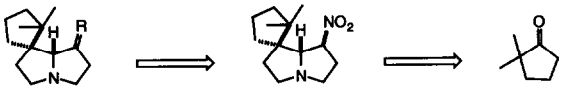
GRAPHICAL ABSTRACTS

Tetrahedron, **1994**, *50*, 6129

SYNTHESIS OF PYRROLIZIDINE OXIMES 222 AND 236: NOVEL ALKALOIDS OF A DENDROBATID POISON FROG

Kira D. Hutchinson *[a], James V. Silverton [b] and John W. Daly [a]; [a]National Institute of Diabetes and Digestive and Kidney Diseases and the [b]National Heart, Lung, and Blood Institute, National Institutes of Health, Bethesda, Maryland 20892.

The structures of two novel spiropentanopyrrolizidine oxime alkaloids **1** and **2** have been confirmed by synthesis via nitropolyzonamine (**4**) starting from 2,2-dimethylcyclopentanone.



1 R = NOH
2 R = $NOCH_3$

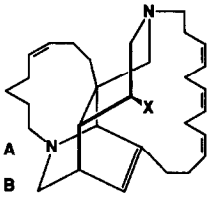
4

Tetrahedron, **1994**, *50*, 6137

INGAMINES A AND B, NEW CYTOTOXIC ALKALOIDS FROM THE MARINE SPONGE *XESTOSPONGIA INGENS*

Fangming Kong and Raymond J. Andersen*, Departments of Chemistry and Oceanography, University of British Columbia, Vancouver, BC, CANADA V6T 1Z4
Theresa M. Allen, Department of Pharmacology, University of Alberta, Edmonton, Alberta, CANADA T6G 2H7

Ingamines A (**2**) and B (**3**), two novel cytotoxic alkaloids, have been isolated from the marine sponge *Xestospongia ingens* collected in Papua New Guinea. The structures of **2** and **3** have been elucidated via extensive spectroscopic analysis.



2 X= OH **Ingamine A**

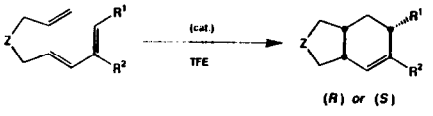
3 X=H **Ingamine B**

Tetrahedron, **1994**, *50*, 6145

On the Asymmetric Rh(I) Catalyzed [4+2] Cycloisomerization Reaction. Electronic and Torsional Ligand Control of Absolute Stereoselection.

Lydia McKinstry and Tom Livinghouse,* Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717-0340, USA.

The use of bisphosphine ligands related to DIOP as chiral modifiers in the Rh(I) catalyzed [4+2] cycloisomerization reaction results in moderate to good levels of enantioselection. The mode of absolute stereoinduction is subject to electronic and torsional modification of the chelating ligand.



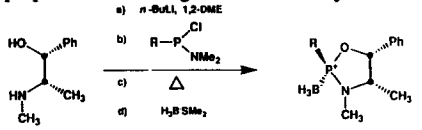
(*R*) or (*S*)

Tetrahedron, **1994**, *50*, 6155

A Flexible, Highly Efficient Method for the Preparation of Homochiral Oxazaphospholidine-boranes

Susan Kult Sheehan, Meiqun Jiang, Lydia McKinstry, Tom Livinghouse* and Donna Garton, Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, USA.

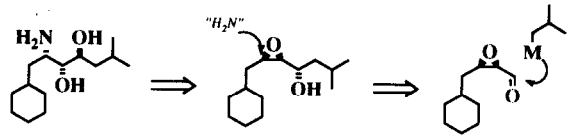
An efficient and operationally simple procedure for the synthesis of 2-substituted 3,4-dimethyl-5-phenyloxazaphospholidine derivatives has been developed. This new method permits the large scale preparation of a range of electronically and sterically differentiated homochiral monophosphine precursors.



