GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 4937

Conformational Analysis of 2-Halotetrahydrothiopyran *S*-Oxides. Diminution of The Anomeric Effect in S(O)-C-X Compared to S-C-X segments.

Eusebio Juaristi* and Mario Ordoñez, Depto. Química, CINVESTAV-IPN, Apdo. Postal 14-740, 07000 México D.F., México.

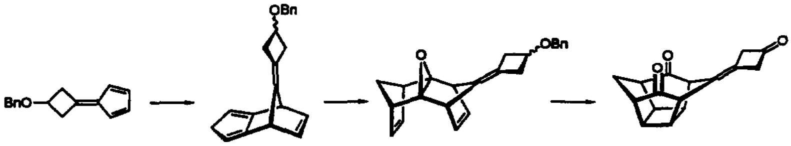
The conformational equilibria of several 2-halothiane sulfoxides support the existence of $n_{S(O)} \rightarrow \sigma^*_{S-X}$ stereoelectronic interactions, which are, nevertheless, less important than $n_S \rightarrow \sigma^*_{C-X}$ interactions in the corresponding thioether analogues.

Tetrahedron, **1994**, *50*, 4949

Development of a Strategy for the Synthesis of the Spherical Hydrocarbon *p*-[4².5⁸]Decahedrane

Chien-Chang Shen and Leo A. Paquette*
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Fulvene **12** has been transformed via **14** into diene epoxide **17**. The latter intermediate undergoes photochemical [2+2] cycloaddition and subsequent oxidative cleavage to provide ultimately the triketone **20**.

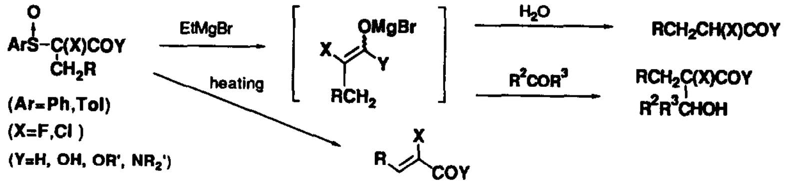


12 **14** **17** **20**

Tetrahedron, **1994**, *50*, 4957

Ligand Exchange Reaction of Sulfoxides in Organic Synthesis: A Novel Method for Generation of Magnesium Enolates and Its Application to Synthesis of α-Halocarboxylic Acid Derivatives and α-Haloaldehydes

Tsuyoshi Satoh, Yasushi Kitoh, Ken-ichi Onda, Koji Takano, and Koji Yamakawa*
Faculty of Pharmaceutical Sciences, Science University of Tokyo;
Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan

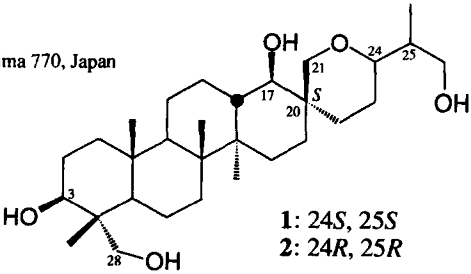


Tetrahedron, **1994**, *50*, 4973

Hosenkosides A, B, C, D, and E, Novel Baccharane Glycosides from the Seeds of *Impatiens balsamina*

Shoji N., Umeyama A., Saito N., Yoshikawa K., Kann Y. and Arihara S.
Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Tokushima 770, Japan

Hosenkol A, the genin of hosenkosides A and D, and hosenkol B, the genin of hosenkosides B and E are formulated as **1** and **2** respectively. Hosenkol C, the genin of hosenkoside C is determed as (3*S*,4*R*,17*R*,20*S*,24*Z*)-3,17,21,26,28-pentahydroxybacchar-24-ene, on the basis of spectral data.



