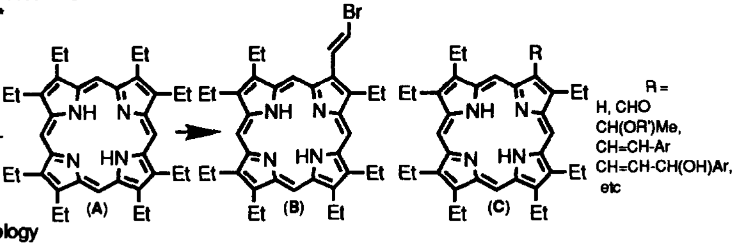
GRAPHICAL ABSTRACTS

Tetrahedron, **1991**, *47*, 6887

FUNCTIONALIZATIONS OF THE ALKYL SUBSTITUENTS IN OCTA-ALKYLPORPHYRINS

M Graça H Vicente and Kevin M Smith,*
Department of Chemistry, University of California, Davis, CA 95616

Treatment of octaethylporphyrin (**A**) with NBS in presence of AIBN yields the trans-(2-bromovinyl)porphyrin (**B**) in high yield Numerous alkyl-functionalized porphyrins [e g (**C**)] can be obtained using extensions and variations of this methodology

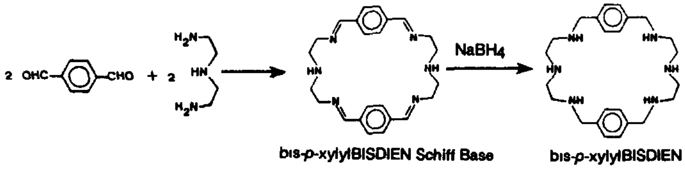


Tetrahedron, **1991**, *47*, 6895

THE SYNTHESIS OF NEW BINUCLEATING POLYAZA MACROCYCLIC AND MACROBICYCLIC LIGANDS: DIOXYGEN AFFINITIES OF THE Co COMPLEXES

*Dian Chen and Arthur E Martell**, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, U S A

A general procedure is described for condensing rigid dialdehydes and bis or tris primary amines to produce macrocyclic or macrobicyclic Schiff bases which are then reduced to the saturated macrocyclic and macrobicyclic polyamines Six of the dicobalt complexes of the reduced macrocyclic and macrobicyclic polyamines were found to be oxygen carriers A typical reaction sequence is the following



Tetrahedron, **1991**, *47*, 6903

NMR STUDY OF THE EFFECT OF NITROGEN-BORANE COORDINATION ON THE CONFORMATIONAL EQUILIBRIUM OF SIX MEMBERED RING HETEROCYCLES.

A Flores-Parra* , N Farfán, A I Hernández-Bautista, L Fernández-Sánchez and R Contreras
Departamento de Química , Centro de Investigación y de Estudios Avanzados del I P N
A P 14-740, México D F , 07000 México

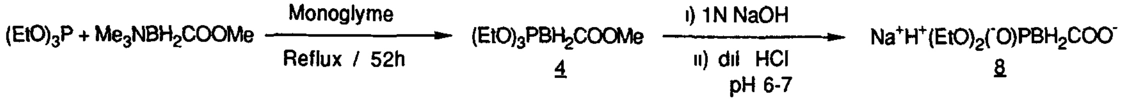
The syntheses, conformational and spectroscopic studies of N-borane adducts of 14 nitrogen six-membered ring heterocycles were performed It was found that borane can act as a conformation and configuration locking agent In addition, it can be very helpful for the assignment of the chemical shifts of other atoms or groups in the molecule as well as to obtain the configuration of substituted carbons

Tetrahedron, **1991**, *47*, 6915

Boron Analogues of Phosphonoacetates Synthesis, Characterization and Antitumor Properties of Sodium Diethylphosphite-carboxyborane and Related Compounds

Anup Sood,[*#] Cynthia K Sood,[*] Iris H Hall[**] and Bernard F Spielvogel[*#]
[*] P M Gross Chemical Laboratory, Duke University, Durham, NC 27706, U S A
[#] Boron Biologicals, Inc, 2811 O'Berry Street, Raleigh, NC 27607, U S A
[**] Division of Medicinal Chemistry and Natural Products, School of Pharmacy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, U S A

Investigations into the synthesis and antitumor properties of substituted borane adducts of phosphites, with a particular emphasis on the boron analogues of phosphonoacetates, are described