Tetrahedron, **1994**, *50*, 6163

A Stereoselective Synthesis of the Dihydroxyethylene Dipeptide Isostere, A-82768

Damian J. Krysan,* Anthony R. Haight, Jerome A. Menzia, and Noel Welch
Process Research, Chemical and Agrigultural Products Division, D54P, R8 Abbott Laboratories, North Chicago, IL 60064



1 2 3

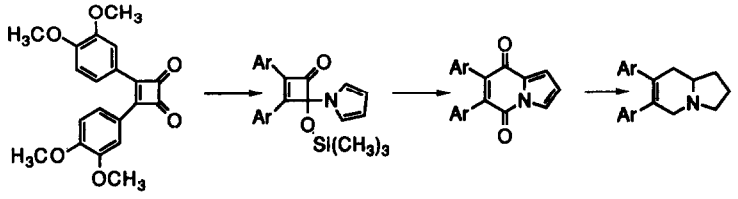
A concise, stereoselective synthesis of the dihydroxyethylene dipeptide isotere A-82768 (**1**) based upon the diastereoselective addition of *i*-BuMgCl to a cis-α,β-epoxy-aldehyde is described.

Tetrahedron, **1994**, *50*, 6173

SYNTHESIS OF (±)-SEPTICINE

Yerxa, B. R.; Yang, K.; Moore, H. W., Department of Chemistry, University of California, Irvine, CA 92717

(±)-Septicine was synthesized in 8 steps from dimethyl squarate in 27% overall yield. The key step is the ring expansion of a 4-(1-pyrrolo)cyclobutenone to the corresponding indolizinedione.

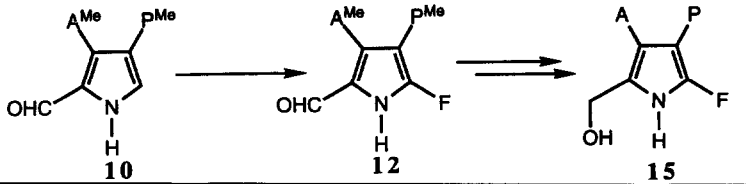


Tetrahedron, **1994**, *50*, 6181

Synthesis of the 2-Fluoro-11-hydroxy Analog of Porphobilinogen, a New Suicide Inhibitor of the Enzyme Porphobilinogen Deaminase.

Jianji Wang and A. Ian Scott*
Center for Biological NMR, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255.

The 2-fluoro-11-hydroxy analog of porphobilinogen (PBG) **15** is synthesized using xenon difluoride as the fluorinating reagent. It is found that **15** is a new suicide inhibitor of the enzyme porphobilinogen deaminase (PBGD).

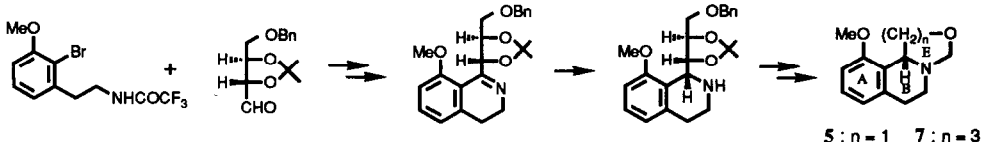


10 **12** **15**

Tetrahedron, **1994**, *50*, 6193

Synthetic Studies on Quinocarcin and Its Related Compounds. 1. Synthesis of Enantiomeric Pairs of the ABE Ring Systems of Quinocarcin

Shoichi Saito, Osamu Tamura, Yuko Kobayashi, Fuyuhiko Matsuda, Tadashi Katoh, Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan



14 **I** **25** **26**

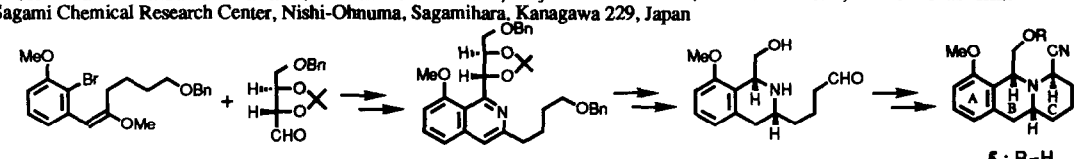
5 : n = 1 **7** : n = 3
6 : n = 2

The title compounds (**5**, *ent*-**5**, **6**, *ent*-**6**, **7**, and *ent*-**7**) were synthesized by featuring novel diastereoselective reduction of 3,4-dihydroisoquinoline derivatives **25** and *ent*-**25**, wherein each enantiomer of threose derivative is employed as a chiral auxiliary.

