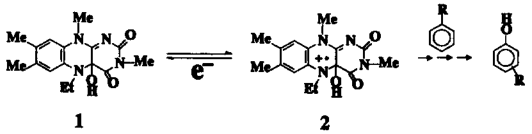
GRAPHICAL ABSTRACTS

AROMATIC HYDROXYLATIONS BY FLAVINS: EVIDENCE ON DIRECT ATTACK OF PHENYLALANINE BY FLAVIN RADICAL SPECIES.

Tetrahedron, **1994**, *50*, 5287

Humphrey I. X. Mager[a] and Shiao-Chun Tu[ab]*
Contribution from the [a]Department of Biochemical and Biophysical Sciences
and the [b]Department of Chemistry, University of Houston, Houston, Texas 77204-5934, U.S.A.

The one-electron oxidation of the flavin pseudobase 1 to the radical 2 provides a novel system for aromatic hydroxylation without involving dihydroflavin hydroperoxide as a starting compound or free $HO^{\bullet}$ radical as the primary attacking species.



Moenomycin A: Reactions at the Lipid Part. New Structure-Activity Relations

Tetrahedron, **1994**, *50*, 5299

S. Marzian, M. Happel, U.-Wagner
D. Müller, P. Welzel*[a]
H.-W. Fehlhaber, A. Stärk, H.-J. Schütz,
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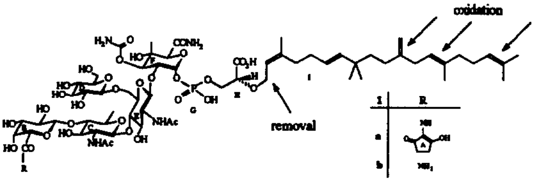
Université Paris-Sud, Orsay (France)



Methods for the removal and the oxidation of the lipid moiety of the antibiotic moenomycin A have been studied. Combined with biochemical studies, the results demonstrate that antibiotic activity is closely related with the integrity of the lipid unit.

ACTIVATION OF N,N-BIS(ALKOXYCARBONYL) AMINO ACIDS. SYNTHESIS OF N-ALKOXYCARBONYL AMINO ACID N-CARBOXYANHYDRIDES AND N,N-DIALKOXYCARBONYL AMINO ACID FLUORIDES, AND THE BEHAVIOR OF THESE AMINO ACID DERIVATIVES

Tetrahedron, **1994**, *50*, 5309

Jaroslav Savrda,[a] Lyubov Chertanova[b] and Michel Wakselman[a]
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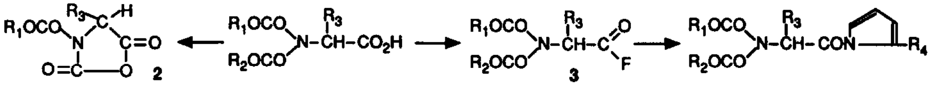
[b]Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France

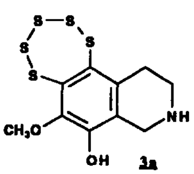


Formation and aminolysis (Young's tests) of the title compounds 2 and 3 and the use of the fluorides (3) for the acylation of pyrrole derivatives.

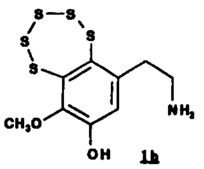
Lissoclinotoxins: Antibiotic Polysulfur Derivatives From The Tunicate *L. perforatum*. Revised Structure of Lissoclinotoxin A

Tetrahedron, **1994**, *50*, 5323

M. Litaudon, F. Trigalo, M.-T. Martin, F. Frappier and M. Guyot*.
Laboratoire de Chimie, URA 401 C.N.R.S., M.N.H.N., 63 rue Buffon, 75005 Paris, France.