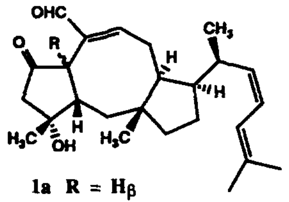
$$(EtO)_3P + Me_3NBH_2COOMe \xrightarrow[\text{Reflux / 52h}]{\text{Monoglyme}} \underset{\underline{4}}{(EtO)_3PBH_2COOMe} \xrightarrow[\text{ii) dil HCl, pH 6-7}]{\text{i) 1N NaOH}} \underset{\underline{8}}{Na^+H^+(EtO)_2(^-O)PBH_2COO^-}$$

Tetrahedron, **1991**, *47*, 6931

Structure and Conformation of Ophiobolin K and 6-Epiophiobolin K from *Aspergillus ustus* as a Nematocidal Agent

Sheo B Singh[*], Jack L Smith, Glory S Sabnis Anne W Dombrowski, James M Schaeffer, Michael A Goetz and Gerald F Bills
Merck Sharp & Dohme Research Laboratories, P O Box 2000, Rahway, N J 07065 (U S A)

The structure, stereochemistry, solution conformation and nematocidal activity of Ophiobolin K (**1a**) and 6-epiophiobolin K (**1b**) isolated from *Aspergillus ustus* has been described Ophiobolin K exhibited nematocidal activity (ED$_{50}$ 10 µg/mL) against the free-living nematode *Caenorhabditis elegans* ,but the A/B trans isomer **1b** was found to be inactive

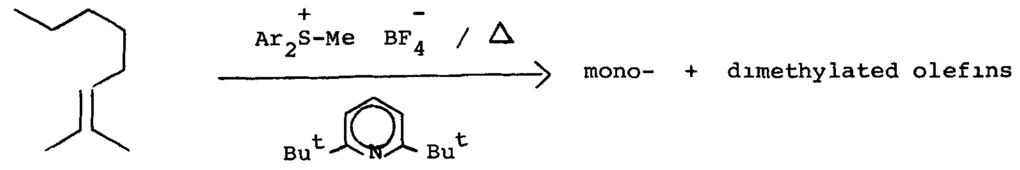


1a R = H$_\beta$
1b R = H$_\alpha$

Tetrahedron, **1991**, *47*, 6939

BIOMIMETIC TRANSALKYLATION OF OLEFINS VIA SULFONIUM SALTS

MARC JULIA and BRIAN McDONALD (Laboratoire de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris 05, France) and MARCOS CAROLI REZENDE (Departamento de Química, Universidade Federal de S.Catarina, Florianópolis, SC 88049, Brasil)

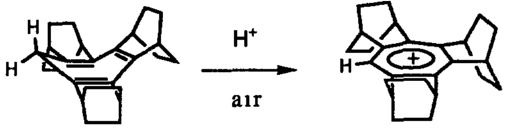


Tetrahedron, **1991**, *47*, 6951

FORMATION, PROPERTIES, AND REACTIONS OF THE 1,2:3,4:,5,6-TRIS(BICYCLO[2.2.2]OCTENO)TROPYLIUM ION

Koichi Komatsu, Hidekazu Akamatsu, Shuji Aonuma, Yasuhisa Jinbu, Naoko Maekawa, and Ken'ichi Takeuchi
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

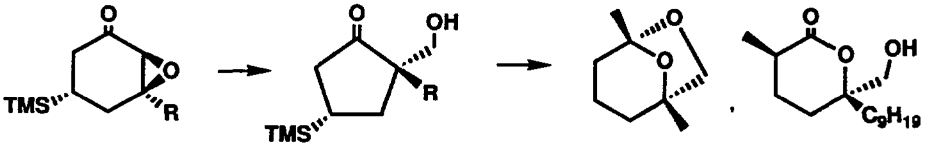
Formation of the title cation by protolytic ionization of the precursor hydrocarbon and the cation's reactions with various heteroatom- and carbon-nucleophiles are described.



