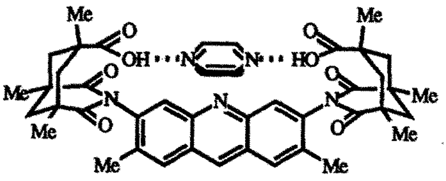
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 8559

MOLECULAR STRUCTURES OF HOST-GUEST COMPLEXES OF REBEK'S DIACID

Robert A. Pascal, Jr., and Douglas M. Ho
Department of Chemistry, Princeton University, Princeton, NJ 08544



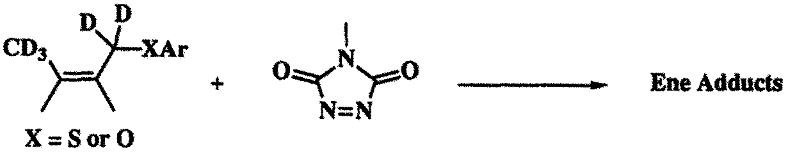
The crystal and molecular structures of 1:1 complexes of Rebek's diacid with pyrazine and quinoxaline, as well as that of Rebek's diacid hydrochloride are reported. The former two complexes exhibit two-point binding of the diamine guest, and the latter shows three-point binding of the chloride ion.

Tetrahedron, **1994**, *50*, 8569

A COMPARISON OF SUBSTITUENT FIELD EFFECTS ON THE REGIOCHEMISTRY OF THE ENE REACTIONS OF ALLYLIC SULFIDES AND ETHERS.

Edward L. Clennan,* Jaya J. Koola, Ming-Fang Chen, Department of Chemistry, University of Wyoming, Laramie WY 82071 USA

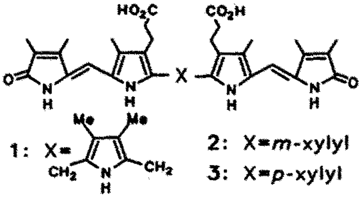
The different regiochemical preferences of 1-Methyl-1,2,4-triazolinedione in its reactions with allylic sulfides and ethers is attributed to the differences in the C-O and C-S bond lengths.



Tetrahedron, **1994**, *50*, 8579

SYNTHESIS AND UNUSUAL PROPERTIES OF EXPANDED BILIRUBIN ANALOGS

Daniel F. Nogales, D. Timothy Anstine and David A. Lightner*
Department of Chemistry, University of Nevada, Reno



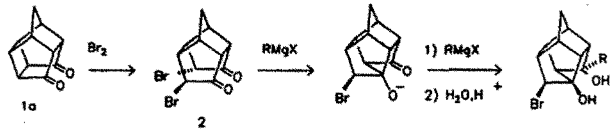
Centrally expanded bilirubin analogs **1**, **2** and **3** were prepared following acid catalyzed condensation of methyl 3-nor-neoxanthobilirubinate with 3,4-dimethyl-2,5-pyrroledialdehyde, isophthalaldehyde and terephthalaldehyde, respectively. They are thought to adopt sandwich-like intramolecularly hydrogen bonded conformations.

Tetrahedron, **1994**, *50*, 8597

NEW ROUTE TO 4,4,6,7-TETRASUBSTITUTED PENTACYCLO[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]UNDECANES.

Alexander M. Aleksandrov,* Susan A. Bourne, Mariusz Krawiec, Tonis J. Pehk, Alexander E. Petrenko and William H. Watson,* Ukrainian Academy of Sciences, 252094 Kiev, Ukraine; Texas Christian University, Fort Worth, TX 76109; Estonian Academy of Sciences, 200001 Tallinn, Estonia.

Reactions of Grignard reagents with 3,6-dibromo-2,7-dioxotetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane lead to the formation of (D_3)-trishomocubane derivatives.



