GRAPHICAL ABSTRACTS

Tetrahedron, 1993, *49*, 6533

Conformation of Taxotere® and Analogues Determined by NMR Spectroscopy and Molecular Modeling Studies

Joëlle Dubois, Daniel Guénard*, Françoise Guéritte-Voegelein , Nourredine Guedira, Pierre Potier, Brigitte Gillet and Jean-Claude Beloeil.
Institut de Chimie des Substances Naturelles - CNRS 91198 Gif sur Yvette - France

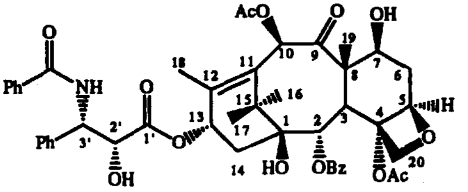
The structures of taxotere, taxol and twelve analogues bearing different substituents at carbon 2' and 3' and showing different *in vitro* biological activity on tubulin, have been investigated by ^1H NMR spectroscopy and molecular modeling studies and compared to that of taxotere 2 obtained from X-ray analysis. We thus propose in this paper a set of active conformations for taxol-like compounds and the most optimal parameters for the drug receptor binding process.

Tetrahedron, 1993, *49*, 6545

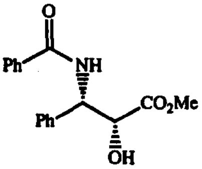
NMR AND MOLECULAR MODELING STUDY OF THE CONFORMATIONS OF TAXOL AND OF ITS SIDE CHAIN METHYLESTER IN AQUEOUS AND NON-AQUEOUS SOLUTION.

Howard J. Williams, A. Ian Scott*, Reiner A. Dieden
Center for Biological NMR, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255
Charles S. Swindell*, Lisa E. Chirlian, Michelle M. Francl, Julia M. Heerding, Nancy E. Krauss
Department of Chemistry, Bryn Mawr College, 101 North Merion Avenue, Bryn Mawr, Pennsylvania 19010-2899

Conformations of taxol 1 and its side chain methyl ester 4 in chloroform and water/d$_6$-DMSO have been determined by NMR spectroscopy and Molecular Modeling calculations.



1 Taxol



4

Tetrahedron, 1993, *49*, 6561

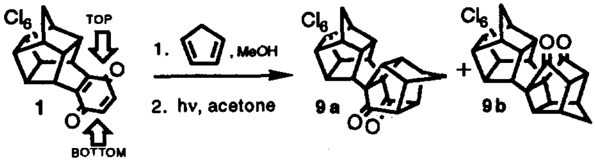
SYNTHESIS AND CHEMISTRY OF A FACIALLY DISSYMMETRIC CAGE-CONDENSED p-BENZOQUINONE: A SYNTHETIC ENTRY INTO NOVEL DOUBLY-CAGED SYSTEMS

Alan P. Marchand*, Simon G. Bott, and Vijay R. Gadgil

Department of Chemistry University of North Texas, Denton, TX 76203

William H. Watson*, Mariusz Krawiec, and Ram P. Kashyap

Department of Chemistry, Texas Christian University, Box 32908, Fort Worth, TX 76129

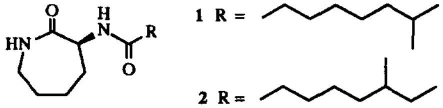


The syntheses of a novel caged quinone, 1, is reported. Diels-Alder cycloaddition of cyclopentadiene to 1 affords 7a and 7b, each of which can be photocyclized to the corresponding "doubly caged" diketone (9a and 9b, respectively)

Tetrahedron, **1993**, *49*, 6569

ISOLATION AND SYNTHESES OF CAPROLACTINS A AND B, NEW CAPROLACTAMS FROM A MARINE BACTERIUM

Bradley S. Davidson* and Robert W. Schumacher
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

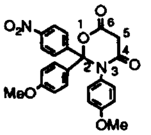


Two new caprolactams have been isolated from an unidentified Gram-positive bacterium obtained from a deep-ocean sediment sample. Caprolactins A (1) and B (2) are composed of cyclic-L-lysine linked to 7-methyloctanoic acid or 6-methyloctanoic acid, respectively. The structures were proposed using spectroscopic methods and confirmed by synthesis.

