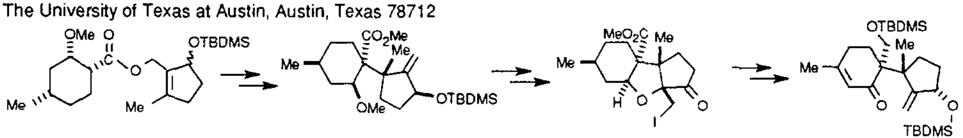
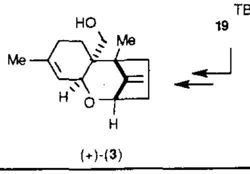
GRAPHICAL ABSTRACTS

Enantioselective Synthesis of an *Ent*-Trichothecene Skeleton

Tetrahedron, **1994**, *50*, 1651

John C. Gilbert* and Robert D. Selliah, Department of Chemistry and Biochemistry
The University of Texas at Austin, Austin, Texas 78712





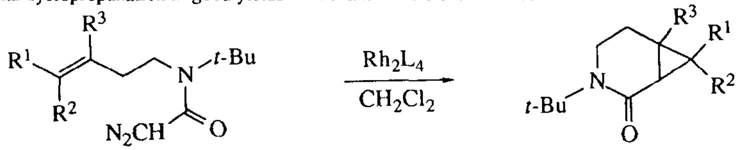
Rearrangement of silylketene acetal derived from 7 occurs with high facial and diastereoselectivity to afford 9a preferentially. Subsequent functional group manipulations yields the *ent*-trichothecene molecular skeleton in the form of 3. This sequence represents a convergent, enantioselective approach to this family of sesquiterpenes.

ENANTIOSELECTIVE INTRAMOLECULAR CYCLOPROPANATION OF *N*-ALLYLIC- AND *N*-HOMOALLYLIC DIAZOACETAMIDES CATALYZED BY CHIRAL DIRHODIUM(II) CATALYSTS.

Tetrahedron, **1994**, *50*, 1665

Michael P. Doyle*, Michail Y. Eismont‡, Marina N. Protopopova, and Michelle M. Y. Kwan, Department of Chemistry, Trinity University, San Antonio, Texas 78212, U.S.A. ‡N.D. Zelinski Institute of Organic Chemistry, Moscow, Russia.

Diazodecomposition of *N*-homoallylic diazoacetamides catalyzed by chiral dirhodium(II) catalysts forms the products from intramolecular cyclopropanation in good yields with enantiomeric excess of 60-90%.

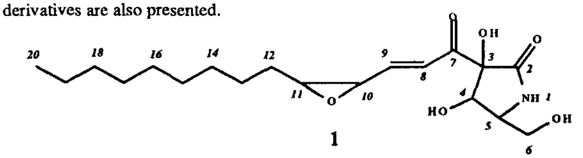


PRAMANICIN, A NOVEL ANTIMICROBIAL AGENT FROM A FUNGAL FERMENTATION.

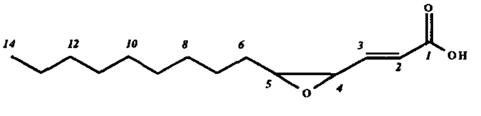
Tetrahedron, **1994**, *50*, 1675

Robert E. Schwartz,* Gregory L. Helms, Evon A. Bolessa, Kenneth E. Wilson, Robert A. Giacobbe, Jan S. Tkacz, Gerald F. Bills, Jerrold M. Liesch, Deborah L. Zink, James E. Curotto, Barnali Pramanik, and Janet C. Onishi, Merck Research Laboratories, P. O. Box 2000, Rahway, N. J. 07065-0900, U. S. A.

The antimicrobial agent pramanicin (1), and a related fatty acid (6), were isolated and the structures determined by a variety of spectral means including UV, IR, and NMR spectroscopy (^1H-^{15}N HMQC was used to detect the lactam NH), as well as mass spectrometry. A number of chemical derivatives are also presented.