Tetrahedron, **1991**, *47*, 6967

New Route to (–)-Frontalin and (–)-Malyngolide via Epoxyketone Rearrangement

Morio Asaoka,* Satoshi Hayashibe, Syuzo Sonoda, and Hisashi Takei
Department of Life Chemistry, Tokyo Institute of Technology, Midoriku, Yokohama 227 Japan



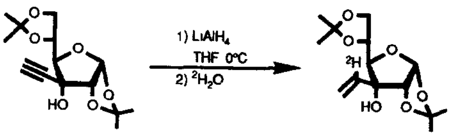
(-)-frontalin (-)-malyngolide

Tetrahedron, **1991**, *47*, 6975

Diacetone Glucose Architecture as a Chirality Template I Crucial Effects of the Intramolecular Oxygens upon the $LiAlH_4$ Reduction of the Propargyl Alcohol of 3-*C*-Ethynyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose Derivatives

Katsumi Kakinuma * Toshihiro Matsuzawa and Tadashi Eguchi
Department of Chemistry, Tokyo Institute of Technology O okayama Meguro-ku Tokyo 152 Japan

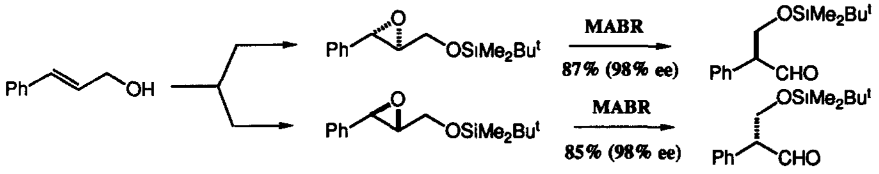
The facile as well as regio- and stereoselective reactivity of 3-*C*-ethynyl-1,2 5,6-di-*O* isopropylidene-α-D allofuranose derivatives for $LiAlH_4$ reduction were investigated The effect of oxygen atoms is discussed by means of semi-empirical MO calculation



Tetrahedron, **1991**, *47*, 6983

Organoaluminum-Catalyzed Rearrangement of Epoxides: A Facile Route to the Synthesis of Optically Active β-Siloxy Aldehydes

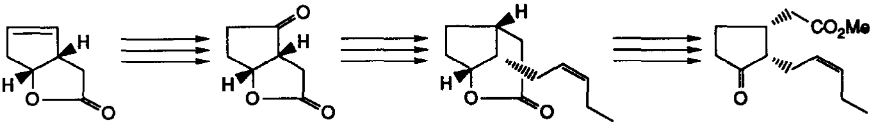
Keiji Maruoka, Takashi Ooi, Shigeru Nagahara, and Hisashi Yamamoto
Department of Appied Chemistry, Nagoya University, Chikusa, Nagoya 464-01, Japan



Tetrahedron, **1991**, *47*, 6999

SYNTHESIS OF BOTH THE ENANTIOMERS OF METHYL EPIJASMONATE

TAKESHI KITAHARA*, TSUNEHIRO NISHI and KENJI MORI, Department of Agricultural Chemistry, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113, Japan



(+)-1 (+)-2 (-)-3 (+)-4

Both the pure enantiomers of methyl epijasmonate 4 with potato-tuber inducing activity were synthesized stereoselectively starting from 2-oxabicyclo[3,3,0]oct-6-en-3-one 1 in 20%yield through 11steps

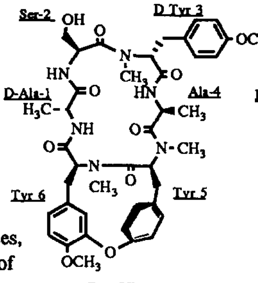
---

Tetrahedron, **1991**, *47*, 7007

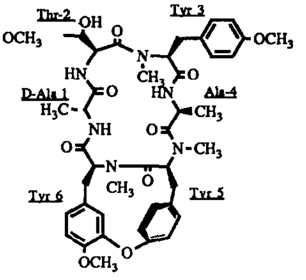
NEW ANTITUMOR BICYCLIC HEXAPEPTIDES, RA-VI AND -VIII FROM RUBIA CORDIFOLIA; CONFORMATIONAL-ACTIVITY RELATIONSHIP II

Hideji Itokawa,*[a] Hiroshi Morita,[a] Koichi Takeya,[a] Nobuo Tomioka,[b] Akiko Itai,[b] and Yoichi Iitaka[c]

Department of Pharmacognosy, Tokyo College of Pharmacy,[a] Horinouchi 1432-1, Hachioji, Tokyo 192-03, Japan, Faculty of Pharmaceutical Sciences, University of Tokyo,[b] Hongo, Bunkyo-ku, Tokyo113, Japan and Faculty of Medicine, Teikyo University,[c] Ohtsuka 359, Hachioji, Tokyo 192-03, Japan