Tetrahedron, **1993**, *49*, 6575

THE EFFECT OF para-SUBSTITUENTS ON THE CONFORMATIONAL BEHAVIOR OF 2,2-DIARYL-1,3-OXAZINE-4,6-DIONES: EVIDENCE FROM A CRYSTAL STRUCTURE DETERMINATION

Masayuki Sato, Shinya Nagashima, Masayuki Murakami, and Chikara Kaneko
Pharamaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan
Toshio Furuya
Tsukuba Research Laboratories, Yamanouchi Pharmaceutical Co. Ltd., 21 Miyukigaoka, Tsukuba, Ibaraki 305, Japan



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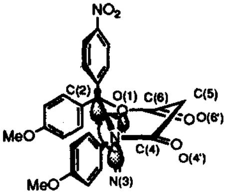


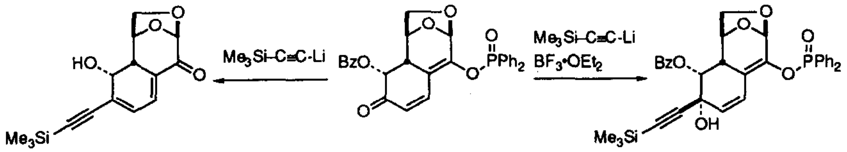
The crystal structure of 9 has revealed that the molecule is in a boat conformation with C(2) and C(5) pointing upward and the 4-nitrophenyl group takes a quasi-axial conformation. The reason for this conformation is presented.

Tetrahedron, **1993**, *49*, 6581

Chemoselective Introduction of Acetylene into Hindered Carbonyl Group using Alkynyltrifluoroborate, A Solution as one Step to (-)-Tetrodotoxin

Noboru Yamamoto and Minoru Isobe*
Laboratory of Organic Chemistry, School of Agriculture, Nagoya University,
Chikusa, Nagoya 464-01, Japan

Several examples for addition of lithium alkynyltrifluoroborates, prepared from lithium acetylides and boron trifluoride etherate, are demonstrated to react chemoselectively with carbonyl groups without addition to phosphorous atom in the vinyl phosphinate.

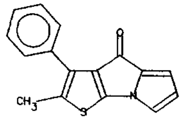


Tetrahedron, **1993**, *49*, 6591

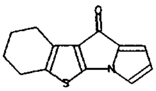
ON THE SYNTHESES AND PHOTOCHEMICAL PROPERTIES OF NOVEL PYRROLIZINONE DERIVATIVES AS PHOTOSENSITIZERS

By Rupert Bauer[a], Günter Heisler[b], and Christian Königstein[a], [a]Department of Physical Chemistry and [b]Department of Organic Chemistry, Technical University of Vienna, Getreidemarkt 9, A - 1060 Wien, Austria)

Abstract : The syntheses as well as the photochemical behavior of compounds **1** - **4** is described.



1



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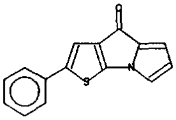

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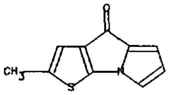

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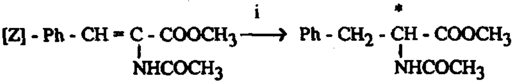
Tetrahedron, **1993**, *49*, 6605

INFLUENCE OF DIFFERENT TYPES OF AMPHIPHILES ON THE RHODIUM(I) COMPLEX-CATALYZED ASYMMETRIC HYDROGENATION OF (Z)-METHYL-α-ACETAMIDOCINNAMATE IN AQUEOUS MEDIUM

Ingrid Grassert, Eckhard Paetzold, Günther Oehme*
Institut für Organische Katalyseforschung an der Universität Rostock e.V.
Buchbinderstraße 5-6, O-2500 Rostock, Germany



$$[Z]\text{-}Ph\text{-}CH=\underset{\displaystyle NHCOCH_3}{C}\text{-}COOCH_3 \xrightarrow{i} Ph\text{-}CH_2\text{-}\underset{\displaystyle NHCOCH_3}{\overset{*}{C}H}\text{-}COOCH_3$$

i. cat.: $[Rh(COD)_2]BF_4$ + 1.1 BPPM, surfactant, water, H_2 (0.1 MPa)

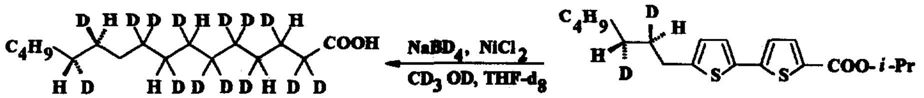
Different types of surfactants (neutral, zwitterionic, ionic) promote reaction rate and enantioselectivity significantly.