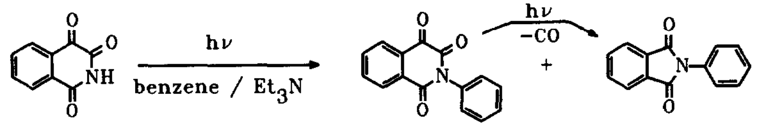
1: 24*S*, 25*S*
2: 24*R*, 25*R*

Tetrahedron, **1994**, *50*, 4987

ON THE PHOTOCHEMICAL REACTIVITY OF PHTHALONIMIDE.

Rafael Suau* and Ezequiel P. de Inestrosa Villatoro.
Departamento de Quimica Organica. Facultad de Ciencias.
Universidad de Málaga, 29071 Malaga, Spain.

Several processes are described from the irradiation of phthalonimide in aromatic solvents: photoreduction, oxetane formation and N-arylation.

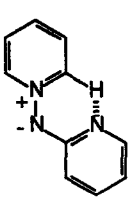


Tetrahedron, **1994**, *50*, 4995

AZINIUM-N-(2′-AZINYL)AMINIDES: SYNTHESIS, STRUCTURE AND REACTIVITY

Rosa Carceller[a], Jose L. García-Navío[a], María L. Izquierdo[a], Julio Alvarez-Builla[a]*, Mariano Fajardo[b], Pilar Gómez-Sal[b] and Federico Gago[c].
Departamentos de Química Orgánica[a], Química Inorgánica[b], Farmacología[c], Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, España.

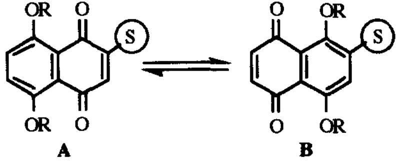
Several Azinium-N-(2′-azinyl)aminides are reported. The structure of pyridinium-N-(2′-pyridyl)aminide has been studied, both in solution and crystalline state, and results have been compared. In non-polar solvents, the aminides present a planar conformation stabilized by an intramolecular hydrogen bond. The reactivity toward electrophiles confirms the structural data, producing either N- or C- substitutions under mild conditions.



Tetrahedron, **1994**, *50*, 5013

TAUTOMERIC EQUILIBRIUM OF NAPHTHAZARIN THIODERIVATIVES.

M. Carmen Carreño, J. Luis García Ruano and Antonio Urbano. Departamento de Química (C-I), Universidad Autónoma. 28049 Madrid. Spain



Ⓢ = STol, SOTol, SO_2Tol

R = H, Me

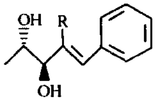
The synthesis of these hydroxy and methoxy naphthoquinones is reported. Their ^{13}C-nmr spectra allows the study of the tautomeric equilibrium.

Tetrahedron, **1994**, *50*, 5021

ON THE ASYMMETRIC DIHYDROXYLATION OF (2S,3R) 5-PHENYLPENT-4-EN-2,3-DIOL DERIVATIVES

Giovanni Fronza, Claudio Fuganti, Piero Grasselli, Andrea Mele
Dipartimento di Chimica del Politecnico, Centro CNR per lo Studio delle Sostanze Organiche Naturali, 20133 Milano, Italy

Sharpless OsO_4 asymmetric dihydroxylation of protected forms of the unsaturated (2S,3R) diols **2** affords a mixture of diastereoisomers ratios depending upon the nature of the ligand, the hydroxyl group protection and the double bond substitution.



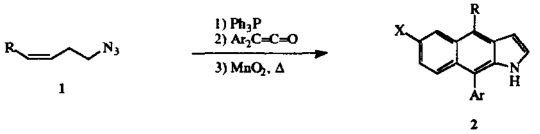
2a R=H
2b R=Me

Tetrahedron, **1994**, *50*, 5027

A STRAIGHTFORWARD PREPARATION OF BENZ[*f*]INDOLES BY AN INTRAMOLECULAR DIELS-ALDER CYCLOADDITION OF UNSATURATED KETENIMINES

Pedro Molina, Carmen López-Leonardo and Julián Alcántara
Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30071, Murcia, Spain.

