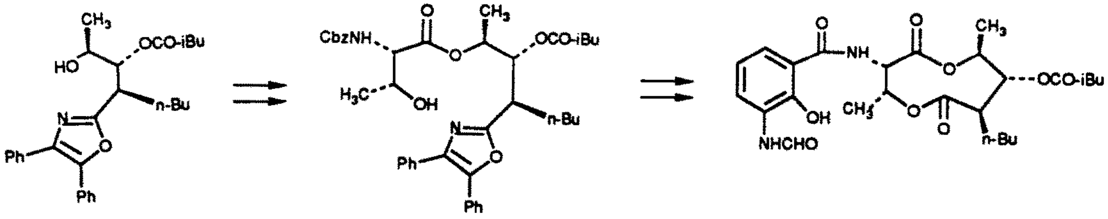
GRAPHICAL ABSTRACTS

Tetrahedron, **1992**, *48*, 7059

SINGLET OXYGEN IN SYNTHESIS. FORMATION OF ANTIMYCIN A3 FROM AN OXAZOLE TEMPLATE.

Harry H. Wasserman, * and Ronald J. Gambale, Department of Chemistry, Yale University, New Haven, CT 06511 USA

Antimycin A3 has been synthesized using an oxazole template for constructing the framework of the dilactone. Formation of the nine-membered ring was accomplished by reaction of an ω-hydroxyl group with an activated carboxylate generated in the reaction of the oxazole with singlet oxygen.

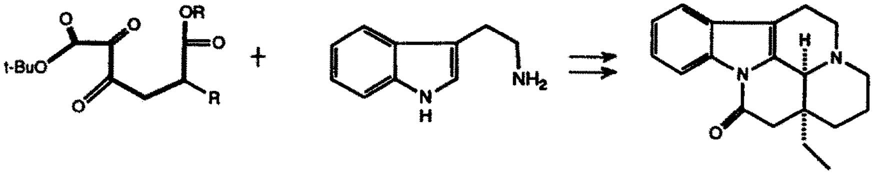


Tetrahedron, **1992**, *48*, 7071

OXIDATION OF YLIDE PRECURSORS TO VICINAL TRICARBONYLS. APPLICATIONS IN VINCAMINE ALKALOID SYNTHESIS.

Harry H. Wasserman* and Gee-Hong Kuo, Department of Chemistry, Yale University, New Haven, CT 06511 USA

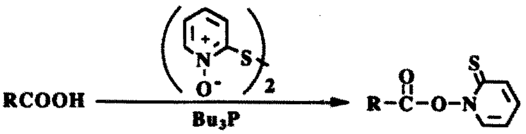
Attachment of carbethoxyalkyl residues to an α,β-diketo ester provides dielectrophilic species applicable to the synthesis of the vincamine alkaloids, eburnamonine and tacamonine. The required vicinal tricarbonyl aggregates were formed by oxidation of suitable ylide precursors with ozone or singlet oxygen.



Tetrahedron, **1992**, *48*, 7083

The Invention of Radical Reactions. Part XXV A Convenient Method for the Synthesis of the Acyl Derivatives of *N*-Hydroxypyridine-2-thione

Derek H.R. Barton* and Mohammad Samadi*
Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A

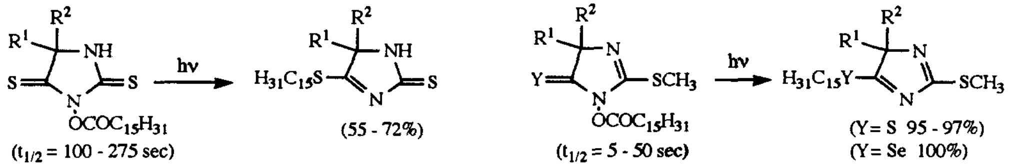


Tetrahedron, **1992**, *48*, 7091

THE INVENTION OF RADICAL REACTIONS. PART XXVI. NEW THIO- AND SELENO-HYDROXAMIC ACIDS; RADICAL CHEMISTRY OF THEIR O-ACYL DERIVATIVES.