3a



1b

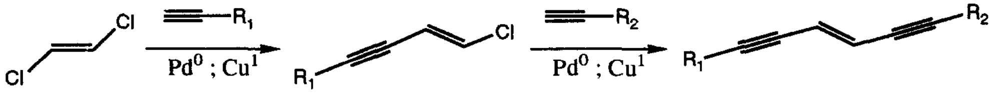
Lissoclinotoxin B 3a a new pentathiepin derivative, was isolated from the tunicate *Lissoclinum perforatum*. Structure elucidation of this compound is described, together with a revised structure 1b for lissoclinotoxin A. A synthesis of tetraacetyl isolissoclinotoxin A is proposed.

Tetrahedron, **1994**, *50*, 5335

PALLADIUM-CATALYZED REACTION OF (E) AND (Z) DICHLOROETHENES WITH 1-ALKYNES. AN EFFICIENT STEREOSPECIFIC SYNTHESIS OF (E) AND (Z)-ENEDIYNES.

Denis Chemin and Gérard Linstrumelle

Ecole Normale Supérieure, Laboratoire de chimie, 24 rue Lhomond, 75231 Paris Cedex 05-France.

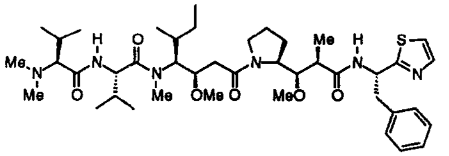


Tetrahedron, **1994**, *50*, 5345

Synthèse de la Dolastatine 10 et de la [R-Doe]-Dolastatine 10.

Florence Roux, Isabelle Maugras, Joël Poncet, Gilles Niel et Patrick Jouin.
Laboratoire des Mécanismes Moléculaires des Communications Cellulaires, UPR 9023 CNRS, Centre CNRS-INSERM, rue de la Cardonille 34094, Montpellier cedex 5, France.

A stepwise synthesis of Dolastatin 10 and its [Doe]-epimer is described. Both residues dolaisoleuine and dolaproine were obtained by stereoselective five-step procedures.



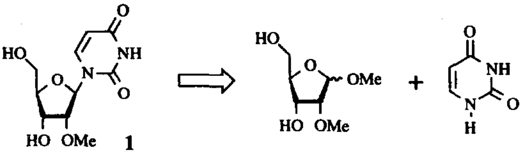
Tetrahedron, **1994**, *50*, 5361

A Convergent Synthesis of 2'-O-Methyl Uridine

Gilles Parmentier, Gaby Schmitt, Frédéric Dollé & Bang Luu*.

Laboratoire de Chimie Organique des Substances Naturelles, associé au CNRS,
Université Louis Pasteur, Centre de Neurochimie, 5 rue Blaise Pascal, 67084 Strasbourg, France.

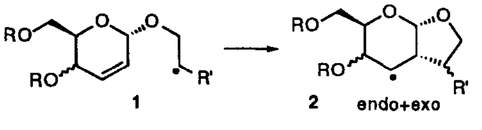
A convergent synthesis of 2'-O-methyl uridine (1) is described. The key steps in our synthesis are : (1) a facile obtention of the 2'-O-methyl sugar synthon using totally selective and efficient methylation conditions; (2) a stereoselective high-yield condensation with an uracil derivative, yielding the desired β-form.



Tetrahedron, **1994**, *50*, 5369

Stereocontrol in Radical Cyclizations on Sugar Templates

Catherine Lesueur[a], Robert Nouguier[a], Michèle Paula Bertrand[a], Pascale Hoffmann[b], Alain De Mesmaeker[b]
a : LCMO - URA 1412 - Boite 562 - Faculté des Sciences Saint -Jérôme, Av. Normandie Niemen - 13397 Marseille Cedex 20 - France
b : Central Research Laboratories, Ciba-Geigy Ltd., CH-4002 Basel, Switzerland



The endo/exo ratio of fused furanopyrans (2) obtained *via* the cyclisation of prochiral radicals (1) is dicussed on the basis of conformational preference in the transition state. The intermediate radical (1) is generated either by the reduction of the corresponding halide (R'=alkyl or Ph) or by the addition of sulfonyl radical to the appropriate allyl ether (R'= CH_2Ts).

