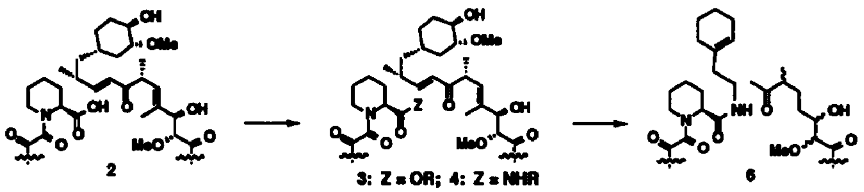
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 197

SYNTHESIS OF SECORAPAMYCIN ESTERS AND AMIDES

J. S. Skotnicki,* R. M. Kearney and A. L. Smith, *Wyeth-Ayerst Research,*
CN 8000, Princeton, New Jersey 08543-8000

Secorapamycin acid **2** has been converted to a variety of functionalized esters **3** and amides **4**. Sequential retroaldol / realdol reaction of a secorapamycin amide provided a truncated analog **6**.

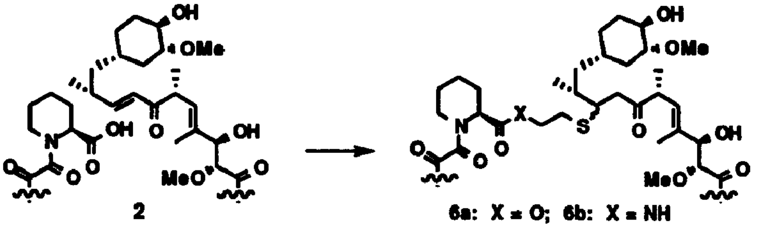


Tetrahedron Letters, **1994**, *35*, 201

RING EXPANDED RAPAMYCIN DERIVATIVES

J. S. Skotnicki* and R.M. Kearney, *Wyeth-Ayerst Research, Princeton, N. J. 08543*

Two ring expanded rapamycin derivatives **6a,b** were synthesized from secorapamycin acid **2**.

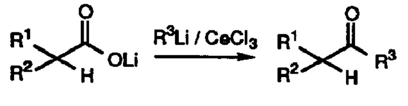


Tetrahedron Letters, **1994**, *35*, 203

CERIUM(III) CHLORIDE REMARKABLY INCREASES THE RATES OF FORMATION AND YIELDS OF KETONES IN THE REACTION OF LITHIUM CARBOXYLATES WITH ORGANOLITHIUMS.

Yoonmo Ahn and Theodore Cohen,* Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260 USA

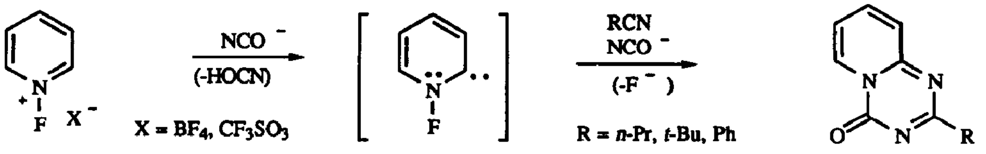
The presence of $CeCl_3$ greatly increases the yield of ketones in the reaction of organolithiums with lithium carboxylates. The $CeCl_3$ suppresses the enolization of the lithium carboxylate and the formation of tertiary alcohols. One reason for the latter effect is an increase in the rate of addition of the organometallic to the lithium carboxylate in the presence of $CeCl_3$.



Tetrahedron Letters, **1994**, *35*, 207

A NOVEL SYNTHESIS OF 2-SUBSTITUTED PYRIDO[1,2-a]-1,3,5-TRIAZIN-4-ONES BY THE REACTION OF *N*-FLUOROPYRIDINIUM SALTS WITH CYANATE ION AND CARBONITRILES: EVIDENCE IN SUPPORT OF A CARBENE INTERMEDIATE

Alexander S. Kiselyov and Lucjan Strekowski, Department of Chemistry, Georgia State University, Atlanta, Georgia 30303

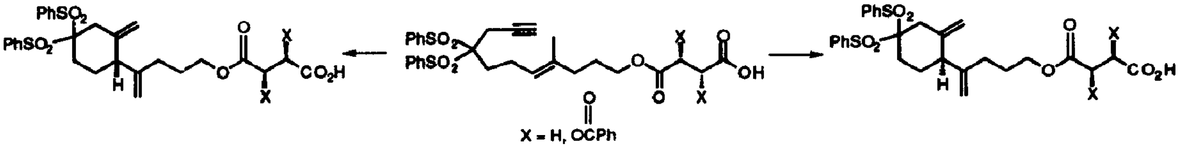


Tetrahedron Letters, **1994**, *35*, 211

Asymmetric Induction in Pd Catalyzed Enyne Cycloisomerizations

Barry M. Trost* and Boris A. Czeskis
Department of Chemistry, Stanford University, Stanford, CA 94305-5080

Control of the absolute stereochemistry in the palladium catalyzed Alder ene reaction was achieved either with chiral auxiliaries or chiral catalysts.

