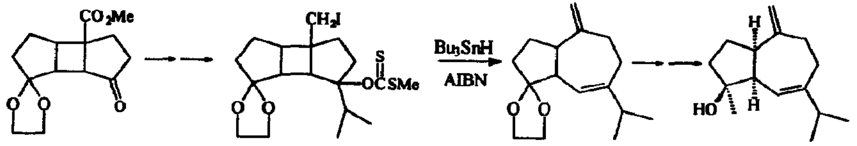
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 8513

SYNTHESIS OF THE GUAIANE (±)-ALISMOL USING A FREE RADICAL FRAGMENTATION/ELIMINATION SEQUENCE

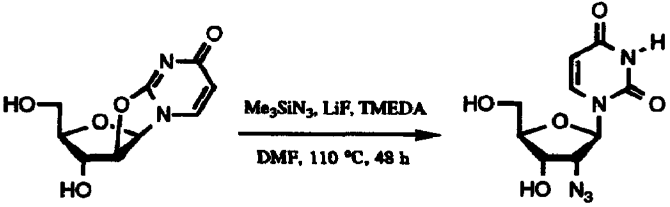
Gordon L. Lange* and Christine Gottardo, Guelph-Waterloo Centre for Graduate Work in Chemistry,
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.



Tetrahedron Letters, **1994**, *35*, 8517

An Improved Synthesis of 2'-Azido-2'-Deoxyuridine

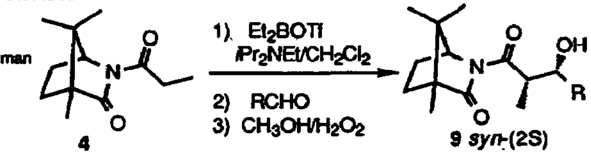
Gary P. Kirschenheuter,* Yansheng Zhai and Wolfgang A. Pieken
NeXagen, Inc. 2860 Wilderness Place, Boulder, CO 80301



Tetrahedron Letters, **1994**, *35*, 8521

TOWARD THE DEVELOPMENT OF A GENERAL CHIRAL AUXILIARY 2. EVALUATION OF CAMPHOR LACTAM IMIDE AUXILIARIES FOR ASYMMETRIC ALDOL REACTIONS

Robert K. Boeckman, Jr.,* Alan T. Johnson, and Rhonda A.. Musselman
Department of Chemistry
University of Rochester
Rochester, New York 14627-0216



4

9 *syn*-(2S)

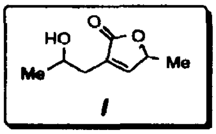
The Z-diethylenolborinate derived from 4 affords very good to excellent syn-2S diastereoselectivity with a variety of aldehydes. The reactivity of these enolates was lower than expected, and the reactivity and stereoselectivity were found to be sensitive to the size of the ligands on boron.

Tetrahedron Letters, **1994**, *35*, 8525

Stereostructural Studies on the 4-Hydroxylated Annonaceous Acetogenins: Synthesis of Model Butenolides of Known Relative and Absolute Configuration Involving an Intriguing Translactonization Reaction

Thomas R. Hoye,* Paul R. Hanson, Linda E. Hasenwinkel,
Elizabeth A. Ramirez and Zhiping Zhuang

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455



I

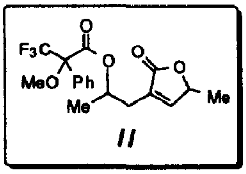
Each diastereomer of model butenolides **I** was synthesized from appropriate antipodes of propylene oxide. Concomitant translactonization reactions have important stereochemical ramifications.

Tetrahedron Letters, **1994**, *35*, 8529

Stereostructural Studies on the 4-Hydroxylated Annonaceous Acetogenins: A Novel Use of Mosher Ester Data for Determining *Relative* Configuration [Between C(4) and C(36)]

Thomas R. Hoye,* Paul R. Hanson, Linda E. Hasenwinkel,
Elizabeth A. Ramirez and Zhiping Zhuang

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455



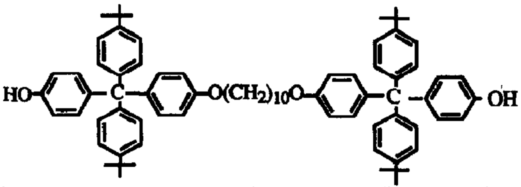
Analysis of MTPA (Mosher) esters of II vis-a-vis the MTPA derivatives of 4-hydroxylated acetogenins provides the first general method for assignment of C(4)/C(36) relative configuration.

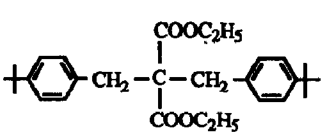
Tetrahedron Letters, **1994**, *35*, 8533

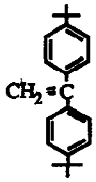
Difunctional Blocking Groups for Rotaxanes and Polyrotaxanes. Shu Liu and Harry W. Gibson*,

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Three difunctional blocking groups for rotaxanes and polyrotaxanes were synthesized:





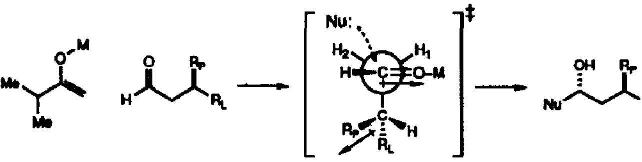


Tetrahedron Letters, **1994**, *35*, 8537

1,3-Asymmetric Induction in the Aldol Addition Reactions of Methyl Ketone Enolates and Enolsilanes to β-Substituted Aldehydes. A Model for Chirality Transfer

David A. Evans,* Joseph L. Duffy, and Michael J. Dart
Department of Chemistry, Harvard University, Cambridge, Mass. 02138, USA

The diastereoselectivities of the indicated aldol reactions were documented for a representative set of enol derivatives (M = Li, TiCl$_n$, BR$_2$, SiMe$_3$) and β-substituted aldehydes (Rp = OR, OAc, Cl). A model for the addition process is proposed to account for the data reported.