1



6

Synthesis, Characterization and Crystal Density Modeling of Four $C_{24}H_{28}$ Cage-Functionalized Alkenes

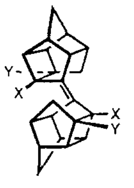
Tetrahedron, **1994**, *50*, 1687

Alan P. Marchand*, Anjali Zope, Florencio Zaragoza, and Simon G. Bott*

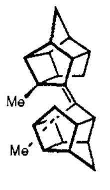
*Department of Chemistry, University of North Texas
Denton, TX 76203-0068*

Herman L. Ammon* and Zuyue Du

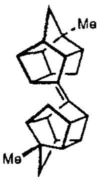
*Department of Chemistry, & Biochemistry
University of Maryland, College Park, MD 20742-2021*



6c: X = Me, Y = H
7c: X = H, Y = Me



6d



9a

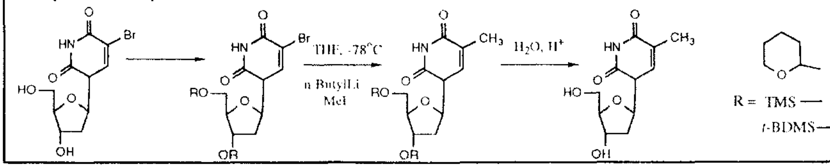
Structures of four isomerically pure "methylated PCU alkene dimers" ($C_{24}H_{28}$) have been synthesized and fully characterized. The crystal density of each alkene (calculated from unit cell parameters) is compared with the results of theoretical density predictions.

Tetrahedron, **1994**, *50*, 1699

SELECTIVE ALKYLATION OF PYRIMIDYL DIANIONS II: SYNTHESIS, CHARACTERIZATION, AND COMPARATIVE REACTIVITY OF 3',5'-O-BIS-TETRAHYDROPYRANYL, TRIMETHYLSILYL AND *tert*-BUTYLDIMETHYLSILYL DERIVATIVES OF 5-BROMO-2'-DEOXYURIDINE

Mian M. Alauddin* and Peter S. Conti; PET Imaging Science Center, University of Southern California, Los Angeles, CA.

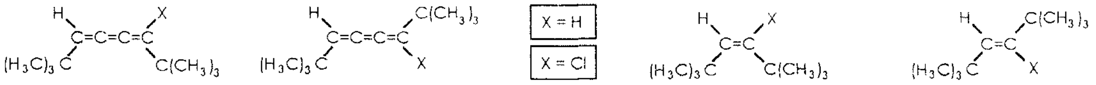
Evaluation of three precursors for radiochemical synthesis of thymidine is reported. 3',5'-o-bis- tetrahydropyranyl,trimethylsilyl and *t*-butyldimethylsilyl ethers were successfully synthesized and alkylated at 5-position. THP and *t*-BDMS ethers were found to be better precursors compared to the TMS ether



Tetrahedron, **1994**, *50*, 1707

Identification of Stereoisomers Based on Dielectric Studies: Dipole Moments of Chloroalkenes and Chlorocumulenes

Paul J. Bauer [a], Otto Exner [b], Renzo Ruzziconi [c,d], Tran Dinh An [d], Claudio Tarchini [d], Manfred Schlosser [d]
[a] Institut für biologische Informations-Verarbeitung, Forschungszentrum Jülich, D-52425 Jülich, Germany
[b] Czechoslovak Academy of Science, CS-16610 Praha 6, Czech Republic
[c] Dipartimento di Chimica Organica dell'Università, I-06100 Perugia, Italy
[d] Institut de Chimie organique de l'Université, CH-1005 Lausanne, Switzerland

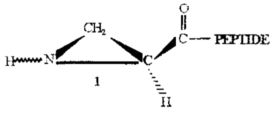


Tetrahedron, **1994**, *50*, 1717

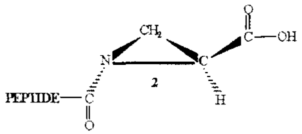
On The Synthesis of (2S)-Aziridine-2-Carboxylic Acid Containing Peptides

Andreas Korn, Sabine Rudolph-Böhner, Luis Moroder*
Max-Planck-Institut für Biochemie, Am Klopferspitz 18a, D-82152 Martinsried

Starting from benzyl (-)-(2S)-1-trityl-aziridine-2-carboxylate peptides **1** and **2** are synthesized in a multi-step reaction sequence.