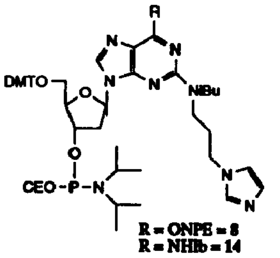


Tetrahedron Letters, **1994**, *35*, 215

Remarkable Enhancement of Binding Affinity of Heterocycle-Modified DNA to DNA and RNA. Synthesis, Characterization and Biophysical Evaluation of N^2-Imidazolylpropylguanine and N^2-Imidazolylpropyl-2-aminoadenine Modified Oligonucleotides.

Kanda S. Ramasamy,* Maryann Zounes, Carolyn Gonzalez, Susan M. Freier, Elena A. Lesnik, Lendell L. Cummins, Richard H. Griffey, Brett P. Monia and P. Dan Cook
ISIS Pharmaceuticals, 2280 Faraday Avenue, Carlsbad, CA 92008, USA

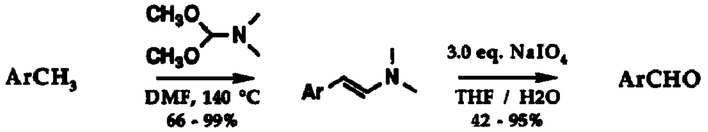
Oligonucleotides containing novel N^2-Imidazolylpropylguanine andN^2-Imidazolylpropyl-2-aminoadenine moieties (8 & 14) were synthesized and studied for their hybridization and biophysical properties.



Tetrahedron Letters, **1994**, *35*, 219

A MILD METHOD FOR THE CONVERSION OF ACTIVATED ARYL METHYL GROUPS TO CARBOXALDEHYDES VIA THE UNCATALYZED PERIODATE CLEAVAGE OF ENAMINES

Michael G. Vetelino and Jotham W. Coe*
Central Research Division, Pfizer Inc., Groton, CT. 06340

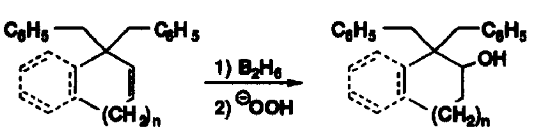


Tetrahedron Letters, **1994**, *35*, 223

UNUSUAL REGIOCHEMISTRY IN THE HYDROBORATION OF 3,3-DIBENZYLCYCLOALKENES

Xiaolian Shi and Bernard Miller*, Department of Chemistry, University of Massachusetts, Amherst, MA 01003 USA

Reaction of 3,3-dibenzylcycloalkenes with diborane results in predominant attack by boron at the more crowded ends of the double bonds.



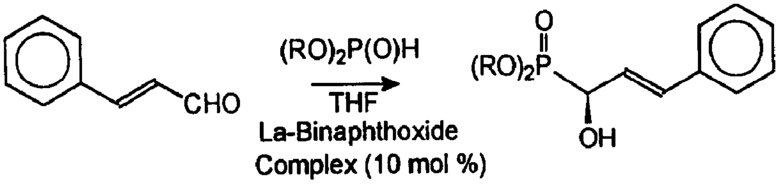
n = 0, 1

principal product

Tetrahedron Letters, **1994**, *35*, 227

THE ENANTIOSELECTIVE ADDITION OF DIALKYLPHOSPHITES TO ALDEHYDES: CATALYSIS BY A LANTHANUM BINAPHTHOXIDE COMPLEX.