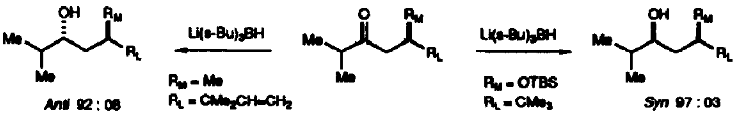


Tetrahedron Letters, **1994**, *35*, 8541

1,3-Asymmetric Induction in Hydride Addition Reactions to β-Substituted Ketones. A Model for Chirality Transfer

David A. Evans,* Michael J. Dart, and Joseph L. Duffy
Department of Chemistry, Harvard University, Cambridge, Mass. 02138, USA

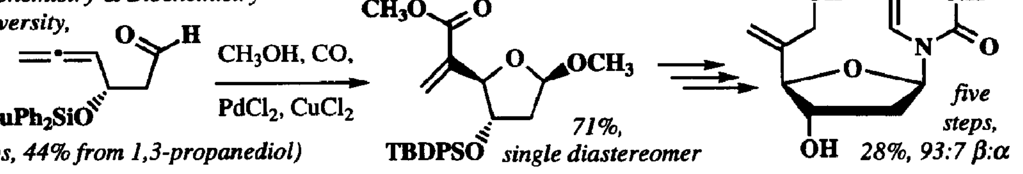
A reversal in carbonyl π-facial selectivity is observed in the reductions of β-substituted ketones depending on the nature of the β-substituent. A polar model is proposed to account for this turnover.



Tetrahedron Letters, **1994**, *35*, 8545

SYNTHESIS OF A NUCLEOSIDE ANALOG BEARING A BRANCHED DIFUNCTIONAL SIDECHAIN USING THE PALLADIUM-MEDIATED CYCLIZATION OF A γ-OXOALLENE

Robert D. Walkup, and Michael D. Mosher*
Department of Chemistry & Biochemistry
Texas Tech University,
Lubbock, Texas
79409-1061



(six steps, 44% from 1,3-propanediol)

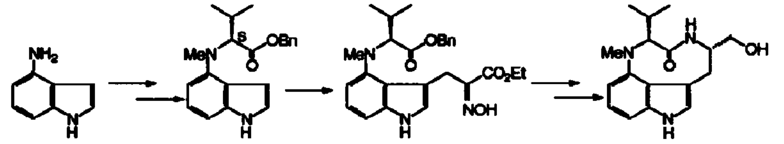
71%, single diastereomer

five steps, 28%, 93:7 β:α

Tetrahedron Letters, **1994**, *35*, 8549

Protein Kinase C Modulators. Indolactams. 1. Efficient and Flexible Routes for the Preparation of (−)-Indolactam V for Use in the Synthesis of Analogs. James Quick*, Bijali Saha and Paul E. Driedger. Procyon Pharmaceuticals, Inc., 165 New Boston St., Woburn, MA 01801.

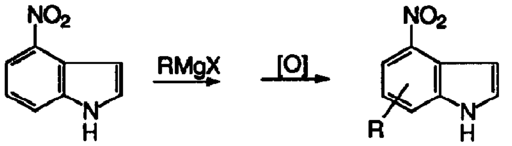
Abstract: Three synthetic routes to the protein kinase C activator, (−)-indolactam V, are described and are compared for their potential utility in the preparation of ILV analogs. In one route the 4-amino functionality is introduced regiospecifically during the construction of the indole portion and enantiomeric control is achieved by the alkylation of the amine with a triflate derived from D-valine.



Tetrahedron Letters, **1994**, *35*, 8553

Protein Kinase C Modulators. Indolactams. 2.[1] Alkylation of 4-Nitroindole by Grignard Reagents. Synthesis of (−)-7-OctylindolactamV. James Quick* and Bijali Saha. Procyon Pharmaceuticals, Inc., 165 New Boston St., Woburn, MA 01801.

Abstract: A method for the C-alkylation of 4-nitroindole at the 5 and 7 positions has been developed. The 4-nitro-7-octylindole thus prepared has been used as a starting material for the synthesis of the lyngbyatoxin analog, (−)-7-octylindolactam V.

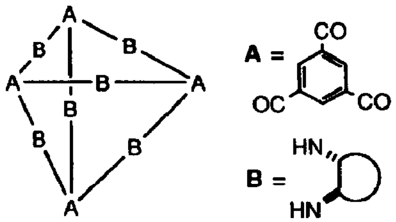


Tetrahedron Letters, **1994**, *35*, 8557

Cyclooligomeric Receptors for the Sequence Selective Binding of Peptides. A Tetrahedral Receptor from Trimesic Acid and 1,2-Diamines.

Seung Soo Yoon and W. Clark Still
Department of Chemistry, Columbia University, New York, NY 10027

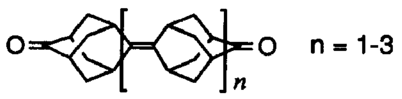
A new, tetrahedrally symmetric A_4B_6 receptor is prepared by simple chemistry and shown to bind certain peptides sequence selectively. The work indicates what general structural features are associated with hosts that bind peptides in organic solvents.



Tetrahedron Letters, **1994**, *35*, 8561

Synthesis and X-ray Crystal Structures of Poly-Adamantane Molecular Rods

Fred D. Ayres,* Saeed I. Khan, Orville L. Chapman, Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90024-1569 USA

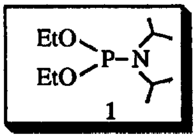


Tetrahedron Letters, **1994**, *35*, 8565

Diethoxy N, N-diisopropyl Phosphoramidite as an Improved Capping Reagent in the Synthesis of Oligonucleotides Using Phosphoramidite Chemistry

Dong Yu, Jin-yan Tang, Radhakrishnan P. Iyer and Sudhir Agrawal*
Hybridon Inc., One Innovation Drive, Worcester, MA 01605.

Reported herein is the use of Diethoxy N, N-diisopropyl Phosphoramidite (1) as an improved capping reagent in the synthesis of oligonucleotides using phosphoramidite chemistry.



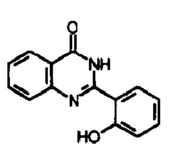
1

Tetrahedron Letters, **1994**, *35*, 8569

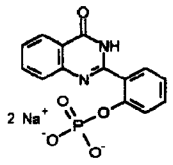
SYNTHESIS AND USE OF NEW FLUOROGENIC PRECIPITATING SUBSTRATES.