Derek H. R. Barton* and Catherine Tachdjian*.
Department of Chemistry, Texas A&M University, College Station, Texas 77843

New thio- and seleno-hydroxamic acids have been synthesized; their corresponding O-acyl derivatives rearrange on irradiation with visible light. A wide range of half-lives was observed.

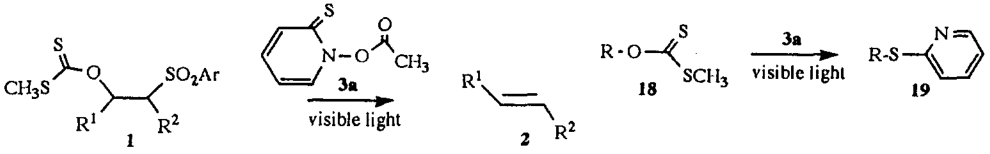


Tetrahedron, **1992**, *48*, 7109

THE INVENTION OF RADICAL REACTIONS. PART XXVII. MODIFIED JULIA SYNTHESIS OF OLEFINS USING RADICAL DEOXYGENATION.

Derek H. R. Barton* and Catherine Tachdjian.
Department of Chemistry, Texas A&M University, College Station, Texas 77843

Xanthate derivatives **1** of β-hydroxy sulfones react with methyl radicals generated from the photolysis of N-acetyloxy-2-thiopyridone **3a** to give the corresponding olefin **2** in good yield. Under identical conditions the xanthate derivative **18** of cyclododecanol is transformed to its thiopyridyl derivative **19**.

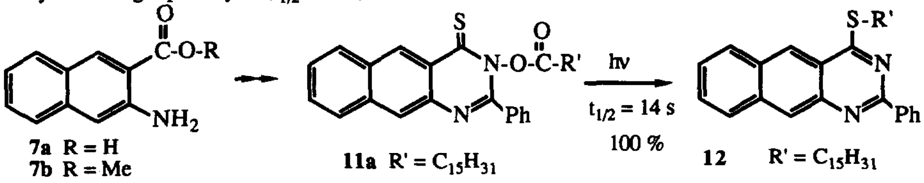


Tetrahedron, **1992**, *48*, 7121

THE INVENTION OF RADICAL REACTIONS. PART XXVIII A NEW VERY PHOTOLABILE *O*-ACYL THIOHYDROXAMIC ACID DERIVATIVE AS PRECURSOR OF CARBON RADICALS

Derek H. R. Barton, Paul Blundell and Joseph Cs. Jaszberenyi*
Department of Chemistry, Texas A&M University, College Station, Texas, 77843

A new radical precursor O-acyl thiohydroxamic acid derivative **11a** was synthesized and converted to **12** by visible light photolysis ($t_{1/2}$ = 14 s).

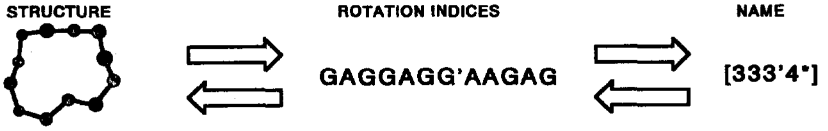


Tetrahedron, **1992**, *48*, 7131

A REVISED NOMENCLATURE FOR THE RING CONFORMATION AND A NOTE ON THE CONFORMATIONAL DISTANCE IN CYCLODODECANE

Hitoshi Goto, Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

A ring nomenclature is presented which covers all the patterns of bond rotation sequences along endocyclic bond and provides a unique name for every ring conformation.



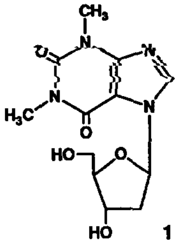
Tetrahedron, **1992**, *48*, 7145

Aplysidine, a New Nucleoside from the Okinawan Marine Sponge *Aplysina* Sp.

Kazuhiko Kondo, Hideyuki Shigemori, Masami Ishibashi,
and Jun'ichi Kobayashi*

Faculty of Pharmaceutical Sciences, Hokkaido University,
Sapporo 060, Japan

A new nucleoside, aplysidine (1), has been isolated from the Okinawan marine sponge *Aplysina* sp. and the structure elucidated by spectroscopic data and confirmed by synthesis of **1**.



