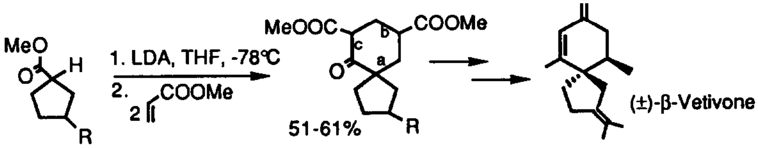
GRAPHICAL ABSTRACTS

Tetrahedron, **1992**, *48*, 4677

A ONE-FLASK MULTICOMPONENT ANNULATION REACTION AS THE KEY STEP IN A TOTAL SYNTHESIS OF SPIROBICYCLIC (±)-β-VETIVONE

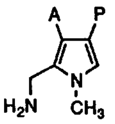
Gary H. Posner* and Ellen M. Shulman-Roskes
Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218, USA



Tetrahedron, **1992**, *48*, 4687

On the Mechanism of Porphobilinogen Deaminase. Design, Synthesis, and Enzymatic Reactions of Novel Porphobilinogen Analogs. Clotilde Pichon, Karen R. Clemens, Alan R. Jacobson*, and A. Ian Scott*. Center for Biological NMR, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255.

Three new derivatives of PBG 12, 29 and 36 were synthesized. Their reactivities with PBG deaminase were examined and mechanistic hypotheses were suggested to explain the biological results.



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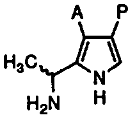

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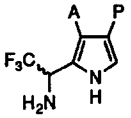


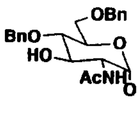
(36)

Tetrahedron, **1992**, *48*, 4713

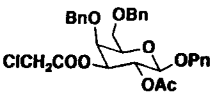
N-PENTENYL GLYCOSIDES IN THE EFFICIENT ASSEMBLY OF THE BLOOD GROUP SUBSTANCE B TETRASACCHARIDE

Uko E. Udodong, C. Srinivas Rao, and Bert Fraser-Reid
Department of Chemistry, Duke University, Durham, NC 27706

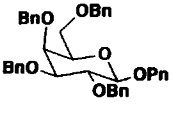
Blood group substance **3** has been assembled in six chemical operations from **6b** and the n-pentenyl glycosides **17b**, **9b** and **19b**, the coupling steps proceeding in 68, 82 and 91% yields.



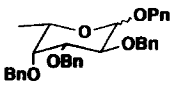
6b



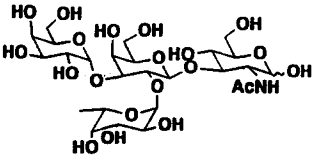
17b



9b



19b

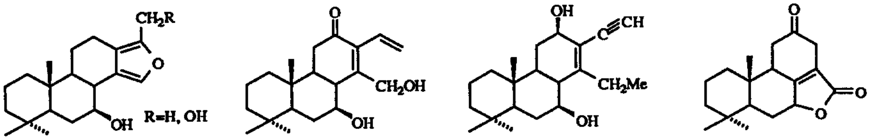


3 (blood group substance B)

Tetrahedron, **1992**, *48*, 4725

UNUSUAL CASSANES FROM A *CHAMAECRISTA* SPECIES

B. Barba, J. G. Díaz, V. L. Goedken, W. Herz, Dept. of Chemistry, Florida State University, Tallahassee, FL 32306, USA; X. A. Dominguez, Dpto. de Química ITESM, Suc. Correos "J", Monterrey, N. L. 64689, México Isolation of the four cassanes and one *bis*-norcassane shown below from *Chamaecrista foliosa* var. *texana* is reported.

