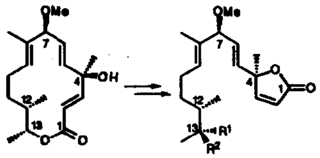
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 2635

RELATIVE AND ABSOLUTE STEREOCHEMISTRY OF THE MELANOGENESIS INHIBITORS OH-3984 K1 AND K2. PARTIAL SYNTHESIS FROM ALBOCYCLINE

Toshiaki Sunazuka, Rika Obata, Li Zhuorong, Satoshi Takamatsu, Kanki Komiyama, and Satoshi Ōmura*
Research Center for Biological Function, The Kitasato Institute, Minato-ku, Tokyo 108, Japan
Amos B. Smith, III,*
Department of Chemistry, Laboratory for Research on the Structure of Matter, and Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

The transformation of the macrolide antibiotic albocycline (3) to the recently isolated melanin synthesis inhibitors OH-3984 K1 (1) and K2 (2) has established the relative and absolute configurations of 1 (4*R*, 7*R*, 12*S*) and 2 (4*R*, 7*R*, 12*S*, 13*R*).



Albocycline (3)

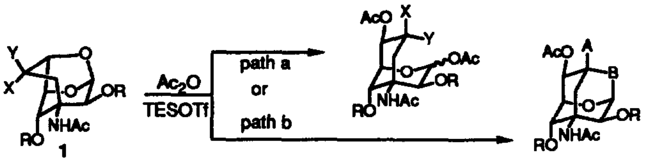
OH-3984 K1 (1) $R^1, R^2 = O$
OH-3984 K2 (2) $R^1 = OH, R^2 = H$

Tetrahedron Letters, **1994**, *35*, 2637

ARMED/DISARMED EFFECTS IN THE SOLVOLYSIS OF CAGED 1,6-ANHYDRO PYRANOSES.

Christopher S. Burgey, Roland Vollerthun and Bert Fraser-Reid*, Department of Chemistry, Duke University, Durham, NC 27708

The reactivity of tricycle 1 towards acetolysis, and the structures of the products obtained are greatly affected by the nature of the protecting groups R, and the nature and orientation of the substituents X and Y.

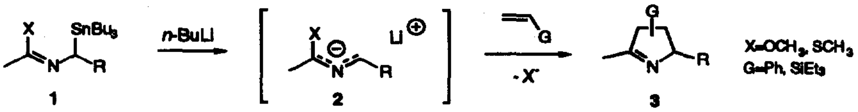


Tetrahedron Letters, **1994**, *35*, 2641

GENERATION AND CYCLOADDITION OF HETEROATOM-SUBSTITUTED 2-AZAALLYL ANIONS WITH ALKENES AND ALKYNES. SYNTHESIS OF 1-PYRROLINES AND PYRROLES.

William H. Pearson* and Erland P. Stevens
Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055

Transmetalation of the tin-substituted imidates and thioimidates 1 gave the heteroatom-substituted 2-azaallyl anions 2, which underwent cycloaddition with alkenes to produce the 1-pyrrolines 3. Use of diphenylacetylene led to the formation of a pyrrole.

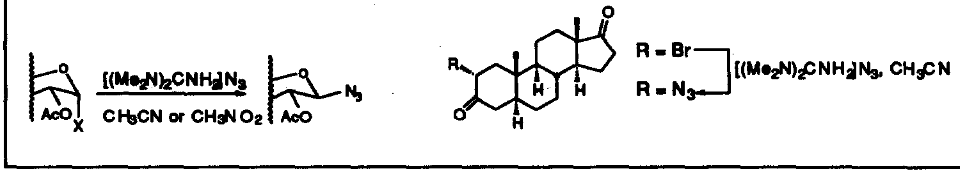


Tetrahedron Letters, **1994**, *35*, 2645

The Use of Tetramethylguanidinium Azide in Non-halogenated Solvents Avoids Potential Explosion Hazards

C. Li, Tzenge-Lien Shih, Jae Uk Jeong, Ashok Arasappan, and P. L. Fuchs*
Department of Chemistry, Purdue University, West Lafayette, IN 47907

Tetramethylganidinium azide was used in the efficient synthesis of glycosyl azides and steroidal azides in non-halogenated solvents, thereby avoiding potential explosion hazards.

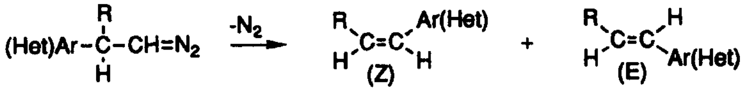


Tetrahedron Letters, **1994**, *35*, 2647

THE STEREOCHEMISTRY OF REARRANGEMENTS OF ARYL AND HETARYL GROUPS TO PRIMARY CARBENIC CENTERS.

W. E. Slack, W. Taylor, C. G. Moseley, K. T. Chang, A. Kraska, L. H. Press, L. Cherney and H. Shechter*
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Aryl and hetaryl migrations in thermal decompositions of 2-substituted-1-diazoalkanes give (Z)- rather than (E)-olefins along with C-H rearrangement and insertion products.

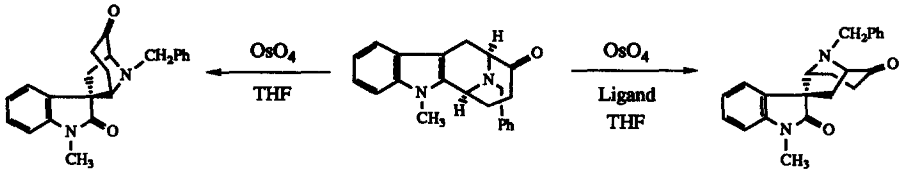


Tetrahedron Letters, **1994**, *35*, 2651

STUDIES ON THE ENANTIOSPECIFIC SYNTHESIS OF OXINDOLE ALKALOIDS

Andrew C. Peterson and James M. Cook*,
Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI 53201 USA

A diastereoselective conversion of N_a-methyl, N_b-benzyltetracyclic ketone **1** into either oxindole **2a** or **2b** was developed.