J.J.Naleway*, C.M.J.Fox, D.Robinhold, E.Terpetschnig, N.A.Olson, and R.P.Haugland, Molecular Probes, Inc., Eugene, OR 97402 USA

Synthesis of novel precipitating fluorogenic enzyme substrates, for example **5b**, from the base quinazolinone dye **4a** is described.



4a

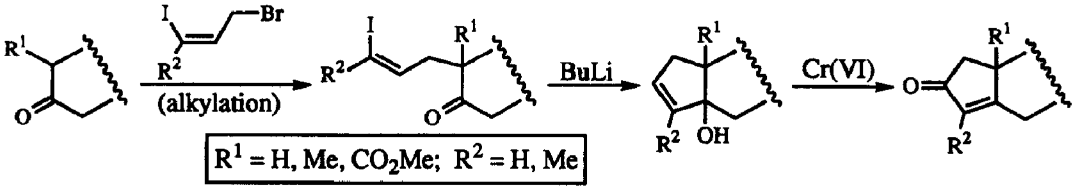


5b

Tetrahedron Letters, **1994**, *35*, 8573

A NEW CYCLOPENTENONE ANNULATION METHOD

Edward Piers,* Katherine L. Cook, and Christine Rogers
Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1



$R^1 = H, Me, CO_2Me;\ R^2 = H, Me$

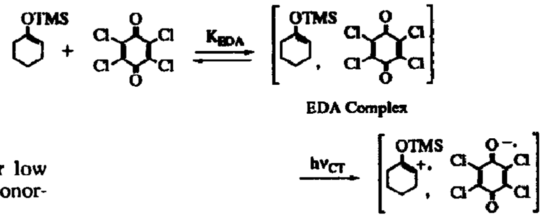
Tetrahedron Letters, **1994**, *35*, 8577

Quantitative Assessment of Electron-Donor Properties of Enol Silyl Ethers: Charge-Transfer Complex Formation, Photoelectron Spectra and Transient Electrochemical Oxidation

Rajendra Rathore and Jay K. Kochi

Chemistry Department, University of Houston
Houston, Texas, 77204-5641, U.S.A.

Enol silyl ethers are excellent electron donors by virtue of their low ionization and oxidation potentials and they readily form electron donor-acceptor complexes with quinones.

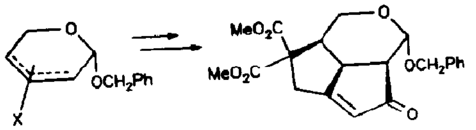


Tetrahedron Letters, **1994**, *35*, 8581

SYNTHESIS OF POLYFUNCTIONALIZED BIS-ANNULATED PYRANOSIDES: USEFUL INTERMEDIATES FOR TRIQUINANE SYNTHESIS.

Noshena Naz, Taleb H. Al-Tel, Yousef Al-Abed and Wolfgang Voelter
Abteilung für Physikalische Biochemie der Universität Tübingen, Hoppe-Seyler-Straße 4, D-72076 Tübingen, Germany

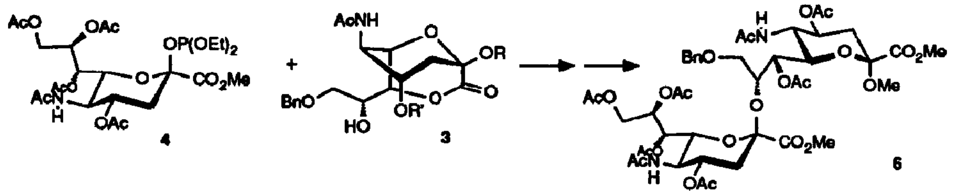
A mild and efficient mehtod for the synthesis of polyfunctionalized bis-annulated pyranosides is described.



Tetrahedron Letters, **1994**, *35*, 8583

8-O-Sialylation of Derivatives of Neuraminic Acid 1,7-Lactone Unusual Stereoselectivity

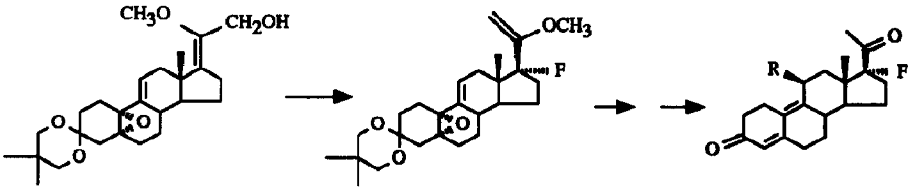
Yury E. Tsvetkov and Richard R. Schmidt
Fakultät Chemie, Universität Konstanz, Postfach 5560 M 725, D-78434 Konstanz, Germany



Tetrahedron Letters, **1994**, *35*, 8587

A Facile Construction of the 17α-Fluoroprogesterone Side Chain

Günter Neef*, Gerhard Ast, Günter Michl, Wolfgang Schwede, and Harry Vierhufe
Research Laboratories of Schering AG,
D-13342 Berlin
Germany



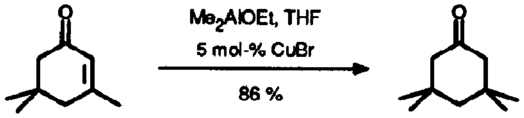
A new process for the synthesis of highly functionalized 17α-fluoroprogesterone derivatives is described.

Tetrahedron Letters, **1994**, *35*, 8591

The Role of Silanes on the Copper-Catalyzed Conjugate Alkylation of Enones by Organoaluminium Reagents.

Jazid Kabbara*, Steffen Flemming, Klaus Nickisch, Harribert Neh, and Jürgen Westermann,
Schering AG, Pharma Process Research, Müllerstrasse 178, D-13342 Berlin, Germany

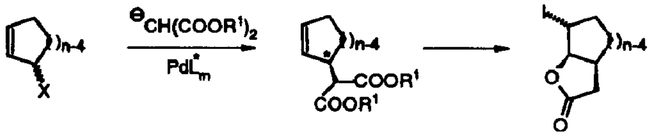
The effect of TMSCl as an additive in the copper-catalyzed conjugate alkylation of enones by various organoaluminium reagents was investigated. Me_2AlOEt turned out to be a useful reagent for methylation without support of additives.