RA-VI

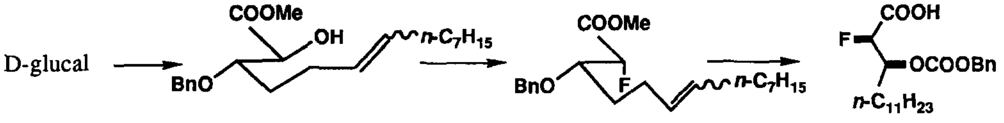


RA-VIII

Tetrahedron, **1991**, *47*, 7021

SYNTHESIS OF (2R,3S)-3-[(BENZYLOXYCARBONYL)OXY]-2-FLUOROTETRADECANOIC ACID

Masao Shiozaki, Yoshiyuki Kobayashi, and Masami Arai
New Lead Research Laboratories, Sankyo Co , Ltd ,
Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140 Japan

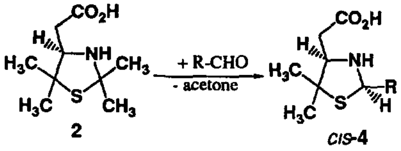


Tetrahedron, **1991**, *47*, 7029

SYNTHESIS AND STEREOCHEMISTRY OF NOVEL 2-SUBSTITUTED 4-THIAZOLIDINE ACETIC ACIDS

Jürgen MARTENS,* Jürgen KINTSCHER and Wolfgang ARNOLD
Fachbereich Chemie (Organische Chemie) der Universität Oldenburg
Ammerländer Heerstraße 114-118, D-2900 Oldenburg i O , Germany

Reaction of isopropylidene-protected ß-homopenicillamine 2 with various aldehydes leads to a number of new 2-monosubstituted 4-thiazolidine acetic acids 4 Thiazolidines *cis*-4 are formed with high diastereoselectivity Assignment of configuration is made by NMR-analysis The diastereomeric pure compounds 4 possess unstable chiral centers in position 2 and undergo rapid epimerisation in solution at higher temperatures

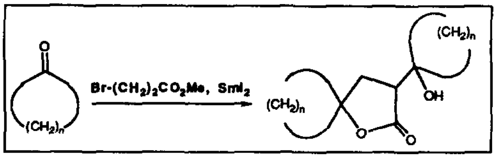


Tetrahedron, **1991**, *47*, 7037

SAMARIUM DIIODIDE PROMOTED SPIROLACTONIZATION OF CYCLOALKANONES

René Csuk * [a], Zhong Hu [a], Mohamed Abdou [b], and Christoph Kratky [b]
a) Pharmazeutisch-Chemisches Institut, Universität Heidelberg, D-W6900 Heidelberg, (FRG),
b) Institut fur Physikalische Chemie, Universität Graz, A-8010 Graz, (Austria)

Reaction of cycloalkanones with methyl 3-bromopropionate and SmI$_2$ afforded formation of spiroanellated γ-lactones, pinacols and unprecedented 3-(1-hydroxycycloalkyl)-1-oxaspiro[n,m]alkan-2-ones

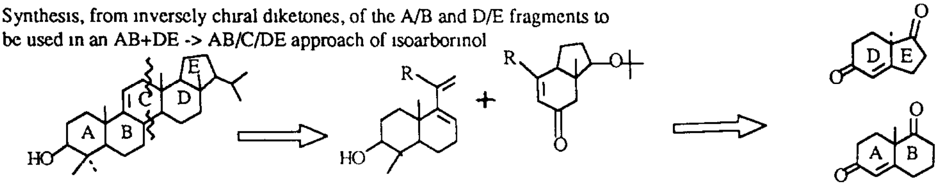


Tetrahedron, **1991**, *47*, 7045

SYNTHETIC APPROACHES TO PENTACYCLIC TRITERPENES OF THE ARBORANE FAMILY

S Arséniyadis, R Rodriguez, E Cabrera, A Thompson & G Ourisson
I C S N , C N R S , F-91198, Gif-sur-Yvette (France)

Synthesis, from inversely chiral diketones, of the A/B and D/E fragments to be used in an AB+DE -> AB/C/DE approach of isoarborinol