Tetrahedron, **1994**, *50*, 5381

Association Constants of Alkaline Complexes of Macrolactones and Crown Ethers Derived from Biphenyl. Influence of the Position and Characteristics of Biphenyl Substituents

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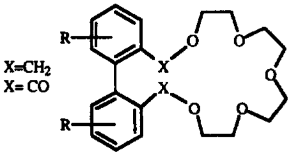
Biphenyl crown ethers and macrolactones have been prepared and their ability to complex alkaline cations tested. The influence of the position and electronic characteristics of substituents in the biphenyl moiety have been established. Macrolactones present a smaller hole and complex Na^+ better than K^+.



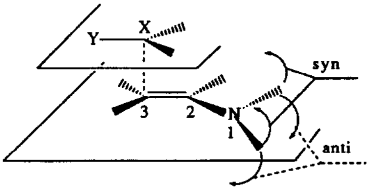
3a $R=4\text{-}NO_2$
3b $R=6\text{-}OCH_3$
3c $R=6\text{-}OH$

Tetrahedron, **1994**, *50*, 5387

ON THE NATURE OF THE ELECTRONIC INTERACTION BETWEEN CONJUGATED NUCLEOPHILES AND ELECTROPHILES

Alain SEVIN and Claude GIESSNER-PRETTRE
Laboratoire de Chimie Organique Théorique, Université Pierre et Marie Curie, Paris, France.

Morokuma's decomposition of interaction energy into 4 terms ES, PL, EX, CT is provided for analyzing the complexes formed between 2 conjugated nucleophiles and 8 model electrophiles. No decisive argument in favor of the HSAB theory emerges.



Tetrahedron, **1994**, *50*, 5401

SYNTHESE DE SELS D'α-AMINOACIDES SULFINIQUES SUBSTITUES A L'AZOTE PAR UN GROUPE METHANE- OU p-TOLUENE-SULFONYLE

Michel Mulliez et Carole Nandy - E.R. du C.N.R.S. n° 76, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse Cédex, France

N methane- or p-toluene-sulfonyl α-aminosulfinic acids salts 1 (table) are synthetized (Scheme 2, path a), in a Mannich like reaction (Scheme 4), by coupling α hydroxysulfinates 5 with methane- or p toluene-sulfonamides 6 in an aqueous basic medium. The isolated products are fairly stable.

$$\underset{\mathbf{6}}{R'SO_2NH_2} + \underset{\mathbf{5}}{HOCHRSO_2Na} \xrightarrow[\text{2) Dicyclohexylammonium citrate}]{} \underset{\mathbf{1}}{R'SO_2NHCHRSO_2^-\ H_2N^+(C_6H_{11})_2}$$

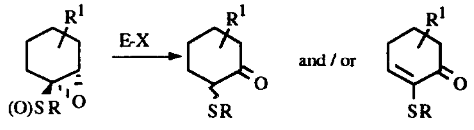
1) H_2O, NaOH cat.
2) Dicyclohexylammonium citrate

$R = H, Me, Ph, CF_3$
$R' = Me, pMeC_6H_4$

Tetrahedron, **1994**, *50*, 5413

Halides-based Electrophiles Mediated Epoxide Ring-opening Reactions of α,β-Epoxy-Sulfoxides in C_6-series : Deoxygenation versus Dehydration and an Overall 1,2-Keto Transposition.

Daniel Barillier, Jocelyne Levillain, and Michel Vazeux*
Laboratoire de Chimie des Composés Thioorganiques, URA CNRS 480, ISMRA,
Université de Caen, 6, bd du Maréchal Juin - 14050 Caen Cedex., France



An efficient and selective method for either deoxygenation or dehydration of six-membered ring α,β-epoxysulfoxides with halides-based electrophiles is described.

Tetrahedron, **1994**, *50*, 5425

REACTION OF NORMAL AND PSEUDO 2-FORMYLBENZENESULFONYL CHLORIDES WITH AMINES: EXPERIMENTAL AND THEORETICAL STUDIES ON THE STRUCTURE OF 2-FORMYLBENZENESULFONAMIDES IN SOLID, SOLUTION AND GAS PHASES.

