#### **GRAPHICAL ABSTRACTS**

Tetrahedron, 1992, 48, 4247

## PYRROLIZIDINE OXIMES: A NOVEL NEW CLASS OF DENDROBATID ALKALOIDS

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Amidine structures 1 - 3 tentatively proposed for three alkaloids, 222, 236 and 252 from the poison frog Dendrobates pumilio, are revised on the basis of GC-FTIR and NMR studies to pyrrolizidine oximes 4 - 6.

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## Synthesis of 2-Aminopurine Nucleosides via Regiocontrolled Glycosylation

Philip Garner,\* Ji Uk Yoo, and Ramakanth Sarabu Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

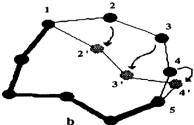
Stereo- and regiocontrolled syntheses of pyranosyl N<sup>9</sup> and N<sup>7</sup>-2-aminopurine nucleosides are described using either Lewis acid or iodonium mediated glycosylation methodology. A convenient NOESY protocol for establishing base regiochemistry and anomeric stereochemistry is also presented.

Tetrahedron, 1992, 48, 4271

### SIMULATED ANNEALING OF RINGS USING AN EXACT RING

#### CLOSURE ALGORITHM

Frank Guarnieri and Stephen R. Wilson, Department of Chemistry, New York University, Washington Square, New York, New York 10003



The method of simulated annealing has been combined with an exact ring closure algorithm to locate the global minimum of hydrocarbon rings without energy minimization. A new program called ANNEAL-RING carries out simulated annealing by computation of the exact new positions of three or more atoms and then application of the Metropolis Monte Carlo accept-reject criterion [exp(-ΔE/RT)] with cooling. Cyclononane, cyclodecane, cycloundecane and cycloheptadecane were studied.

Intramolecular Aldol Condensation Applied to D-Glucose-derived δ-Ketoaldehydes : Access to Enantiomerically Pure Six-membered Carbocycles

Kin-ichi Tadano,\* Satoshi Kanazawa, Ken-ichi Takao, and Seiichiro Ogawa Department of Applied Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan

Highly functionalized six-membered carbocycles, represented by 1 and 2, were stereoselectively synthesized. For the key carbocyclization, base-catalyzed intramolecular aldol condensation applied to a D-glucose-derived δ-ketoaldehyde was utilized.

### REDUCTION OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES USING SAMARIUM DIIODIDE-ACID SYSTEM

Tetrahedron, 1992, 48, 4301

Yasuko Kamochi<sup>\*</sup> and Tadahiro Kudo Daiichi College of Pharmaceutical Sciences, 22-1 Tamagawa-cho, Minami-ku, Fukuoka 815, Japan

R-COOH SmI<sub>2</sub> in THF/R'OH/85%H<sub>3</sub>PO<sub>4</sub> R-CH<sub>2</sub>OH

R=Aryl: yield 91-96%

 $R-CONH_2 = \frac{SmI_2 \text{ in THF/R'OH/85\%H}_3PO_4}{RT/Ar, 3-220sec} R-CHO$ 

R=Aryl: yield >97 % R=Alkyl: yield 6-14 %

SmI<sub>2</sub> in THF/R'OH/50%KOH or 85%H<sub>3</sub>PO<sub>4</sub> 50%KOH; k=Ary1: yield 58% R=CH<sub>2</sub>NH<sub>2</sub> 85%H<sub>3</sub>PO<sub>4</sub>; R=Ary1: yield 52-99% R=PhCH<sub>2</sub>: yield 52-99% R=PhCH<sub>2</sub>: yield 48%

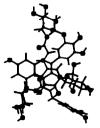
R=PhCH<sub>2</sub>: yield 48%

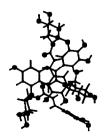
Tetrahedron, 1992, 48, 4313

#### Intramolecular Stacking Conformation of Gentiodelphin, a Diacylated Anthocyanin from Gentiana Makinoi

Kumi Yoshida\*, Tadao Kondo+\* and Toshio Goto++ School of Life Studies, Sugiyama Jogakuen University, Hoshigaoka, Chikusa, Nagoya 464, Japan +\*Chemical Instrument Center, and ++Laboratory of Organic Chemistry, Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464-01, Japan

Intramolecular stacking conformation of gentiodelphin in acidic methanol was studied by <sup>1</sup>H NMR and computer assisted molecular modeling. One of two caffeic acid residue, C2, was stacked to the anthocyanidin nucleus.