Azides 1 by sequential treatment with triphenylphosphine, diaryl ketenes and further heating in the presence of manganese dioxide led to the tricyclic compounds 2

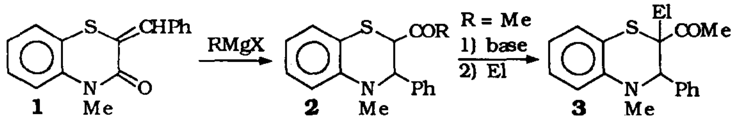


Tetrahedron, **1994**, *50*, 5037

STEREOSELECTIVE SYNTHESIS OF 2-ACYL-3,4-DIHYDRO-2H-1,4-BENZOTHIAZINES.

S. Florio,* E. Epifani, L. Ronzini, G. Gasparri Fava, G.Pelosi and V. Lucchini
Dip. Farmaco-Chimico, Univ. Bari, Via Orabona 4, 70125 Bari, Italy. Dip. Biologia, Univ. Lecce, Italy. Centro Studio Strutturistica Diffrattometrica , CNR, Univ. Parma, Italy. Dip. Scienze Ambientali, Univ. Venezia, Italy.

The title benzothiazines have been prepared by reacting the benzylidene 1 with Grignard reagents and via metallation-alkylation of the 2-acetyl derivative 2.

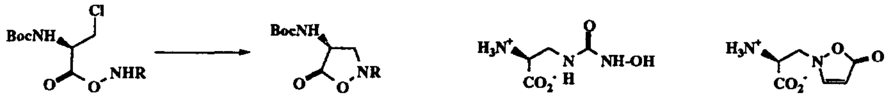


Tetrahedron, **1994**, *50*, 5049

Synthesis of Chiral Isoxazolidin-5-ones and their Applications to the Synthesis of β-Amino-Alanines and β-(N-Hydroxyamino)-Alanines

Jack E. Baldwin*, Robert M. Adlington, Lisa C. Mellor
The Dyson Perrins Laboratory and Oxford Centre for Molecular Sciences, South Parks Road, Oxford OX1 3QY

Abstract: A new route to isoxazolidin-5-ones (1) and (2) is described. Amino acids (3) and (4) were obtained *via* hydrogenation of (2) and hydrolysis of (1) respectively.



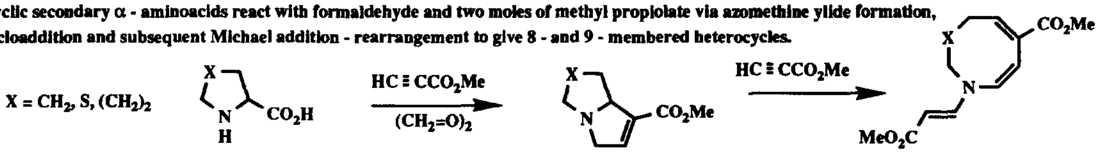
(1) R=Boc, (2) R=Z (3) (4)

Tetrahedron, **1994**, *50*, 5067

X = Y - ZH SYSTEMS AS POTENTIAL 1,3 - DIPOLES. PART 42[1]. DECARBOXYLATIVE THREE CARBON RING EXPANSION OF CYCLIC α - AMINO ACIDS VIA AZOMETHINE YLIDE FORMATION

Harriet Ardill[a], Ronald Grigg[*, b], John F. Malone[a], Visuvanathar Sridharan[b], and W. Anthony Thomas[c] a. Department of Chemistry, Queens University, Belfast BT9 5AG, N. Ireland. b. School of Chemistry, Leeds University, LS2 9JT. c. Roche Products, Welwyn Garden City AL7 3AY.

Cyclic secondary α - aminoacids react with formaldehyde and two moles of methyl propiolate via azomethine ylide formation, cycloaddition and subsequent Michael addition - rearrangement to give 8 - and 9 - membered heterocycles.