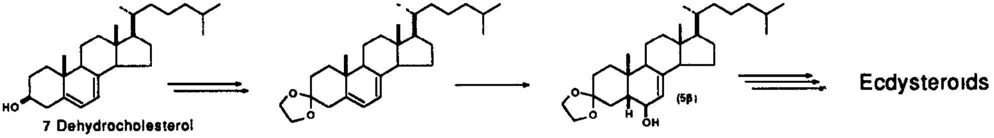


Tetrahedron, **1991**, *47*, 7059

A NEW ROUTE TO PRECURSORS OF ECDYSTEROIDS, USING A REGIO- AND STEREOSELECTIVE HYDROBORATION

Frédéric DOLLE, Charles HETRU# and Bang LUU*
Laboratoire de Chimie Organique des Substances Naturelles, associé au CNRS, 5 rue Blaise Pascal, 67084 Strasbourg, France
#Laboratoire de Biologie Générale, associé au CNRS, 12 rue de l'Université, 67000 Strasbourg, France

Hydroboration-oxidation of 3,3-(ethylenedioxy)-cholesta-5,7-diene produces 3,3-(ethylenedioxy)-5β-cholest-7-en-6β-ol (the same reaction with 7-dehydrocholesterol leads only to the 5α-alcohol (OH-6α), prohibiting the synthesis of 5β-steroids)

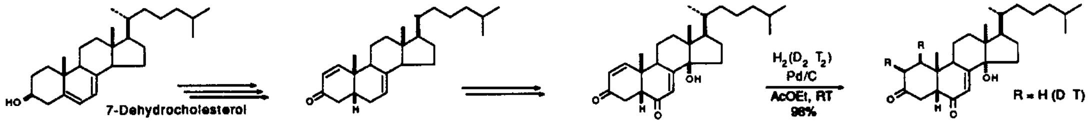


Tetrahedron, **1991**, *47*, 7067

SYNTHESIS OF A TRITIATED 3-DEHYDROECDYSTEROID, PUTATIVE PRECURSOR OF ECDYSTEROID BIOSYNTHESIS IN *LOCUSTA MIGRATORIA*

Frédéric DOLLE[1], Charles HETRU[2], Jean-Pierre ROUSSEL[2], Bernard ROUSSEAU[3], Franck SOBRIO[3], Bang LUU[1*], Jules A. HOFFMANN[2]
[1]Laboratoire de Chimie Organique des Substances Naturelles, associé au CNRS, 5 rue Blaise Pascal, 67084 Strasbourg, France. [2]Laboratoire de Biologie Générale, associé au CNRS, 12 rue de l'Université, 67000 Strasbourg, France. [3]Service des Molécules Marquées, CE de Saclay, 91191 Gif-sur-Yvette, France

[^{3}H-1,2]-14α-hydroxy-5β-cholest-7-ene-3,6-dione have been synthesized with high specific activity (1 74 TBq/mmol) from 7-dehydrocholesterol
The tritiated molecule was very efficiently converted to ecdysone and to 3-dehydroecdysone.

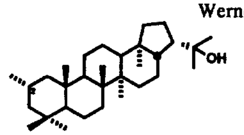


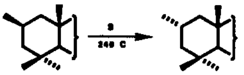
Tetrahedron, **1991**, *47*, 7081

2α-METHYLHOPANOIDS: FIRST RECOGNITION IN THE BACTERIUM ***Methylobacterium organophilum*** AND OBTENTION VIA SULPHUR INDUCED ISOMERIZATION OF 2β-METHYLHOPANOIDS.

AN ACCOUNT FOR THEIR PRESENCE IN SEDIMENTS.

P Stampf, D Herrmann, P Bisseret and M Rohmer* (Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue A Werner, 68093 Mulhouse Cedex, France)

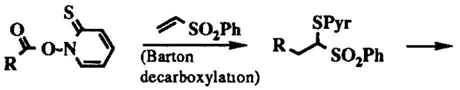




Tetrahedron, **1991**, *47*, 7091

DECARBOXYLATIVE RADICAL ADDITION TO VINYLSULPHONES AND VINYLPHOSPHONIUM BROMIDE SOME FURTHER NOVEL TRANSFORMATIONS OF GEMINAL (PYRIDINE-2-THIYL) PHENYLSULPHONES

Derek H R Barton[a,b]*, Jean Boivin[c], Elisabeth Crépon (née da Silva)[c], Jadab Sarma[a], Hideo Togo[b,d], and Samir Z Zard[b,c]*
a) Texas A&M University, U S A b) Institut de Chimie des Substances Naturelles, France c) Ecole Polytechnique, France.
d) Chiba University, Japan