#### STEREOSELECTIVE SYNTHESIS OF GIROLLINE

Alain AHOND\*, Ali AL MOURABIT, Manuel BEDOYA ZURITA, Richard HENG, Raquel MARQUES BRAGA, Christiane POUPAT\* and Pierre POTIER

Institut de Chimie des Substances Naturelles, C.N.R.S.,

91198 Gif/Yvette Cedex, France

The stereoselective synthesis of girolline has been achieved from 4-carboxaldehyde imidazole or D(-) arabinose.

Tetrahedron, 1992, 48, 4347

## MACROCYCLIC POLYETHER TETRALACTAMS I: SYNTHESIS AND CYCLIZATION STUDIES

M. C. Duriez, T. Pigot, C. Picard, L. Cazaux and P. Tisnès Laboratoire de synthèse et physicochimie organique, Université Paul Sabatier, 31062 TOULOUSE (FRANCE)

A versatile approach to macrocyclic tetralactams with two dimethyleneoxy moieties is reported. The key step is the cyclization of a bis-secondary amine with a diamide diacid activated by the thiazolidine-2-thione group.

Tetrahedron, 1992, 48, 4359

# MACROCYCLIC POLYETHER TETRALACTAMS II: A STUDY OF THEIR BINDING PROPERTIES WITH ALKALINE-EARTH CATIONS

Laboratoire de synthèse et physicochimie organique, Université Paul Sabatier, 31062 TOULOUSE (FRANCE)

Binding properties (picrate extraction and stability constants) of title macrocycles were assessed. A high selectivity of these tetralactams for Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> with respect to Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Zn<sup>2+</sup> was observed..

$$n = 0, 1$$
  
 $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ 

### AN EFFICIENT STEREOCONTROLLED SYNTHESIS OF 12(R)-HETE

AND 12(S)-HETE.

#### Denis Chemin, Sylvie Gueugnot and Gérard Linstrumelle

UR 402 du C.N.R.S., Ecole Normale Supérieure, Laboratoire de chimie, 24 rue Lhomond, 75231 Paris Cedex 05-France.

HO Co<sub>2</sub>Me 
$$\frac{1) Pd^0/Cu^1}{2) Zn}$$
 HO COOMe COOMe

Tetrahedron, 1992, 48, 4379

## ELECTRONIC CONTROL OF STEREOSELECTIVITY IN

THE CHLORINATION OF 1,4-DIHYDRO-1,4-IMINO-

NAPHTHALENES (7-AZABENZONORBORNADIENES) WITH N-CHLOROSUCCINIMIDE

John W. Davies, Michael W. Durrant, Matthew P. Walker and John R. Malpass Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

AB=CH2-CH2, CH=CH, benzo-

X=H, Cl, F, Me, OMe

Y=H, Cl, F, Mc, YY=benzo

(kinetic control)

(thermodynamic control)

Tetrahedron, 1992, 48, 4399

## SYNTHESIS, X-RAY STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF A NEW CROWN ETHER WITH A CIS AZO UNIT IN THE MACROCYCLE

Jan F. Biernat, Elżbieta Luboch and Andrzej Cygan, Technical University of Gdańsk, Poland; Yurij A. Simonov, Aleksandr A. Dvorkin, Academy of Sciences of Mołdova, Kishiniev, 277028 Republic of Mołdova; Elżbieta Muszalska and Renata Bilewicz, University of Warsaw, Poland.