K.G. Rajeev, M.S. Shashidhar*, K. Pius and M.V. Bhatt
Bioorganic Chemistry Unit, Organic Chemistry Division
(Synthesis), National Chemical Laboratory
Pune 411008, India.

2-Formylbenzenesulfonamides are cyclic in the solid state, exist as a mixture of open and cyclic forms in solution and are open in the gas phase.

X = O, NR; R = Alkyl/Aryl

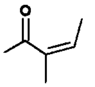
Tetrahedron, **1994**, *50*, 5439

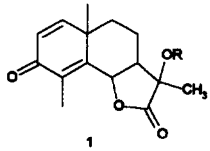
STUDIES ON THE STEREOSTRUCTURE OF EUDESMANOLIDES FROM UMBELLIFERAE: SYNTHESIS OF 11B-ANGELOYLOXY-A-SANTONIN

Francisco A. Macías, José María Aguilar, José María G. Molinillo, Guillermo M. Massanet* and F. R. Fronczek[a]; Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Cádiz.Apdo. 40, 11510 Puerto Real, Cádiz, Spain..[a]Department of Chemistry. Louisiana State University. Baton Rouge. Louisiana, 70803, U.S.A.

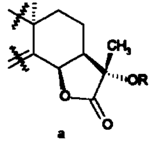
Decipienin A (**1**) having the stereostructure **b** (11β-angeloyloxy-α-santonin) have been synthesized following three different synthetic routes.

R = Ang =

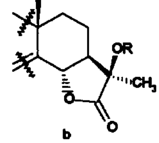




1



a

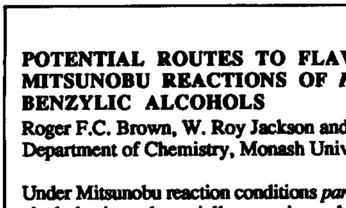


b

Tetrahedron, **1994**, *50*, 5451

OXIRANE -OPENING REACTIONS OF SOME 6,19-OXYGENATED 4α,18-EPOXY-*NEO*-CLERODANES ISOLATED FROM *TEUCRIUM*. BIOGENESIS AND ANTIFEEDANT ACTIVITY OF THEIR DERIVATIVES

B. Rodríguez[a], M.C. de la Torre[a], A. Perales[b], P.Y. Malakov[c], G.Y. Papanov[c], M.S.J. Simmonds[d] and W.M. Blaney[e]
Institutos de Química Orgánica[a] and "Rocasolano"[b], CSIC, 28006 Madrid, Spain; [c]Department of Organic Chemistry, University, 4000 Plovdiv, Bulgaria; [d]Jodrell Laboratory, Royal Botanic Gardens, Kew, U.K.; [e] Department of Biology, Birkbeck College, London, U.K.



4α-Hydroxy-18-chloro derivatives

4α-Hydroxy-18-chloro or methoxy derivatives and 18-acetoxy- or chloro- 4α,6α,19-orthoacetates

4α-Hydroxy-6β,18-epoxy or 18-methoxy and 18-acetoxy-3,4-didehydro derivatives, and 19-acetoxy-4β,6β,18-orthoacetates

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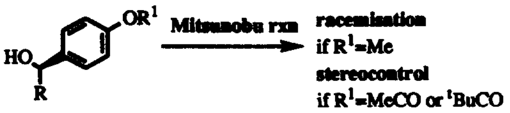
Tetrahedron, **1994**, *50*, 5469

POTENTIAL ROUTES TO FLAVAN-3-OLS, PART 2: THE MITSUNOBU REACTIONS OF *PARA*-OXYGENATED BENZYLIC ALCOHOLS

Roger F.C. Brown, W. Roy Jackson and Tom D. McCarthy*
Department of Chemistry, Monash University, Wellington Road, Clayton, 3168, Victoria, Australia.

Under Mitsunobu reaction conditions *para*-methoxy benzylic alcohols give substantially racemic products, whereas *para*-pivaloyloxy and *para*-acetoxy benzylic alcohols give products resulting from inversion.