Tetrahedron Letters, **1994**, *35*, 8595

Enantiomerically Pure Cycloalkenylacetic Acid Derivatives *via* Pd-Catalyzed Asymmetric Allylic Alkylation and Subsequent Enantiomeric Enrichment *via* Iodolactones

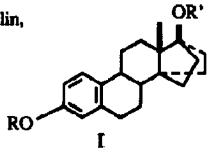
Peter Sennhenn, Bert Gabler and Günter Helmchen*
Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany



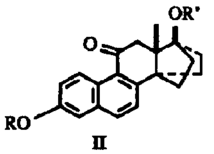
Tetrahedron Letters, **1994**, *35*, 8599

SYNTHESIS OF 14,17α-ETHANO-BRIDGED EQUILENIN DERIVATIVES

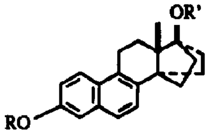
H. Künzer,* M. Thiel, and G. Sauer
Research Laboratories, Schering AG Berlin,
Müllerstrasse 170-178,
1000 Berlin 65,
Germany



I



II



III

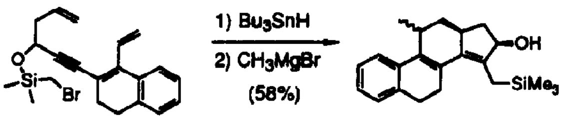
The conversion of I into II by ceric ammonium nitrate is reported. Intermediate II serves as starting point in the synthesis of biologically interesting steroids, e. g., III.

Tetrahedron Letters, **1994**, *35*, 8601

RADICAL CYCLIZATION OF BROMOMETHYLDIMETHYLSILYL PROPARGYL ETHERS; SYNTHESIS OF A CARBOCYCLIC CORE OF STEROID SKELETON BY A TANDEM RADICAL CYCLIZATION.

Sashuang Wu, Michel Journet and Max Malacria*
Université P. et M. Curie, Laboratoire de Chimie Organique de Synthèse, associé au CNRS, B.229, 4 Place Jussieu,
75252 Paris cédex 05, France.

The radical cyclization of a bromomethyldimethylsilyl propargyl ether allowed the formation of a carbocyclic core steroid skeleton in a one-pot reaction.

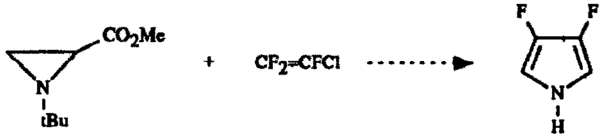


Tetrahedron Letters, **1994**, *35*, 8605

FIRST ACCESS TO 3,4-DIFLUORO-1*H*-PYRROLE

Jacques Leroy and Claude Wakselman
CNRS-CERCOA, 2, rue H. Dunant, F94320 Thiais, France

3,4-Difluoropyrrole is prepared from a *N*-alkylaziridine and chlorotrifluoroethylene.

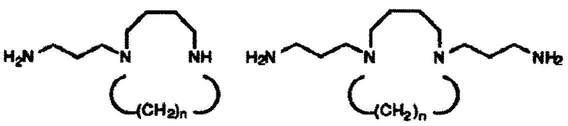


Tetrahedron Letters, **1994**, *35*, 8609

CYCLOPOLYAMINES: SYNTHESIS OF CYCLOSPERMIDINES AND CYCLOSPERMINES ANALOGUES OF SPERMIDINE AND SPERMINE

Guy Brand, Mir Wais Hosseini* and Romain Ruppert
Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France

The synthesis of a series of cyclic analogues of naturally occurring polyamines putrescine, spermidine and spermine was achieved.

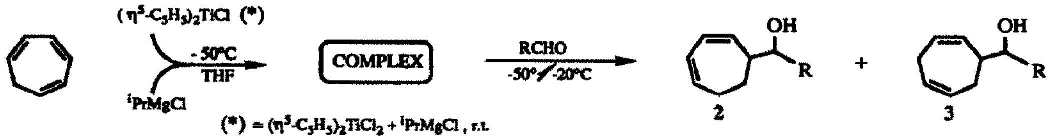


4 n=4, [4,4]cyclospermidine
5 n=5, [4,5]cyclospermidine
6 n=3, [4,3]cyclospermine
7 n=4, [4,4]cyclospermine
8 n=5, [4,5]cyclospermine

Tetrahedron Letters, **1994**, *35*, 8613

TITANIUM-MEDIATED REACTION OF CYCLOHEPTATRIENE WITH ALDEHYDES : A NEW 'ELECTRON-REVERSED' APPROACH TO THE FUNCTIONALIZATION OF SEVEN-MEMBERED RING

Jan Szymoniak, Didier Felix and Claude Moïse, Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS, Faculté des Sciences, 6 bd Gabriel, 21000 Dijon, France.

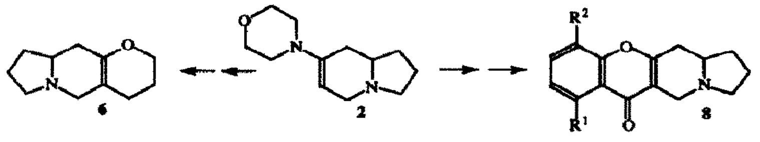


Tetrahedron Letters, **1994**, *35*, 8617

Synthesis of Uncommon heterocyclic Systems : Pyrano- and [1]Benzopyrano[3,2-f]indolizines

Guy Cordonnier, Clarisse Randria, and Henri Sliwa*, Laboratoire de Chimie Organique et Environnement, Université des Sciences et Technologies de Lille 59655, Villeneuve d'Ascq Cedex, France.

Regioselective preparation of the enamine **2** allows the synthesis of the pyrano[3,2-f)]indolizine derivative **6** and gives an entry to a new heterocyclic series the [1]benzopyrano[3,2-f]indolizines **8**.