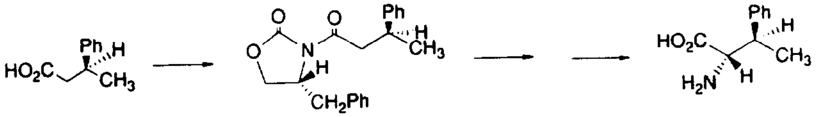


Tetrahedron, **1992**, *48*, 4733

ASYMMETRIC SYNTHESIS OF UNUSUAL AMINO ACIDS: AN EFFICIENT SYNTHESIS OF OPTICALLY PURE ISOMERS OF β-METHYLPHENYLALANINE

Ramalinga Dharanipragada, Katia Van Hulle, Anne Bannister, Soaring Bear, Lisa Kennedy and Victor J. Hruby,
Department of Chemistry, University of Arizona, Tucson, Arizona 85721

The asymmetric synthesis of (2S,3R)-(2R,3S)-, (2S,3S)-, and (2R,3R)-β-methylphenylalanines are reported. The isomer obtained is determined by the β-phenylbutyric acid and chiral axiliary chosen.

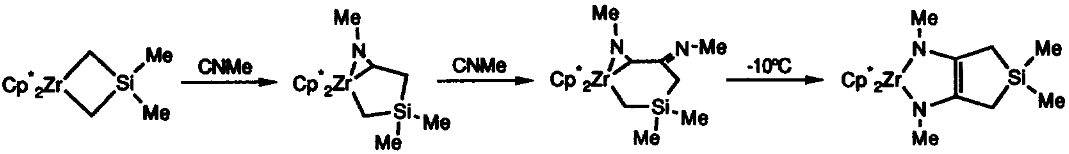


Tetrahedron, **1992**, *48*, 4749

LOW-TEMPERATURE NMR STUDY OF THE REDUCTIVE C,C-COUPLING OF CNMe BY $(C_5Me_5)_2Zr(CH_2SiMe_2CH_2)$ AND STRUCTURAL CHARACTERIZATION OF $(C_5Me_5)_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$

Frederic J. Berg and Jeffrey L. Petersen,* Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045

Low-temperature NMR measurements indicate that the reductive coupling of CNMe by $Cp^*{}_2Zr(CH_2SiMe_2CH_2)$ involves the participation of two η^2-iminoacyl intermediates and leads to the formation of $(C_5Me_5)_2Zr(N(Me)C(CH_2SiMe_2CH_2)=CN(Me))$.

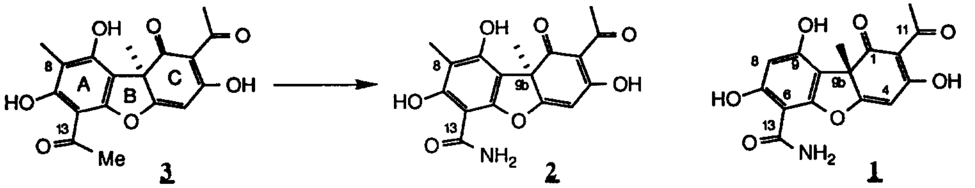


Tetrahedron, **1992**, *48*, 4757

Synthesis of (+)-8-Methyl Cercosporamide: Stereochemical Correlation of Natural (-)-Cercosporamide with (+)-Usnic Acid

Alan B. Cooper, James Wang, Anil K. Saksena, Viyyoor Girijavallabhan, Ashit K. Ganguly, and Tze-Ming Chan
Schering-Plough Research, Bloomfield, New Jersey 07003, U.S.A. and Andrew T. McPhail Paul M. Gross Chemical Laboratories, Duke University, Durham, N.C. 27706, U.S.A.

Synthesis of (+)-8-methyl cercosporamide from (+)-usnic acid is described and the absolute configuration of cercosporamide established as C-9b-(-)-(s).



3 (+)-Usnic Acid

2 (+)-8-Me-Cercosporamide

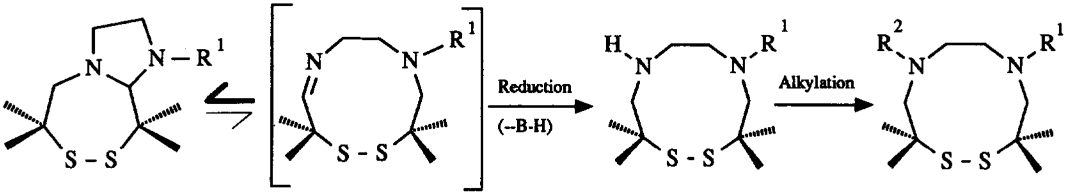
1 (-)-Cercosporamide

Tetrahedron, **1992**, *48*, 4767

BOROHYDRIDE REDUCTION OF IMIDAZOLIDINO[1,2-D]DITHIADIAZEPINES

Nicholas Bodor, Erno Koltai, and Laszlo Prokai; Center for Drug Discovery,
College of Pharmacy, Box 100497, JHMHC, University of Florida, Gainesville, FL 32610.