Synthetic Studies on Quinocarcin and Its Related Compounds. 2. Synthesis of an Enantiomeric Pair of the ABC Ring System of Quinocarcin

Tetrahedron, **1994**, *50*, 6209

Shoichi Saito, Katsunori Tanaka, Kazuhiko Nakatani, Fuyuhiko Matsuda, Tadashi Katoh, Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan



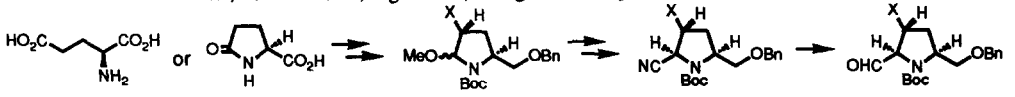
21 11 29 6 5 : R=H 39 : R=Ac

The title compounds (**5**, *ent*-**5**, **39**, and *ent*-**39**) were synthesized by featuring novel diastereoselective reduction of 1,3-disubstituted isoquinoline derivatives **29** and *ent*-**29** and intramolecular *N,O*-acetal formation of amino aldehydes **6** and *ent*-**6**.

Synthetic Studies on Quinocarcin and Its Related Compounds. 3. Synthesis of 5-Substituted- and 3,5-Disubstituted-2-formyl-pyrrolidine Derivatives, the Key D-Ring Fragments of Enantiomeric Pairs of Quinocarcin and 10-Decarboxyquinocarcin

Tetrahedron, **1994**, *50*, 6221

Tadashi Katoh, Yuriko Nagata, Yuko Kobayashi, Katsuko Arai, Junko Minami, Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan



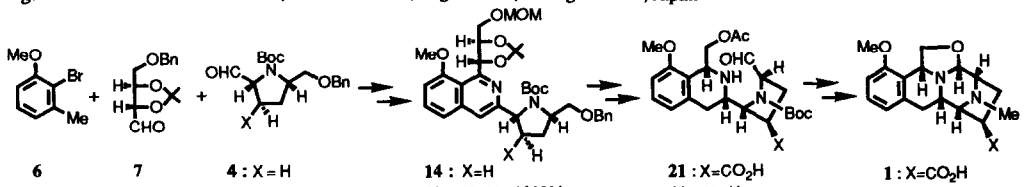
13 14 21 : X=H 43 : X=CH_2OMOM 27 : X=H 45 : X=CH_2OMOM 29 : X=H 47 : X=CH_2OMOM

The title compounds (**29**, *ent*-**29**, **47**, and *ent*-**47**) were prepared by employing each enantiomer of glutamic acid (**13**) and pyroglutamic acid (**14**) as chiral starting materials.

Synthetic Studies on Quinocarcin and Its Related Compounds. 4. Total Synthesis of Enantiomeric Pairs of Quinocarcin and 10-Decarboxyquinocarcin

Tetrahedron, **1994**, *50*, 6239

Tadashi Katoh, Masayuki Kirihara, Yuriko Nagata, Yuko Kobayashi, Katsuko Arai, Junko Minami, Shiro Terashima*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan



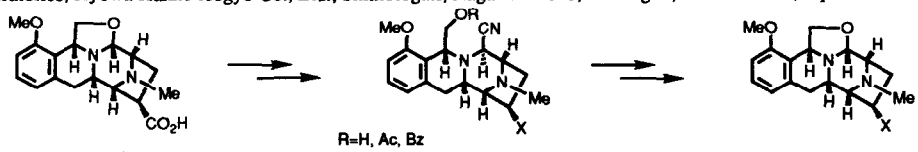
6 7 4 : X = H 5 : X=CH_2OMOM 14 : X=H 33 : X=CH_2OMOM 21 : X=CO_2H 41 : X=H 1 : X=CO_2H 2 : X=H

The title synthesis was accomplished by featuring diastereoselective reduction of isoquinolines (**14**, *ent*-**14**, **33**, and *ent*-**33**).