RCH_2CO_2H REt

$RCH_2CH(SO_2Ph)R'$ $R(CH_2)_2R'$

$R(CH_2)_2SO_2Ph$ $RCH{=}CH_2$

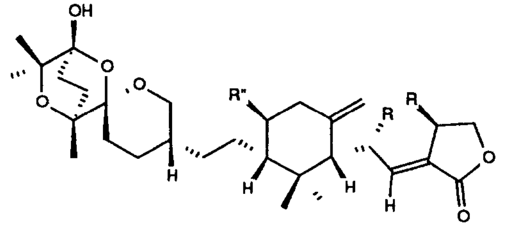
RCH_2COR' $R'CH{=}CH\text{-}CH{=}CH_2$, etc

Tetrahedron, **1991**, *47*, 7109

Fungal Metabolites XXVI. the Structure of Saponaceolides B, C and D, New C-30 Terpenoids from *Tricholoma saponaceum*

Maria De Bernardi, Luigi Garlaschelli, Lucio Toma, Giovanni Vidari* and Paola Vita-Finzi
Dipartimento di Chimica Organica, Università di Pavia, Viale Taramelli 10, 27100 Pavia, Italy

Absolute configuration has been established for saponaceolide A (1), along with the stereostructures of saponaceolides B (2), C (3) and D (4), new cytotoxic triterpenoids from *Tricholoma saponaceum*



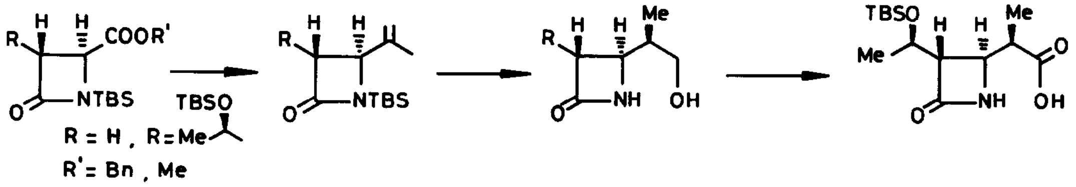
1 R = OH, R' = R" = H
2 R = R' = R" = H
3 R = R' = OH, R" = H
4 R = R" = OH, R' = H

Tetrahedron, **1991**, *47*, 7117

1 β-METHYLTHIENAMYCIN : SOME STEREOCONTROLLED APPROACHES TOWARDS THE KEY INTERMEDIATE

Mukund K Gurjar , Manjunath N Bhanu, Vivek B Khare, Ashok Bhandari, Madhusudan N Deshmukh and A V Rama Rao
Indian Institute of Chemical Technology, Hyderabad 500 007, India

The synthesis of key intermediates of 1β-methylthienamycin based on stereocontrolled reduction and hydroboration-oxidation have been described.



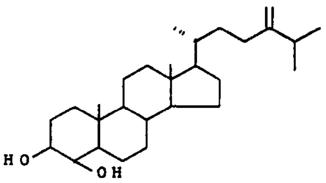
Tetrahedron, **1991**, *47*, 7129

NEW OXYGENATED STEROLS FROM THE WEED *EICHHORNIA CRASSIPES* SOLMS

M. Della Greca, P. Monaco and L. Previtera

Dipartimento di Chimica Organica & Biologica
Via Mezzocannone 16, I-80134 Napoli, Italy.

The phytotoxic sterols 1 - 3 with the unique 4β-hydroxy function have been isolated from *E crassipes* and characterized mainly by spectral analysis



1 Δ8,14 2 Δ8 3 Δ7

Tetrahedron, **1991**, *47*, 7135

SYNTHESIS OF TETRAMERIC BRANCHED RNA-DNA CONJUGATE & BRANCHED-RNA ANALOGUE & THEIR COMPARATIVE CONFORMATIONAL STUDIES BY 500 MHZ NMR SPECTROSCOPY

A Földesi, P Agback, C Glemarec & J Chattopadhyaya*

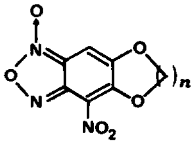
Department of Bioorganic Chemistry, Box 581, Biomedical Center, University of Uppsala,
S-751 23 Uppsala, Sweden