Tetrahedron, **1993**, *49*, 6613

SYNTHESIS OF DEUTERIUM LABELLED (11*S*,12*R*)- AND (11*R*,12*S*)-[$^2H_{14}$]-PALMITIC ACIDS; A FACILE ROUTE TO HIGHLY LABELLED FATTY ACIDS

Christian Fröẞl and Wilhelm Boland*
Institut für Organische Chemie der Universität, Richard-Willstätter-Allee 2, D-76131 Karlsruhe 1, Germany

Highly deuterated (11*S*,12*R*)- and (11*R*,12*S*)-[$^2H_{14}$]-palmitic acids are available from bithienyl by two successive alkylations and desulfurisarion.



(11*S*, 12*R*) - 1

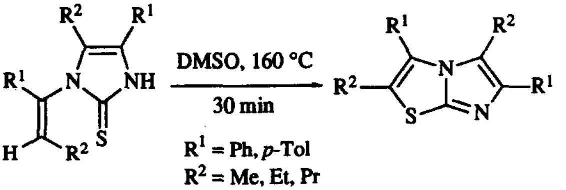
(2*S*, 3*R*) - 11

Tetrahedron, **1993**, *49*, 6619

SYNTHESIS AND NMR CONFIGURATIONAL STUDY OF IMIDAZO[2,1-b]THIAZOLES FROM 1*H*-1,4-DIAZEPINE-7(6*H*)THIONES

José Barluenga*[a], Raquel Pérez Carlón[a], Jesús Joglar[a], Fernando López Ortiz*[a] and Santos Fustero*[b]
[a]Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33012 Oviedo, Spain. [b]Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, 46100 Burjassot (Valencia), Spain

A thermal intramolecular cyclization of 1-vinyl-2,3-dihydro-3*H*-imidazole-2-thiones to imidazo[2,1-b]thiazoles is reported. A heteronuclear correlation study established the configuration of the products.



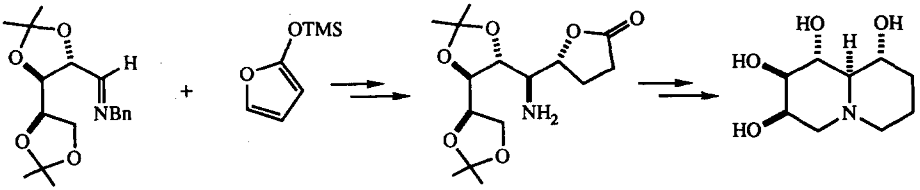
R^1 = Ph, *p*-Tol
R^2 = Me, Et, Pr

Tetrahedron, **1993**, *49*, 6627

EFFICIENT TOTAL SYNTHESES OF (1*R*, 2*R*, 3*R*, 9*R*, 9a*R*)-1,2,3,9-TETRAHYDROXYQUINOLIZIDINE AND ITS ENANTIOMER

Gloria Rassu,* Giovanni Casiraghi,* Luigi Pinna, Pietro Spanu, Fausta Ulgheri, Mara Cornia and Franca Zanardi
Dipartimento di Chimica dell'Università and CNR, Via Vienna 2, I-07100 Sassari, Italy.

The quinolizidine **10** and its enantiomer *ent*-**10** have been synthesized in five steps (>35% overall yields) by starting with arabinose imine derivative (*e.g.* **5**) and 2-(trimethylsiloxy)furan (TMSOF).



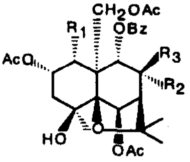
5 TMSOF 7 **10**

Tetrahedron, **1993**, *49*, 6637

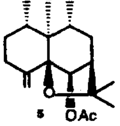
MINOR SESQUITERPENES FROM *MAYTENUS CANARIENSIS* WITH INSECTICIDAL AND ANTIFEEDANT ACTIVITY

Antonio G. González*, Ignacio A. Jiménez, Angel G. Ravelo and Isabel L. Bazzocchi
C.P.N.P."Antonio González", Universidad de La Laguna, Tenerife, Canary Islands, Spain.

One known and four new sesquiterpenes with dihydro-β-agarofuran skeletons were isolated from *Maytenus canariensis* (Celastraceae). Their structures and absolute configurations were determined by spectroscopic and CD studies. Two of the compounds which had a new basic polyhydroxylated 3,13-dideoxy-evoninol skeleton exhibited powerful insecticidal activity against *Spodoptera littoralis* and the others proved antifeedant against the same insect in an election test.