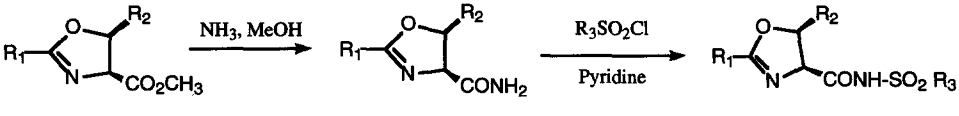


Tetrahedron, **1994**, *50*, 5083

UNUSUAL REACTIVITY OF 4-CARBOXYAMIDO-2-OXAZOLINE SYSTEMS: NEW SYNTHESIS OF OPTICALLY ACTIVE *N*-SULPHONYL DERIVATIVES.

S. Cossu,* G. Giacomelli, S. Conti, and M. Falorni, Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

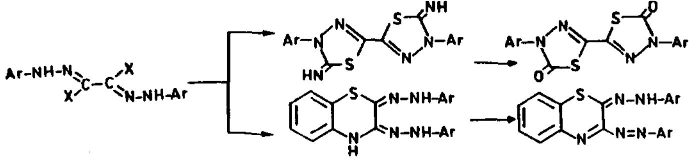
An improved synthesis of *N*-alkylsulphonyl- and *N*-arylsulphonyl 2-alkyl-4-carboxyamido-2-oxazoline is presented.



Tetrahedron, **1994**, *50*, 5091

ONE-STEP SYNTHESIS OF NOVEL 2,2'-BI(4,5-DIHYDRO-1,3,4-THIADIAZOLE) AND 2,3-DISUBSTITUTED 1,4-BENZOTHIAZINE DERIVATIVES

Ahmad M. Farag*, Ahmad S. Shawali, Mohamad S.Algharib and Kamal M. Dawood
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

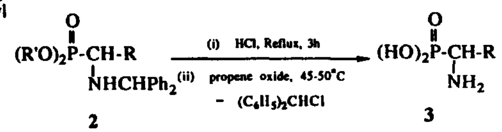


Tetrahedron, **1994**, *50*, 5099

THE SYNTHESIS OF 1-AMINOBENZYLPHOSPHONIC ACIDS FROM BENZYLIDENEDIPHENYLMETHYLAMINES, FOR USE AS STRUCTURAL UNITS IN ANTITHROMBOTIC TRIPEPTIDES

Donovan Green*, Geeta Patel, Said Elgendy, Jehan A. Baban, Goran Claeson,Vijay V. Kakkar, and John Deadman
Thrombosis Research Institute, Emmanuel Kaye Building, 1B, Manresa Road, Chelsea, London SW3 6LR, U.K.

Acid hydrolyses of *O,O*-dimethyl or *O,O*-diethyl 1-(diphenylmethylamino)benzylphosphonate intermediates **2**, generates 1-aminobenzylphosphonic acids **3**, in good yield.



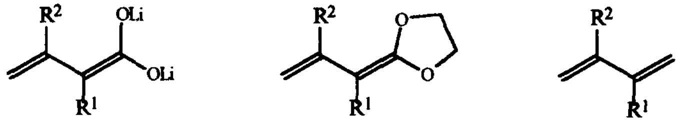
$$\underset{\mathbf{2}}{(R'O)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{NHCHPh_2}{CH}\text{-}R} \xrightarrow[\text{(ii) propene oxide, 45-50°C} \; - \; (C_6H_5)_2CHCl]{\text{(i) HCl, Reflux, 3h}} \underset{\mathbf{3}}{(HO)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{NH_2}{CH}\text{-}R}$$

Tetrahedron, **1994**, *50*, 5109

^{13}C NMR STUDIES OF DIANIONS OF UNSATURATED CARBOXYLIC ACIDS

María J. Aurell, Salvador Gil, Ramon Mestres*, Margarita Parra and Amparo Tortajada.
Departament de Química Orgànica, Universitat de València, Burjassot, València, Spain.

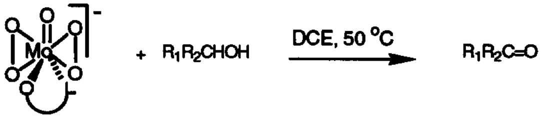
^{13}C NMR Spectra of the dianions resulting from double deprotonation of unsaturated carboxylic acids are examined. Electron densities at C-1 to C-4 are calculated by comparison of dianion chemical shifts with those of the corresponding ethylene vinylketene acetals, dienes, and other neutral models.