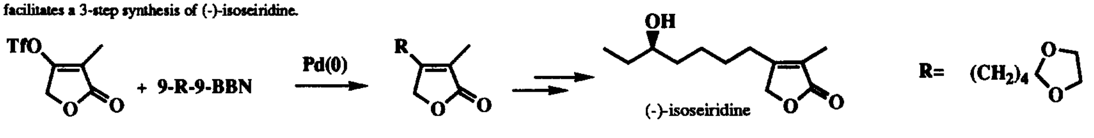


Tetrahedron, **1994**, *50*, 5489

PALLADIUM CATALYSED CROSS-COUPLING OF VINYL TRIFLATES WITH 9-ALKYL-9-BORABICYCLO[3.3.1]NONANES. TOTAL SYNTHESIS OF (-)-ISOSEIRIDINE

Ronald Grigg,*[a] Peter Kennewell,[b] Vladimir Savic[a]
a) School of Chemistry, Leeds University, Leeds LS2 9JT , b) Roussel Scientific Institute, Kingfisher Drive, Swindon SN3 5BZ

Pd (0) cross-coupling of butenolide-3-triflates with 9-alkyl-9-borabicyclo[3.3.1]nonanes occurs in moderate to good yield. This coupling facilitates a 3-step synthesis of (-)-isoseiridine.

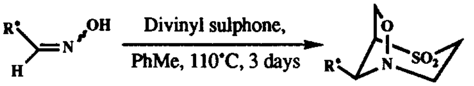


Tetrahedron, **1994**, *50*, 5495

HOMOCHIRAL CYCLOADDUCTS DERIVED FROM SUGAR ALDOXIMES *VIA* NITRONE INTERMEDIATES

Martyn Frederickson,[a] Ronald Grigg,*[a] James Redpath,[b] and Mark Thornton-Pett[a]
a. School of Chemistry, The University of Leeds, Leeds, U.K., LS2 9JT.
b. Organon Laboratories Ltd., Newhouse, Lanarkshire, U.K., ML1 5SH.

Aldoximes derived from D-galactose and D-ribose react regiospecifically with one mole of divinyl sulphone in toluene at 110°C to afford good yields of homochiral cycloadducts with high diastereoselectivity.



R* = D-pyranosyl or D-furanosyl residue

Yield : 52-86%
d.e. : 95-100%

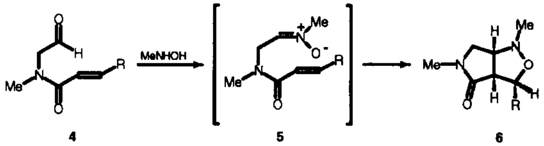
Tetrahedron, **1994**, *50*, 5503

STEREOSELECTIVE SYNTHESIS OF FUSED γ-LACTAMS BY INTRAMOLECULAR NITRONE CYCLOADDITION

Ugo Chiacchio,[a*] Giuseppe Buemi,[a] Francesco Casuscelli,[b] Antonio Procopio,[c] Antonio Rescifina,[a] and Roberto Romeo.[b]

[a]Dipartimento di Scienze Chimiche, Università di Catania; [b]Dipartimento Farmaco-Chimico, Università di Messina; [c]Dipartimento di Chimica, Università di Arcavacata di Rende

A series of nitrones **5** joined by amides to olefines were prepared *in situ* from the related aldehydes **4** with *N*-methyl hydroxylamine. The nitrones added intramolecularly to the olefin, and the cycloadditions gave fused γ-lactams **6** stereoselectively.



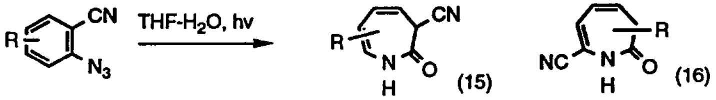
4 **5** **6**

Tetrahedron, **1994**, *50*, 5515

3H-AZEPINES AND RELATED SYSTEMS. PART 5. PHOTO-INDUCED RING-EXPANSIONS OF o-AZIDO-BENZONITRILES TO 3-CYANO- AND 7-CYANO-3H-AZEPIN-2(1H)-ONES.