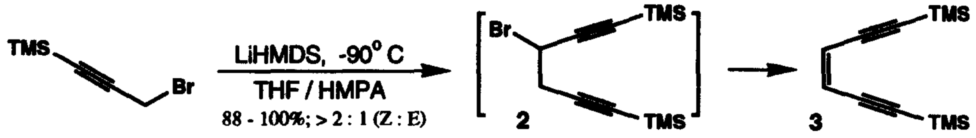


2a **1** **2b**

Tetrahedron Letters, **1994**, *35*, 2655

A Mild and Efficient Route to the Pharmacophore of the Enediyne Antitumor Agents: (Z)-1,6-[Bis(trimethylsilyl)]-Hex-3-ene-1,5-diyne *via* a Novel Carbenoid Coupling Reaction

Robert S. Huber and Graham B. Jones* *Department of Chemistry, Clemson University, Clemson, SC 29634-1905 USA*



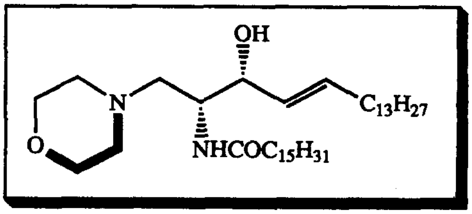
An efficient, palladium-free route to **3** has been found which exhibits unusual stereoselectivity.

Tetrahedron Letters, **1994**, *35*, 2659

STUDIES ON MORPHOLINOSPHINGOLIPIDS: POTENT INHIBITORS OF GLUCOSYLCERAMIDE SYNTHASE

Kenneth G. Carson and Bruce Ganem*
Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, NY 14853-1301 USA

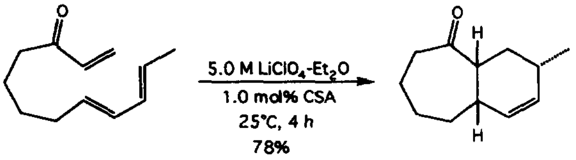
Norman S. Radin, Akira Abe, and James A. Shayman
Nephrology Division, Department of Internal Medicine
University of Michigan, Ann Arbor, MI 48109 USA



Tetrahedron Letters, **1994**, *35*, 2663

ACID CATALYZED INTRAMOLECULAR DIELS-ALDER REACTIONS IN LITHIUM PERCHLORATE-DIETHYL ETHER: ENHANCED REACTION RATES AND DIASTEREOSELECTIVITY

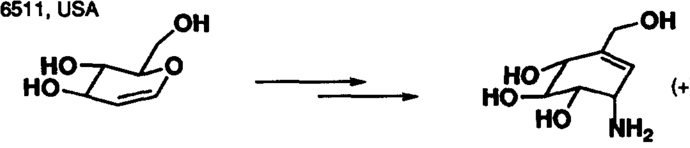
Paul A. Grieco,* Scott T. Handy and James P. Beck, Department of Chemistry, Indiana University, Bloomington, Indiana 47405



Tetrahedron Letters, **1994**, *35*, 2667

A SYNTHETIC ROUTE TO VALIENAMINE: AN INTERESTING OBSERVATION CONCERNING STEREOELECTRONIC PREFERENCES IN THE S_N2' REACTION

Tae Kyo Park* and Samuel J. Danishefsky, Department of Chemistry, Yale University, New Haven, CT 06511, USA

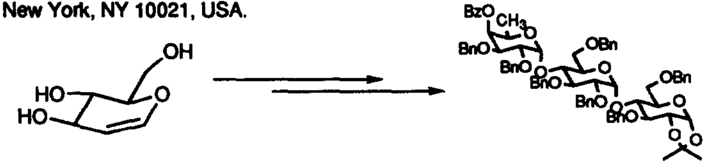


(+) - valienamine

Tetrahedron Letters, **1994**, *35*, 2671

STUDIES DIRECTED TOWARD THE TOTAL SYNTHESIS OF ACARBOSE: THE TRISACCHARIDE DOMAIN.

Tae Kyo Park*, John M. Peterson and Samuel J. Danishefsky, Department of Chemistry, Yale University, New Haven, CT 06511, USA and Laboratory for Bioorganic Chemistry, Sloan-Kettering Institute for Cancer Research, 1275 York Avenue, New York, NY 10021, USA.

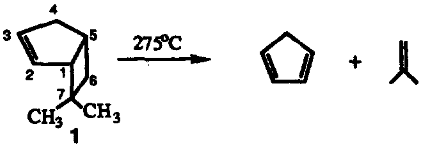


Tetrahedron Letters, **1994**, *35*, 2675

THE THERMAL REARRANGEMENT OF 7,7-DIMETHYLBICYCLO[3.2.0]HEPT-2-ENE

Timothy E. Glass, Phyllis A. Leber, and Patricia L. Sandall
Department of Chemistry, Franklin & Marshall College, Lancaster, PA 17604-3003

The title compound, when subjected to gas-phase pyrolysis at 275°C, undergoes predominantly fragmentation to cyclopentadiene and isobutylene.