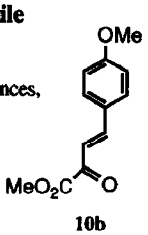


Tetrahedron Letters, **1994**, *35*, 8619

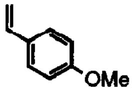
High Yield Endoselective Heterocycloadditions involving Benzylidenepyruvic Esters as the Heterodiene and an Alkoxystyrene as the Dienophile

Gilles Dujardin, Mickaël Maudet and Eric Brown
Laboratoire de Synthèse Organique (URA 482), Faculté des Sciences,
Avenue Olivier Messiaen, BP 535, F-72017 Le Mans, France

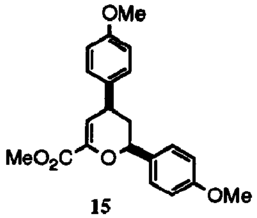
For instance, methyl p-methoxybenzylidenepyruvate **10b** reacted with p-methoxystyrene **12** in the presence of 5% molar amount of $Eu(fod)_3$, in refluxing hexane for 3 days, and afforded the adduct **15** in 98% yield (endo/exo ratio >97/3)



10b



12



15

Tetrahedron Letters, **1994**, *35*, 8623

AN EFFICIENT INEXPENSIVE ELECTROCHEMICAL PREPARATION OF RUPPERT'S REAGENT

Frédéric Aymard, Jean-Yves Nédélec*, and Jacques Périchon, Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS, 2, Rue Henri Dunant, 94320 THIAIS, France

The electrochemical reduction of CF_3Br in DMF in the presence of Me_3SiCl and a sacrificial aluminum anode provides Me_3SiCF_3 (Ruppert's reagent) in high faradaic yield.

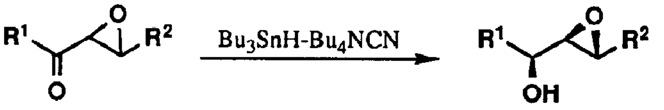
$$CF_3Br + Me_3SiCl \xrightarrow[\text{DMF, -15 °C} \atop \text{Al-anode}]{2\,e^-} CF_3SiMe_3 + Br^- + Cl^-$$

Tetrahedron Letters, **1994**, *35*, 8625

Novel Synthesis of *syn*-α,β-Epoxy Alcohols by Diastereoselective Carbonyl Reduction of α,β-Epoxy Ketones

Takayo Kawakami, Ikuya Shibata,* Akio Baba, Haruo Matsuda and Noboru Sonoda
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

A novel tin hydride reagent, $Bu_3SnH-Bu_4NCN$, reduced α,β-epoxy ketones to the corresponding *syn*-α,β-epoxy alcohols in high diastereoselectivities.

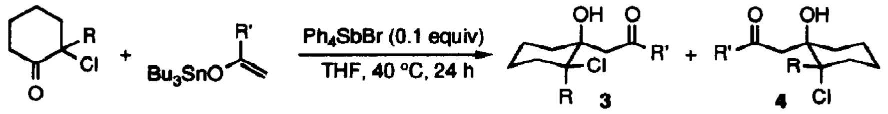


Tetrahedron Letters, **1994**, *35*, 8627

HIGHLY STEREOSELECTIVE ADDITION OF TIN ENOLATE TO α-CHLORO CYCLIC KETONE DERIVATIVES CATALYZED BY Ph_4SbBr

Makoto Yasuda, Tatsuhiro Oh-hata, Ikuya Shibata, Akio Baba,* Haruo Matsuda and Noboru Sonoda
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

Under catalytic conditions, chlorohydrins 3 could be obtained in the range of 86-100% diastereoselectivities in the title reaction.

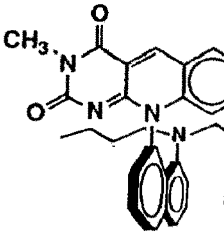


Tetrahedron Letters, **1994**, *35*, 8631

STEREOCHEMISTRY OF ASYMMETRIC "(NET) HYDRIDE TRANSFER" IN AN INTERCOENZYME MODEL REACTION SYSTEM

Tetsuji Kawamoto[1)], Toru Taga[1)], Kiyoshi Bessho[1)], Fumio Yoneda[1)] and Jun-ichi Hayami[2)]
1)Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku Kyoto 60601, Japan.
2)Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku
Kyoto 60601, Japan.

Absolute structure of a flavoenzyme model 1, a 5-deazaflavin possessing both axial and planar chirality, has been revealed. Unequivocal stereochemistry in the model reactions of asymmetric "(net) hydride transfer" between the flavoenzyme model and an NAD(P)H model is described.



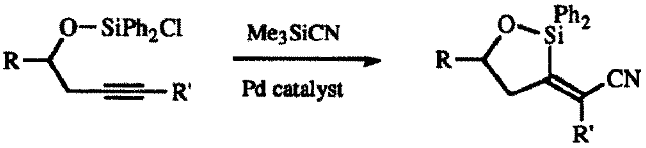
(S)-(+)-1

Tetrahedron Letters, **1994**, *35*, 8635

Palladium-Catalyzed Intramolecular Cyanosilylation of Alkynes Leading to Stereoselective Synthesis of α,β-Unsaturated Nitriles

Michinori Suginome, Hiroshi Kinugasa, and Yoshihiko Ito*
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01

Palladium-catalyzed reaction of chlorodiphenylsilyl ethers of homopropargylic alcohols with trimethylsilylcyanide gave (*Z*)-3-(1-cyanoalkylidene)-2-silatetrahydrofurans, which were transformed into various α,β-unsaturated nitriles in good yields.