1

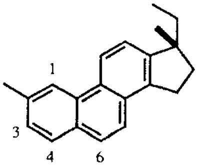


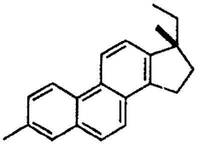
2

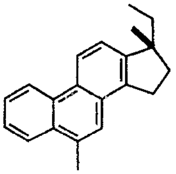
Tetrahedron, **1994**, *50*, 1731

SYNTHESIS OF TRIAROMATIC STEROID HYDROCARBONS METHYLATED AT POSITION 2, 3 OR 6: MOLECULAR FOSSILS OF YET UNKNOWN BIOLOGICAL ORIGIN.

Eric LICHTFOUSE*[1] and Pierre ALBRECHT[2]
[1]Université Pierre et Marie Curie, Paris, France. [2]Université Louis Pasteur, Strasbourg, France.





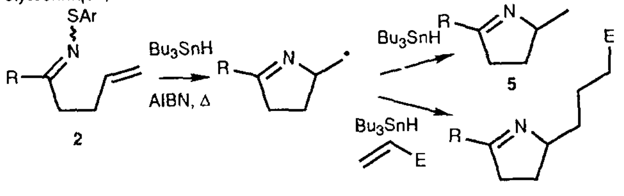


Tetrahedron, **1994**, *50*, 1745

Iminyl Radicals: Part I. Generation and Intramolecular Capture by an Olefin.

Jean Boivin, Eric Fouquet and Samir Z. Zard*
Laboratoire de Synthèse Organique associé au CNRS, Ecole Polytechnique, 91128 Palaiseau, France

Slow addition of tributylstannane to sulphenylimines **2** give the corresponding Δ1- pyrrolenines **5** by an intramolecular addition of the intermediate iminyl radical, a process which can be easily coupled to an intermolecular addition to an electrophilic olefin.

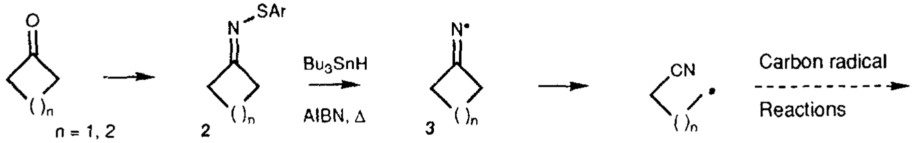


Tetrahedron, **1994**, *50*, 1757

Iminyl Radicals: Part II. Ring Opening of Cyclobutyl- and Cyclopentyliminyl Radicals.

Jean Boivin, Eric Fouquet and Samir Z. Zard*
Laboratoire de Synthèse Organique, Ecole Polytechnique, 91128 Palaiseau, France

Slow addition of tributylstannane to sulphenylimines **2** give the corresponding cycloiminyl radicals **3** which can undergo ring opening, a process that is easily incorporated into complex reaction sequences.

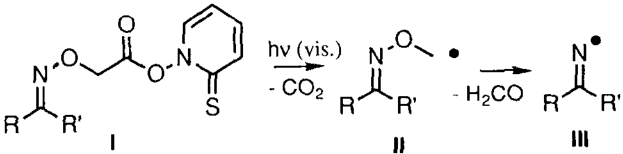


Tetrahedron, **1994**, *50*, 1769

Iminyl Radicals: Part III. Further Synyhetically Useful Sources of Iminyl Radicals.

