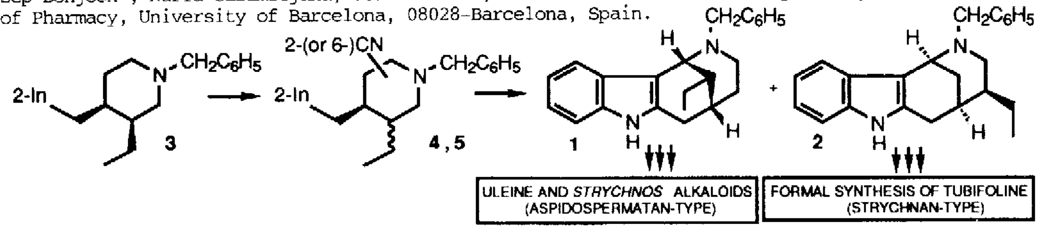
Tetrahedron Lett. 30, 5659 (1989)

## STEREOCONTROLLED ACCESS TO DASYCARPIDAN-TYPE COMPOUNDS AND FORMAL TOTAL SYNTHESIS OF *STRYCHNOS* INDOLE ALKALOIDS OF THE STRYCHNAN-TYPE.

Josep Bonjoch*, Núria Casamitjana, Jordi Gràcia, and Joan Bosch*. Laboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, 08028-Barcelona, Spain.



ULEINE AND *STRYCHNOS* ALKALOIDS (ASPIDOSPERMATAN-TYPE)

FORMAL SYNTHESIS OF TUBIFOLINE (STRYCHNAN-TYPE)

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Tetrahedron Lett. 30, 5663 (1989)

## A SIMPLE CONVENIENT PROCEDURE FOR IODINATION OF ALCOHOLS AND REDUCTIVE IODINATION OF CARBONYL COMPOUNDS USING N,N-DIETHYLANILINE-BORANE-$I_2$ SYSTEM

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School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 134, India

Alcohols, carboxylic acids and carbonyl compounds on reaction with N,N-diethylaniline:$BH_3$-$I_2$ reagent give the corresponding alkyl iodides.