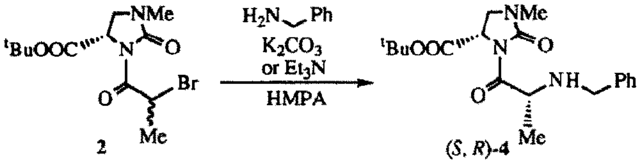


Tetrahedron Letters, **1994**, *35*, 8639

DYNAMIC KINETIC RESOLUTION BY STEREOSPECIFIC AMINATION UTILIZING 2-OXOIMIDAZOLIDINE-4-CARBOXYLATE AS A NOVEL CHIRAL AUXILIARY

Ken-ichi Nunami,*Hitoshi Kubota and Akira Kubo
Research Laboratory of Applied Biochemistry, Tanabe Seiyaku Co. Ltd., 16-89, Kashima-3-chome, Yodogawa-ku, Osaka 532, Japan

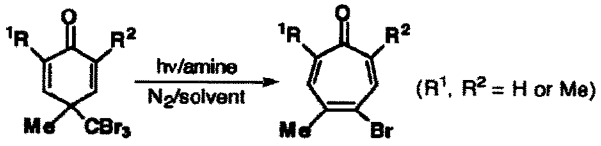
A dynamic kinetic resolution by stereospecific amination was investigated. The reaction of 2 with benzylamine predominantly afforded (*S*, *R*)-4 in nearly quantitative yield.



Tetrahedron Letters, **1994**, *35*, 8643

Novel Photoreaction of 4-Tribromomethyl-4-methyl-2,5-cyclohexadienone with Amine.

Eietsu Hasegawa,*
Yukinobu Tamura, Takaaki Horaguchi, Koji Isogai, and Toshio Suzuki,
Department of Chemistry, Faculty of Science, Department of Chemistry and Chemical Engineering, Faculty of Engineering, and Graduate School of Science and Technology, Niigata University, Ikarashi, Niigata, 950-21,Japan



Tetrahedron Letters, **1994**, *35*, 8647

SYNTHESIS OF BRANCHED-CHAIN AZAFURANOSE DERIVATIVES FROM SECONDARY NITROALKANES. FACILE SYNTHESIS OF (±) 4-AMINO-4,4-BIS(HYDROXYMETHYL)-4-DEOXYTHREONIC-1,4-LACTAM

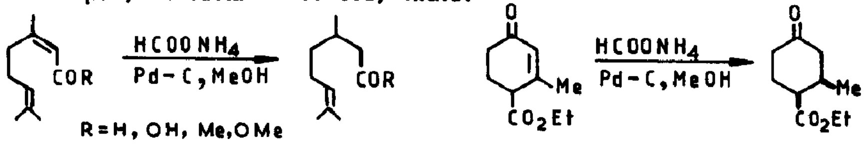
Renata Kuciak and Wojciech Sas*
Faculty of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3, 00 664 Warszawa, Poland

The title lacatm 6 was readily prepared from 2,2-dimethyl-5-nitro-1,3-dioxane in 4 steps.

Tetrahedron Letters, **1994**, *35*, 8649

REGIO- AND STEREOSELECTIVE HYDROGENATION OF CONJUGATED CARBONYL COMPOUNDS VIA PALLADIUM ASSISTED HYDROGEN TRANSFER BY AMMONIUM FORMATE

Brindaban C. Ranu and Arunkanti Sarkar
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

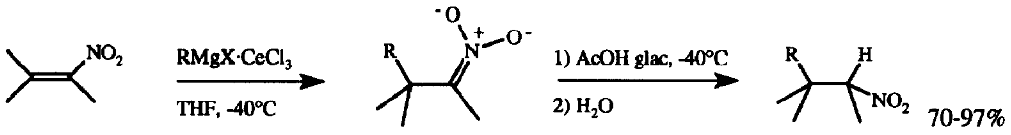


Tetrahedron Letters, **1994**, *35*, 8651

Cerium(III) Chloride Mediated Michael Addition of RMgX to Nitroenes: a Very Efficient Access to Complex Nitroalkanes.

Giuseppe Bartoli*, Marcella Bosco and Letizia Sambri, Dipartimento di Chimica Organica "A.Mangini", v.le Risorgimento, 4, I-40136, Bologna, Italy; Enrico Marcantoni, Dipartimento di Scienze Chimiche, via S.Agostino 1, I-62032, Camerino (MC), Italy

Reactions of $RMgX\text{-}CeCl_3$ complexes with nitroenes lead to functionalized nitroalkanes in very good yields.

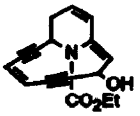


Tetrahedron Letters, **1994**, *35*, 8655

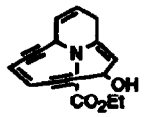
SYNTHESIS OF A NEW BICYCLIC TETRAHYDROPYRIDINE SYSTEM RELATED TO ENEDIYNE ANTIBIOTICS

Miguel F. Braña*, Marina Morán, María Jesús Pérez de Vega
and Isabel Pita-Romero.
Laboratorios KNOLL S.A., Avda de Burgos 91, 28050 Madrid, Spain.

Enediynes 1 and 2 related to dynemicin A have been synthesized.



1

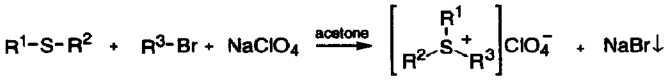


2

Tetrahedron Letters, **1994**, *35*, 8659

SYNTHESIS OF SULFONIUM SALTS BY SULFIDE ALKYLATION; AN ALTERNATIVE APPROACH

Varinder K. Aggarwal[a]*, Alison Thompson[a] and Ray V.H. Jones.[b]
(a) Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England.
(b) Zeneca FCMO, Process Technology Department, Earls Road, Grangemouth, Stirlingshire FK3 8XG, UK.



$$R^1{-}S{-}R^2 + R^3{-}Br + NaClO_4 \xrightarrow{\text{acetone}} \left[\overset{R^1}{\underset{R^2 \quad R^3}{S^+}} \right] ClO_4^- + NaBr\downarrow$$

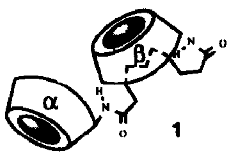
Sulfides undergo alkylation reactions in the presence of $NaClO_4$ in acetone. Reactions are cleaner and it is easier to isolate the resulting sulfonium salts than using the conventional procedure involving $AgClO_4$.

Tetrahedron Letters, **1994**, *35*, 8661

Synthesis and Conformational Behaviour of Novel Cyclodextrin Hetero-Dimers.