J. Boivin, E. Fouquet, Anne-Marie Schiano, and S.Z. Zard
Laboratoire de Synthèse Organique, Ecole Polytechnique, 91128, Palaiseau, France.

Iminyl radicals **III** are produced by various methods, including the Barton's radical decarboxylation of esters **I** into **II** which looses formaldehyde. Radicals **III** are exploited in several radical chain reactions (addition to intramolecular olefins, fragmentation) to afford highly functionalised molecules.



Tetrahedron, **1994**, *50*, 1777

SOLUTION CONFORMATION OF HEXAMERIC & HEPTAMERIC LARIAT-RNAS AND THEIR SELF-CLEAVAGE REACTIONS WHICH GIVE PRODUCTS MIMICKING THOSE FROM SOME CATALYTIC RNAS (RIBOZYMES)

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

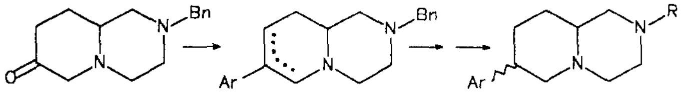
The unique self-cleavage reactions of lariat-RNAs at various temperature, concentration, pH, both in the presence and in the absence of Mg^{2+} ions, have been examined in details. Subsequently, their conformational analysis, using 500 MHz NMR spectroscopy, molecular mechanics and dynamics calculations, have shown the conformational requirement at the self-cleavage site.

THE SYNTHESIS OF 2,7-SUBSTITUTED OCTAHYDRO-2H-PYRIDO-[1,2-a]PYRAZINES, ANALOGUES OF QUINOLIZIDINE AND PIPERAZINE DRUGS

Tetrahedron, **1994**, *50*, 1811

M. Ashty Saleh, Frans Compernolle*, Suzanne Toppet and Georges J.Hoornaert; Laboratorium voor Organische Synthese, K.U.Leuven, Celestijnenlaan 200F, B-3001 Leuven-Heverlee, Belgium

The *cis*- and *trans*- compounds **10** and **11** were prepared via a sequence involving Grignard reaction of **2**, acidic elimination, hydrogenation., and final introduction of the 2-substituent.



2

10 R= 2-Py

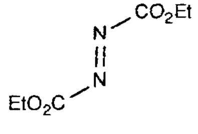
11 R= $4\text{-}FC_6H_4CO$

Ar= $4\text{-}FC_6H_4$

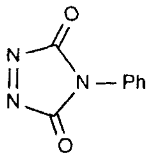
SOLVENT EFFECT IN PERICYCLIC REACTIONS. XI. THE ENE REACTION.

Tetrahedron, **1994**, *50*, 1821

G. Desimoni, G. Faita, P.P. Righetti, A. Sfulcini, and D. Tsyganov
Dipartimento di Chimica Organica dell'Università, V.le Taramelli 10, 27100 Pavia, Italy.



1



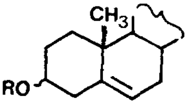
4

The solvent effect on the ene reactions of diethylazodicarboxylate **1** and triazolindione **4** was determined. The solvent effects are the same observed in Diels-Alder reactions with **1** and **4** as dienophiles: the former depends on the solvent acidity, the latter on the nucleophilic character of the medium and correlations with Acceptor resp. Donor Numbers of the solvent were obtained. The salt effects of inorganic perchlorates support this.