Tetrahedron, **1994**, *50*, 8603

SYNTHESIS OF 3-SUBSTITUTED (AZIDO, ACYLTHIO, CHLORO or FLUORO)-2,3-DIDEOXY-D-*ERYTHRO*-PENTOSES AND 3-METHYL-3-SUBSTITUTED-2,3-DIDEOXY-D-*ERYTHRO*-PENTOSES

Y.E. Raifeld[1], A.A. Nikitenko[1], B.M. Arshava[1], I.E. Mikerin[1], L.L. Zilberg[1], G.Y. Vid[2], S.A. Lang, Jr. [2] and V.J. Lee[2]
[1]Laboratory of Carbohydrates and Nucleoside Synthesis - Moscow Institute of Fine Chemical Technology and JV"Angarex"
Moscow 117571, RUSSIA
[2]Medical Research Division, American Cyanamid Company, Pearl River, New York 10965

The synthesis of various 3-substituted-2,3-dideoxy-D-*erythro*-pentoses and furanosides *via* the tandem Sharpless epoxidation and epoxide cleavage with Ti(O-*i*-Pr)$_3$X [or Ti(O-*i*-Pr)$_4$ - TiF$_4$] reagents is discussed in detail, including regioselectivity issues.

R = H; CH_3
R' = $CH(OEt)_2$, $CH=CH_2$

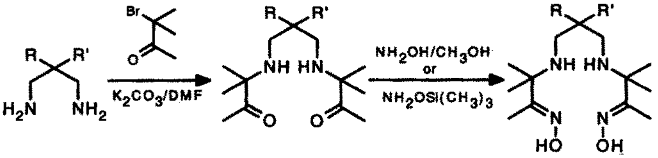
X = N_3, Cl, F, SCOPh, H

Tetrahedron, **1994**, *50*, 8617

AN EFFICIENT SYNTHESIS OF SOME 6-SUBSTITUTED 4,8-DIAZA-3,3,9,9-TETRAMETHYL-UNDECANE-2,10-DIONE DIOXIMES (PROPYLENE AMINE OXIMES, PnAOs): LIGANDS FOR ^{99m}Tc COMPLEXES USED IN STRUCTURE-DISTRIBUTION RELATIONSHIP (SDR) STUDIES.

Palaniappa Nanjappan, Natarajan Raju, Kondareddiar Ramalingam, David P. Nowotnik
The Bristol-Myers Squibb Pharmaceutical Research Institute, Princeton, NJ 08543-4000

A number of 6-substituted propylene amine oxime (PnAO) derivatives were prepared in good yields from the corresponding 2-substituted 1,3-diaminopropane by reacting with 3-bromo-3-methylbutan-2-one followed by oximation.

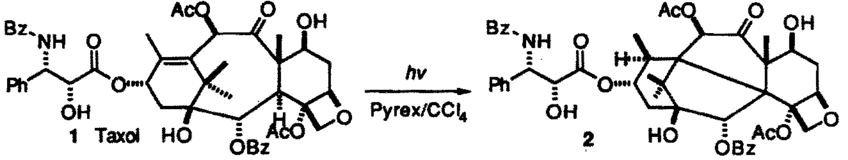


Tetrahedron, **1994**, *50*, 8633

STUDIES ON THE PHOTOCHEMISTRY OF TAXOL®

Shu-Hui Chen*, Vittorio Farina, Stella Huang, Qi Gao, Jerzy Golik and Terrence W. Doyle
Bristol-Myers Squibb Pharmaceutical Research Institute, 5 Research Parkway, Wallingford, CT 06492

Abstract: The mechanistic aspects of the photoisomerization of taxol were investigated.



1 Taxol

2

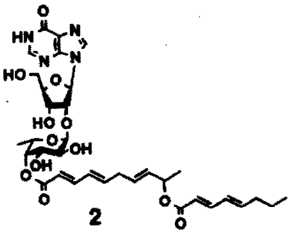
Tetrahedron, **1994**, *50*, 8651

Isolation and Structure of Shimofuridins B ~ G from the Okinawan Marine Tunicate *Aplidium multiplicatum*

Yukiko Doi, Masami Ishibashi, and Jun'ichi Kobayashi*

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

Shimofuridins B (2) ~ G, six new analogs of shimofuridin A, have been isolated from the Okinawan marine tunicate *Aplidium multiplicatum* by careful HPLC separation and their structures elucidated on the basis of spectroscopic data.