Nigam P. Rath and Christopher D. Spilling* *Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121*

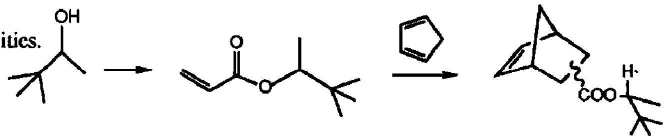


Tetrahedron Letters, **1994**, *35*, 231

STEREOSELECTIVITIES OF THERMAL AND LEWIS ACID CATALYZED DIELS-ALDER REACTIONS OF 1,2,2-TRIMETHYLPROPYL ACRYLATE WITH CYCLOPENTADIENE

Beatriz de Pascual-Teresa and K. N. Houk*
Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

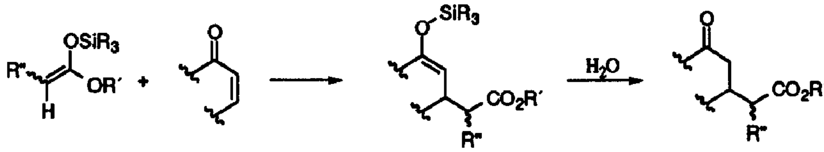
Results are in agreement with previous experimental work on the catalyzed process and quantitate the lower thermal stereoselectivities.



Tetrahedron Letters, **1994**, *35*, 233

Highly Effective Catalysts for the Conjugate Addition of Silyl Ketene Acetals to Enones (Mukaiyama-Michael Reaction)

Valérie Berl, Günter Helmchen* and Stephanie Preston
Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, FRG



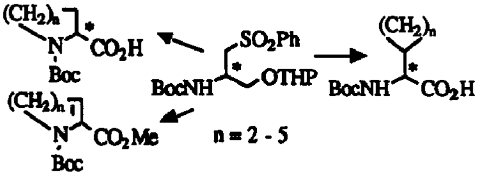
Conjugate additions of O-silyl ketene acetals to enones can be catalysed by as yet unknown species formed from P_4O_{10} in acetonitrile, while non-catalysed reactions gave low yield.

Tetrahedron Letters, **1994**, *35*, 237

A VERSATILE METHOD FOR THE SYNTHESIS OF (S)- OR (R)-CYCLOALKYLGLYCINES, (S)- OR (R)-N-HETEROCYCLIC AND α,β-UNSATURATED N-HETEROCYCLIC α-AMINO ACIDS

Régine Pauly, N. André Sasaki* and P. Potier
Institut de Chimie des Substances Naturelles, CNRS,
Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex France

The title compounds were prepared from the same chiral synthon simply by altering the quantity or type of base required for anion formation.



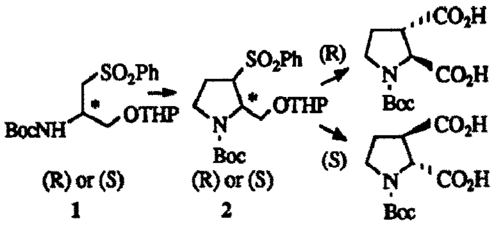
Tetrahedron Letters, **1994**, *35*, 241

ENANTIOSELECTIVE SYNTHESIS OF (2S,3S)- AND (2R,3R)-PYRROLIDINE-2,3-DICARBOXYLIC ACIDS : CONFORMATIONALLY CONSTRAINED (S)- AND (R)-ASPARTIC ACID ANALOGUES

N. André Sasaki*, Régine Pauly, Catherine Fontaine, Angèle Chiaroni,
Claude Riche and Pierre Potier

Institut de Chimie des Substances Naturelles, CNRS,
Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex France

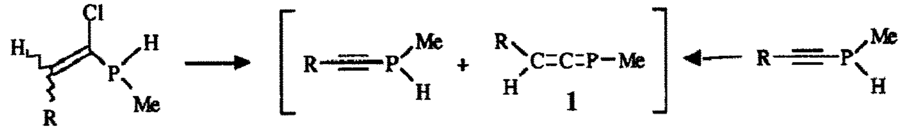
The title compounds were synthesized from the chiral synthons 1- (R) and 1- (S) via the key heterocyclic intermediate 2 and its enantiomer in 6 steps.



Tetrahedron Letters, **1994**, *35*, 245

UNSTABILIZED 1-PHOSPHAALLENES : SYNTHESIS AND CHARACTERIZATION.

J.-C. Guillemin*, T. Janati, P. Guenot, P. Savignac, J.-M. Denis*.
Groupe de Physicochimie Structurale; Université de Rennes 1, F-35042 Rennes. CRMPO, Université de Rennes 1, F-35042 Rennes. DCPH; Ecole Polytechnique, F-91128 Palaiseau.

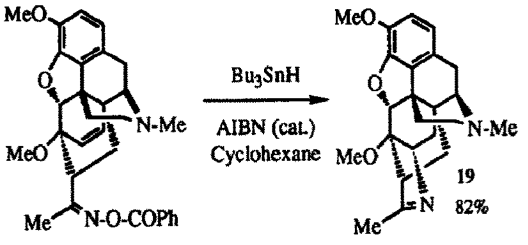


Unstabilized 1-phosphaallenes **1** are prepared by a base-induced dehydrohalogenation of 1-chlorovinyl-methylphosphines or rearrangement of 1-alkynyl-methylphosphines.