Synthetic Studies on Quinocarcin and Its Related Compounds. 5. Synthesis and Antitumor Activity of Various Structural Types of Quinocarcin Congeners

Tetrahedron, **1994**, *50*, 6259

Tadashi Katoh,[a] Masayuki Kirihara,[a] Toshiharu Yoshino,[a] Osamu Tamura,[a] Fumiaki Ikeuchi,[a] Kazuhiko Nakatani,[a] Fuyuhiko Matsuda,[a] Kaoru Yamada,[a] Katsushige Gomi,[b] Tadashi Ashizawa,[b] Shiro Terashima[a]*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan[a] and Pharmaceutical Research Laboratories, Kyowa Hakko Kogyo Co., Ltd., Shimotogari, Nagaizumi-cho, Sunto-gun, Shizuoka 411, Japan[b]

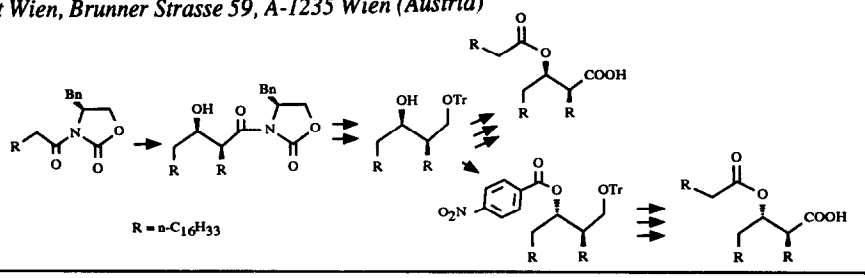


quinocarcin R=H, Ac, Bz X=H, CH_2OH, CH_2OAc, CH_2OBz, CHO, CH_2F X=H, CH_2OH

Synthesis of the 4 possible stereoisomers of 3-O-stearoyl C_{36}-corynomycolic acid and derived lipopeptides.

Tetrahedron, **1994**, *50*, 6271

Jacques Eustache* **and Alfred Grob**
Sandoz Forschungsinstitut Wien, Brunner Strasse 59, A-1235 Wien (Austria)

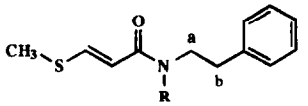


SYNTHESIS AND CORRECTED STRUCTURES OF SULPHUR-CONTAINING AMIDES FROM GLYCOSMIS SPECIES: SINHARINES, PENIMIDES, AND ILLUKUMBINS

Tetrahedron, **1994**, *50*, 6279

Sabine Hinterberger [a], **Otmar Hofer** [a*], **and Harald Greger** [b]
[a] Institute of Organic Chemistry, University of Vienna, Währingerstraße 38, A-1090 Wien, Austria. [b] Comparative Phytochemistry Department, Institute of Botany, University of Vienna, Rennweg 14, A-1030 Wien, Austria.

The structures of 5 amides and 2 imides from *Glycosmis* species were revised on the basis of synthesis and NOE measurements. The compounds represent derivatives of 3-(methylthio)-propenoic acid and not cinnamides as described previously. Synthesis: H-C≡C-COOH + MeSH ⟶ Me-S-CH=CH-COOH, followed by reaction with the proper amines. All products can be derived from 3-(methylthio)-propenoic acid phenthylamide with modifications at positions a and b (see formula).