	R_1	R_2	R_3
1	OAc	=O	=O
2	OBz	=O	=O
3	OBz	OBz	H
4	OAc	OBz	H



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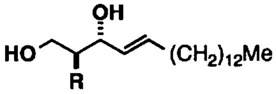
Tetrahedron, **1993**, *49*, 6645

An Enantiospecific Synthesis of D-*erythro*-Sphingosine from D-Tartaric Acid

Peter Somfai* and Roger Olsson, Organic Chemistry 2, Chemical Center
Lund Institute of Technology, P. O. B. 124
S-221 00 Lund, Sweden

An efficient enantiospecific synthesis of D-*erythro*-sphingosine (**1**) via azidospingosine (**2**) is described, the absolute stereochemistry being deived from D-tartaric acid.

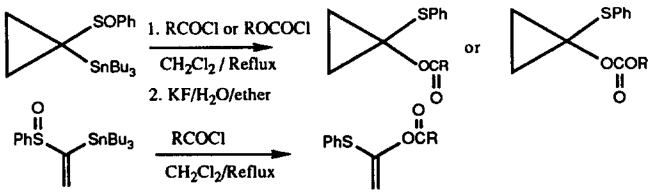


1 $R=NH_2$
2 $R=N_3$

Tetrahedron, **1993**, *49*, 6651

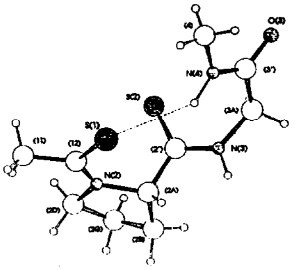
DESTANNYLATIVE PUMMERER-TYPE REARRANGEMENT OF 1-(TRIBUTYLSTANNYL)-1-(PHENYLSULFINYL)- CYCLOPROPANE AND -ETHENE.

M. Pohmakotr*, S. Sithikanchanakul and S. Khosavanna; Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Rd., Bangkok 10400, Thailand.



Tetrahedron, **1993**, *49*, 6661

REVERSE TURN CONFORMATION OF N-THIOACETYL THIOPROLYL GLYCINE N'-METHYLAMIDE IN THE CRYSTAL AND IN SOLUTION.



M. Czugler[#], A. Kálmán[#], M. Kajtár-Peredy[#], E. Kollát[+], J. Kajtár[+], Zs. Majer[+], Ö. Farkas[+], and M. Hollósi[+]
[#] Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O.B. 17, Hungary; [+]Institute of Organic Chemistry, Eötvös University, H-1518 Budapest 112, P.O.B. 32, Hungary

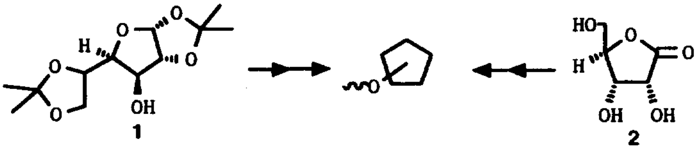
Turn conformation of N-thioacetyl thioprolyl glycine N'-methylamide in the crystal. The torsion angles ($\Phi_2 = -73.2°$, $\Psi_2 = 151.9°$, $\Phi_3 = 83.5°$, $\Psi_3 = 5.5°$) are close to those of a type II (oxo)amide turn.

Tetrahedron, 1993, *49*, 6669

STRATEGIES AND TACTICS FOR FREE RADICAL CARBOCYCLIZATION: SYNTHESIS OF POLYFUNCTIONALIZED CYCLOPENTANOID MOLECULES FROM CARBOHYDRATES

José Marco-Contelles*, Pilar Ruiz, Luis Martínez and Angeles Martínez-Grau.

Instituto de Química Orgánica General (CSIC); Juan de la Cierva, 3. 28006-Madrid.



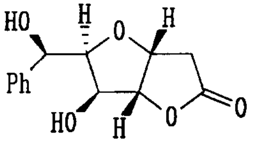
From diacetone glucose 1 or D-ribonolactone 2 synthetic strategies are described for the preparation of polyfunctionalized cyclopentanes.

Tetrahedron, 1993, *49*, 6695

THE TOTAL SYNTHESIS OF GONIOFUFURONE

Patrick J. Murphy* and Shelagh T. Dennison.
Department of Chemistry, University of Wales, Bangor, Gwynedd, UK, LL57 2UW.