Tetrahedron Letters, **1994**, *35*, 249

IMINYL RADICALS BY STANNANE MEDIATED CLEAVAGE OF OXIME ESTERS.

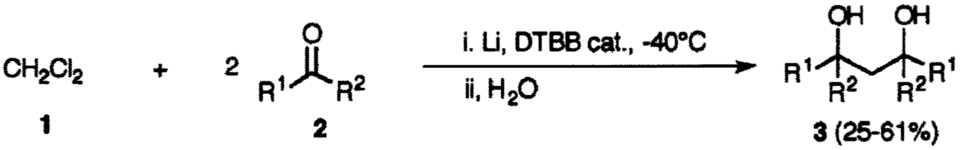
Jean Boivin, Anne-Marie Schiano and Samir Z. Zard*
Laboratoire de Synthèse Organique Associé au C. N. R. S., Ecole Polytechnique, F-91128 Palaiseau, France.



Tetrahedron Letters, **1994**, *35*, 253

DICHLOROMETHANE AS A SOURCE OF THE CH_2^{2-} SYNTHON: A COMBINATION OF AN ARENE-CATALYSED LITHIATION AND A BARBIER-TYPE REACTION

A. Guijarro and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain



1

2

3 (25-61%)

Tetrahedron Letters, **1994**, *35*, 257

MOLECULAR CHIRAL RECOGNITION IN SUPERCRITICAL SOLVENTS

Elemér Fogassy*, Mária Ács, Timea Szili, Béla Simándi[1], János Sawinsky[1]
Department of Organic Chemical Technology, Technical University of Budapest, Budapest POB 91, 1521 Hungary
[1]Technical University of Budapest, Department of Chemical Industrial Processes

A novel optical resolution method involving extraction with CO_2 of supercritical state is described.

$$2\ \underset{\text{DL-acid}}{R_1\text{-COOH}} + \underset{\text{chiral base}}{R_2\text{-NHR}_3} \xrightarrow{\text{extraction by supercritical } CO_2} \underset{\text{residue}}{L(D)\text{-}R_1\text{-COOH.NHR}_2R_3} + \underset{\text{extract}}{D(L)\text{-}R_1\text{-COOH}}$$

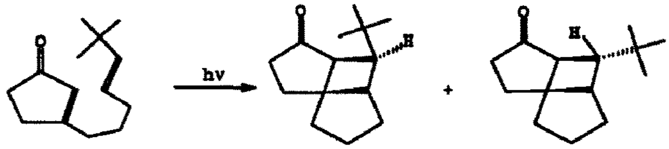
R_1 : substituted aryl-, substituted cikloalkyl- group
R_2 : substituted alkyl-, substituted aryl-alkyl- group
R_3 : alkyl-, aryl-alkyl- group

Tetrahedron Letters, **1994**, *35*, 261

REGIO AND STEREOCHEMISTRY IN 2+2 INTRAMOLECULAR PHOTO-CYCLOADDITION OF SUBSTITUTED OLEFINS TO CYCLOPENTENONES.

D. Becker* and N. Klimovich
Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel

The influence of substituents on the regio- and stereochemistry on intramolecular [2+2] photocycloaddition of olefins to cyclopentenones has been studied.

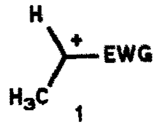


Tetrahedron Letters, **1994**, *35*, 265

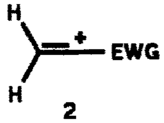
Destabilized Vinyl Cations. An MO Study of the Influence of Electron-Withdrawing Substituents.

Yitzhak Apeloig*, Rivka Biton, Han Zuilhof, and Gerrit Lodder*
Technion-Israel Institute of Technology, Haifa 32000, Israel;
Gorlaeus Laboratories, Leiden University, 2300 RA Leiden, The Netherlands.

Theoretical calculations up to the MP3/6-31G*//6-31G* level have been used to delineate the destabilization of cations 1 and 2 by electron-withdrawing groups (EWG: Cl, F, CN, CHO and CF_3).