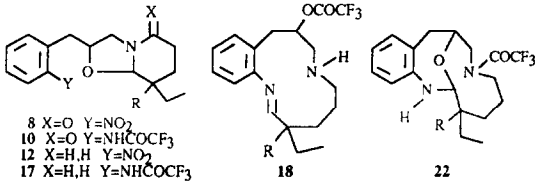


SYNTHESIS AND REACTIVITY OF OXAZOLOPIPERIDINES AND OXAZOLOPIPERIDONES

Tetrahedron, **1994**, *50*, 6287

J.-P.Alazard, C. Terrier, A. Mary and C.Thal
Institut de Chimie des Substances Naturelles,CNRS,91198 Gif / Yvette Cedex, France

The reaction of compouds **8**, **10** and **12** with the system TMSOTf (or TBDMSOTf)-TMSCN -$ZnBr_2$ shows a reversible ring opening of the heterocycle leading to the thermodynamical products. In the case of **17**, the participation of the amide group in various conditions leads to the imine **18** and aminoether **22**.

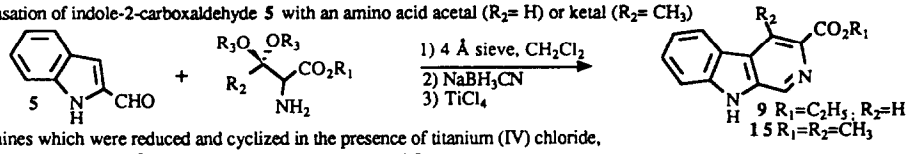


A NEW EFFICIENT SYNTHESIS OF ETHYL β- CARBOLINE-3-CARBOXYLATE (β-CCE) AND METHYL 4-METHYL- β-CARBOLINE-3-CARBOXYLATE (4-METHYL-β-CCM) STARTING FROM INDOLE-2-CARBOXALDEHYDE

Tetrahedron, **1994**, *50*, 6299

Mouloud Dekhane and Robert H. Dodd*
Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France

Condensation of indole-2-carboxaldehyde **5** with an amino acid acetal (R_2= H) or ketal (R_2= CH_3)



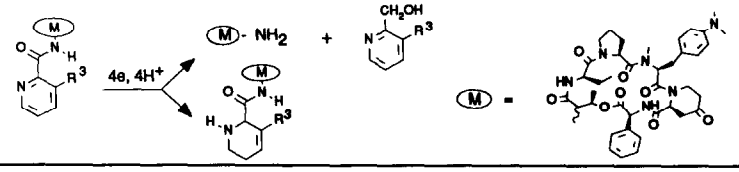
gave imines which were reduced and cyclized in the presence of titanium (IV) chloride, affording high yields of β-carboline-3-carboxylates **9** and **15**.

ELECTROCHEMICAL REDUCTION OF PRISTINAMYCIN I_A AND RELATED STREPTOGRAMINS IN AQUEOUS ACIDIC MEDIUM.

Tetrahedron, **1994**, *50*, 6307

M. Largeron[#], M. Vuilhorgne[o], I. Le Potier[#], N. Auzeil[#], E. Bacqué[o], J.M. Paris[o] and M.B. Fleury[#*].
[#]*Laboratoire de Chimie Analytique, URA CNRS 1310, Faculté de pharmacie, 4 avenue de l'Observatoire, 75270 Paris cedex 06, France.*
[o]*Rhone-Poulenc-Rorer, Centre de Recherches de Vitry-Alfortville, 13 quai Jules Guesde, 94403 Vitry sur Seine cedex, France.*

The cathodic electrolysis of pristinamycin I_A (R^3 = OH) proceeds by two major competitive routes: splitting of the pyridyl carboxamide C-N bond and reduction of the pyridine nucleus.

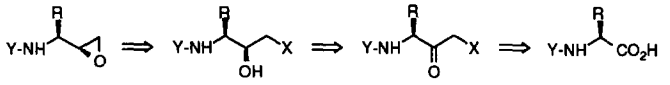


STEREOCONTROLLED SYNTHESIS OF *ERYTHRO* N-PROTECTED α-AMINO EPOXIDES AND PEPTIDYL EPOXIDES.