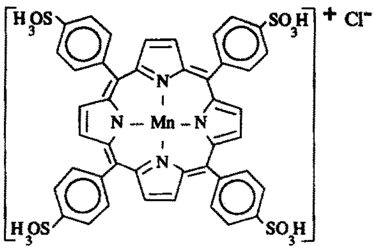
2

An Optimized Synthesis of Manganese *meso*-Tetra(4-sulfonato-phenyl)porphine: A Tumor-Selective NMR Imaging Contrast Agent

Tetrahedron, **1994**, *50*, 8657

Kurt Bockhorst and Mathias Hoehn-Berlage*, Max-Planck Institut
für neurologische Forschung, Gleueler Str. 50, D-50931 Köln, Germany

The synthesis and purification of manganese meso-tetra(4-sulfonato-phenyl)porphine is described. This synthetic porphyrin is a potential tumor-selective contrast agent in magnetic resonance tomography.

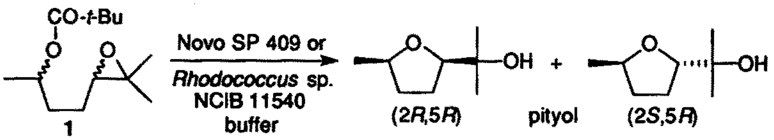


ENZYME-TRIGGERED OPENING OF AN EPOXIDE - CHEMO-ENZYMATIC SYNTHESIS OF (2*R*,5*R*)- AND (2*S*,5*R*)-PITYOL

Tetrahedron, **1994**, *50*, 8661

M. Mischitz, A. Hackinger, I. Francesconi and K. Faber*
Institute of Organic Chemistry, Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria

Enzymatic ester-hydrolysis of 1 did not lead to the formation of the epoxy-alcohol but furnished rearranged products.

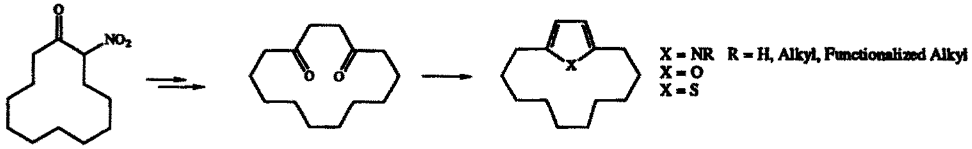


SYNTHESIS OF [10]HETEROPHANES USING A RING ENLARGEMENT REACTION

Tetrahedron, **1994**, *50*, 8665

Ferrid Hadj-Abo, Stefan Bienz, and Manfred Hesse*, Org.-chem. Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich.

The Paal-Knorr cyclization of cyclotetradecane-1,4-dione, obtained from 2-nitrocyclododecanone by a reaction sequence comprising a ring enlargement step, gave rise to a number of [10](2,5)pyrrolophanes (X = NR, R = H, alkyl, functionalized alkyl) and to [10](2,5)furanophane (X = O) in good to excellent yields. The corresponding [10](2,5)thiophenophane (X = S) was formed in less satisfactory yield.

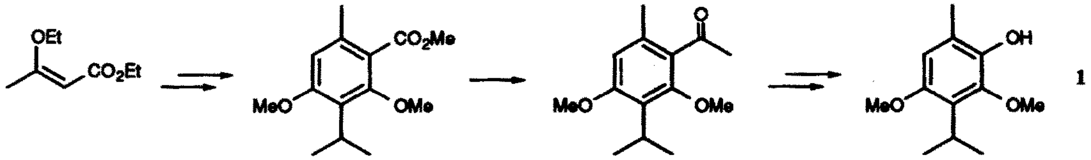


A SHORT SYNTHESIS OF THE AROMATIC MONOTERPENE ESPINTANOL

Tetrahedron, **1994**, *50*, 8673

David J Wadsworth* and Sabine Losch, Ciba Animal Health Division, CH-4002 Basel, Switzerland

A flexible and expedient synthesis of the naturally-occurring monoterpene espintanol 1 is outlined.

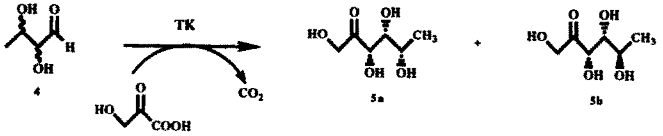


Tetrahedron, **1994**, *50*, 8677

Chemoenzymatic Synthesis of 6-Deoxy-D-Fructose and 6-Deoxy-L-Sorbose using Transketolase

Laurence Hecquet, Jean Bolte, and Colette Demuynck*, Laboratoire de Chimie Organique Biologique associé au CNRS, Université BlaisePascal, 63177 Aubière, France.