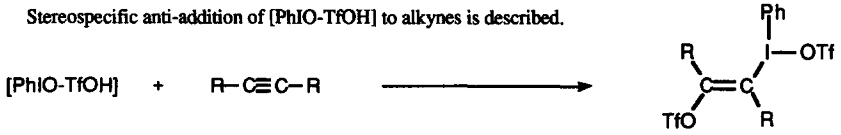
1

Tetrahedron, **1992**, *48*, 7149

ELECTROPHILIC ADDITIONS OF IODOSYLBENZENE ACTIVATED BY TRIFLUOROMETHANESULFONIC ACID, [PhIO-TfOH], TO ALKYNES

Tsugio Kitamura*, Ryuji Furuki, and Hiroshi Taniguchi*, Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812, Japan; Peter J. Stang, Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U. S. A.

Stereospecific anti-addition of [PhIO-TfOH] to alkynes is described.

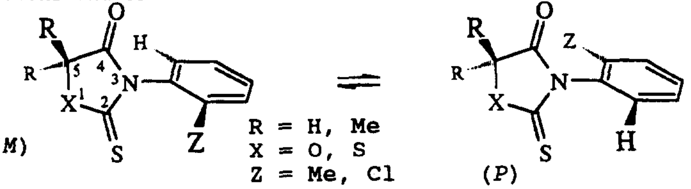


Tetrahedron, **1992**, *48*, 7157

SYNTHESIS AND NMR STUDIES OF CHIRAL 4-OXAZOLIDINONES AND RHODANINES

İ.Doğan[a,*], T. Burgemeister[b], S. İçli[c], and A. Mannschreck[b]; [a]Boğaziçi University, İstanbul, (Turkey), [b]Universität Regensburg, D-8400 Regensburg, (Germany), [c]Ege University, İzmir, (Turkey)

2-Thioxo-4-oxazolidinones and -thiazolidinones (rhodanines) forming enantiomers by steric hindrance to rotation around the C-N bond are synthesized. Chirality is proven by NMR of diastereotopic protons and carbon atoms.

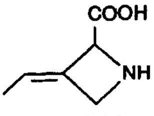


R = H, Me
X = O, S
Z = Me, Cl

Tetrahedron, **1992**, *48*, 7165

Synthesis of (2RS,E)-3-Ethylidene-azetidine-2-carboxylic acid (rac. Polyoximic acid)

Gerhard Emmer
Sandoz Forschungsinstitut, Brunnerstrasse 59
A-1230 Wien, Austria.



(±)1

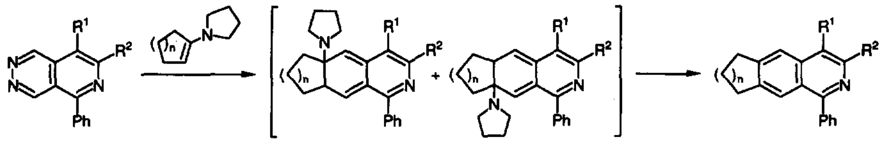
An efficient seven step synthesis of polyoximic acid (1) based on a rhodium carbenoid intramolecular N-H insertion reaction is described.

Tetrahedron, **1992**, *48*, 7173

INVERSE-ELECTRON-DEMAND DIELS-ALDER REACTIONS OF CONDENSED PYRIDAZINES, PART 2. SYNTHESIS OF ISOQUINOLINE DERIVATIVES FROM PYRIDO[3,4-*d*]PYRIDAZINES.

Norbert Haider
Institute of Pharmaceutical Chemistry, University of Vienna, Währinger Straße 10, A-1090 Vienna, Austria

Pyrido[3,4-*d*]pyridazines undergo [4+2] cycloaddition reactions with cyclic enamines to afford, after aromatisation of intermediate dihydroisoquinoline derivatives, annelated isoquinolines in good overall yields.