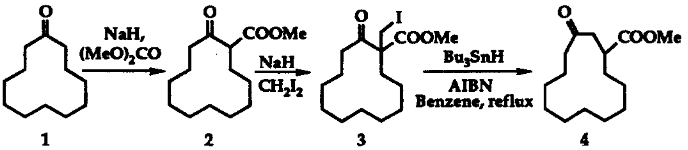
The title compounds are reduced with sodium borohydride in acidic media, or with borane. Alkylation is observed as a side reaction.



Tetrahedron, **1992**, *48*, 4773

HOMOLOGATION OF LARGE RINGS

Paul Dowd* and Soo-Chang Choi
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260



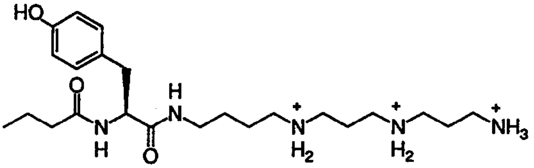
Free radical promoted one-carbon ring expansion of twelve-, fourteen- and fifteen-membered cyclic β-keto esters is described. The method is then extended to include a three-carbon ring expansion of cyclododecanone, the targets being (±)-muscone and nautrally occuring (R)-(−)muscone.

Tetrahedron, **1992**, *48*, 4793

Synthesis Of Novel And Photolabile Philanthotoxin Analogs: Glutamate Receptor Antagonists

S.-K. Choi, R. A. Goodnow, A. Kalivretenos, G. W. Chiles, S. Fushiya, K. Nakanishi*
Department of Chemistry, Columbia University, New York, N.Y. 10027

The syntheses of 27 philanthotoxins including photoaffinity labeled analogs are described.



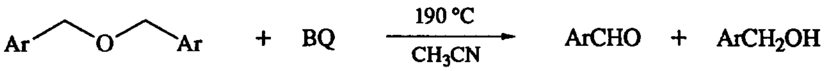
Philanthotoxin-433

Tetrahedron, **1992**, *48*, 4823

π-Acceptor Induced Reactions: Radicals vs. Ions in Thermally Induced Ether Cleavage Reactions

John H. Penn* and Dao-Li Deng
Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045

The reaction products and reaction rates of aryl ethers with a variety of quinones have been determined. A hydride transfer mechanism is used when the quinone is highly electron deficient. A radical mechanism is used when the quinone is less electron deficient.



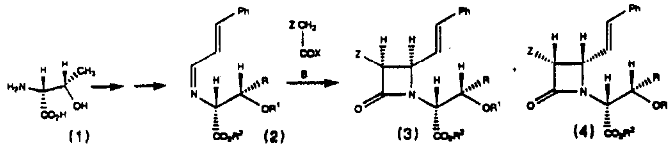
Tetrahedron, **1992**, *48*, 4831

STEREOREGULATED SYNTHESIS OF β-LACTAMS FROM SCHIFF BASES DERIVED FROM THREONINE ESTERS [1]

Ajay K. Bose*, Maghar S. Manhas, James M. van der Veen, Shamsher S. Bari and Dilip R. Wagle
Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030

A variety of optically active 3-substituted-2-azetidinones has been prepared by the annelation of Schiff bases (2) derived from cinnamaldehyde and D-threonine esters (1).
When R^1 = H, (3) : (4) = about 50:50; when R^1 = $SiPh_3$, (3) : (4) = about 95:5.