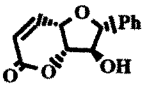
A chemoenzymatic route to 6-deoxy (D-Fructose **5b** and L-sorbose **5a**) is described.This method is based on conversion of racemic 2,3-dihydroxybutyraldehyde to **5a** and **5b** catalyzed by spinach leaves Transketolase (TK). Only the (R,R) and (R,S) isomers of 2,3-dihydroxybutyraldehyde react, yielding 6-deoxy-D-fructose and 6-deoxy-L-sorbose.



Tetrahedron, **1994**, *50*, 8685

ENANTIOSPECIFIC SYNTHESIS OF (+)-ALTHOLACTONE AND ITS THREE STEREOISOMERS

Tony K. M. Shing*[a] and John G. Gillhouley[b]
a Department of Chemistry, The Chinese University of Hong Kong,
Shatin, Hong Kong.
b Department of Chemistry, The Victoria University of Manchester,
Manchester M13 9PL, U.K.



1

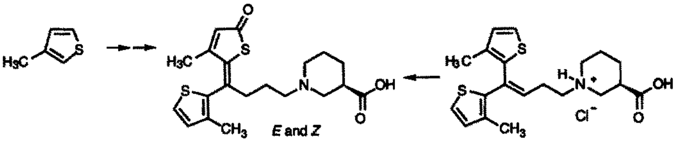
(+)-Altholactone 1 and its three stereoisomers have been constructed from D-mannose or D-gulonolactone.

Tetrahedron, **1994**, *50*, 8699

THE SYNTHESIS OF NOVEL GABA UPTAKE INHIBITORS. PART 2. SYNTHESIS OF 5-HYDROXYTIAGABINE, A HUMAN METABOLITE OF THE GABA REUPTAKE INHIBITOR TIAGABINE

Knud E. Andersen [a], Mikael Begtrup [b], Mukund S. Chorghade [c], Jesper Lau [a], Elaine C. Lee [c], Behrend F. Lundt [a], Hans Petersen [a], Per O. Sørensen [a]*, and Henning Thøgersen [a] [a] Novo Nordisk A/S, Novo-Nordisk Park, DK-2760 Måløv Denmark. [b] Department of Organic Chemistry, The Royal Danish School of Pharmacy, Universitetsparken 2 DK-2100 Copenhagen Denmark. [c] Department 54P, Abbott Laboratories, Abbott Park, Illinois 60064.

5-Hydroxytiagabine, a metabolite of tiagabine, has been prepared from 3-methylthiophene and by biomimetic metalloporphyrin assisted hydroxylation of tiagabine. The structure was confirmed by NMR.



Tetrahedron, **1994**, *50*, 8711

REMARKABLE CONFORMATIONAL CHANGE PROMOTED BY 3'-ETHYLPHOSPHATE AT THE BRANCH-POINT OF A TETRAMERIC LARIAT-RNA DICTATES ITS SELF-CLEAVAGE REACTION MODELLING SOME CATALYTIC RNAS (RIBOZYMES)

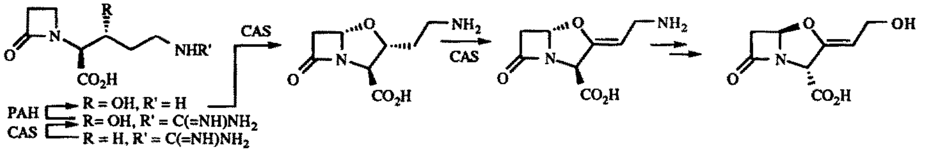
*B. Rousse, C. Sund, C. Glemarec, A. Sandström, P. Agback & J. Chattopadhyaya**
Department of Bioorganic Chemistry, Box 581, Biomedical Center,
University of Uppsala, S-751 23 Uppsala, Sweden

The unique 3'-ethylphosphate function at the branch-point in a tetrameric lariat-RNA orchestrates its self-cleavage reaction ($k = 0.15 \times 10^{-4}$ min^{-1} at 19 °C) modelling the active cleavage site of the natural self-cleaving catalytic RNAs; its conformational feature by 500 MHz NMR and Molecular dynamics simulations in water is reported.

