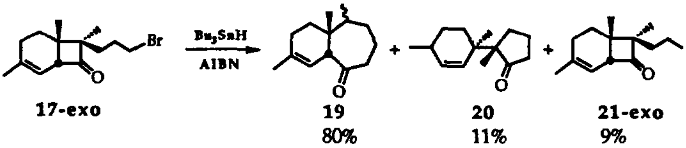
Tetrahedron, **1993**, *49*, 1965

FREE RADICAL REARRANGEMENT OF BICYCLO[2.2.2]- AND BICYCLO[4.2.0]OCTENONE SYSTEMS

Wei Zhang and Paul Dowd*
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260



Generation of the free radical from 17-exo, leading to intramolecular cyclization to the carbonyl group, yields the ring expansion product 19. Mechanistic questions surrounding this transformation are examined.

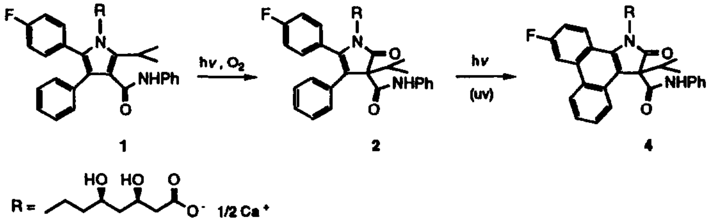
PHOTODECOMPOSITION OF CI-981, AN HMG-CoA REDUCTASE INHIBITOR

Tetrahedron, **1993**, *49*, 1979

Timothy R. Hurley*†, Charles E. Colson†, Scott A. Clippert†, Susan E. Uhlendorf‡ and Michael D. Reily‡

Parke-Davis Pharmaceutical Research Division, Warner-Lambert Company, 2800 Plymouth Road, Ann Arbor, MI 48106, USA

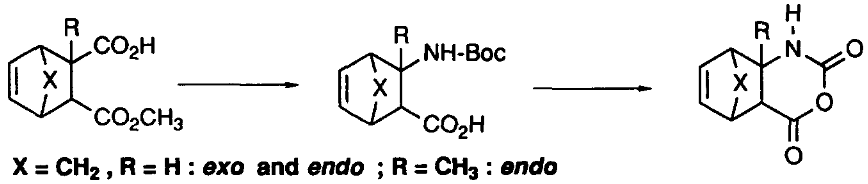
The photodecomposition of pyrrole 1 leads to the formation of lactam 2 and phenanthrene 4.



Tetrahedron, **1993**, *49*, 1985

A CONVENIENT SYNTHESIS OF BRIDGED AZATRICYCLIC ANHYDRIDES

P. Canonne, Département de chimie, Université Laval, Québec, Canada GlK 7P4
M. Akssira, A. Dahdouh, H. Kasmi and M. Boumzebra, Laboratoire de chimie organique, Département de chimie, Faculté des Sciences, Université Abdelmalek Essaadi, B.P. 2121, Tétouan, Maroc.



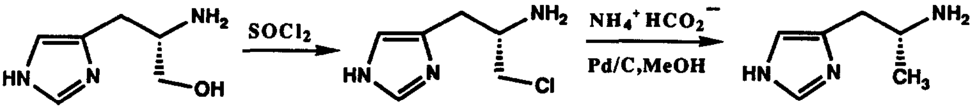
X = CH_2 , R = H : *exo* and *endo* ; R = CH_3 : *endo*
X = O , R = H : *exo*

Tetrahedron, **1993**, *49*, 1993

TRANSFER HYDROGENOLYSIS: AN IMPROVED SYNTHESIS OF (R)-(-)-α-METHYL HISTAMINE.

Richard J. Friary, Pietro Mangiaracina*, Mehdi Nafissi, Steven C. Orlando,
Stanley Rosenhouse, Vera A. Seidl, and Neng-Yang Shih
Schering-Plough Research Institute, 60 Orange Street, Bloomfield, N. J. 07003, U. S. A.

R-(-)-α-methyl histamine was prepared via a new and convenient method.