Fokke Venema, Chantal M. Baselier, Martinus C. Feiters, and Roeland J.M. Nolte,*
Department of Organic Chemistry, NSR-Center, University of Nijmegen,
Toernooiveld, 6525 ED Nijmegen, The Netherlands

The synthesis of novel cyclodextrin heterodimers (e.g. 1) derived from α- and β-cyclodextrin is reported. NMR-studies in D_2O indicate that the spacer is bound in one of the two cavities of the dimer, which results in lower affinities for guest molecules.



1

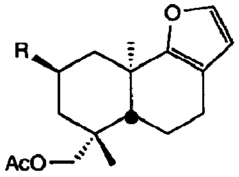
Tetrahedron Letters, **1994**, *35*, 8665

NEW ACETOXY-*ent*-PALLESCENSIN-A SESQUITERPENOIDS FROM THE SKIN OF THE POROSTOME NUDIBRANCH *DORIOPSILLA AREOLATA*

Aldo Spinella, Luis A. Alvarez, Conxita Avila and Guido Cimino

Istituto per la Chimica di Molecole di Interesse Biologico, C. N. R.
Via Toiano, 6 - 80072 Arco Felice (NA) - Italy

The first chemical study of an European *Doriopsilla* mollusc is reported. Two acetoxy derivatives (5, 6) of *ent*-pallescensin-A were isolated from the border of the dorsal mantle of *D. areolata*.



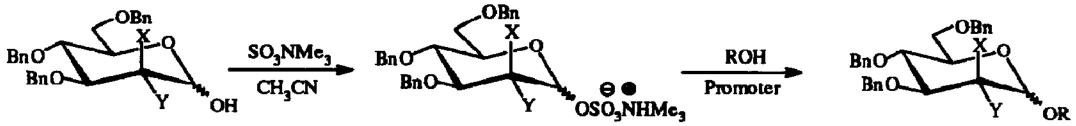
5 R = H; **6** R = OAc

Tetrahedron Letters, **1994**, *35*, 8669

GLYCOSYL SULFATES AS GLYCOSYL DONORS.

Laura Cipolla, Luigi Lay, Francesco Nicotra, Luigi Panza and Giovanni Russo*
Dipartimento di Chimica Organica e Industriale, Centro per lo Studio
delle Sostanze Organiche Naturali del CNR, via Venezian 21, 20133 Milano - Italy

Glycosyl sulfates, easily synthesised from tetrabenzyl pyranoses, can act as glycosyl donors under Lewis acid catalysis.



Tetrahedron Letters, **1994**, *35*, 8671

Mapping the Stereochemical Course of Carbonyl Phosphonylation *via* Chiral Phosphorodiamidites

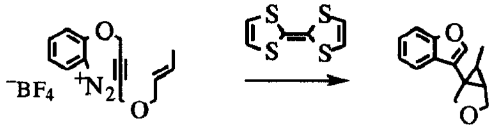
Mark J. Cain, Christopher A. Baird and Terence P. Kee*
School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Comparison of N-Me and N-^{i}Pr-(1*R*,2*S*)-ephedrine auxiliaries in the asymmetric Abramov reaction reveals that the latter has a stronger preference for (S_P,S_C) stereochemistry.

Tetrahedron Letters, **1994**, *35*, 8675

NOVEL SYNTHETIC APPLICATIONS OF ARENEDIAZONIUM SALTS

Christopher Lampard, John A. Murphy* and Faiza Rasheed, Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD; Norman Lewis, SmithKline Beecham Pharamaceuticals, Old Powder Mills, Leigh, Tonbridge, Kent TN11 9AN; Michael B. Hursthouse and D. E. Hibbs, EPSRC X-Ray Crystallography Service, P.O. Box 912, Cardiff, CF1 3TB.

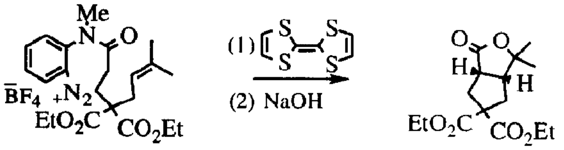


(64%)

Tetrahedron Letters, **1994**, *35*, 8679

TETRATHIAFULVALENE AS A TRIGGER FOR SEQUENTIAL RADICAL TRANSLOCATION AND FUNCTIONALISATION.

Michael J. Begley†, John A. Murphy* and Stephen J. Roome,
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD



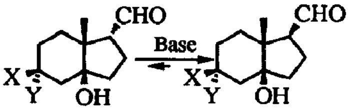
(45%)

Tetrahedron Letters, **1994**, *35*, 8683

STEREOCHEMICAL CONTROL OF PERHYDROINDANES FOR THE SYNTHESIS OF CARDENOLIDE ANALOGS

Manuel Medarde*, Fernando Tomé, Jose Luis López, Esther Caballero, Melchor Boya, Concepción P. Melero and Arturo San Feliciano
Dept . Química Orgánica y Farmacéutica. Fac. Farmacia. Av. Campo Charro s/n. E-37007 SALAMANCA. Spain. (FAX-34-23-294515).

Molecular modeling of *cis*-perhydroindane compounds predicted the higher stability of the C-1-β-epimer for the dithiane derivative at C-5. So, the control of the stereochemistry at C-1 has been achieved in these compounds, required for the synthesis of cardenolide analogs.



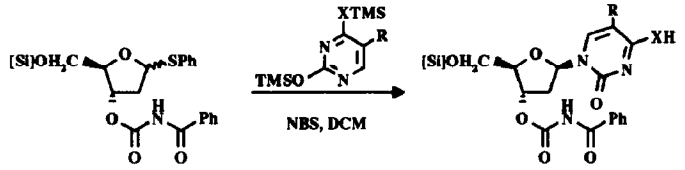
X,Y=S(CH$_2$)$_3$S

Tetrahedron Letters, **1994**, *35*, 8687

β-ANOMER SELECTIVITY IN 2'-DEOXYNUCLEOSIDE SYNTHESIS: A NOVEL APPROACH USING AN ACYL CARBAMATE DIRECTING GROUP.

Robert J. Young*, Sue Shaw-Ponter, George W. Hardy and Gail Mills.
Department of Medicinal Chemistry, The Wellcome Foundation Ltd., Beckenham, Kent, BR3 3BS, U.K.