Tetrahedron, **1994**, *50*, 8737

EXPRESSION IN *E.COLI* OF A CLAVAMINIC ACID SYNTHASE ISOZYME: A TRIFUNCTIONAL OXYGENASE INVOLVED IN CLAVULANIC ACID BIOSYNTHESIS

Elizabeth J. Lawlor[†], Stephen W. Elson[†], Susan Holland[†], Robert Cassels[†], John E. Hodgson[†], Matthew D. Lloyd[ø], Jack E. Baldwin[ø], and Christopher J. Schofield[ø]. [†] SmithKline Beecham Pharmaceuticals, Brockham Park, Betchworth, Surrey, RH3 7AJ, U.K.[ø] The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

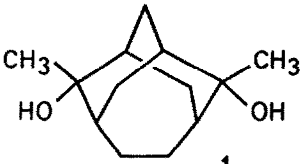


Tetrahedron, **1994**, *50*, 8749

2,7-Dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol as a Host for Volatile and Odorous Guest Molecules

Roger Bishop,* Donald C. Craig, Athanasios Marougkas and Marcia L. Scudder
School of Chemistry, University of New South Wales, Sydney 2052, Australia

The title compound **1** forms two predictable types of lattice inclusion compound depending on the size and shape of the guest molecule chosen. This paper examines the potential of **1** for inclusion of small volatile or odorous guests, and the crystal structures of the helical tubulate $(\mathbf{1})_3\cdot(CBr_2F_2)$ and ellipsoidal clathrate $(\mathbf{1})_4\cdot(CS_2)$ are presented. The guest in the latter is trapped between two interpenetrating sublattices and thus **1** has excellent prospects as a trapping or storage agent.

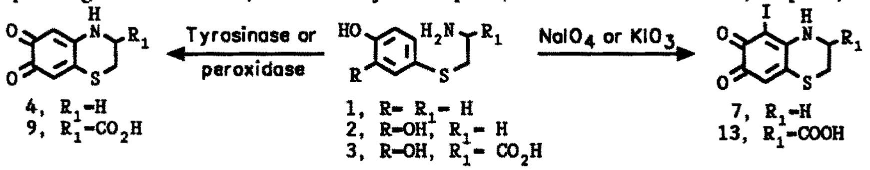


1

Tetrahedron, **1994**, *50*, 8757

BIOMIMETIC OXIDATION OF THE ANTIMELANOMA AGENT 4-S-CYSTEAMINYLPHENOL AND RELATED CATECHOL THIOETHERS: ISOLATION AND REACTION BEHAVIOUR OF NOVEL DIHYDROBENZOTHIAZINEQUINONES.

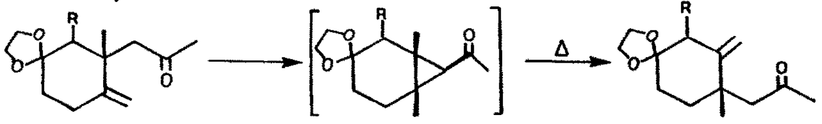
D. Mascagna, C. Costantini, M. d'Ischia and G. Prota*
Dept. Org. Biol. Chem., University of Naples, Via Mezzocannone 16, Naples, Italy



Tetrahedron, **1994**, *50*, 8765

ISOMERISATION OF 1-METHYLENE-2-METHYL-2-(2-OXOPROPYL)-CYCLOHEXANES TO 2-METHYLENE-1-METHYL-1-(2-OXOPROPYL)-CYCLOHEXANES BY ENE AND RETRO-ENE REACTION

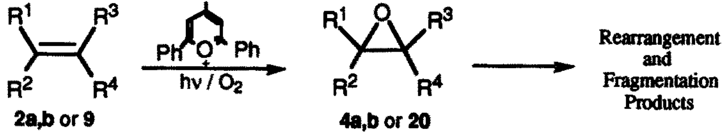
A. Srikrishna,* S. Venkateswarlu, S. Nagaraju and K. Krishnan
Department of Organic Chemistry, Indian Institute of Science
Bangalore - 560 012, India.