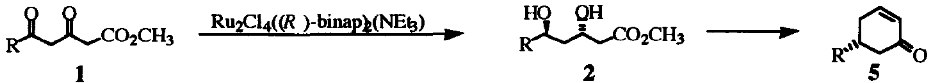


Tetrahedron, **1993**, *49*, 1997

Asymmetric Hydrogenation of 3,5-Dioxoesters Catalyzed by Ru-binap Complex: A Short Step Asymmetric Synthesis of 6-Substituted 5,6-dihydro-2-pyrones

Liming Shao, Hiroyuki Kawano, Masahiko Saburi*, and Yasuzo Uchida
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 Japan

Asymmetric hydrogenation of 3,5-dioxoesters **1a-c** using $Ru_2Cl_4((R)$ or (S)-binap$)_2(NEt_3)$ as the catalyst gave dominantly *anti* 3,5-dihydroxyesters **2**, which were then converted into unsaturated lactones **5a-c** (70-80% e.e.). It was revealed that the Ru-binap catalyzed hydrogenation of **1a-b** proceeds mainly via the β-diketone mode A convenient asymmetric synthesis of hydroxylactone **3c** and unsaturated lactone **5c** was presented

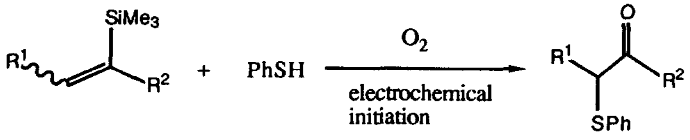


R a=CH_3; b=^nPr; c=$BnOCH_2$

Tetrahedron, **1993**, *49*, 2011

Electro-Initiated Oxygenation of Alkenylsilanes in the Presence of Thiophenol.

Shogo Nakatani, Jun-ichi Yoshida,* Sachihiko Isoe*
Institute of Organic Chemistry, Faculty of Science, Osaka City University,
Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

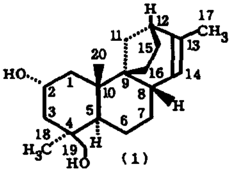


Tetrahedron, **1993**, *49*, 2025

Oryzalexin S Structure: A New Stemarane-type Rice Plant Phytoalexin and its Biogenesis.

Shigeru Tamogami* and Masahiro Mitani
Central Research Laboratories Idemitsu Kosan Co. Ltd., 1280 Kamiizumi Sodegaura-shi, Chiba 299-02 Japan
Osamu Kodama and Tadami Akatsuka
Laboratories of Bio-organic and Pesticide Chemistry, Faculty of Agriculture, Ibaraki University, Ami, Ibaraki 300-03, Japan

Oryzalexin S (1) is a new phytoalexin from rice plants. Details of its structure and of its biogenesis, including stereoselective cyclizations are described.



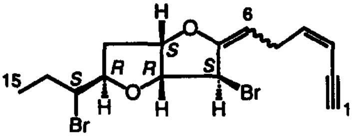
(1)

Tetrahedron, **1993**, *49*, 2033

STRUCTURES OF LAURENENYNE-A AND -B, NOVEL HALOGENATED ACETOGENINS FROM A SPECIES OF THE RED ALGAL *LAURENCIA*

Minoru Suzuki*, Yoshihide Matsuo, and Michio Masuda†
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan; †Department of Botany, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Two novel halogenated metabolites, laurenenyne-A (1) and -B (2) have been isolated as an inseparable mixture from an undescribed *Laurencia* species collected in Japan.

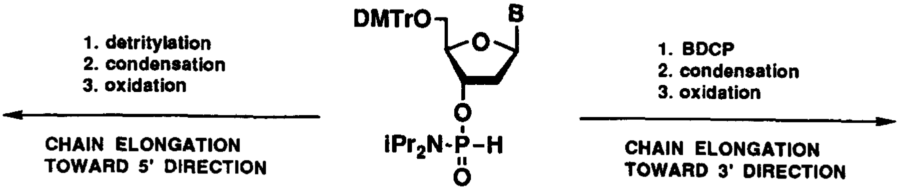


1: 6*E*
2: 6*Z*

Tetrahedron, **1993**, *49*, 2043

Nucleoside 3'-*N*,*N*-Dialkylphosphonamidates as Novel Nucleotide Units for the Solution-Phase Oligonucleotide Synthesis

Takeshi Wada, Kazushige Ishikawa, and Tsujiaki Hata*
Department of Life Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midoriku, Yokohama 227, Japan

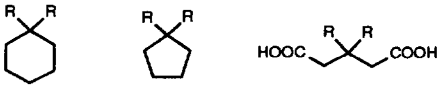


THE STRUCTURAL BASIS OF THE GEMINAL-DIMETHYL EFFECT

Tetrahedron, **1993**, *49*, 2055

Reinhart Keese* and Marc Meyer
Institut fur organische Chemie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland

Scissor-type deformations at C_q are absent, C-C-C bond angles in α-position of C_q are significantly larger.