1



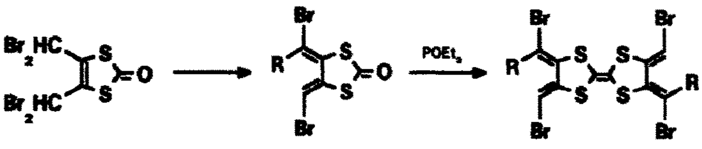
2

Tetrahedron Letters, **1994**, *35*, 269

4,5-BIS(METHYLENE)-1,3-DITHIOLE-2-ONES FROM BROMINATED 4,5-DIMETHYL-1,3-DITHIOLE-2-ONES: PRECURSORS FOR TETRAMETHYLENE-TETRATHIAFULVALENES

R. M. Renner and G. R. Burns*
Chemistry Department, Victoria University,
P.O. Box 600, Wellington, New Zealand

Dienes 1 and 2 are crystalline compounds. They react with triethyl phosphite, and spectroscopic data indicates that stable tetramethylene-tetrathiafulvalenes 3 are formed.



1 R = H
2 R = Br

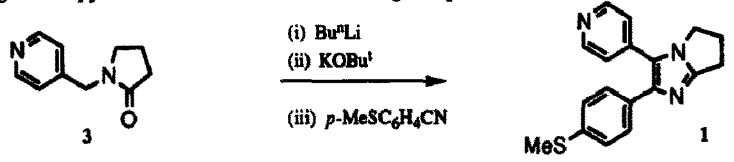
3 R = H, Br

Tetrahedron Letters, **1994**, *35*, 273

A NOVEL AND EFFICIENT SYNTHESIS OF A TETRA-SUBSTITUTED IMIDAZOLE.

Jerome F. Hayes* and Michael B. Mitchell,
Synthetic Chemistry Department, SmithKline Beecham Pharmaceuticals R&D, Old Powder Mills, Tonbridge, Kent TN11 9AR.
Garry Procter, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT.

A novel synthesis of a tetra-substituted imidazole is described. Regioselective deprotonation of picolylpyrrolidinone 3 and reaction of this anion with an aryl nitrile gives the pyrrolidinoimidazole nucleus in a single step.



Tetrahedron Letters, **1994**, *35*, 275

A Short, Flexible Approach to Vitamin D_3 Analogues with Modified Side Chains

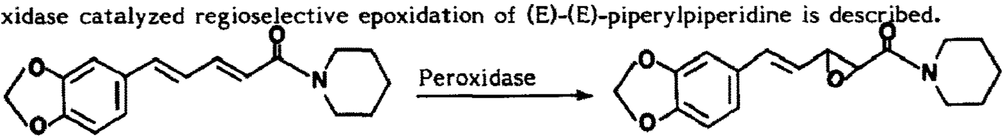
J. Pérez-Sestelo, J.L. Mascareñas, L. Castedo, A. Mouriño*
Departamento de Química Orgánica y Sección de Alcaloides del CSIC
Universidad de Santiago, 15706 Santiago de Compostela, Spain

Tetrahedron Letters, **1994**, *35*, 279

REGIOSELECTIVE ENZYMATIC EPOXIDATION OF (E)-(E)-PIPERYL PIPERIDINE

A Bhaskar Rao[a], M Venkateswara Rao[a]
Anil Kumar[b], G L David Krupadanam[b] and G Srimannarayana[b]
[a] Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b] Department of Chemistry, Osmania University, Hyderabad 500 007, India

Peroxidase catalyzed regioselective epoxidation of (E)-(E)-piperylpiperidine is described.

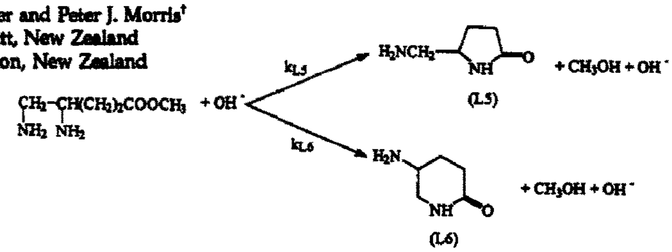


Tetrahedron Letters, **1994**, *35*, 281

COMPETITIVE INTRAMOLECULAR AMINOLYSIS: RELATIVE RATES OF 5- AND 6-MEMBERED LACTAM RING CLOSURE

Kevin H. Patterson*, Gary J. Depree, Johannes A. Zender and Peter J. Morris†
*Industrial Research Limited, PO Box 31310, Lower Hutt, New Zealand
†Chemistry Department, University of Waikato, Hamilton, New Zealand

Methyl 4,5-diaminopentanoate provides an ideal case for assessing the relative rates of 5- and 6-membered lactam ring closure