Photochemically Induced Mercuric Oxide - Iodine Oxidation of Some Unsaturated Steroid Compounds

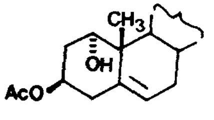
Tetrahedron, **1994**, *50*, 1833

M. Dabović, M. Bjelaković, V. Andrejević, Lj. Lorenc, and M. Lj. Mihailović Faculty of Chemistry, University of Belgrade, Studentski trg 16, P.O. Box 550, YU-11001 Belgrade, and Institute of Chemistry, Technology and Metallurgy, Belgrade

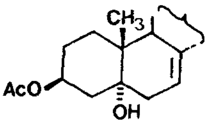


6 R=H (3α) **10** R=Ac (3α)

7 R=H (3β) **11** R=Ac (3β)



8



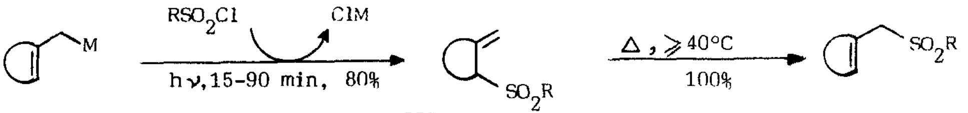
9

HgO/I_2 oxidations of the alcohols and acetates shown above, which were found to proceed *via* alkoxy radicals and/or by I_2O attack at the olefinic double bond, are described.

SH2' REACTION IN ORGANOCOBALOXIMES: SYNTHESIS AND 1,3-REARRANGEMENT OF EXO-METHYLENE ALICYCLIC ALLYL SULFONES

Tetrahedron, **1994**, *50*, 1847

S. Roy[a,*], I. Das[a], K. Bhanuprakash[a,*] and B.D. Gupta[b,*]
[a]IPC Divn., IICT, Hyderabad, India; [b]Chem. Dept., IIT, Kanpur, India.



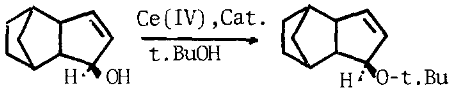
○ = cy-5, cy-6, bicy-[2.2.1]; M=$Co^{III}(dmgH)_2Py$

Tetrahedron, **1994**, *50*, 1859

CERIUM(IV), AS A SELECTIVE AND EFFICIENT CATALYST FOR ALCOHOLYSES OF ALLYLIC AND TERTIARY BENZYLIC ALCOHOLS

N. Iranpoor*, E. Mothaghineghad
Department of Chemistry, Shiraz University, Shiraz, 71454 Iran

An efficient and catalytic method is described for alcoholyses of allylic and tertiary benzylic alcohols with Ce(IV) as ceric ammonium nitrate.

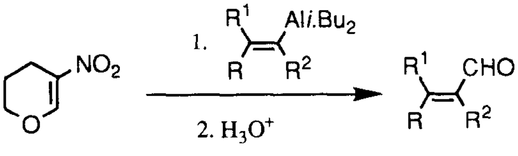


Tetrahedron, **1994**, *50*, 1871

Reactivity of 3-Nitro-5,6-Dihydro-4H-Pyran with Organoalanes: Preparation of (E)-α, β-Ethylenic Aldehydes.

Rita Menicagli,* Vito Guagnano, Corrado Malanga
Dipartimento di Chimica e Chimica Industriale and Centro di Studi del CNR per le Macromolecole Stereordinate ed Otticamente Attive
Via Risorgimento 35, 56126 Pisa - Italy.

3-Nitro-5,6-dihydro-4H-pyran reacts with (E)-diisobutyl, 1'-alkenylaluminum to give, in suitable hydrolysis conditions, (E)-α, β-ethylenic aldehydes.



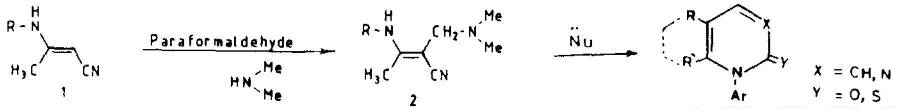
70-85%

Tetrahedron, **1994**, *50*, 1877

ß-ENAMINONITRILES IN HETEROCYCLIC SYNTHESIS: A NOVEL SYNTHESIS AND TRANSFORMATIONS OF α-SUBSTITUTED-ß-ENAMINONITRILES

Ayman Wahba Erian,[a*] Sherif M. Sherif,[a] Abdel-Zaher A. Alassar,[b] and Yehya M. Elkholy[b]
[a]Department of Chemistry, Faculty of Science, Cairo University, Giza, A.R. Egypt
[b]Department of Chemistry, Faculty of Science, Helwan University, Helwan, Cairo, A.R. Egypt