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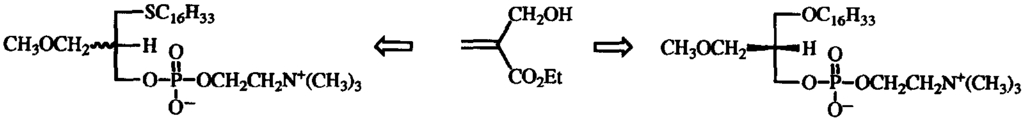
Tetrahedron Letters, **1994**, *35*, 2679

ANTITUMOR ETHER LIPIDS: AN IMPROVED SYNTHESIS OF ILMOFOSINE AND AN ENANTIOSELECTIVE SYNTHESIS OF AN ILMOFOSINE ANALOG.

Kasireddy Chandraprakash Reddy, Hoe-Sup Byun, and Robert Bittman,* Department of Chemistry & Biochemistry, Queens College of The City University of New York, Flushing, New York 11367-1597 USA

Abstract: Efficient routes to racemic Ilmofosine (1) and to the enantiomers of its oxygen analog, (*R*)- and (*S*)-2, are described starting from ethyl α-(hydroxymethyl)acrylate (3) or 2-methylene-1,3-propanediol (6).



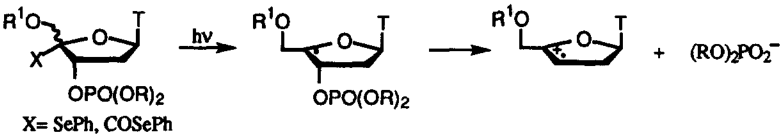
rac-1 3 (*R*)-2

Tetrahedron Letters, **1994**, *35*, 2683

HETEROLYTIC C,O-BOND CLEAVAGE OF 4'-NUCLEOTIDE RADICALS

Bernd Giese,* Peter Erdmann, Luc Giraud, Thomas Göbel,
Mario Petretta, Thomas Schäfer, Institute of Organic Chemistry, University of Basel,
St. Johannsring 19, CH-4056 Basel, Switzerland
Markus von Raumer, Institute of Physical Chemistry,University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

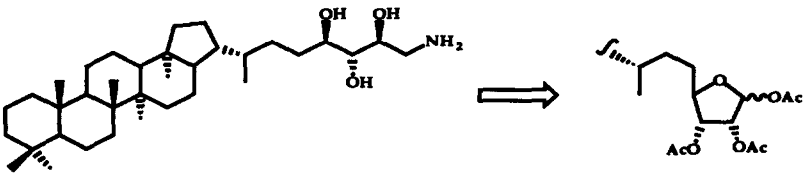
Photocurrent studies of 4'-nucleotide radicals bearing β-phosphate substituents proved the heterolytic cleavage of the C,O-bond.



Tetrahedron Letters, **1994**, *35*, 2687

DIMETHYLDIOXIRANE OXIDATION OF AMINOBACTERIOHOPANETRIOL: OBTENTION OF A PUTATIVE INTERMEDIATE IN BACTERIAL HOPANOID BIOSYNTHESIS.

P. Bisseret, M. Seemann and M. Rohmer*, *Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue A. Werner, 68093 Mulhouse, France.*

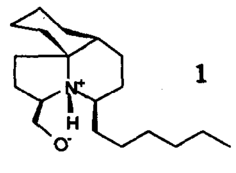


Tetrahedron Letters, **1994**, *35*, 2691

LEPADIFORMINE, A NEW MARINE CYTOTOXIC ALKALOID FROM *CLAVELINA LEPADIFORMIS* MÜLLER

J.F. Biard*, S. Guyot, C. Roussakis and J.F. Verbist, SMAB, Faculté de Pharmacie, BP 1024, 44035 NANTES, France;
J. Vercauteren and J.F. Weber, Laboratoire de Pharmacognosie Faculté de Pharmacie, 3 ter, Place de la Victoire 33076 BORDEAUX, France;
K. Boukef, Centre d'Etude des Plantes Médicinales, rue Djebel Lakhdar, Bab Saadoun, TUNIS, Tunisie.

Lepadiformine **1**, a pyrroloperhydroquinoleine alkaloid isolated from *Clavelina lepadiformis* Müller, exhibits a unique new heterocyclic structure with a zwitterionic moiety. This structure has been established on the basis of chemical and spectroscopic proofs. The antiproliferative activity of **1**, studied on a continuous human non-small cell bronchopulmonary carcinoma line, resulted from a partial blockade of G1 phase cells.



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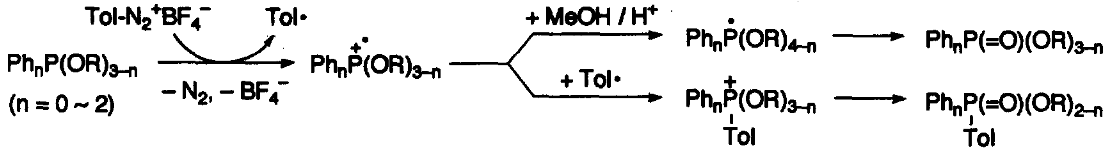
Tetrahedron Letters, **1994**, *35*, 2695

REACTION OF A CATION RADICAL GENERATED FROM TRIVALENT PHOSPHORUS COMPOUND THROUGH SINGLE-ELECTRON TRANSFER TO ARENEDIAZONIUM SALT

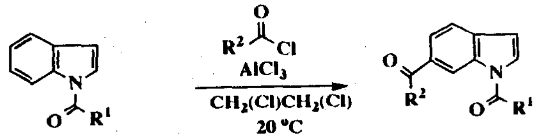
Shinro Yasui,* Kosei Shioji,† and Atsuyoshi Ohno†
Tezukayama College, Gakuen-Minami, Nara 631 Japan
†Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 Japan