Z = N_3
= NHC(Me) = CHCOOMe

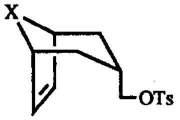


Tetrahedron, **1992**, *48*, 4845

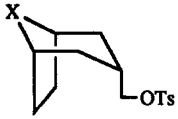
HIGH π-ROUTE REACTIVITY IN THE TROPENE SYSTEM. ABSENCE OF A NITROGEN ACCELERATION EFFECT.

Brown L. Murr,* Billy J. Parkhill, and Alex Nickon
Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218, U.S.A.

Compounds 4-6 have been prepared and their solvolyses studied. Both unsaturated tosylates gave only tricyclic products from alkene bond participation. The ratios are: $k_4/k_5 = 2.1 \times 10^5$; $k_6/k_5 = 16.6 \times 10^5$; $k_4/k_6 = 1/8$. This last ratio reveals that nitrogen does not enhance the π participation but diminishes it, probably inductively.



4 X = NCH_3
6 X = CH_2



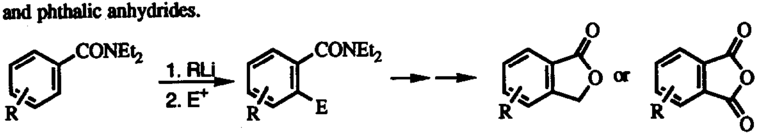
5 X = NCH_3
7 X = CH_2

Tetrahedron, **1992**, *48*, 4863

DIRECTED *ortho* METALATION OF N,N-DIETHYL BENZAMIDES. METHODOLOGY AND REGIOSPECIFIC SYNTHESIS OF USEFUL CONTIGUOUSLY TRI- AND TETRA-SUBSTITUTED OXYGENATED AROMATICS, PHTHALIDES AND PHTHALIC ANHYDRIDES

S.O. de Silva, J.N. Reed, R.J. Billedeau, X. Wang, D.J. Norris, and V. Snieckus*, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Simple *ortho*-substituted and contiguously 1,2,3- and 1,2,3,4-substituted N,N-diethyl benzamides are prepared by directed *ortho* metalation. Some of these benzamides are subsequently converted into pthalides and phthalic anhydrides.

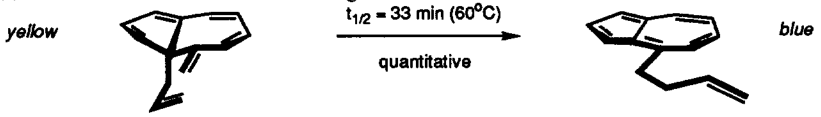


Tetrahedron, **1992**, *48*, 4879

Isomerization of Dihydroazulenes to Substituted Azulenes - Naked Eye Observation of a Novel Cope-Type Rearrangement.

Klaus Hafner*, Jens Hartung and Claudia Syren

Yellow bridgehead substituted dihydroazulenes 9 rearrange in a low activation enthalpy process to substituted azulenes. Activation parameters and limitations of this novel reaction are given.



9a

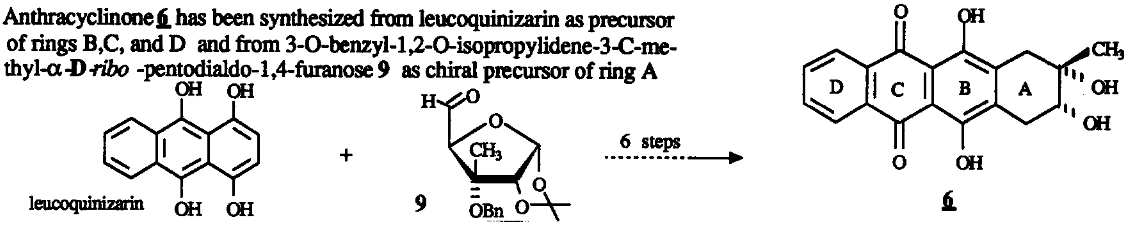
10a

Tetrahedron, **1992**, *48*, 4885

ANTHRACYCLINONES. SYNTHESIS OF A 9-METHYL ANTHRACYCLINONE FROM D-GLUCOSE

B. Deguin, E. Bertounesque, G. Gaudel, J.-C. Florent, and C. Monneret
Service de Chimie , URA 1387, Section de Biologie, Institut Curie, 26 rue d'Ulm, 75005 Paris, France