Tetrahedron, **1994**, *50*, 8773

INVOLVEMENT OF OXIRANE INTERMEDIATES IN THE ELECTRON TRANSFER PHOTOOXYGENATION OF 1,1- AND 1,2-DIARYLETHYLENES SENSITIZED BY 2,4,6-TRIPHENYLPYRYLIUM TETRAFLUOROBORATE

Hermenegildo García, Miguel A. Miranda,* Fatemeh Mojarrad and María J. Sabater
Departamento de Química/Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Valencia, Spain

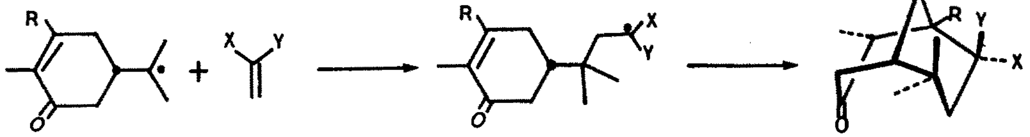


2a and **4a**: $R^1=R^3=Ph$; $R^2=R^4=H$
2b and **4b**: $R^1=R^4=Ph$; $R^2=R^3=H$
9 and **20**: $R^1,R^2=C_6H_4CH_2CH_2C_6H_4$; $R^3=R^4=H$

Tetrahedron, **1994**, *50*, 8781

A REGIOSPECIFIC RADICAL ANNULATION STRATEGY TO FUNCTIONALISED CHIRAL BICYCLO[3.3.1]NONANES

A. Srikrishna, P. Hemamalini and S. Venkateswarlu
Department of Organic Chemistry, Indian Institute of Science
Bangalore - 560 012, India.

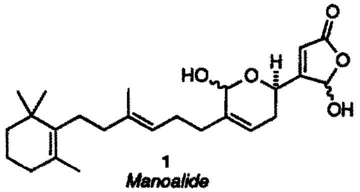


Tetrahedron, **1994**, *50*, 8793

TWO SYNTHESES OF MANOALIDE VIA HETEROATOM-ASSISTED ALKYNE CARBOMETALLATION

P. Bury, G. Hareau, P. Kocieński, Department of Chemistry,
The University, Southampton, SO17 1BJ, U.K.
D. Dhanak, SmithKline Beecham Pharmaceuticals, The Fryth,
Welwyn Garden City, AL6 9AR, U.K.

Two approaches to the sesterterpenoid phospholipase A2 inhibitors seco-manoalide (3) and manoalide (1) are described based on carbometallation of propargylic alcohols to generate the functionalised C6-C7 trisubstituted alkene. Both syntheses also deploy the photooxidation of a furan in order to generate a 4-substituted-5-hydroxy-2(5H)-furanone moiety.



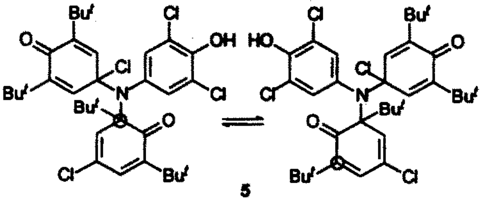
1
Manoalide

Tetrahedron, **1994**, *50*, 8809

The Mechanism of the Gibbs Reaction. Part 2:
The *Ortho* $\rightleftharpoons$ *Ortho* 2,4-Cyclohexadiene-1-one Rearrangement of the Reaction Product of 2,6-Di-*tert*-butyl-4-chlorophenol and 2,6-Dichlorobenzoquinone N-chloroimine

István Pallagi*, András Toró and József Müller
Institute for Drug Research Ltd.,
47-49 Berlini utca, 1045 Budapest, Hungary

The saturation transfers which were observed during the ^1H NOE difference measurements prove an *ortho* $\rightleftharpoons$ *ortho* 2,4-cyclohexadiene-1-one rearrangement of the compound 5. This process is an intramolecular rearrangement.



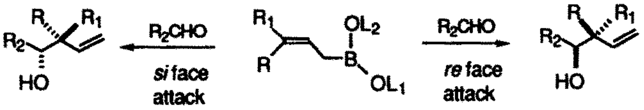
5

Tetrahedron, **1994**, *50*, 8815

ORIGINS OF STEREOSELECTIVITY IN THE ADDITION OF ALLYL- AND CROTYLBORONATES TO ALDEHYDES : THE DEVELOPMENT AND APPLICATION OF A FORCE FIELD MODEL OF THE TRANSITION STATE

Cesare Gennari, Elena Fioravanzo, Anna Bernardi, Anna Vulpetti
Dipartimento di Chimica Organica e Industriale, Universita' di Milano, via Venezian 21, 20133 Milano, Italy

A molecular mechanics model of the transition state for the addition of allyl and crotyl boronates to aldehydes was developed. The force field is used to analyse the stereoselectivity of various synthetically interesting reactions.