Tetrahedron, **1994**, *50*, 5119

MECHANISM OF ALCOHOL OXIDATIONS BY ANIONIC PEROXOMOLYBDENUM COMPLEXES

Sandro Campestrini and Fulvio Di Furia*
Centro CNR di Studio sui Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, Universita' di Padova, Via Marzolo 1, 35131 Padova (Italia).

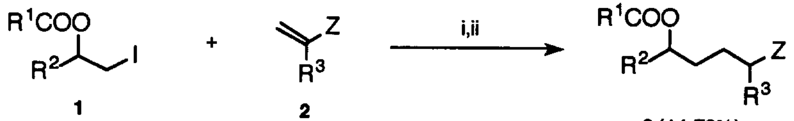


A kinetic study is reported which allows to propose a common general scheme for the oxidation of various alcohols by different anionic peroxomolybdenum complexes.

Tetrahedron, **1994**, *50*, 5131

β-FUNCTIONALISED RADICALS IN ORGANIC SYNTHESIS: 2-ACYLOXYALKYL RADICALS FROM 2-ACYLOXYALKYL IODIDES BY THE TIN ROUTE

F. Foubelo, F. Lloret and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain



1 2 3 (14-72%)

[R^1=Me, Ph; R^2=H, Me, Ph; R^3=H, Me; Z=CO_2Me, CN. *Reagents*: i, $Bu^n{}_3SnCl$, $NaBH_4$, AIBN cat., EtOH; ii, NaF, H_2O]

Tetrahedron, **1994**, *50*, 5139

AROMATIC IODINATION WITH THE I_2-HgX_2 COMBINATION

A. Bachki, F. Foubelo and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

$$\underset{\mathbf{1a\text{-}t}}{ArH} + I_2 + \underset{\mathbf{2a\text{-}c}}{HgX_2} \xrightarrow{i} \underset{\mathbf{3a\text{-}t}\ (34\text{-}98\%)}{ArI} + HX + HgXI$$

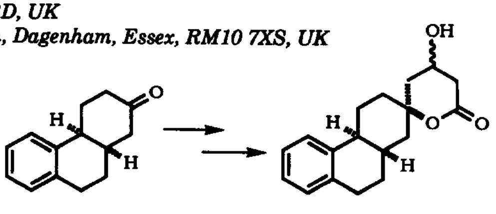
[X=Cl, NO_3, CF_3SO_3. *Conditions* : CH_2Cl_2, 20°C, overnight]

Tetrahedron, **1994**, *50*, 5147

Synthesis of Conformationally Restricted Relatives of the Mevinic Acids

Frank Bennett,[a] Garry Fenton[b] and David W. Knight[a]*
[a] *Chemistry Department, University Park, Nottingham, NG7 2RD, UK*
[b] *Rhone-Poulenc-Rorer, Central Research, Rainham Road South, Dagenham, Essex, RM10 7XS, UK*

A series of *spiro*-hydroxy valerolactones have been prepared, in some cases stereospecifically, by the addition of acetoacetate dianions to examples of hexahydrobenz[e]indenones and hexahydrophenanthrenones, as potential HMGCoA reductase inhibitors.

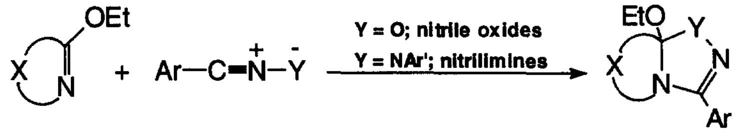


Tetrahedron, **1994**, *50*, 5159

REACTIONS OF NITRILE OXIDES AND NITRILIMINES WITH IMIDATE ESTERS, THE NITROGEN ATOM OF WHICH FORMS PART OF A HETEROCYCLIC RING.