$$\bigcirc \bigcap_{NO_2} \bigcap_{O} \bigcirc \bigcap_{N=N} \bigcap_{O} \bigcap_{N=N} \bigcap_{N=N} \bigcap_{O} \bigcap_{N=N} \bigcap_{N=$$

# SYNTHETIC EXPLOITATION OF THE RING-OPENING OF 3.4-DINITROTHIOPHENE. ACCESS TO

1,4-DISUBSTITUTED 2,3-DINITRO-1,3-BUTADIENES AND 2,3-BUTANEDIONE DIOXIMES
C. Dell'Erba, A. Mele, M. Novi,\* G. Petrillo and P. Stagnaro

$$O_2N$$
 $O_2N$ 
 $O_2N$ 

Tetrahedron, 1992, 48, 4419

SILICON-MEDIATED ISOQUINOLINE SYNTHESIS: PREPARATION AND STEREOCHEMICAL CHARACTERIZATION OF 4-HYDROXY-3-PHENYLISOQUINOLINES.

Dolores Badía, Esther Domínguez and Imanol Tellitu

Departamento de Química Orgánica, Facultad de Ciencias, Universidad del País Vasco. P.O. Box 644-48080 Bilbao (Spain).

The silicon-mediated synthesis of 4-hydroxy-6,7-dimethoxy-3-phenylisoquinoline derivatives is reported. The described procedure implies synthetically useful yields and a high degree of stereoselectivity.

Tetrahedron, 1992, 48, 4431

### Reduction of DDHQ and TCC Esters by NaBH<sub>4</sub>-Its Specificity in the Presence of Alkyl/Aryl Esters

Tirumalai R. Kasturi \* and Palle V.P. Pragnacharyulu Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, INDIA.

Preparation of different DDHQ and TCC esters 3, 7 and their reduction by NaBH<sub>4</sub> to corresponding alcohols in good yields are described. The observed facile reduction has been rationalised.

R,R'=Carbonyl Unit,CH3 or H.

## DIASTEREOFACIAL SELECTIVITY IN THE ALDOL REACTIONS OF CHIRAL α-METHYL ALDEHYDES: A COMPUTER MODELLING APPROACH.

Cesare Gennari\*. Siegfried Vieth. Angiolina Comotti. Anna Vulpetti. Jonathan M. Goodman. and Ian Paterson

- (a) Dipartimento di Chimica Organica e Industriale, Università di Milano, Centro C.N.R. Sost.Org.Nat., 20133 Milano, Italy
- (b) University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

A transition state modelling-force field approach was used to investigate  $\pi$ -facial selectivity in Z-enol borinate aldol additions to chiral  $\alpha$ -methyl aldehydes.

Tetrahedron, 1992, 48, 4459

## BICYCLO[3.3.1] NONANE APPROACH TO TRIQUINANES. FORMAL SYNTHESIS OF $(+/-)\Delta^{9(12)}$ CAPNELLENE AND $(+/-)\Delta^{9(12)}$ CAPNELLENE-8 $\beta-10\alpha-$ DIOL

Augusto Gambacorta, \* Giovanni Fabrizi, Paolo Bovicelli
Centro CNR di Studio per la Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica,
Università "La Sapienza",00185 Roma, Italy.

Ketone 4, a known key intermediate in the synthesis of the capnellenes 3a,b, has been prepared, in a model study, by skeletal rearrangement of the bicyclo[3.3.1]nonanic precursor 6. The synthesis of 6 is described.

Tetrahedron, 1992, 48, 4465

STEREOSELECTIVE SYNTHESIS OF (S)-13-HYDROXY
OCTADECA-(9Z,11E)-DI- AND (9Z,11E,15Z)-TRIENOIC ACIDS: SELFDEFENSIVE SUBSTANCES
AGAINST RICE BLAST DISEASE

J S Yadav<sup>\*</sup>, P K Deshpande and G V M Sharma Organic Chemistry Division-I, Indian Institute of Chemical Technology Hyderabad 500007, India

Synthesis of 1 and 2 is described.