Tetrahedron Letters, **1994**, *35*, 2699

FORMATION OF 6-ACYLINDOLES FROM 1-ACYLINDOLES

Shin-ichi Nakatsuka,#* Katsunori Teranishi,## and Toshio Goto†
School of Agriculture, Nagoya University, Chikusa, Nagoya 464-01, Japan

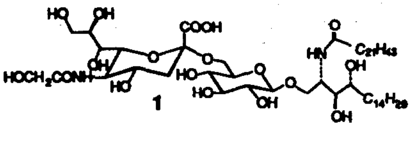


Tetrahedron Letters, **1994**, *35*, 2701

SYNTHESIS OF GANGLIOSIDE M5 FROM SEA URCHIN EGG

Toshihiro Yamamoto, Tadashi Teshima, Umihito Saitoh+, Motonori Hoshi+, and Tetsuo Shiba*,
Peptide Institute, Protein Research Foundation, 4-1-2 Ina, Minoh, Osaka 562, Japan
+Department of Life Science, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan

One component of the ganglioside M5 (1), containing *N*-glycolylneuraminic acid and phytosphingosine, was first synthesized from *N*-acetylneuraminic acid.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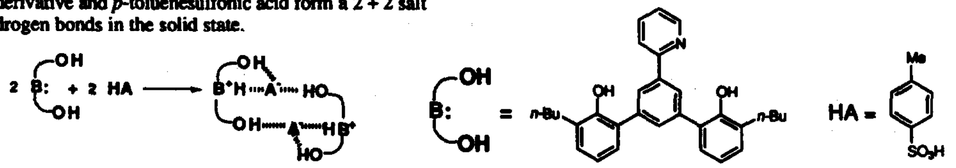
Tetrahedron Letters, **1994**, *35*, 2705

2 + 2 SALT FORMATION INDUCED BY HYDROGEN BONDING.

Kei Manabe,*a Kimio Okamura,b Tadamasa Date,b and Kenji Koga,*a aFaculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan
bOrganic Chemistry Research Laboratory, Tanabe Seiyaku Co., Ltd., 2-2-50, Kawagishi, Toda, Saitama 335, Japan

A pyridine derivative and *p*-toluenesulfonic acid form a 2 + 2 salt with six hydrogen bonds in the solid state.

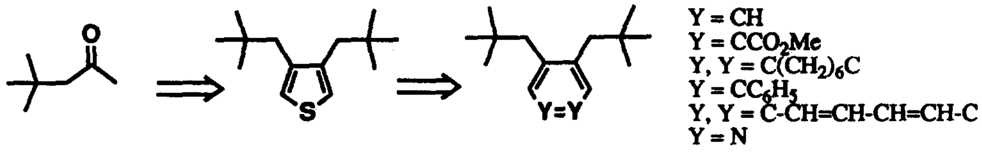


Tetrahedron Letters, 1994, 35, 2709

A General Synthesis of Aromatic Compounds Carrying Two Neopentyl Groups on Adjacent Positions

Juzo Nakayama and Koichi Yoshimura*

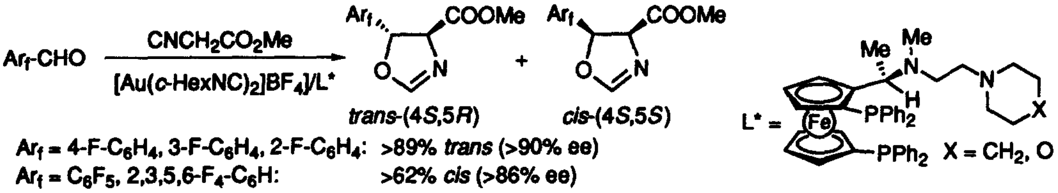
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan



Tetrahedron Letters, 1994, 35, 2713

Gold(I)-Catalyzed Asymmetric Aldol Reaction of Methyl Isocyanoacetate with Fluorinated Benzaldehydes

V. A. Soloshonok and T. Hayashi,* *Catalysis Research Center, Hokkaido University, Sapporo 060, Japan*



Ar_f = 4-F-C_6H_4, 3-F-C_6H_4, 2-F-C_6H_4: >89% *trans* (>90% ee)

Ar_f = C_6F_5, 2,3,5,6-F_4-C_6H: >62% *cis* (>86% ee)

Monofluorobenzaldehydes gave *trans*-oxazolines (>90% ee) while polyfluorobenzaldehydes gave *cis*-isomers (>86% ee) predominantly.

Tetrahedron Letters, 1994, 35, 2717

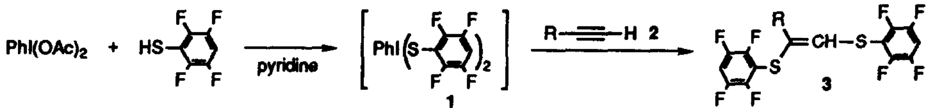
Preparation of Bis(arylthio)iodobenzene and Reaction with 1-Alkynes. A Novel Route to 1,2-Bis(arylthio)alkenes

Yasuyuki Kita,[a] Takayuki Okuno,[a] Hirofumi Tohma,[a] Shuji Akai,[a] and Keita Matsumoto[b]

[a] *Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka 565, JAPAN*

[b] *Research Center, Taisho Pharmaceutical Co., Ltd, Yoshino-cho, Omiya, Saitama 330, JAPAN*

A novel hypervalent iodine reagent 1 having arylthio ligand was *in situ* prepared from phenyliodine diacetate and 2,3,5,6-tetrafluorothiophenol and reacted with 1-alkynes 2 to give 1,2-bis(arylthio)alkenes 3 in good yields.