David J. Miller and Richard M. Scrowston. School Of Chemistry, University of Hull, HULL, HU6 7RX, U.K.
Peter D. Kennewell and Robert Westwood. Roussel Laboratories Ltd., Covingham, SWINDON. SN3 5BZ, U.K.

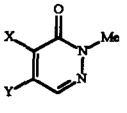
The reaction of heterocycles containing the imidate ester function C(OEt)=N with a range of 1,3-dipoles was studied.



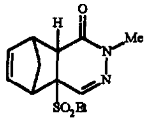
Tetrahedron, **1994**, *50*, 5169

DIELS-ALDER REACTIONS WITH 2-METHYLPYRIDAZIN-3(2*H*)-ONES BEARING ELECTRON-WITHDRAWING SUBSTITUENTS AT THE 4- OR 5-POSITION

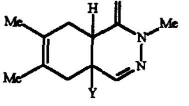
Francisco Fariña, M. Victoria Martín, and Magali Romañach
Instituto de Química Orgánica General , C.S.I.C., Juan de la Cierva, 3, 28006 Madrid, Spain.



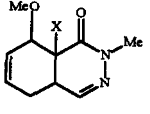
2, Y=H **3**, X=H



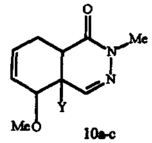
6a



7a,c



9b,c



10a-c

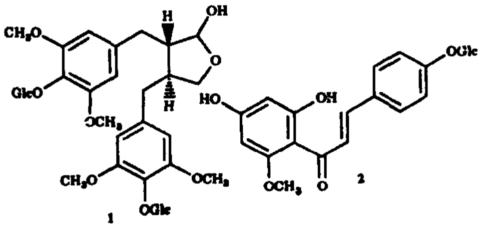
Pyridazinones **2, 3** (X, Y: **a**, SO_2Et; **b**, CN; **c**, CO_2Me) react with several dienes to afford adducts **6a, 7a,c, 9b,c** and **10a-c**.

Tetrahedron, **1994**, *50*, 5181

TWO GLUCOSIDES FROM *PYRACANTHA COCCINEA* ROOTS: A NEW LIGNAN AND A NEW CHALCONE

Anna Rita Bilia*, Ivano Morelli, and Antonio Marsili.
Dipartimento di Chimica Bioorganica, Universita' di Pisa,
via Bonanno 33, I-56126 Pisa, Italy.

The structure of two new glucosides 1 and 2 from *Pyracantha coccinea* were determined using spectroscopic techniques, mainly by detailed NMR spectral studies including COSY, NOESY, HETCOR and COLOC nmr experiments.



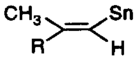
1 2

Tetrahedron, **1994**, *50*, 5189

REGIO- AND STEREOSELECTIVE SYNTHESIS OF (*E*)-2-METHYL-1-ALKENYLTRIMETHYLSTANNANES FROM 1-ALKYNES

Fabio Bellina*, Adriano Carpita*, Elisabetta Adorni Fontana and Renzo Rossi.
Dipartimento di Chimica e Chimica industriale – University of Pisa. – Via Risorgimento 35, I-56126 Pisa, Italy.

Compounds of general formula **4** have been regio- and stereoselectively synthetized by procedures involving the Zr-catalyzed carboalumination of 1-alkynes (**5**).



4a-f

$R-C\equiv C-H$ **5a-f**

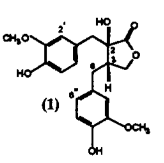
a : R = n-C_4H_9
b : R = C_6H_{13}
c : R = C_6H_5
d : R = TBDMSO$(CH_2)_3$
e : R = 1-cyclohexenyl
f : R = 4-F-$C_6H_4CH_2$

Tetrahedron, **1994**, *50*, 5203

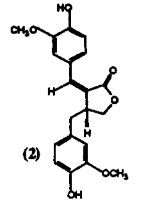
STRUCTURAL ELUCIDATION AND CONFORMATIONAL ANALYSIS OF NEW LIGNAN BUTENOLIDES FROM THE LEAVES OF *BUPLEURUM SALICIFOLIUM.*

Ana Estévez-Braun *, Rafael Estévez-Reyes and Antonio G. González.
C.P.N.O. "Antonio González". Instituto Universitario de Bio-Orgánica, Universidad de La Laguna, Tenerife, Canary Island, Spain.