Kaddour Lamara, Alan D. Redhouse, Robert K. Smalley, and J. Robin Thompson, Department of Chemistry and Applied Chemistry, University of Salford, Salford, M54WT, U.K.

Photolysis of o-azidobenzonitriles in aqueous -THF yields mixtures of the expected 3-cyano-3H-azepin-2(1H)-ones (15) and the unexpected isomeric 7-cyano-3H-azepin-2(1H)-ones (16). X-ray data are provided.

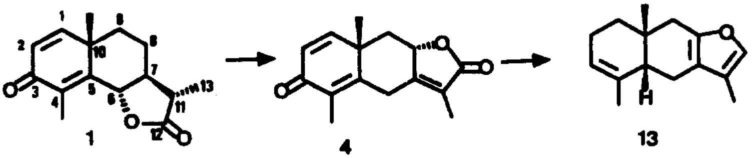


Tetrahedron, **1994**, *50*, 5527

SYNTHETIC STUDIES TOWARD NATURAL FURANOSESQUITERPENOIDS FROM SANTONIN. SYNTHESIS OF (+)-1,2-DIHYDROTUBIPOFURAN

Luz Cardona, Begoña García, José R. Pedro* and Desamparados Ruiz
Departament de Química Orgànica, Facultat de Química, Universitat de València, 46100-Burjassot (València) Spain

Santonin (1) was converted into (+)-1,2-dihydrotubipofuran (13) via a synthetic pathway involving a very easy preparation of 7,11-ene-8,12-olide (4) and 8,12-furan moieties and A-ring elaboration of the eudesmane framework.

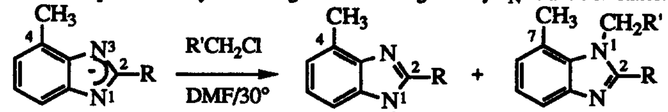


Tetrahedron, **1994**, *50*, 5535

AMBIDENT HETEROCYCLIC REACTIVITY: ALKYLATION OF 2-SUBSTITUTED-4-METHYLBENZIMIDAZOLES

M.Rezaul Haque and Malcolm Rasmussen* Chemistry Department, Australian National University, Canberra, ACT 0200, Australia.

*N*1/*N*3-alkylation regioselectivities of 2-substituted-4-methylbenzimidazole anions are under *steric approach control*; steric effects are critically dependent on the partial *N*-alkyl bond lengths in variable geometry S_N2 transition states.



R' = $PhCH_2O$, Ph, Pr, *t*-BuOCO, PhCO

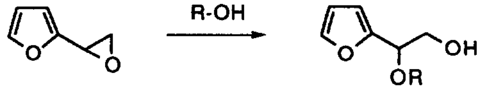
a) R = H
b) R = CH_3
c) R = OCH_2CH_3
d) R = Cl
e) R = NH_2
f) R = OH

Tetrahedron, **1994**, *50*, 5555

THE UNCATALYZED ALCOHOLYSIS OF FURYL-2-OXIRANE. A MECHANISTIC STUDY BASED ON KINETIC DATA.

Benito Alcaide, Cristina Biurrun, and Joaquín Plumet.*
Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense, 28040-Madrid, Spain

Kinetic data for the uncatalyzed methanolysis of furyl-2-oxirane in solvolytic conditions indicates that the reaction occurs by a solvent-assisted S_N process through a solvent-separated ion pair intermediate.



Tetrahedron, **1994**, *50*, 5561

THEORETICAL AND EXPERIMENTAL STUDY OF THE REGIOSELECTIVITY OF THE REACTION OF DIAZOMETHANE WITH ALLENE.

Augusto Rastelli,*[a] Marisa Bagatti,[a] Remo Gandolfi*[b]
a) Dip. di Chimica, Universita' di Modena, Modena-Italy; b) Dip. di Chimica Organica, Universita' di Pavia, Pavia-Italy

Ab-initio calculations (e.g., MP4SDTQ//6-31G*//HF/6-31G* and MP4SDTQ//6-31G*//MCSCF/3-21G) qualitatively reproduce the revised regiochemical ratio of the reaction between diazomethane and allene.