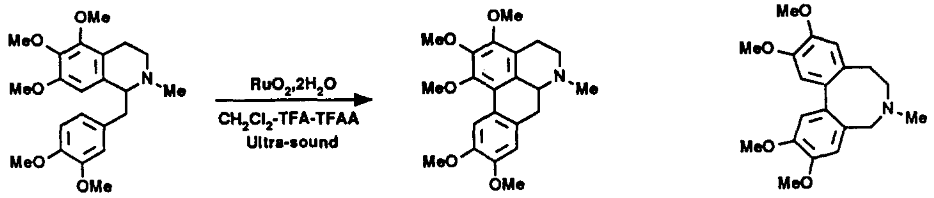


Tetrahedron, **1992**, *48*, 7185

RUTHENIUM DIOXIDE IN FLUORO ACID MEDIUM. III. APPLICATION TO THE SYNTHESIS OF APORPHINIC, HOMOAPORPHINIC AND DIBENZAZOCINIC ALKALOIDS. STUDIES TOWARDS THE PREPARATION OF AZAFLUORANTHENIC SKELETON.

Yannick Landais and Jean-Pierre Robin*

Département de Chimie, Institut Universitaire de Technologie, Université du Maine, Route de Laval, 72017 Le Mans Cedex, France.

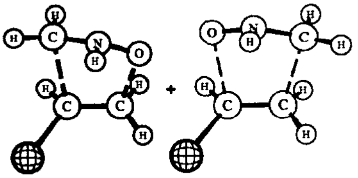


Tetrahedron, **1992**, *48*, 7197

THEORETICAL STUDY OF 1,3-DIPOLAR CYCLOADDITIONS . EFFECT OF THE SUBSTITUENT OF AN ACTIVATED ALKENE ON THE TRANSITION STATES SPECTRUM AND THE REGIOSELECTIVITY OF THE ADDITION OF NITRONE .

Y.L. Pascal[1], J. Chanet-Ray[2], R. Vessière[2] and A. Zeroual[2]
[1])Laboratoire de Chimie Organique Structurale,Université Blaise Pascal,63177 Aubière,France.
[2])Laboratoire de Chimie Organique II,Université Blaise Pascal,63177 Aubière,France.

$H_2C{=}NHO + YCH{=}CH_2 \longrightarrow$



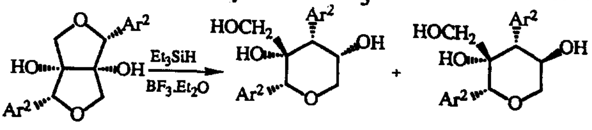
$Y = H, CF_3, CN, COCH_3, NO_2, SO_2F, CH_3, OH, OCH_3$
Determination of the transition states with AM1 method.

Tetrahedron, **1992**, *48*, 7209

REARRANGEMENTS OF 2,6-DIARYL-3,7-DIOXABICYCLO[3.3.0]OCTANE LIGNANS[1] REACTIONS OF PAULOWNIN AND WODESHIOL WITH TRIETHYLSILANE AND BF_3-ETHERATE

By Andrew Pelter and Robert S. Ward
(Chemistry Department, University of Swansea, Singleton Park, Swansea SA2 8PP, U.K.)
and Revuru Venkateswarlu and Chakicherla Kamakshi
(Andhra University Postgraduate Centre, Nuzvid 521201 India).

Treatment of wodeshiol with triethylsilane and BF_3-etherate affords two isomeric tetrahydropyran derivatives.



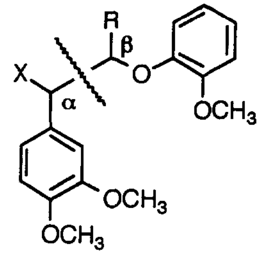
Tetrahedron, **1992**, *48*, 7221

ANODIC CLEAVAGE OF LIGNIN MODEL DIMERS IN METHANOL

Vera L. Pardini, Reinaldo R. Vargas and Hans Viertler*, Instituto de Quimica, Universidade de São Paulo, SP, Brazil ;

James H.P. Utley, Department of Chemistry, Queen Mary and Westfield College (University of London), London E1 4NS, UK.