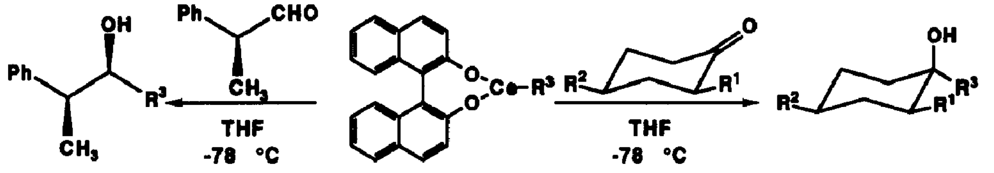


Tetrahedron Letters, **1994**, *35*, 285

LIGAND EFFECTS ON DIASTEREOSELECTIVE ADDITION OF ORGANOCERIUM REAGENTS TO ALDEHYDES AND CYCLIC KETONES

Nicholas Greeves,* Lisa Lyford and J. Elizabeth Pease
Robert Robinson Laboratories, Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K.

A new class of diaryloxyorganocerium reagent has been prepared and the diastereoselectivity of carbonyl addition reactions has been compared with that of conventional organocerium reagents.

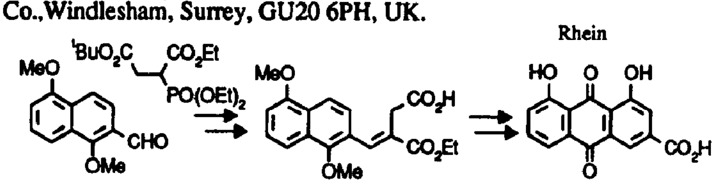


Tetrahedron Letters, **1994**, *35*, 289

A NEW SYNTHESIS OF RHEIN.

Peter T. Gallagher*, Terry A. Hicks, Andrew P. Lightfoot and W. Martin Owton.
Lilly Research Centre, Eli Lilly & Co.,Windlesham, Surrey, GU20 6PH, UK.

Rhein has been synthesised by coupling a novel phosphonosuccinate with a naphthaldehyde, followed by cyclisation to an anthracene and subsequent oxidation to the anthraquinone.

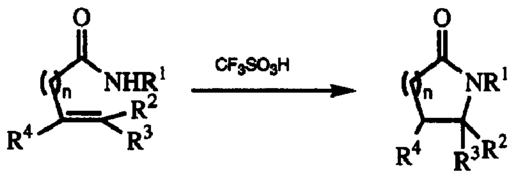


Tetrahedron Letters, **1994**, *35*, 293

PREPARATION OF γ- AND δ-LACTAMS BY RING CLOSURE OF β,γ-UNSATURATED AMIDES USING TRIFLUOROMETHANESULFONIC ACID

Charles M. Marson* and Asad Fallah, Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K.

γ-Lactams and δ-lactams can be prepared by cyclization of β,γ-unsaturated amides with trifluoromethanesulfonic acid

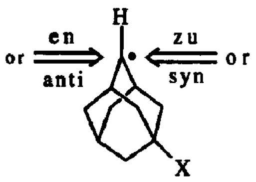


Tetrahedron Letters, **1994**, *35*, 297

THE NATURE OF ELECTRONIC INTERACTIONS GOVERNING THE CONTROL OF Π-FACIAL SELECTIVITY IN THE CAPTURE OF 5-SUBSTITUTED(X)-2-ADAMANTYL RADICALS: ELECTROSTATIC *VERSUS* HYPERCONJUGATIVE EFFECTS

William Adcock*, Christopher I. Clark and Neil A. Trout, School of Physical Sciences, The Flinders University of South Australia, Adelaide, South Australia, 5001

An electrostatic rather than a hyperconjugative effect appears to be the dominant factor governing the control of Π-facial selectivity in the capture of 5-substituted(X)-2-adamantyl radicals.

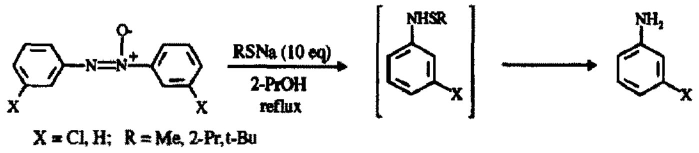


Tetrahedron Letters, **1994**, *35*, 301

A NEW REACTION OF THE AZOXY GROUP WITH ALKYL THIOLATES: REDUCTION TO AMINO *VIA* A SULFENAMIDO INTERMEDIATE

Maria Teresa Dario, Stefano Montanari, Cristina Paradisi* and Gianfranco Scorrano
Centro Studio Meccanismi Reazioni Organiche del CNR, Dipartimento di Chimica Organica, Via Marzolo 1, 35131 Padova, Italy