Tetrahedron, **1994**, *50*, 6333

Amnon Albeck* and Rachel Persky
Department of Chemistry, Bar Ilan University, Ramat Gan 52900, Israel

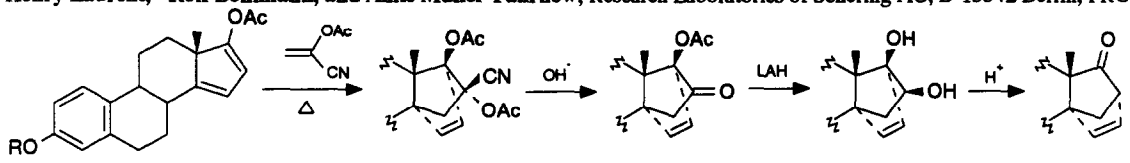
Stereoselective synthesis of *erythro* α-amino epoxides and *erythro* peptidyl epoxides, based on the sequence: peptide (amino acid) --> peptidyl haloketone --> peptidyl halohydrin --> peptidyl epoxide is described.



CYCLOADDITION MEDIATED SYNTHESIS AND REARRANGEMENT OF 16-FUNCTIONALISED 14α,17α-ETHENO-19-NORSTEROIDS

Tetrahedron, **1994**, *50*, 6347

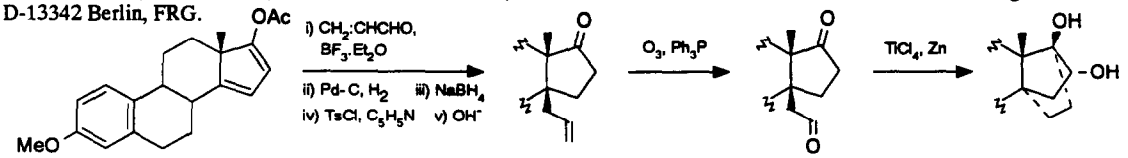
James R. Bull* and Claudia Grundler, University of Cape Town, Rondebosch 7700, RSA.
Henry Laurent,* Rolf Bohlmann, and Anke Müller-Fahrnow, Research Laboratories of Schering AG, D-13342 Berlin, FRG.



CYCLOADDITION-FRAGMENTATION ROUTE TO 14β-ALLYLESTRONE AND THE DERIVED 14α,17α-ETHANO ANALOGUE OF ESTRIOL

Tetrahedron, **1994**, *50*, 6363

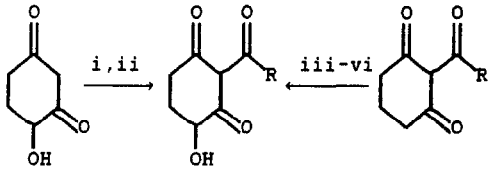
James R. Bull* and Pia G. Mountford University of Cape Town, Rondebosch 7700, RSA
Gerald Kirsch, Günter Neef,* Anke Müller-Fahrnow, and Rudolf Wiechert Research Laboratories of Schering AG, D-13342 Berlin, FRG.



SYNTHESIS OF 2-ACYL-4-HYDROXYCYCLOHEXANE-1,3-DIONES, KAIROMONES AND DEFENSIVE COMPOUNDS OF SOME INSECTS

Tetrahedron, **1994**, *50*, 6377

[a]Vladimir G.Zaitsev,[b]Genrich I.Polozov and [a]Fyodor A.Lakhvich* [a]Institute of Bioorganic Chemistry, Acad. of Sci. of Belarus', Zhodinskaja 5/2, Minsk 220141:/b/Byelorussian State University, Leningradskaja 14, Minsk 220080, (BELARUS')



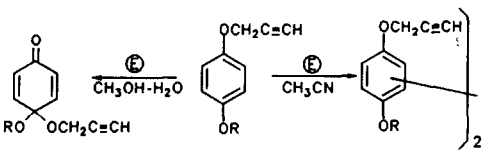
i:RCOCl,Py,THF;ii:acetone cyanhydrin, MeCN,r.t.,2h;iii:$NH_2OH.HCl$,NaOH; iv:LTA,AcOH; v :Ni/Ra,$AlCl_3$,$MeOH_{aq}$; vi:NaOH,then HCl; R=$C_{11}H_{23}$;$C_{15}H_{31}$; $C_{17}H_{35}$;/Z/-heptadec-8-enyl; /Z,Z/-heptadec-8,11-dienyl

Anodic Oxidation of Aryl Propargyl and Aryl Allyl Ethers at a Platinum Electrode

Tetrahedron, **1994**, *50*, 6387

S. Dhanalekshmi, K.K. Balasubramanian* and C.S. Venkatachalam*
Department of Chemistry, Indian Institute Of Technology, Madras 600 036, INDIA.