Anthracyclinone **6** has been synthesized from leucoquinizarin as precursor of rings B,C, and D and from 3-O-benzyl-1,2-O-isopropylidene-3-C-methyl-α-D-*ribo* -pentodialdo-1,4-furanose 9 as chiral precursor of ring A



leucoquinizarin

9

6

Tetrahedron, **1992**, *48*, 4893

CRYSTAL ENGINEERING OF CYTIDINE AND DEOXYCYTIDINE SULPHATE. I. PREPARATION AND UNUSUAL PROPERTIES.

M. D. Bratek-Wiewiórowska, M. Alejska, N. Malinowska, J. Sarzynska, M. Figlerowicz, E.Utzig[a], W. Zielenkiewicz[a], M. Jaskólski[b] and M. Wiewiórowski
Institute of Bioorganic Chemistry, Poznan and [a]Institute of Physical Chemistry, Warsaw, Polish Academy of Sciences; [b]Department of Chemistry, A. Mickiewicz University, Poznan, POLAND

$$\begin{tikzcd}
2\,\mathrm{dCydH^{+}.SO_4^{2-}\cdot 1/2\,CH_3OH} \arrow[dr, "30\ \mathrm{min}"] & & \\
& {} \arrow[r, "+\ 2\ \mathrm{NaCl}", "\mathrm{rt}"'] & 2(\mathrm{dCydH^{+}Cl^{-}}) + \mathrm{Na_2SO_4} \\
2\,\mathrm{dCydH^{+}\cdot SO_4^{2-}} \arrow[ur, "60\ \mathrm{min}"'] & &
\end{tikzcd}$$

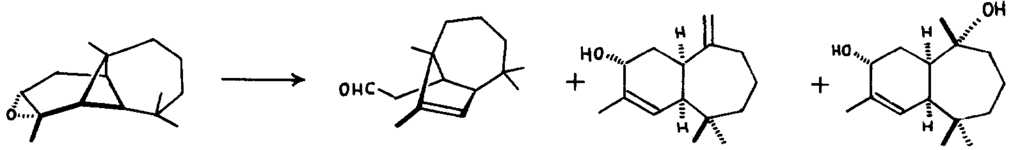
$$2\,\mathrm{CydH^{+}\cdot SO_4^{2-}} + 2\,\mathrm{NaCl} \xrightarrow{\mathrm{rt},\ 240\ \mathrm{min}} 2(\mathrm{CydH^{+}Cl^{-}}) + \mathrm{Na_2SO_4}$$

The unidirectional ion exchange reactions take place in **100 %** in ***crystalline phase only***, revealing the significance of information coded in crystal structures of nucleosides.

Tetrahedron, **1992**, *48*, 4905

STUDIES IN SESQUITERPENES-LX. REVERSION OF LONGIPINANE TO HIMACHALANE SYSTEM : REVISION OF STRUCTURE OF ISOCENTDAROL

Mayank H. Shastri and Sukh Dev*
Malti-Chem Research Centre, Nandesari,Vadodara, India



18 19 21 29

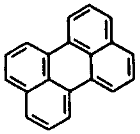
Tetrahedron, **1992**, *48*, 4919

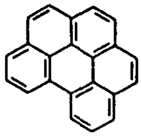
FORMATION OF POLYCYCLIC AROMATIC COMPOUNDS UPON ELECTRIC DISCHARGES IN LIQUID TOLUENE

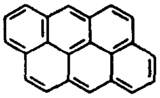
Mihály T. Beck,* Zoltán Dinya and Sándor Kéki
Department of Physical Chemistry, Lajos Kossuth University and
Research Group of Antibiotics of the Hungarian Academy of Sciences
Debrecen 10, Hungary 4010

The formation of a great number of polycyclic aromatic compounds occurs when electric discharges are made in liquid toluene.