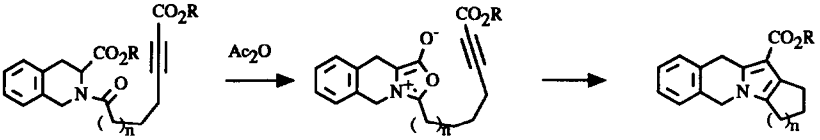
a) R = H, b) R = CH_3

THE INTRAMOLECULAR 1,3-DIPOLAR CYCLISATION OF MESOIONIC SPECIES GENERATED THROUGH THE THERMOLYSIS OF THE MIXED ANHYDRIDES OF ACETIC AND *N*-ALKYNOYL-1,2,3,4-TETRAHYDROISOQUINOLINE 3-CARBOXYLIC ACIDS

Tetrahedron, **1993**, *49*, 2065

Malcolm Sainsbury[a], Rosalind H. Strange[a], and Peter R. Woodward,[b] and Paul A. Barsanti[a]
[a]School of Chemistry, University of Bath, Bath BA2 7AY;
Medicinal Chemistry II, Glaxo Group Research Ltd., Greenford, Middlesex UB6 0HE.

Octahydropentaleno[2,3-*a*]isoquinolines and hexahydroindeno[2,3-*a*]isoquinolines are formed from *N*-alkynoyl-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acids via mesoionic intermediates

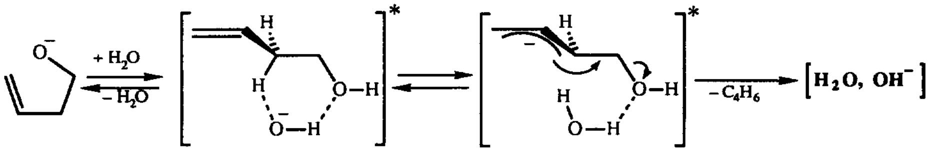


Anionic Ether Cleavage of Tetrahydrofuran in the Gas Phase

Tetrahedron, **1993**, *49*, 2077

F. Matthias Bickelhaupt, Leo J. de Koning, and Nico M.M. Nibbering*
Instituut voor Massaspectrometrie, Universiteit van Amsterdam (The Netherlands)

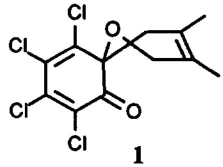
In the gas phase THF reacts with anionic bases predominantly via a 1,2-elimination. The resulting $(THF-H)^-$ ions very efficiently react with water under formation of $[H_2O, OH^-]$ via a mechanism which involves a hydroxide-induced $(E1cb)_{rev}$ process.



SOLVENT EFFECT IN PERICYCLIC REACTIONS. VIII. THE RETRO CLAISEN REARRANGEMENT.

Tetrahedron, **1993**, *49*, 2093

G. Desimoni*, G. Faita, S. Gatti Comini, P.P. Righetti, and G. Tacconi.
Dipartimento di Chimica Organica dell'Università, V.le Taramelli 10, 27100 Pavia, Italy.



1

The solvent effect on the retro-Claisen rearrangement of **1** was investigated in 17 solvents and 3 lithium perchlorate-methanol solutions. The kinetic data are a linear function of Reichardt's $E_T(30)$ solvent polarity parameter, giving evidence for a transition state with partial charge separation.
A comparison between the solvent effect in forward and retro process will be discussed.

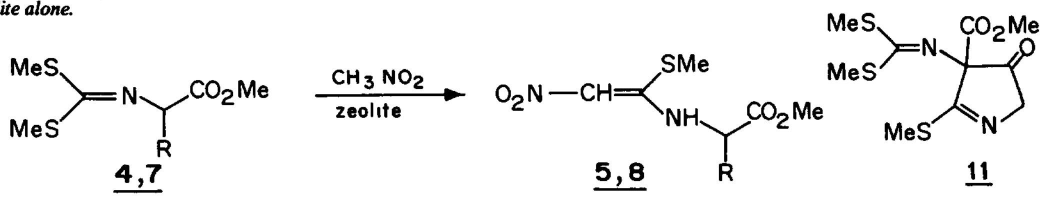
UNIQUE ZEOLITE-CATALYZED SYNTHESIS OF NITROKETENE S,N-ACETALS

Tetrahedron, **1993**, *49*, 2101

T. Indrasena Reddy, B.M. Bhawal and S. Rajappa*

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, India.

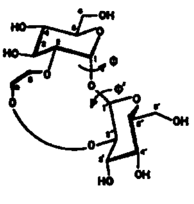
Abstract: Dimethyl carbonimidodithioates (4 & 7) derived from amines and amino acid esters have been condensed with nitromethane in the presence of RE(~70%)Na Y to give S,N-acetals (5 & 8). The glycine derivative (7a) gives a dimeric product (11) when heated with zeolite alone.



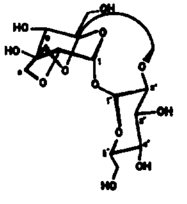
The *Exo*-Anomeric Effect Does not Govern the Conformation of Some 2,2'-*O*-Substituted α,α'-Trehalose Derivatives. Solid State and Solution Evidences.