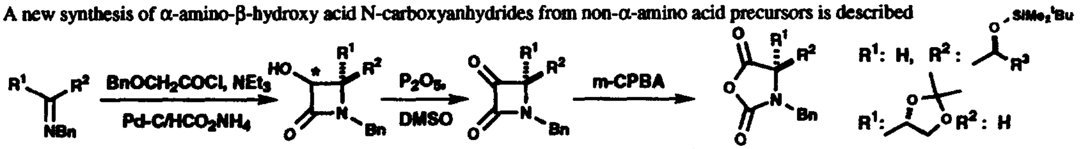
Tetrahedron Letters, 1994, 35, 2721

SYNTHESIS OF β-ALKYLSERINE-N-CARBOXYANHYDRIDES THROUGH β-LACTAMS VIA CYCLOADDITION REACTION OF ALKOXYKETENES TO CHIRAL α-ALKOXYALDEHYDE-DERIVED IMINES

Claudio Palomo, Jesus M. Aizpurua, Françesc Cabré, Jesus M. García, Jose M. Odriozola

Departamento de Química Orgánica. Facultad de Química. Universidad del País Vasco. Aptdo 1072. 20080, San Sebastian.Spain.

A new synthesis of α-amino-β-hydroxy acid N-carboxyanhydrides from non-α-amino acid precursors is described

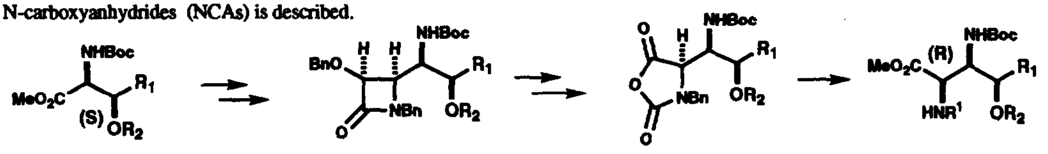


FROM (S) α-AMINO β-HYDROXYACIDS TO (R)-α,β-DIAMINO-γ-HYDROXYACID N-CARBOXYANHYDRIDES VIA β-LACTAMS.

Tetrahedron Letters, **1994**, *35*, 2725

Claudio Palomo, Jesus M. Aizpurua, Francesc Cabré, Carmen Cuevas, Simon Munt and José M. Odriozola
Departamento de Química Orgánica. Facultad de Química. Universidad del País Vasco. Aptdo 1072. 20080, San Sebastian.Spain.

A new synthesis of α,β-diamino-γ-hydroxyacids through optically pure non-naturally available amino acid-derived N-carboxyanhydrides (NCAs) is described.



DIRECT CONVERSION OF CARBOXYLIC ACIDS INTO CARBAMOYL AZIDES.

Tetrahedron Letters, **1994**, *35*, 2729

Hilman Affandi, Aristea V. Bayquen and Roger W. Read*, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia

Optimal conditions are described and the conversion illustrated with 8 examples.

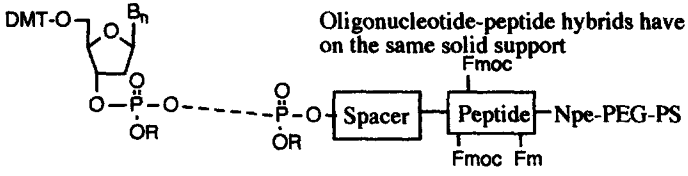
$$\mathrm{RCOOH}\ \xrightarrow[\substack{2.\ \mathrm{NaN_3}\ (5\ \mathrm{equiv}),\ 0^\circ \\ 3.\ 0^\circ \rightarrow \mathrm{r.t.}}]{\substack{1.\ [(\mathrm{CH_3})_2{}^{+}\mathrm{N{=}CHCl}]\ \mathrm{Cl^-}\ (1.5\ \mathrm{equiv}) \\ \mathrm{pyridine}\ (1.0\ \mathrm{equiv})\ \mathrm{in}\ \mathrm{CH_3CN-THF}}}\ \mathrm{RNHCON_3}$$

STEPWISE SOLID-PHASE SYNTHESIS OF OLIGONUCLEOTIDE-PEPTIDE HYBRIDS

Tetrahedron Letters, **1994**, *35*, 2733

Beatriz G. de la Torre, Anna Aviñó, Gemma Tarrason, Jaume Piulats, Fernando Albericio, Ramon Eritja.
CID-CSIC, Laboratori de BioInvestigació Merck-Igoda, Life Sciences Research Group Millipore Corp.

Oligonucleotide-peptide hybrids have been synthesized stepwise on the same solid support



SOLID PHASE PHOSPHORYLATION OF A PEPTIDE BY THE H-PHOSPHONATE METHOD.

Tetrahedron Letters, **1994**, *35*, 2737

Elisabeth Larsson and Björn Lüning,*
Dept. of Organic Chemistry Stockholm University, S-10691 Stockholm Sweden.