For example:





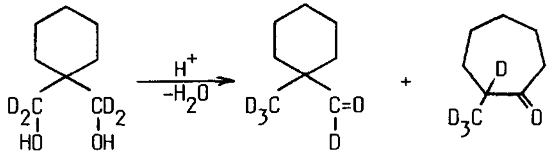


Tetrahedron, **1992**, *48*, 4929

STUDIES ON THE CHEMISTRY OF DIOLS AND CYCLIC ETHERS-53. DEHYDRATION OF 1,1-BISHYDROXYMETHYLCYCLOALKANES: A QUEST FOR A 1,3-HYDRIDE SHIFT

Árpád Molnár, Imre Bucsi and Mihály Bartók*
Department of Organic Chemistry, József Attila University, Szeged, Hungary

Mechanistic studies of the sulphuric acid-catalysed dehydration of 1,1-bishydroxymethylcycloalkanes and 1,1-bis[dideuteriohydroxymethyl] cyclohexane to carbonyl compounds furnished evidence of a 1,3-hydride shift.

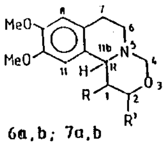


Tetrahedron, **1992**, *48*, 4937

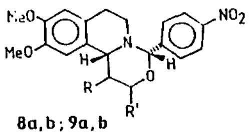
SYNTHESIS AND CONFORMATIONAL ANALYSIS OF STEREOISOMERIC 1- AND 2-METHYL-2*H*,4*H*-1,6,7,11b-TETRAHYDRO-1,3-OXAZINO[4,3-*a*]ISOQUINOLINES[1]

Pál Sohár, László Lázár[a], Ferenc Fülöp[a], Gábor Bernáth[a] and Jenő Kóbor[b]; Spectroscopic Department, EGIS Pharmaceuticals, POB 100, H-1475 Budapest, Hungary, [a]Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, POB 121, H-6701 Szeged, Hungary, [b]Chemical Department, Pedagogical Training College, H-6720 Szeged, Hungary

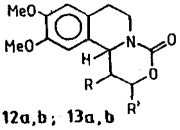
From 1-(ß-hydroxyethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines, 1- or 2-methyl-9,10-dimethoxy-2*H*,4*H*-1,6,7,11b-tetrahydro-1,3-oxazino[4,3-*a*]isoquinoline diastereomers (**a** and **b**) (**6-9**, **12** and **13**) were prepared, and the predominant conformations were determined.



6a,b; 7a,b



8a,b; 9a,b



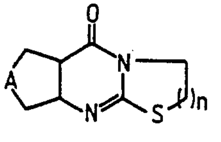
12a,b; 13a,b

Tetrahedron, **1992**, *48*, 4949

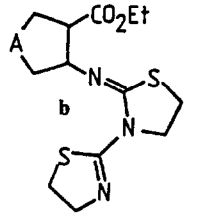
SYNTHESIS AND STRUCTURE DETERMINATION OF ALICYCLE-FUSED THIAZOLO- AND THIAZINO[2,3-*b*]-QUINAZOLONES AND CYCLOALKYLIMINO-3(*N*)-THIAZOLINYLTHIAZOLIDINES

I.Huber, Á.Szabó, F.Fülöp, G.Bernáth*, P.Sohár*; Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6720 Szeged, POB 121, (Hungary), *Spectroscopic Department, EGIS Pharmaceuticals, H-1475 Budapest, POB 100, (Hungary)

In the reactions of chloroalkyl isothiocyanates and stereoisomeric alicyclic ethyl 2-aminocarboxylates, sixteen new derivatives of products **a** and **b** were prepared, and their structure were proved by means of IR, ^{1}H and ^{13}C NMR spectroscopy, use also being made of DR, DNOE, DEPT and 2D-HSC measurements.



a



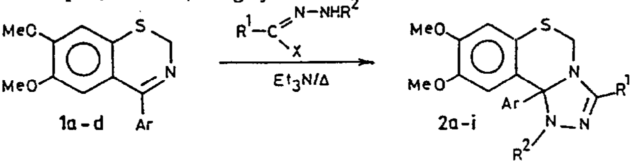
b

Tetrahedron, **1992**, *48*, 4957

CONFORMATIONAL ANALYSIS OF *s*-TRIAZOLOBENZOTHIAZINE DERIVATIVES PREPARED BY INTERMOLECULAR 1,3-DIPOLAR CYCLOADDITION OF NITRILIMINES TO 4-ARYL-2*H*-1,3-BENZOTHIAZINES[1]