Lignin model compounds, C_{17} - C_{18}, are oxidised anodically in methanol with a view to understanding the mode of cleavage of the C_α - C_β bond, typically to methoxylated benzaldehydes. Detailed product analyses and information from voltammetric experiments indicates that the α-hydroxyl function is necessary for rapid cleavage of the first formed radical-cation.



X = HO, =O ; R includes H CH_3 CH_2OH

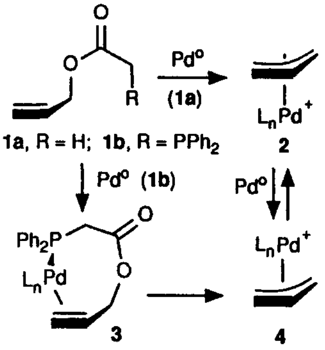
Tetrahedron, **1992**, *48*, 7229

STEREOCHEMISTRY OF THE PALLADIUM-CATALYZED ALLYLIC SUBSTITUTION: THE SYN-ANTI DICHOTOMY IN THE FORMATION OF (π-ALLYL)PALLADIUM COMPLEXES AND THEIR EQUILIBRATION†

I. Starý, J. Zajíček, and P. Kočovský*
Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Whereas (π-allyl)palladium complexes are known to arise from allylic esters in an anti fashion (**1a** ⟶ **2**), (diphenylphosphino)acetates (DPPAcO) of sterically biased substrates have been found to prefer a syn-mechanism (**1b** ⟶ **3** ⟶ **4**). This reversal of stereochemistry is attributed to pre-coordination of Pd(0) to the leaving group in the latter case (**3**). Substrates free of steric hindrance prefer the anti-mechanism even if the DPPAcO group is employed. At higher temperatures, Pd(0) in the presence of DPPAcOH facilitates equilibration of the complexes (**2** ⇄ **4**).

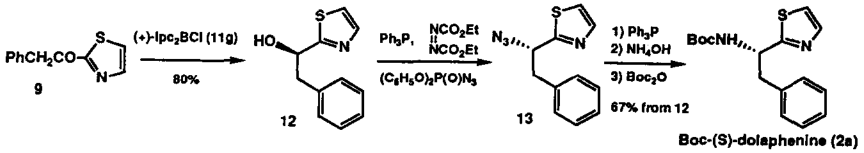
†Prelim. report: Starý, I.; Kočovský, P.: J. Am. Chem. Soc. 111, 4981 (1989).



Tetrahedron, **1992**, *48*, 7251

A New Efficient Synthesis of (S)-Dolaphenine ((S)-2-Phenyl-1-(2-thiazolyl)ethylamine), the C-Terminal Unit of Dolastatin 10

Naoko Irako, Yasumasa Hamada,* and Takayuki Shioiri*
Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, JAPAN

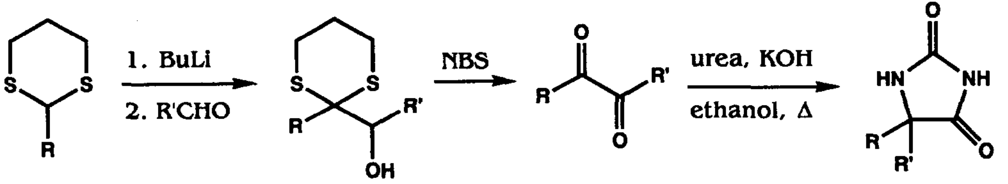


Tetrahedron, **1992**, *48*, 7265

A Convenient Preparation of Symmetrical and Unsymmetrical 1,2-Diketones: Application to Fluorinated Phenytoin Synthesis

Philip C. Bulman Page,* Andrew E. Graham and B. Kevin Park†
Robert Robinson and Donnan Laboratories, Department of Chemistry, and
†Department of Pharmacology and Therapeutics,
University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, England

1,2-Diketones are produced by reaction of aldehydes with dithiane anions followed by treatment of the resulting alcohols with NBS. Several phenytoin derivatives were prepared from these diketones.