Synthesis of tetrameric branched RNA-DNA conjugate $A3'p5'G^{2'p5'[dC]}_{3'p5'C}$ (**13**) found naturally in gram-negative bacterium *Stigmatella aurantiaca*, and corresponding branched RNA analogue $A3\ p5'G^{2'p5'C}_{3'p5'C}$ (**14**) are reported Subsequently, the conformational features of branched tetramers **13** and **14** have been elucidated and compared with those of $A^{2'p5'G}_{3'p5'C}$ and $U3'p5'A^{2'p5'G}_{3'p5'C}$ found as the branch-point in the lariat formed in the pre-mRNA processing reaction (Splicing)

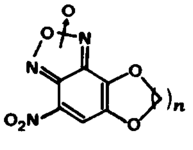
Tetrahedron, **1991**, *47*, 7157

Influence of the Heterocyclic Side Ring During the Boulton-Katritzky Rearrangement of 1,2-Alkylenedioxy-nitrobenzofuroxans

Ioannis M. Takakis*, Phaedon M. Hadjimihalakis and Georgia G. Tsantali
Laboratory of Organic Chemistry, University of Thessaloniki, GR-540 06, Thessaloniki, Greece.



1



2

	n
a	1
b	2
c	3
d	4
e	5
f	6

$$\mathbf{1b,c,d,e}\ \overset{\Delta}{\underset{\Delta}{\substack{\longrightarrow \\ \not\longleftarrow}}}\ \mathbf{2b,c,d,e} \qquad (1)$$

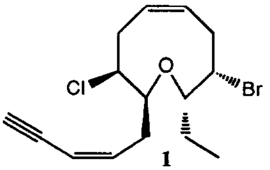
$$\mathbf{1f}\ \overset{\Delta}{\underset{\Delta}{\rightleftarrows}}\ \mathbf{2f} \qquad (2)$$

$$\mathbf{1a}\ \overset{\Delta}{\underset{\Delta}{\substack{\not\longrightarrow \\ \longleftarrow}}}\ \mathbf{2a} \qquad (3)$$

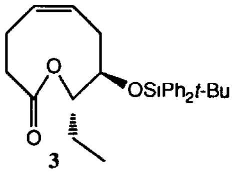
Tetrahedron, **1991**, *47*, 7171

STUDIES TOWARDS THE SYNTHESIS OF OBTUSENYNE. A CLAISEN REARANGEMENT APPROACH TO UNSATURATED NINE-MEMBERED LACTONES

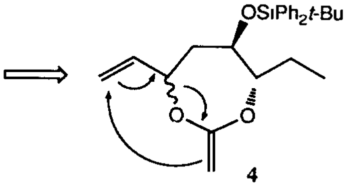
Neil R Curtis, Andrew B Holmes,* and Mark G Looney
University Chemical Laboratory, Lensfield Road, CAMBRIDGE CB2 1EW, U K



1



3



4

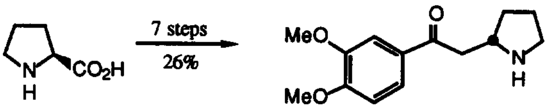
Claisen rearrangement of the racemic vinyl ketene acetal 4, generated *in situ* by selenoxide elimination, gave the unsaturated lactone 3 which is an advanced precursor for the *Laurencia*-derived natural product obtusenyne 1

Tetrahedron, **1991**, *47*, 7179

A TOTAL SYNTHESIS OF (-)-RUSPOLINONE

Keith Jones* and King-Chung Woo, Department of Chemistry, King's College London, Strand, London WC2R 2LS U K

A synthesis of the pyrrolidine alkaloid (-)-ruspolinone (1) from (2S)-proline in 7 steps and 26% overall yield is presented which assigns the (2S) configuration to (-)-(1)



(1)

Tetrahedron, **1991**, *47*, 7185

PHTHALIMIDOSULPHENYL CHLORIDE PART 2[1]. SYNTHESIS OF UNUSUAL THIIRANE DERIVATIVES

Giuseppe Capozzi*, Luciano Gori and Stefano Menichetti
Centro C N R Chimica Composti Eterociclici, Dipartimento di Chimica Organica, Universita' di Firenze,
Via G Capponi 9, 50121 Firenze, Italy

Vinylthio phthalimides **1** react with hydrides to give stereoselectively vinylthio thiiranes **3** and di-vinyl disulphides **6**