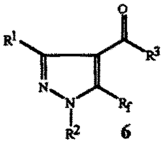


Tetrahedron, **1994**, *50*, 8827

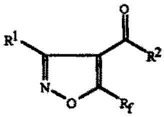
An Efficient Entry to Perfluoroalkyl Substituted Azoles Starting from β-Perfluoroalkyl-β-dicarbonyl Compounds.

Pierfrancesco Bravo, Dario Diliddo, Giuseppe Resnati* - C.N.R. - Centro Studio Sostanze Organiche Naturali, Dipartimento Chimica, Politecnico, 7 via Mancinelli, I-20131 Milano, Italy

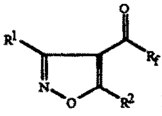
β-Perfluoroalkyl-β-dicarbonyls **2** are shown to be convenient precursors of 5-perfluoroalkypyrazoles **6**, 5-perfluoroalkylisoxazoles **11**, and 4-perfluoroacylisoxazoles **13**.



6



11



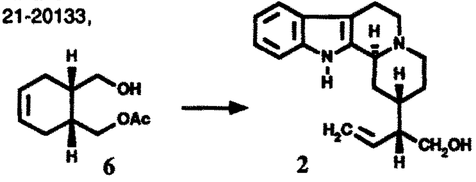
13

Tetrahedron, **1994**, *50*, 8837

A HIGHLY ENANTIOSELECTIVE SYNTHESIS OF (-)-ANTIRHINE BY CHEMO-ENZYMATIC APPROACH

Bruno Danieli, Giordano Lesma*, Marina Mauro, Giovanni Palmisano and Daniele Passarella
Dipartimento di Chimica Organica e Industriale, Universita' degli Studi di Milano-
Centro CNR di Studio per le Sostanze Organiche Naturali-Via Venezian 21-20133,
Milano-Italy.

(-)-Antirhine **2** has been synthesized in high enantioselective fashion and in 13.3% overall yield from **6**, readily available by enzymatic desymmetrization.



Tetrahedron, **1994**, *50*, 8853

COPPER-CATALYSED N-ACYLIMINIUM ION CYCLISATION TO 3-AZABICYCLO[3.3.1]NONANES; SYNTHESIS OF 2,4-DISUBSTITUTED 1-AZA-ADAMANTANES

Jan H. Udding, Nadine Papin, Henk Hiemstra* and W. Nico Speckamp*
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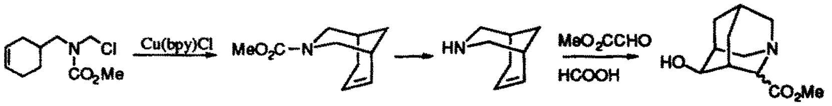
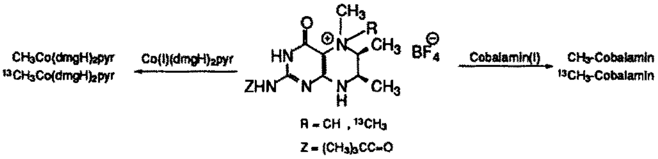
An efficient Cu(bpy)Cl-catalyzed *N*-acyliminium cyclisation to *N*-protected 3-azabicyclo[3.3.1]non-6-ene is reported. This compound is a useful intermediate in the synthesis of 2,4-disubstituted 1-aza-adamantanes.



ALKYL TRANSFER FROM QUATERNARY AMMONIUM SALTS TO COBALT (I): MODEL FOR THE COBALAMIN DEPENDENT METHIONINE SYNTHASE REACTION.

Tetrahedron, **1994**, *50*, 8863

Ellen Hilhorst, Atef S. Iskander, Tjoe B.R.A. Chen and Upendra K. Pandit*. Organic Chemistry Laboratory, University of Amsterdam, (The Netherlands).



Chemistry of Insect Antifeedants from *Azadirachta Indica* (Part 16): Synthesis of Several Derivatives of Azadirachtin Containing Fluorescent or Immunogenic Reporter Groups.

Tetrahedron, **1994**, *50*, 8871

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