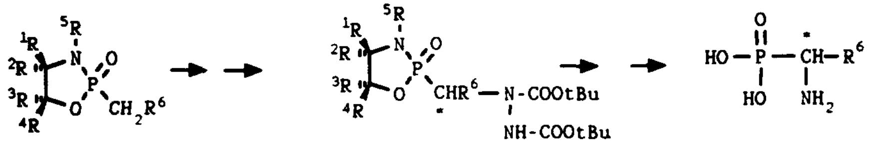


Tetrahedron, **1992**, *48*, 7275

STUDIES TOWARD A MODEL FOR PREDICTING THE DIASTEREOSELECTIVITY IN THE ELECTROPHILIC AMINATION OF CHIRAL 1,3,2-OXAZAPHOSPHOLANES.

Giancarlo Jommi, Giuliana Miglierini, Roberto Pagliarin, Guido Sello, Massimo Sisti.
Dipartimento di Chimica Organica e Industriale, Universita' di Milano,
via Venezian 21, Milano, Italy.

A model has been developed and applied for predicting the diastereoselectivity of the title reaction. The theoretical and experimental results are compared.

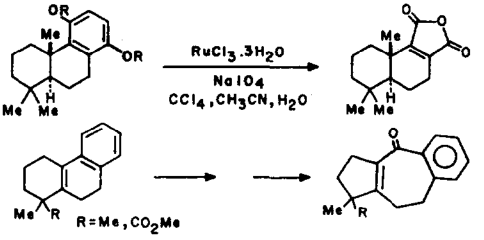


Tetrahedron, **1992**, *48*, 7289

INFLUENCE OF ELECTRON DONATING AROMATIC SUBSTITUENTS ON THE RUTHENIUM TETROXIDE-CATALYSED OXIDATION OF (±)-PODOCARPA-8,11,13-TRIENES

Sukumar Ghosh and Usha Ranjan Ghatak
Department of Organic Chemistry, Indian Association for the
Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

Ruthenium tetraoxide catalysed oxidation of (±)-podocarpa-8,11,13-trienes, incorporating a phenolic hydroxyl or ether functionality at C-11 and C-14 or at C-14 give (±) winterin. Hexahydrophenanthrenes on similar oxidation lead to the respective diketones and the benzazulenes.

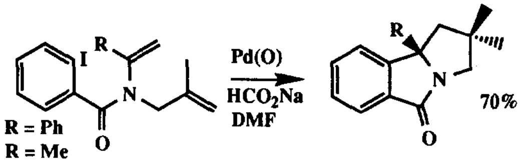


Tetrahedron, **1992**, *48*, 7297

PALLADIUM CATALYSED TANDEM CYCLISATION – ANION CAPTURE PROCESS. PART 1. BACKGROUND AND HYDRIDE ION CAPTURE BY ALKYL - AND Π - ALLYL - PALLADIUM SPECIES[1].

Barry Burns,[a] Ronald Grigg,[*,b] Vijayaratnam Santhakumar,[b] Visuvanathar Sridharan[b], Paul Stevenson[a] and Tanachat Worakun[a]
a. Chemistry Department, Queens University, Belfast BT9 5AG.
b. School of Chemistry, Leeds University, Leeds LS2 9JT.

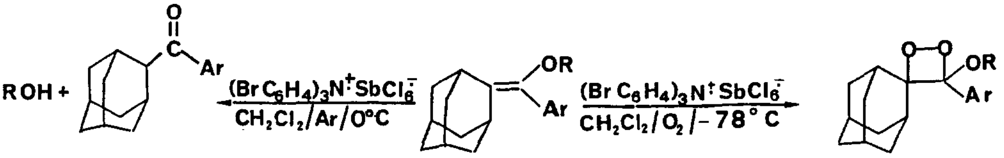
A new wide ranging, synthetically powerful, catalytic, tandem cyclisation anion capture process is proposed and exemplified for hydride capture.