János Szabó[a]*, Lajos Fodor[a], Ernest Bani-Akoto[a], Gizella S. Talpas[a], Gábor Bernáth[a] and Pál Sohár[b]*
Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6701 Szeged, POB 121, Hungary,
[b]Spectroscopic Department, EGIS Pharmaceuticals, H-1475 Budapest, POB 100, Hungary

A series of new 1,3,10b-trisubstituted-8,9-dimethoxy-1,10b-dihydro-5*H*-1,2,4-triazolo[4,3-*c*][1,3]benzothiazines (**2a-i**) have been synthesized by cycloaddition of nitrilimines to 4-aryl-6,7-di-methoxy-2*H*-1,3-benzothiazines (**1a-d**). Conformational analysis of the *s*-triazolobenzothiazine derivatives **2a-i** was performed.

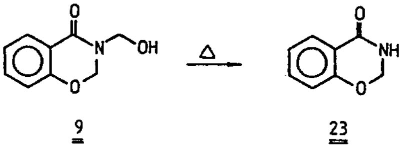


Tetrahedron, **1992**, *48*, 4963

Synthesis, Reactions and Stereochemistry of 3-Hydroxymethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one and some Perhydrogenated Derivatives[1]

Ferenc Fülöp[a,b,*], Kalevi Pihlaja[a,*], Imre Huber[b], Gábor Bernáth[b], Béla Ribár[c], Gyula Argay[d] and Alajos Kálmán[d]
Department of Chemistry, University of Turku, SF-20500 Turku, Finland; [b]Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6701 Szeged, POB 121, Hungary; [c]Institute of Physics, Faculty of Sciences, 21000 Novi Sad, Ilije Djuricica 4, Yugoslavia; [d]Central Research Institute for Chemistry, Hungarian Academy of Sciences, POB 17, H-1525 Budapest, Hungary

3-Hydroxymethyl-2,3-dihydro-4*H*-1,3-benzoxazin-4-one (9) and a number of its perhydrogenated derivatives were prepared. Thermal decomposition of the 3-hydroxymethyl derivatives led to the previously unknown parent compounds. According to the NMR and X-ray structure investigations in the cyclopentane and cyclohexane-fused derivatives the oxazinone ring predominantly attains a single half-chair conformation.

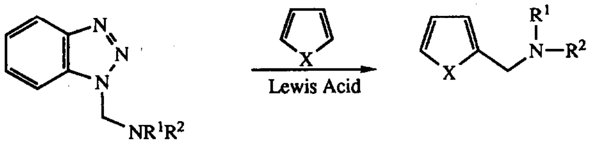


Tetrahedron, **1992**, *48*, 4971

AMINOALKYLBENZOTRIAZOLE: A REAGENT FOR THE AMINOALKYLATION OF ELECTRON RICH HETEROCYCLES

Alan R. Katritzky,* Zhijun Yang, and Jamshed N. Lam
Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville FL 32611-2046

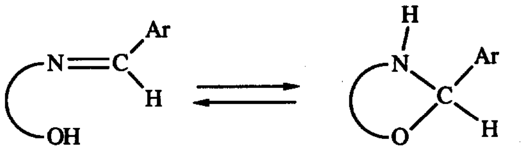
Secondary and tertiary aminoalkylbenzotriazoles react with indoles, pyrroles and 2-methylfuran under mild conditions in the presence of a Lewis acid to afford selectively the corresponding C-aminoalkylated secondary and tertiary amines.



Tetrahedron, **1992**, *48*, 4979

A Solid-State NMR Study of Ring-Chain Tautomerism in 1,3-*O*,*N*-Heterocycles

Frank G. Riddell and S. Arumugam,
Department of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, Scotland, U.K.
Ferenc Fülöp and Gábor Bernáth,
Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, H-6701 Szeged, POB 121, Hungary.