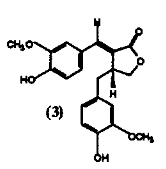
Three new lignan butenolides were isolated from *Bupleurum salicifolium* (Umbelliferae). Their structures were determined by means of spectroscopic studies and chemical evidence. A study of the conformational analysis of these lignans using Molecular Mechanics Calculations is also included.



(1)



(2)



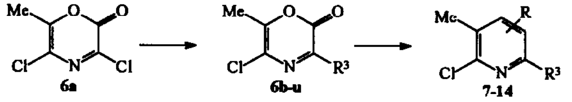
(3)

Tetrahedron, **1994**, *50*, 5211

THE SYNTHESIS OF 3-FUNCTIONALIZED 5-CHLORO-6-METHYL-2*H*-1,4-OXAZIN-2-ONES AND OF PYRIDINES FROM CYCLOADDITION-ELIMINATION REACTIONS WITH SUBSTITUTED ACETYLENIC COMPOUNDS.

Koen J. Van Aken, Gerrit M. Lux, Geert G. Deroover, Lieven Meerpoel, Georges J. Hoornaert*
Laboratorium voor Organische Synthese, Department of Chemistry, K.U.Leuven, Celestijnenlaan 200F, B-3001 Leuven (Belgium)

Selective functionalisation of the chlorimine group in 3,5-dichloro-6-methyl-2*H*-1,4-oxazin-2-one is realised in appropriate conditions. The azadiene system is shown to react easily with monosubstituted acetylenic compounds yielding new polyfunctionalized pyridines.



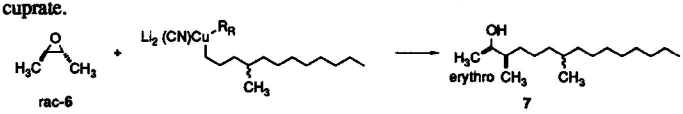
R^3=alkyl, (hetero)aryl, thioalkyl, thioaryl, alkoxy, dialkylamino, bromo, sulfinyl, sulfonyl
R=COOMe, Ph, CH_2Cl, OEt

Tetrahedron, **1994**, *50*, 5225

EFFICIENT OPENING OF *TRANS*-2,3-EPOXYBUTANE BY A HIGHER ORDER CUPRATE: SYNTHESIS OF *ERYTHRO*-3,7-DIMETHYLPENTADECAN-2-YL ACETATE, PHEROMONE OF PINE SAWFLIES.

Erik Hedenström* and Hans-Erik Högberg.
Chemistry, Department of Science and Technology in Sundsvall, Mid Sweden University, S-851 70 Sundsvall, Sweden.

A higher order cuprate reacted with racemic *trans*-2,3-epoxybutane (rac-6) furnishing a mixture of the four erythro-isomers of diprionol (3,7-dimethyl-2-pentadecanol, 7) in high yield both counted on the epoxide (96%) and the haloalkane (85%) used as the starting material for the cuprate.

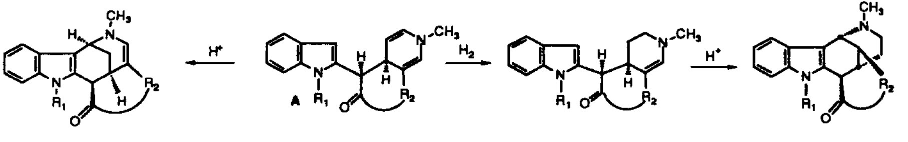


Tetrahedron, **1994**, *50*, 5233

NUCLEOPHILIC ADDITIONS TO PYRIDINIUM SALTS. REDUCTION OF THE INTERMEDIATE DIHYDROPYRIDINES.