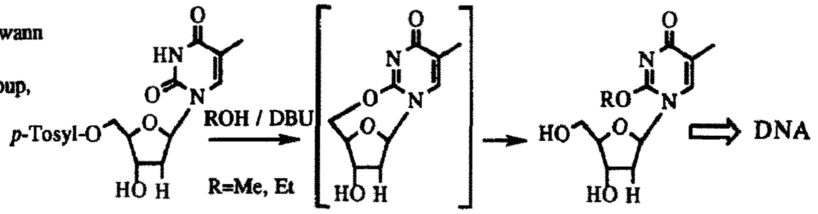
Sulfenamides (R = *t*-Bu) or anilines are obtained in good yields *via* an unprecedented reduction of the NNO moiety.



Tetrahedron Letters, **1994**, *35*, 303

OLIGODEOXYNUCLEOTIDES CONTAINING O^2-ALKYLTHYMINE: SYNTHESIS AND CHARACTERIZATION

Yao-Zhong Xu* and Peter F. Swann
Cancer Research Campaign,
Nitrosamine-Induced Cancer Group,
Department of Biochemistry and
Molecular Biology, University
College London, Gower Street,
London WC1E 6BT, England

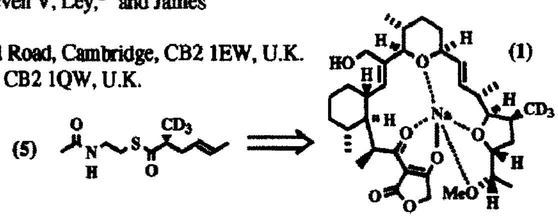


Tetrahedron Letters, **1994**, *35*, 307

Biosynthesis of Tetronasin: Part 1. Introduction and Investigation of the Diketide and Triketide Intermediates Bound to the Polyketide Synthase.

Helen C. Hailes,[a] Catherine M. Jackson,[a] Peter F. Leadlay,[b] Steven V, Ley,[a*] and James Staunton.[a*]
[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.
[b] Department of Biochemistry, Tennis Court Road, Cambridge, CB2 1QW, U.K.

In biosynthetic incorporation studies with intact cells, the N-acetyl cysteamine analogue of the proposed triketide intermediate (5) was incorporated intact into tetronasin (1).

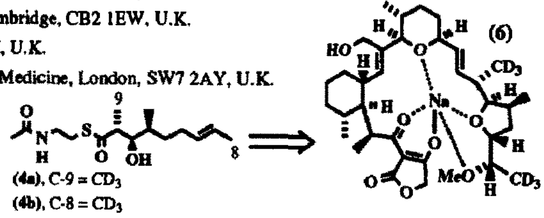


Tetrahedron Letters, **1994**, *35*, 311

Biosynthesis of Tetronasin: Part 2. Identification of the Tetraketide Intermediate Attached to the Polyketide Synthase.

Helen C. Hailes,[a] Sandeep Handa,[a] Peter F. Leadlay,[b] Ian C. Lennon,[c] Steven V, Ley,[a*] and James Staunton.[a*]
[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.
[b] Department of Biochemistry, Tennis Court Road, Cambridge, CB2 1QW, U.K.
[c] Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, U.K.

In biosynthetic incorporation studies with intact cells, the N-acetyl cysteamine analogues (4a) and (4b) of the proposed tetraketide intermediate (4) were incorporated intact into tetronasin (6). Diastereoisomers of (4), however, were not incorporated into (6).



Biosynthesis of Tetronasin: Part 3. Preparation of Deuterium Labelled Tri- and Tetraketides as Putative Biosynthetic Precursors of Tetronasin.

Tetrahedron Letters, **1994**, *35*, 315

Helen C. Hailes,[a] Sandeep Handa,[a] Peter F. Leadlay,[b] Ian C. Lennon,[c] Steven V. Ley[a*] and James Staunton.[a*]
[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.
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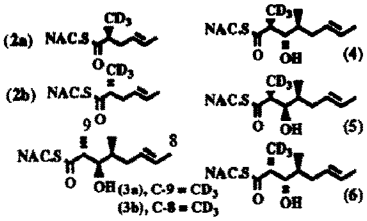
Seven deuterium labelled N-acetyl cysteamine thioesters, (2a), (2b), (3a), (3b), (4), (5) and (6) were prepared as putative biosynthetic precursors of the acyl tetronic acid ionophore tetronasin (1).