A 3-*O*-carbamate group induced excellent β-anomeric selectivity in glycosidations yielding 2'-deoxyribonucleosides.



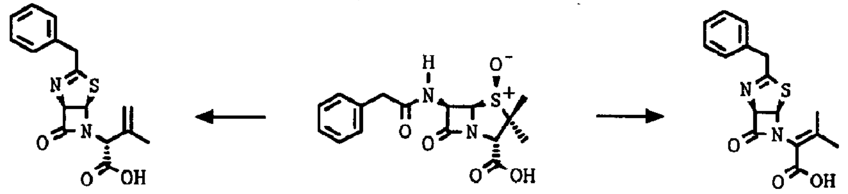
β:α ratios
up to 14:1

Tetrahedron Letters, **1994**, *35*, 8691

REDUCTIVE REARRANGEMENTS OF SILYLATED PENICILLIN G 1-OXIDE.

Pieter A.M. van der Klein, Henk A. Witkamp and Erik de Vroom*. Gist-brocades B.V., P.O. Box 1, 2600 MA Delft, The Netherlands.

Silylation of penicillin G 1-oxide with BSU followed by reduction gives thiazoline azetidinones.

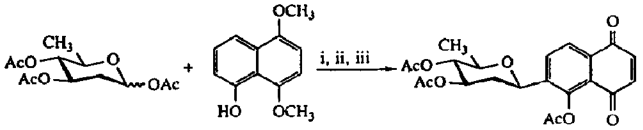


Tetrahedron Letters, **1994**, *35*, 8693

SYNTHETIC APPROACHES TO THE ANGUCYCLINE ANTIBIOTICS: SYNTHESIS OF THE *C*-GLYCOSIDIC CD RING SYSTEM.

Fleur L. Andrews and David S. Larsen, Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand.

The protected *C*-glycosyl substituted CD ring system (**22**) of the angucycline antibiotics has been prepared by the boron trifluoride promoted reaction of the sugar electrophile (**16**) and the naphthol (**9**) followed by acetylation and oxidation.



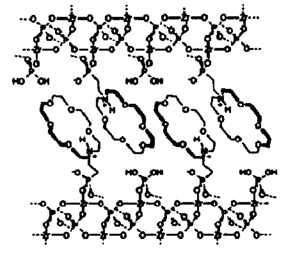
(16) (9) (22)

Reagents. i BF$_3$.Et$_2$O, 0°C, CH$_3$CN, 15 min, ii. Ac$_2$O, C$_6$H$_5$N, iii. CAN, CH$_3$CN/H$_2$O.

Tetrahedron Letters, **1994**, *35*, 8697

COVALENT BONDING OF AZA-18-CROWN-6 TO γ-ZIRCONIUM PHOSPHATE. A NEW LAYERED ION-EXCHANGER WITH POTENTIAL RECOGNITION CAPABILITIES.

Ernesto Brunet*, Manuel Huelva and Juan Carlos Rodríguez-Ubis* ***Departamento de Química Orgánica, C-I. Facultad de Ciencias. Universidad Autónoma de Madrid, 28049-Madrid, Spain.*** **Fax 34 1 397 3966**



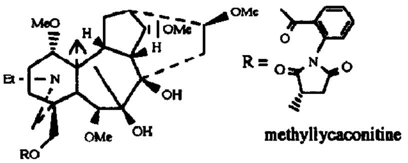
Reaction of *N*-(2-ethylphosphonic)-aza-18-crown-6 with γ-zirconium phosphate is described as well as ^{31}P NMR data, powder XRD pattern and preliminary ion-exchange experiments of the resulting material whose structure is discussed with the aid of molecular modeling.

Tetrahedron Letters, **1994**, *35*, 8701

RAPID AND EFFICIENT ISOLATION OF THE NICOTINIC RECEPTOR ANTAGONIST METHYLLYCACONITINE FROM *DELPHINIUM* : ASSIGNMENT OF THE METHYLSUCCINIMIDE ABSOLUTE STEREOCHEMISTRY AS *S*

P. A. Coates, I. S. Blagbrough, D. J. Hardick, M. G. Rowan, S. Wonnacott, B. V. L. Potter
School of Pharmacy and Pharmacology, and School of Biology and Biochemistry,
University of Bath, Bath BA2 7AY, UK.

The potent nicotinic antagonist methyllycaconitine has been isolated from *Delphinium* and the chirality of the methylsuccinimide moiety has been proven using 13C NMR spectroscopy and optical rotation.



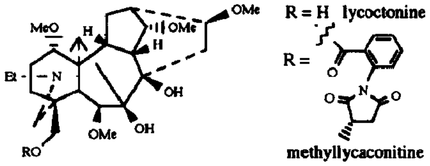
methyllycaconitine

Tetrahedron Letters, **1994**, *35*, 8705

ACYLATION OF LYCOCTONINE: SEMI-SYNTHESIS OF INULINE, DELSEMINE ANALOGUES AND METHYLLYCACONITINE

I. S. Blagbrough, P. A. Coates, D. J. Hardick, T. Lewis, M. G. Rowan, S. Wonnacott, and B. V. L. Potter. School of Pharmacy and Pharmacology, and School of Biology and Biochemistry,
University of Bath, Bath BA2 7AY, and Zeneca Agrochemicals, Jealott's Hill, Bracknell, UK.

Lycoctonine has been regioselectively acylated to produce the potent nicotinic receptor antagonist methyllycaconitine.



methyllycaconitine

Tetrahedron Letters, **1994**, *35*, 8709

RAPID AND EFFICIENT ENTRY TO SUBSTITUTED 2-SUCCINIMIDOBENZOATE-3-AZABICYCLO[3.3.1]NONANES: AE-BICYCLIC ANALOGUES OF METHYLLYCACONITINE

P. A. Coates, I. S. Blagbrough, M. G. Rowan, and B. V. L. Potter
School of Pharmacy and Pharmacology, University of Bath, Bath BA2 7AY, U.K. and
D. P. J. Pearson and T. Lewis, Zeneca Agrochemicals, Bracknell RG12 6EY, U.K.

AE-Bicyclic analogues of the potent nicotinic antagonist methyllycaconitine have been prepared by a double Mannich reaction and subsequent transformations.