Rodolfo Lavilla*, Teresa Gotsens, Francisco Gullón and Joan Bosch*
Laboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, 08028 Barcelona, Spain

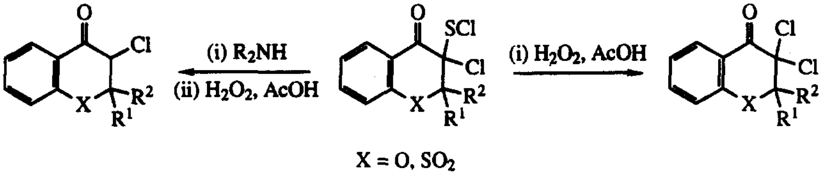
The reduction and subsequent acid cyclization of dihydropyridines A is studied. The introduction of a linkage between R_2 and the carbonyl group greatly improves the process regarding to yields, regio- and stereoselectivity.



Tetrahedron, **1994**, *50*, 5245

A New Reaction of α-Chloro-α-chlorosulfenyl Ketones: Facile Syntheses of 3,3-Dichloro- and 3-Chloro- Chroman-4-ones and Thiochroman-4-ones

Christopher D. Gabbutt, John D. Hepworth and B. Mark Heron.
Department of Chemistry, University of Central Lancashire, Preston, PR1 2HE, England.

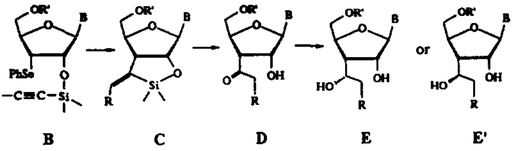


Tetrahedron, **1994**, *50*, 5255

Diastereospecific Synthesis of 2'- or 3'-*C*-Branched Nucleosides through Intramolecular Free-radical Capture by Silicon-tethered Acetylene

Zhen Xi, Jianhui Rong and Jyoti Chattopadhyaya*
Department of Bioorganic Chemistry, Box 581, Biomedical Center, S-751 23 Uppsala, University of Uppsala, Sweden

The intramolecular free-radical trapping by a silicon tethered acetylene function in (B) gave only the [3.3.0]-*cis*-fused *Z*-vinylsiloxane (C) which was transformed to (E) or (E') through an oxidation to (D) and its subsequent diastereospecific reduction.

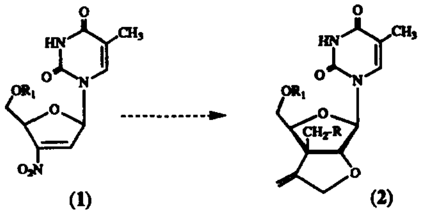


Tetrahedron, **1994**, *50*, 5273

THE SYNTHESIS OF NEW 3'-BIS-C-SUBSTITUTED-3'-DEOXY-3'-DEHYDRO-[3.3.0]-α-FUSED THYMIDINES BY INTRAMOLECULAR RADICAL TRAPPING BY TETHERED ACETYLENES

*Neeraj Garg, Nafizal Hossain and Jyoti Chattopadhyaya**
Department of Bioorganic Chemistry, Box 581, Biomedical Center, University of Uppsala, S-751 23 Uppsala, Sweden

3'-bis-C-substituted ribothymidine (2) was synthesized for the first time from 3'-nitro-olefin (1) in 4 steps.



Tetrahedron, **1994**, *50*, 5279

NEW DIASTEREOSPECIFIC SYNTHESIS OF 2',3'-DIDEOXY-2'- OR 3'-C_2-BRANCHED- OR 2',3'-α-FUSED-ISOXAZOLIDINE NUCLEOSIDES DIRECTLY FROM THE SECONUCLEOSIDE

*A. Papchikhin & J. Chattopadhyaya**
Department of Bioorganic Chemistry, Box 581, Biomedical Center,
University of Uppsala, S-751 23 Uppsala, Sweden