Tetrahedron, **1993**, *49*, 2109

F.H. Cano[a], J.L. G. de Paz[b], C. Foces-Foces[a],
J Jiménez-Barbero[c], M. Martín-Lomas[c], S. Penadés*[c]
and C. Vicent[c].
[a] Instituto Rocasolano, CSIC, 28006 Madrid, Spain
[b] Departamento de Química-Física Aplicada C-XIV-505,
Universidad Autónoma de Madrid, 28049 Madrid, Spain
[c] Instituto de Química Orgánica, CSIC,
Juan de la Cierva 3, 28006 Madrid, Spain



Isomer A ($\Phi,\Phi' \simeq 70°$)



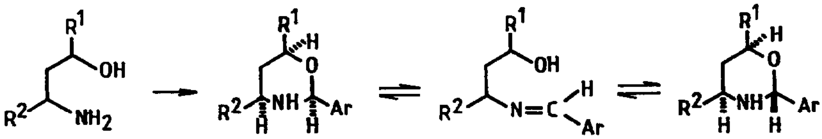
Isomer B ($\Phi,\Phi' \geq 100°$)

The crystal structure and solution conformation of the chiral mono-trehalo-15-crown 5 1 shows what is probably the first case of a disaccharidic structure where the anomeric effect does not dominate. This unexpected conformational change seems to be a general tendency in 2,2'-polyethylene glycol substituted trehalose derivatives.

SUBSTITUENT EFFECTS ON THE RING-CHAIN TAUTOMERISM OF 1,3-OXAZINES

Tetrahedron, **1993**, *49*, 2115

Ferenc Fülöp,[a,b]* László Lázár,[a] Gábor Bernáth,[a] Reijo Sillanpää[b] and Kalevi Pihlaja[b]*
[a]Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6701 Szeged, POB 121, Hungary;
[b]Department of Chemistry, University of Turku, SF-20500 Turku, Finland



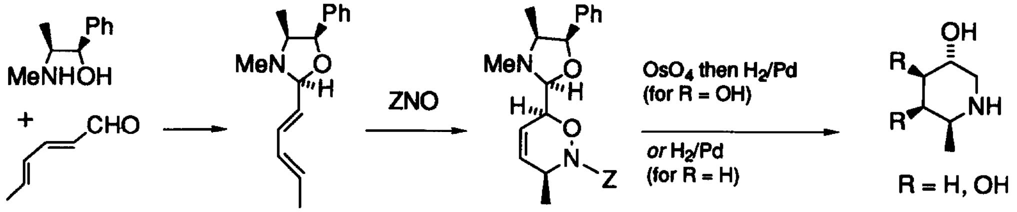
The electronic effects of the aryl substituents at positions 2, 4 and 6 on the ring-chain tautomeric ratios of 2,4- or 2,6-diarylsubstituted-tetrahydro-1,3-oxazines are discussed.

Tetrahedron, **1993**, *49*, 2123

2-(Penta-1, 3-dienyl)oxazolidines: Synthesis of Hydroxylated Piperidines by a Stereoselective Diels-Alder Reaction

Abid Hussain and Peter B Wyatt*
Department of Chemistry, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, UK

A stereoselective Diels-Alder reaction of benzyl nitrosoformate with the chiral diene obtained by condensation of (-)-ephedrine with hexa-2,4-dienal gave a cycloadduct which could be converted into hydroxylated piperidine derivatives.

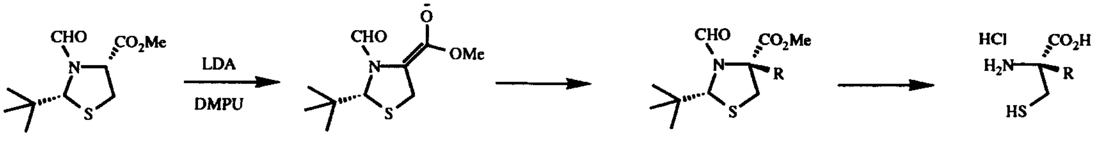


ENANTIOSELECTIVE SYNTHESIS OF 2-ALKYL SUBSTITUTED CYSTEINES.

Tetrahedron, **1993**, *49*, 2131

Gerald Pattenden,* Stephen M. Thom and Martin F. Jones†
Department of Chemistry, The University, Nottingham, NG7 2RD
†Glaxo Group Research Ltd., Greenford, Middlesex UB6 0HE

An enantioselective synthesis of 2-alkyl substituted cysteines is described based on a modification of Seebach's "self-reproduction of chirality" protocol.



R = alkyl