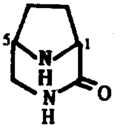
An investigation of the tautomeric equilibrium in tetrahydrooxazines and oxazolidines in the solid state is reported.

Tetrahedron, **1992**, *48*, 4985

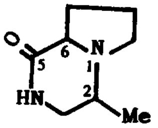
LACTAM & AMIDE ACETALS XXI. USE OF PYROGLUTAMIC ACID AND PROLINE IN CHIRAL SYNTHESIS OF CONFORMATIONALLY CONSTRAINED PIPERAZINONES.

S.Jain, K.Sujatha, K.V.Rama Krishna, R.Roy, J.Singh & N.Anand*, Medicinal Chemistry Division, Central Drug Research Institute, Lucknow 226 001, India.

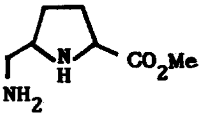
Synthesis of (1S,5R)- and (1R,5S)-diazabicyclo-octanones of 5-aminomethylprolines 1 and 2, 12a & 15 therefrom, and of (2R,6S)-, (2S,6S)-, (2S,6R)- and (2R.6R)-bicyclononanones 3 and 4 has been carried out from (S)- and (R)-pyroglutamates and (S)- and (R)-prolines respectively via nitroenamine intermediates.



1: 1S,5R
2: 1R,5S



3a: 2R,6S
3b: 2S,6S
4a: 2S,6R
4b: 2R,6R



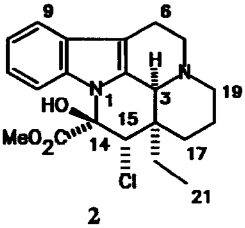
12a: 2S,5R
15: 2R,5S

Tetrahedron, **1992**, *48*, 4999

Synthesis of Vinca Alkaloids and Related Compounds LX. A Simple Transformation of Apovincamine into Vincamine

István Moldvai,[a] Csaba Szántay Jr.,[b] Kari Rissanen[c] and Csaba Szántay[a]
[a] Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest, POB 17, Hungary.
[b] Chemical Works of Gedeon Richter, NMR Laboratory, H-1475, Budapest, POB 27, Hungary.
[c] University of Jyväskylä, Department of Chemistry, Kyllikinkatu 1-3, SF-40100 Jyväskylä, Finland.

The 15α-chloro-vincamine derivative 2 was prepared and proved to be key intermediate of a two-step transformation of apovincamine into vincamine. The structure of 2 was established via detailed NMR and X-ray investigations. Full NMR assignments for related compounds are also given.

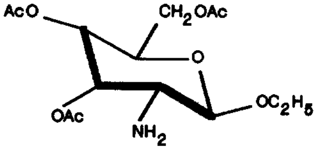


2

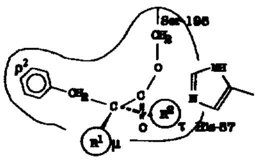
Tetrahedron, **1992**, *48*, 5009

Nitrogen Participation in the Deacylation of D-Glucosamine and α-Chymotrypsin Derivatives. Explanation of the Stereospecificity of Acyl-α-Chymotrypsin Hydrolysis

László Ötvös* and Ferenc Kraicsovits Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary



ethyl 3,4,6-tri-O-acetyl-2-deoxy-2--amino-β-D-glucopyranoside



active site of α-chymotrypsin acylated with substituted β-phenylpropionic acid.

Tetrahedron, **1992**, *48*, 5015

Synthesis of *Vinca* Alkaloids and Related Compounds, LXII

SYNTHESIS OF DESMETHOXY "DECARBOMETHOXY APOCUANZINE"

Ferenc Sóti*, Zsuzsanna Kardos-Balogh, Mária Incze,
Mária Kajtár-Peredy, and Csaba Szántay*

Central Research Institute for Chemistry,
Hungarian Academy of Sciences,
H-1525 Budapest, POB 17, Hungary

Starting from the intermediate product of the desmethoxy cuanzine synthesis (±)-desmethoxy "decarbomethoxy apocuanzine" was synthesized.