The total synthesis of natural (+)-Goniofufurone 1 and related compounds from D-glucose is reported utilising as the key step a non-classical Wittig reaction.



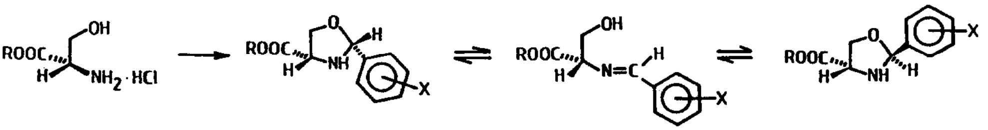
1

Tetrahedron, 1993, *49*, 6701

RING-CHAIN TAUTOMERISM OF OXAZOLIDINES DERIVED FROM SERINE ESTERS

Ferenc Fülöp[a,b,*] and Kalevi Pihlaja[a]

[a]Department of Chemistry, University of Turku, SF-20500 Turku, Finland;
[b]Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6701 Szeged, POB 121, Hungary



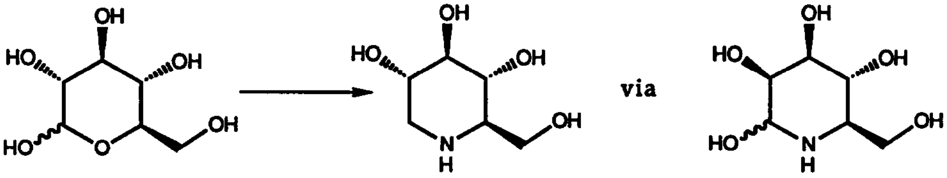
Ring-chain tautomeric mixtures were obtained from serine methyl or ethyl ester with aromatic aldehydes.

Tetrahedron, **1993**, *49*, 6707

THE BIOSYNTHESIS OF 1-DEOXYNOJIRIMYCIN IN *BACILLUS SUBTILIS VAR NIGER*

Hardick, D. J., Hutchinson, D. W.
Department of Chemistry, University of Warwick, Coventry, CV4 7AL.

Glucose is the precursor to the anti-HIV alkaloid, 1-deoxynojirimycin, in *Bacillus subtilis var niger*.



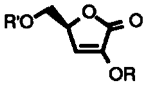
1-deoxynojirimycin

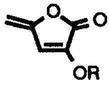
Tetrahedron, **1993**, *49*, 6717

SYNTHETIC APPROACHES TO EITHER HOMOCHIRAL OR ACHIRAL DERIVATIVES OF 3-HYDROXY-2(5*H*)-FURANONE (ISOTETRONIC ACID)

Joaquim Bigorra, Josep Font, Cristina Ochoa de Echagüen, and Rosa M. Ortuño*
Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain.

Several title compounds were synthesized from D-ribonolactone as a chiral precursor or from 2,4-dioxopentanoic acid as a suitable achiral precursor. Base-induced elimination and subsequent acid promoted ring-size contraction has proved to be an efficient protocol to prepare isotetronic acids from 2-*O*-alkyl-3,4-*O*-benzylidene-*D*-ribono-1,5-lactone derivatives.



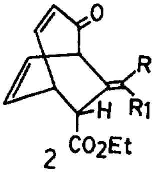


Tetrahedron, **1993**, *49*, 6729

PERI-, REGIO- AND STEREOSELECTIVITIES IN THERMAL ADDITION OF TROPONE TO ALLENIC ESTERS

M.P.S. Ishar and R.P. Gandhi*, Department of Chemistry, Indian Institute of Technology-Delhi, Hauz Khas, New Delhi-110016.

Tropone reacts with allenic esters, $RR_1C=C=CHCO_2Et$, to furnish major cycloadducts 2-6 and minor products 7,8.



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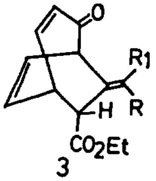

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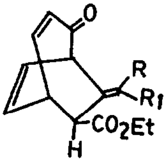

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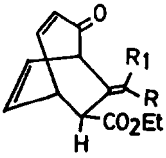

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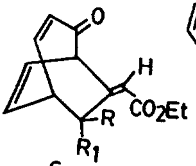

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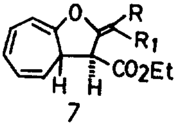

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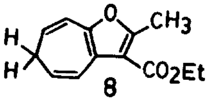

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