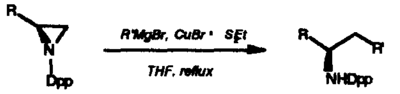
The SerValSerGluAla was phosphorylated at Ser3 by benzyl H-phosphonate followed by in situ oxidation with iodine.

$$\mathrm{PEPTIDE{-}OH}\ \xrightarrow[(\mathrm{CH_3})_3\mathrm{C{-}COCl\ /\ Pyridine\ /\ DCM}]{\mathrm{C_6H_5{-}CH_2{-}O{-}\overset{O}{\overset{\|}{P}}H{-}O^-}}\ \mathrm{PEPTIDE{-}O{-}P({=}O)H{-}OBz}\ \xrightarrow{\mathrm{I_2\ /\ Pyridine\ /\ H_2O}}\ \mathrm{PEPTIDE{-}O{-}P({=}O)OH{-}OBz}$$

Tetrahedron Letters, **1994**, *35*, 2739

A PRACTICAL ALTERNATIVE TO SULFONYL ACTIVATION OF AZIRIDINES: RING-OPENING OF N-DIPHENYLPHOSPHINOYL AZIRIDINES BY CARBON NUCLEOPHILES

Helen M.I. Osborn and J.B. Sweeney,* School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K., and William Howson, Parke-Davis Neuroscience Research Centre, Cambridge, CB2 2QB



53-89%
(Dpp=Diphenylphosphinoyl)

N-Diphenylphosphinoyl aziridines are ring-opened with regiospecificity by Copper (I)-modified Grignard reagents

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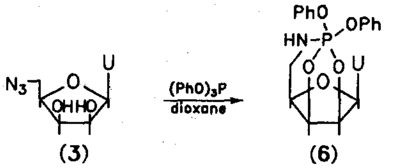
Tetrahedron Letters, **1994**, *35*, 2743

A NOVEL TYPE OF NUCLEOSIDE ANALOGUE WITH PENTA-COORDINATED PHOSPHORUS

Darinka Katalenić*, Vinko Škarić, and Branimir Klaić
Department of Organic Chemistry and Biochemistry, "Ruđer Bošković" Institute, 41001 Zagreb, P.O.B. 1016, Croatia

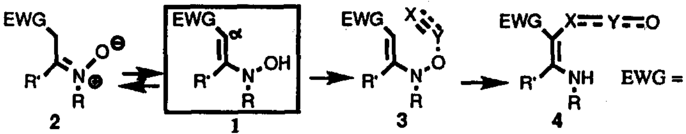
The reaction of 1-(5-azido-5-deoxy-ß-D-lyxofuranosyl)uracil (3) with triphenyl phosphite afforded a cyclic phosphorane (6) rather than the anticipated 5'-phosphoramido lyxoside (4). The structural assignment of this novel nucleoside analogue with penta-coordinated phosphorus is based on ^{1}H, ^{13}C and ^{31}P NMR data.



Tetrahedron Letters, **1994**, *35*, 2747

ENEHYDROXYLAMINES AS VERSATILE COMPOUNDS IN 3,3-SIGMATROPIC REARRANGEMENTS

L. V. Reis, A. M. Lobo,* and S. Prabhakar*
Secção de Química Orgânica Aplicada, FCT-UNL, 2825 Monte da Caparica, Portugal



EWG = electron-withdrawing group

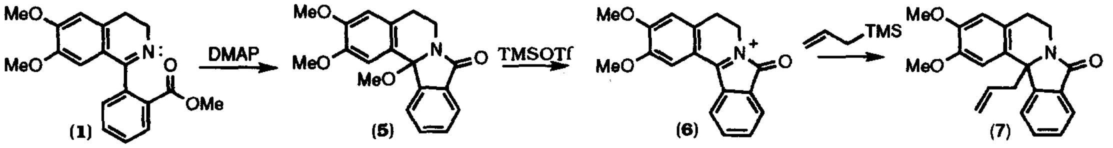
Enehydroxylamines **1** react with electrophiles to give a variety of α-substituted compounds **4** *via* 3,3-sigmatropic rearrangements.

Tetrahedron Letters, **1994**, *35*, 2751

ACYLIMINIUM IONS DERIVED FROM THE REARRANGEMENT OF BISCHLER-NAPIERALSKI CYCLISATION PRODUCTS

H. Heaney and K.F. Shuhaibar, Department of Chemistry, Loughborough University of Technology, Leicestershire, LE11 3TU, England.

6,7-Dimethoxy-1-(2-methoxycarbonylphenyl)-3,4-dihydroisoquinoline rearranges quantitatively in methanol in the presence of DMAP to the acylaminol ether (5); the related acyliminium ion can be generated by TMSOTf and reacts with allyltrimethylsilane.



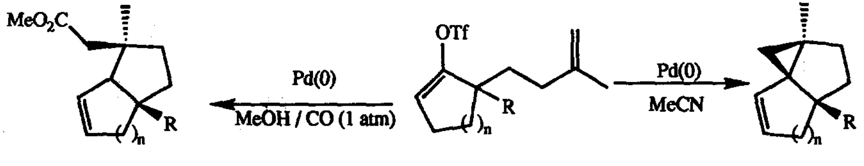
PALLADIUM CATALYSED CYCLISATION-CYCLOPROPANATION AND CYCLISATION - ANION CAPTURE PROCESSES OF VINYL TRIFLATES.