Oxidation reactions of aromatic 3,3-sigmatropic systems have been investigated under different conditions.

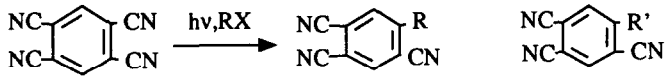


SCOPE AND MECHANISM OF THE ELECTRON TRANSFER PHOTOINDUCED ALKYLATION OF AN AROMATIC NITRILE

Tetrahedron, **1994**, *50*, 6401

Maurizio Fagnoni, Mariella Mella, and Angelo Albini,
Dip.Chimica Organica, Università, v.Taramelli 10, 27100 Pavia, Italy.

1,2,4,5-Tetracyanobenzene is alkylated by donors R-X (R=cyclopropylmethyl or 5-hexenyl) through a photoinduced SET process. The effect of structure and medium on the alkylation quantum yield (both with and without radical rearrangement) support a free radical process with silanes and stannnanes, and a S_N2-like process for dioxolanes.

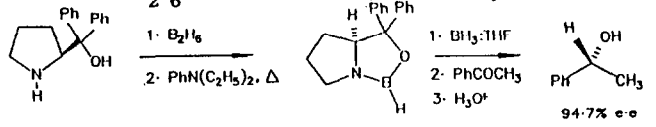


CONVENIENT PROCEDURES FOR THE ASYMMETRIC REDUCTIONS UTILIZING α,α-DIPHENYLPYRROLIDINEMETHANOL AND BORANE COMPLEXES GENERATED USING THE $I_2/NaBH_4$ SYSTEM

Tetrahedron, **1994**, *50*, 6411

Mariappan Periasamy*, J.V.Bhaskar Kanth and A.S.Bhanu Prasad, School of Chemistry, University of Hyderabad, Central University P.O, Hyderabad-500134, India.

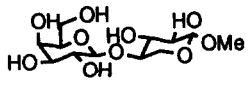
Formation of the oxazaborolidine *in situ* in the reaction of α,α-diphenylpyrrolidine-methanol and B_2H_6 is facilitated by N,N-diethylaniline.



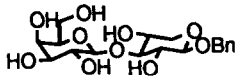
Tetrahedron, **1994**, *50*, 6417

CONFORMATIONAL STUDIES ON ß-GALACTOPYRANOSYL-(1->3) AND (1->4)-XYLOPYRANOSIDES BY NMR, MOLECULAR MECHANICS, MOLECULAR DYNAMICS, AND SEMIEMPIRICAL CALCULATIONS. Juan Luis Asensio, Rosa López, Alfonso Fernández-Mayoralas, and Jesús Jiménez-Barbero*, Grupo de Carbohidratos, Departamento de Química Orgánica Biológica, Instituto de Química Orgánica, (C.S.I.C)., Juan de la Cierva 3, 28006 Madrid (Spain)

The conformation of galactosyl xyloses **1** and **2** has been studied in water solution by NMR spectroscopy, assisted by molecular mechanics, molecular dynamics, and semiempirical methods.



1



2

Tetrahedron, **1994**, *50*, 6433

NUCLEOPHILIC 1,2-ADDITION OF BROMINE TO ELECTRON DEFICIENT DOUBLE BONDS BY PERBROMIDE REAGENTS

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Perbromide compounds prove to be excellent reagents for achieving nucleophilic 1,2 addition of bromine to the double bond of α,ß-unsaturated compounds. This reaction proved to be highly selective in eudesmanolides with an electronegative substituent at C-1.In others subtrates with additional non-conjugated double bonds, competitive electrophilic addition of bromine can be minimized in the presence of alkenes with electron-rich double bonds.