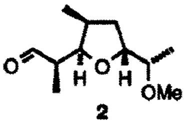


Two New Routes to the C19-C26 Tetrahydrofuran Fragment of the Acyl Tetronic Acid Ionophore Tetronasin (ICI M139603)

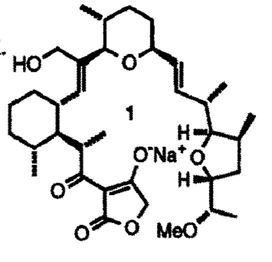
Tetrahedron Letters, **1994**, *35*, 319

Geert-Jan Boons[a], Dearg S. Brown[b], J. Andrew Clase[a], Ian C. Lennon[b] and Steven V. Ley[a]
a)Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.
b)Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, UK

Two highly efficient and complementary synthetic routes to the C19-C26 tetrahydrofuran fragment (2) of the novel acyltetronic acid ionophore tetronasin (ICI M139603) (1) are described.



2



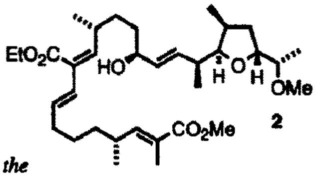
1

Novel Polyene Cyclization Routes to the Acyl Tetronic Acid Ionophore Tetronasin (ICI M139603)

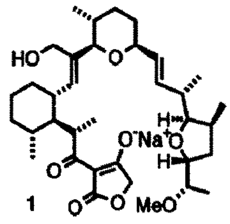
Tetrahedron Letters, **1994**, *35*, 323

Geert-Jan Boons[a], Ian C. Lennon[b], Steven V. Ley[a], Elaine S.E. Owen[b], James Staunton[a] and David J. Wadsworth[b]
a) Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.
b) Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, UK.

An approach to the total synthesis of the ionophore antibiotic tetronasin (1) is reported, in which the key step is a novel base catalysed cascade cyclisation of an activated polyene (2). This establishes two rings and four stereogenic centres in one step. A related polyene has been cyclised in a similar manner, illustrating the generality of this procedure



2



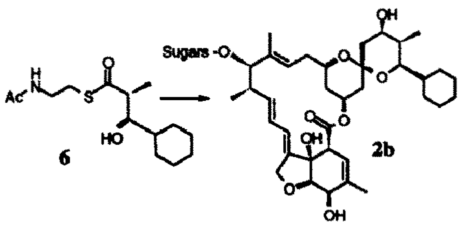
1

Avermectin Biosynthesis. Intact Incorporation Of A Diketide Chain-Assembly Intermediate Into The Polyketide Macrocyclic Ring

Tetrahedron Letters, **1994**, *35*, 327

Christopher J. Dutton,[a] Antony M. Hooper,[b] Peter F. Leadlay[c] and James Staunton[b*]
[a] Central Research Division, Pfizer Ltd., Ramsgate Road, Sandwich, Kent CT13 9NJ, U.K;[b] University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K;[c] Department of Biochemistry, Tennis Court Road, Cambridge CB2 1QW, U.K.

The diketide analogue (6) incorporates intact into the polyketide core of avermectin (2b) showing that chain assembly follows the processive mode

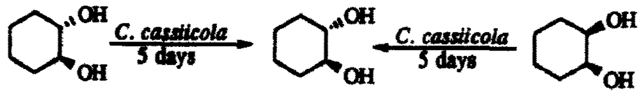


Tetrahedron Letters, **1994**, *35*, 331

Preparation of Optically Active Cyclohexanediols and (+)-α-Hydroxycycloheptanone by an Enzyme Catalysed Stereoinversion/Oxidation Process

Andrew J. Carnell*[a], Gilles Iacazio[a], Stanley M. Roberts[a], Andrew J. Willetts[b].
[a]Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD. [b]Department of Biological Sciences, University of Exeter, Prince of Wales Road, Exeter EX4 4QG.

Incubation of the (±)-diol 1 or the *meso* diol 2 with the fungus *C. cassiicola* gives optically pure (+)-1.



(±)-1 (+)-1*S*, 2*S*-1 2

Tetrahedron Letters, **1994**, *35*, 335

UNPRECEDENTED FORMATION OF SPIROBICYCLO[3.1.0]HEXANES THROUGH TANDEM ACETYLENE-ADDITION - MICHAEL CYCLIZATION

A.I.A. Broess, M.B. Groen and H. Hamersma*, Organon International, PO Box 20, 5340 BH Oss, the Netherlands

Treatment of pinacolone-type ketones with 4-pentynyltriphenylphosphonium bromide efficiently produces 6-acylbicyclo[3.1.0]hexane systems.