Tetrahedron Letters, **1994**, *35*, 2753

Alan Brown[a], Ronald Grigg [b*], Thangavelauthum Ravishanker[b] and Mark Thornton-Pett.[b]
a. Pfizer Central Research, Sandwich, Kent CT13 9NJ
b. School of Chemistry, Leeds University , Leeds, LS2 9JT

Cyclisation-anion capture involving carbomethoxylation or transfer of groups from boron can compete effectively with cyclisation- cyclopropanation under appropriate conditions

n= 1, R= CO_2Me
n= 2, R= CO_2Et
n= 3, R= CO_2Me

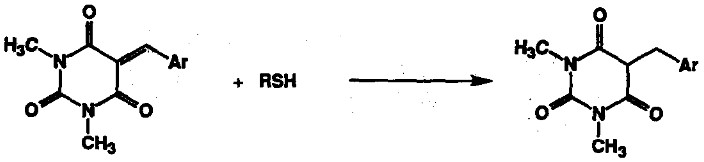


REDUCTION OF 5-ARYLIDENEBARBITURATE DERIVATIVES BY THIOLS

Tetrahedron Letters, **1994**, *35*, 2757

J.W.G. Meissner, A.C. van der Laan, U.K. Pandit
University of Amsterdam, The Netherlands

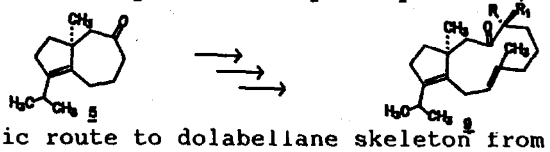
Reduction of arylidenebarbiturates containing different aryl groups by thiols, is consistent with a radical mechanism for the reaction



An Oxy-Cope Rearrangement Route for the Enantioselective Construction of 5,11-Fused Framework of Dolabellane Diterpenes

Tetrahedron Letters, **1994**, *35*, 2761

G.Mehta,* S.R.Karra and N.Krishnamurthy
School of Chemistry, University of Hyderabad, Hyderabad, India.

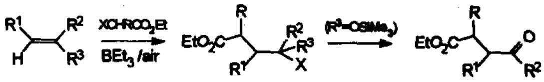


A synthetic route to dolabellane skeleton from (R)-limonene is described.

SYNTHESIS OF γ-HALOESTERS AND γ-KETOESTERS BY HOMOLYTIC ADDITION OF CARBON RADICALS GENERATED BY α-HALOESTERS AND TRIETHYLBORANE TO ALKENES AND SILYL ENOL ETHERS.

Tetrahedron Letters, **1994**, *35*, 2763

Enrico Baciocchi*, Ester Muraglia
Dipartimento di Chimica Università "La Sapienza" and Centro CNR per lo Studio dei Meccanismi di Reazione, P.le A. Moro 5, 00185 Rome, Italy

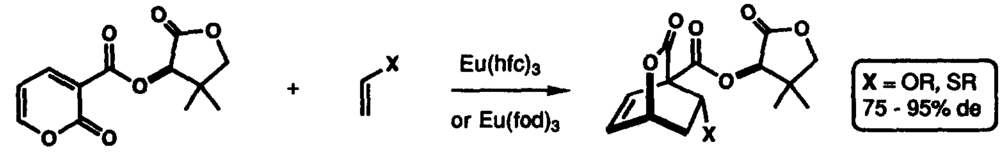


The synthesis of γ-haloesters and γ-ketoesters has been achieved with good yields by addition of carbon radicals $\cdot CH(R)CO_2Et$ generated by $XCH(R)CO_2Et$ (X= Br, I; R= H, Me, CO_2Et) / BEt_3 / air to linear and cyclic alkenes an silyl enol ethers, respectively (R^1= H, alkyl; R^2= alkyl; R^3= H,$OSiMe_3$).

Tetrahedron Letters, **1994**, *35*, 2767

Diastereoselective, Lanthanide-Catalysed, Inverse Electron-Demand Diels-Alder (IEDDA) Reactions of 3-Carbomethoxy-2-Pyrone (3-CMP) Derivatives

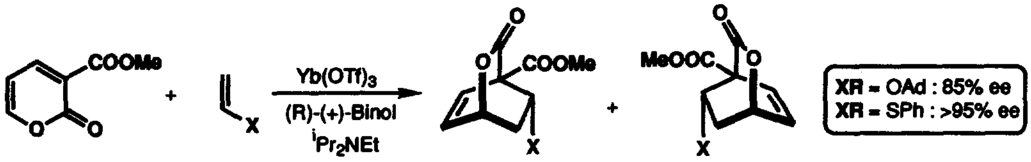
István E Markó * and Graham R Evans.
Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium



Tetrahedron Letters, **1994**, *35*, 2771

Catalytic, Enantioselective, Inverse Electron-Demand Diels-Alder Reactions of 3-Carbomethoxy-2-pyrone

István E Markó * and Graham R Evans
Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium

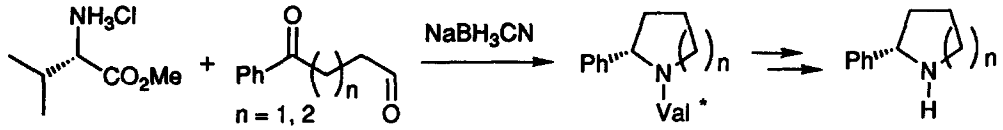


Tetrahedron Letters, **1994**, *35*, 2775

REDUCTIVE AMINATION OF 1,4- AND 1,5-DICARBONYL COMPOUNDS WITH (S)-VALINE METHYL ESTER. SYNTHESIS OF (S)-2-PHENYLPYRROLIDINE AND (S)-2-PHENYLPIPERIDINE.

Francesco Manescalchi, Anna R. Nardi, and Diego Savoia,*
Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy

(S)-2-Phenylpyrrolidine and -piperidine were prepared through reductive amination of 4-phenyl-4-oxobutanal and 5-phenyl-5-oxohexanal



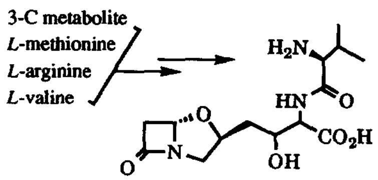
Tetrahedron Letters, **1994**, *35*, 2779

BIOSYNTHETIC PRECURSORS OF VALCLAVAM

Jack E. Baldwin, Kee-Chuan Goh and Christopher J. Schofield

The Dyson Perrins Laboratory and the Oxford Centre for Molecular Sciences, South Parks Road, Oxford OX1 3QY, U.K.