Tetrahedron, **1992**, *48*, 7321

Electron-Transfer Reactions On Enol-Ethers Induced By Aminium Salts Syntheses Of 1,2-Dioxetanes And/Or Ketones

L. Lopez,[a] L. Troisi [b]
Centro CNR "MISO", Dipartimento di Chimica, Università di Bari, Via Amendola 173, 70126 Bari Italy
Laboratorio di Chimica Organica, Dipartimento di Biologia, Università di Lecce, Monteroni 73100 Italy

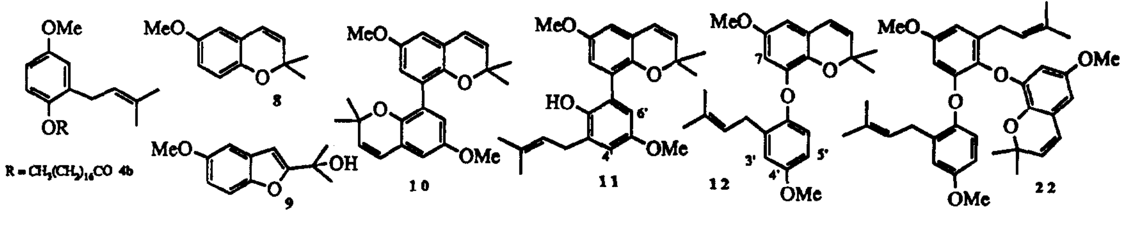


Tetrahedron, **1992**, *48*, 7331

THE CHEMISTRY OF *LACTARIUS FULIGINOSUS* AND *LACTARIUS PICINUS*

Maria De Bernardi, Giovanni Vidari*, Paola Vita-Finzi* and Giovanni Fronza
Dipartimento di Chimica Organica, Università di Pavia, 27100 Pavia (Italy)

Taste and colour changes of the title Lactarius species (Basidiomycetes) are related to chemical transformations of 2-(3-methyl-2-butenyl)-4-methoxyphenyl stearate (**4b**) in benzofuran (**9**), 2,2-dimethyl-6-methoxychromene (**8**) and oligomers as **10-12** and **22.**

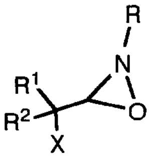


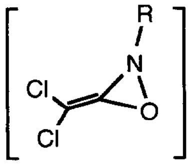
Tetrahedron, **1992**, *48*, 7345

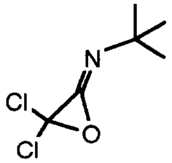
SYNTHESIS, FRAGMENTATIONS AND REARRANGEMENTS OF 3-(1-HALOALKYL)OXAZIRIDINES

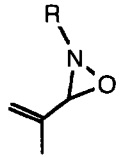
N. De Kimpe, B. De Corte
Laboratory of Organic Chemistry, Fac. Agric. Sciences, B-9000 Gent, Belgium

Fragmentations of new halogenated oxaziridines via elusive hetero(methylenecyclopropanes) are reported.









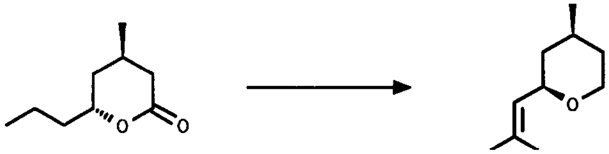
Tetrahedron, **1992**, *48*, 7363

ON THE MODE OF BAKER'S YEAST REDUCTION OF METHYL SUBSTITUTED ARYLALKYL γ- AND δ-KETO ACIDS. SYNTHESIS OF CIS-(+)-ROSE OXIDE

G. Fronza, C. Fuganti, P. Grasselli and M. Terreni.
Dipartimento di Chimica del Politecnico, Centro CNR per lo Studio delle Sostanze Organiche Naturali, 20133, Milano, Italy.

Lactone **13**, obtained in a study on the mode of baker's yeast reduction of keto acids **1-6**, is converted into cis-(+)-rose oxide **23a**.

13



23a

Tetrahedron, **1992**, *48*, 7373

A Practical Route to C-8 Substituted Fluoroquinolones

Juan C. Carretero, José L. García Ruano and Mercedes Vicioso
Departamento de Química. Universidad Autónoma de Madrid. 28049 Madrid. Spain

The highly regioselective ortho metalation of N-BOC-3,4-difluoroaniline has been applied to the synthesis of C-8 fluoroquinolones