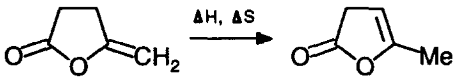
Novel synthesis of α-substituted-ß-enaminonitriles 2 could be obtained from reaction of ß-enaminonitriles 1 with paraformaldehyde and dimethylamine. Such compounds reacted readily with a wide variety of reagents to give unique heterocyclic systems.



Tetrahedron, **1994**, *50*, 1885

RELATIVE THERMODYNAMIC STABILITIES OF γ-METHYLENE-γ-BUTYROLACTONE AND α-ANGELICALACTONE

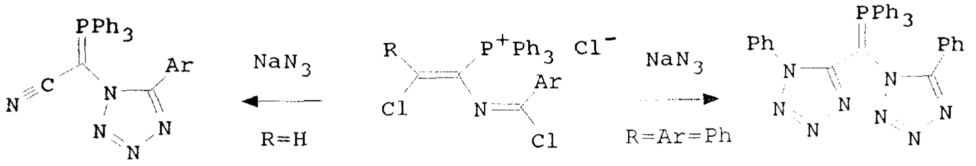
Esko Taskinen, Department of Chemistry, University of Turku, FIN-20500 Turku, Finland



STRUCTURE AND PROPERTIES OF PHOSPHONIUM YLIDES OBTAINED BY THE REACTION OF 3-PHOSPHORYLATED 1,4-DICHLORO-2-AZA-1,3-DIENES WITH SODIUM AZIDE.

Tetrahedron, **1994**, *50*, 1889

Luc Van Meervelt*, Chemistry Department, K.U. Leuven, Belgium, Roman N. Vydzhak, Vladimir S. Bovarets, Nikolai I. Mishchenko and Boris S. Drach, Institute of Bioorganic Chemistry and Petrochemistry, Academy of Sciences of Ukraine, Kiev, Ukraine.

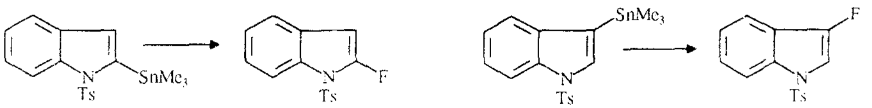


Electrophilic Fluorination in the Synthesis of new Fluoroindoles

Tetrahedron, **1994**, *50*, 1899

Harold F. Hodson[a], David J. Madge[a], Alexandra N.Z. Slawin[c], David A. Widdowson[b]*and David J.Williams[c]
[a] Department of Medicinal Chemistry, Wellcome Research Laboratories, Beckenham, Kent, BR3 3BS, England.
[b] Department of Chemistry, Imperial College of Science, Technology and Medicine, London, SW7 2AY, England.
[c] Chemical Crystallography Laboratory, Imperial College of Science, Technology and Medicine, London, SW7 2AY, England.

Trimethylstannylindoles were fluorinated with caesium fluoroxysulfate or Selectfluor™ to provide the corresponding fluoroindoles.



TRANSITION METAL-CATALYZED CHLORINE TRANSFER CYCLIZATIONS OF CARBON-CENTERED GLYCINE RADICALS; A NOVEL SYNTHETIC ROUTE TO CYCLIC α-AMINO ACIDS

Tetrahedron, **1994**, *50*, 1907

Jan H. Udding, C. (Kees) J. M. Tuijp, Henk Hiemstra, W. Nico Speckamp
Department of Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The copper(I)-catalyzed chlorine transfer radical cyclization of α-chloroglycine derivatives to 3-(1-chloroalkyl)-substituted prolines is described.