Results of feeding experiments indicate that the primary metabolic precursors of valclavam are a 3-C pool metabolite, *L*-valine, *L*-arginine and probably *L*-methionine and suggest a common biosynthetic origin for clavulanic acid and valclavam.



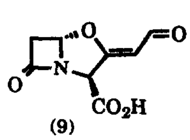
Tetrahedron Letters, **1994**, *35*, 2783

ENZYMES OF VALCLAVAM BIOSYNTHESIS

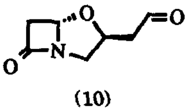
Jack E. Baldwin, Y. Fujishima, Kee-Chuan Goh and Christopher J. Schofield

The Dyson Perrins Laboratory and the Oxford Centre for Molecular Sciences, South Parks Road, Oxford OX1 3QY, U.K.

The enzymes, proclavaminic acid amidinohydrolase (PAH) and clavaminic acid synthase (CAS) were detected in *Streptomyces antibioticus*, indicating a shared biosynthetic pathway between clavulanic acid and valclavam. The aldehydes (9) and (10) are proposed as branch-points in clavam biosynthesis in different *Streptomyces* spp.



(9)

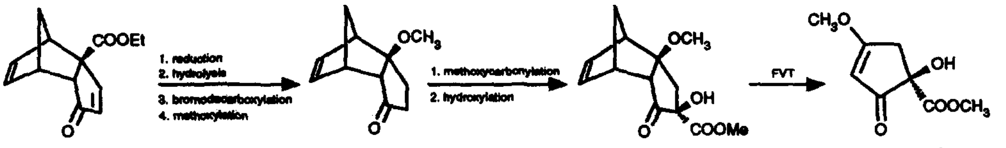


(10)

Tetrahedron Letters, **1994**, *35*, 2787

STEREOSPECIFIC TOTAL SYNTHESIS OF (-)-KJELLMANIANONE AND A REVISION OF ITS ABSOLUTE CONFIGURATION

Jie Zhu, Antonius J.H. Klunder and Binne Zwanenburg*, Department of Organic Chemistry, NSR Center for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands



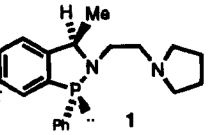
$[\alpha]_D = +105^0$, ee>98%

$[\alpha]_D = -113.0^0$

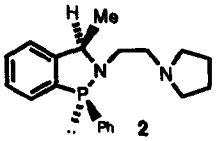
Tetrahedron Letters, **1994**, *35*, 2791

A NEW CLASS OF CHIRAL PHOSPHORUS CATALYST FOR ASYMMETRIC PALLADIUM CATALYSED ALLYLIC SUBSTITUTION REACTIONS.

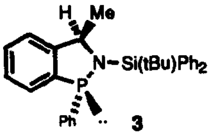
Guy Brenchley, Eric Merifield and Martin Wills.*
School of Chemistry, University of Bath,
Claverton Down, Bath, BA2 7AY.
Michael Fedouloff
SmithKline Beecham Pharmaceuticals, Coldharbour
Road, The Pinnacles, Harlow, Essex, CM19 5AD.



1



2



3

Ligands 1 to 3 were employed in asymmetric palladium catalysed allylation reactions. Enantiomeric excesses of up to 91.5% were obtained.

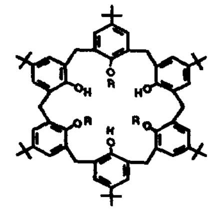
Tetrahedron Letters, **1994**, *35*, 2795

On the Occurrence of the 1,3,5-Trisubstitution Pattern in the *O*-Alkylation of *p*-*tert*-Butylcalix[6]arene

Placido Neri,* Grazia M. L. Consoli, Francesca Cunsolo and Mario Piattelli

Istituto per lo Studio delle Sostanze Naturali di Interesse Alimentare e Chimico-Farmaceutico, C.N.R.,
Via del Santuario 110, I-95028 Valverde (CT), Italy

Alkylation of *p*-*tert*-butylcalix[6]arene (1, R = H) with alkyl iodides (Et, *n*-Pr, *n*-Bu) or *p*-X-benzyl bromides (X = *tert*-Bu, Me, Br, NO_2) in the presence of K_2CO_3 or CsF gives the corresponding trisubstituted derivatives 3-9 with the "rare" 1,3,5-substitution pattern.



Tetrahedron Letters, 1994, *35*, 2799

MOLECULAR DECOMPOSITION OF ACETONE

Josef Pola[a]* and Roger Taylor[b]*
[a] Institute of Chemical Process Fundamentals, Academy of Sciences
of the Czech Republic, 162 02 Prague, Czech Republic
[b] School of Chemistry and Molecular Sciences, University of Sussex,
Brighton BN1 9QJ, UK

The absence of a radical-scavenging effect by [$^2H_4$]germane in ArF laser-induced photolysis of acetone at relatively high radiation fluences is consistent with molecular expulsion of ethane from acetone.

$$(CH_3)_2C{=}O \longrightarrow H_3C\text{-}CH_3 + CO$$

Tetrahedron Letters, 1994, *35*, 2801

Silver(I) Induced Conformational Change in a Molecular Clip.

Joost N.H. Reek Rintje P. Sijbesma and Roeland J.M. Nolte
Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld 6525 ED Nijmegen, The Netherlands.

Binding of Ag$^+$ changes the conformation of clip **1** from *sa* to *aa* and *ss*.