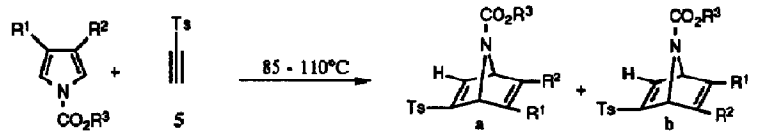
GRAPHICAL ABSTRACTS

Tetrahedron Letters, **1994**, *35*, 9649

Synthesis of Highly Functionalized 7-Azabicyclo[2.2.1]heptadienes

Zhengming Chen and Mark L. Trudell*, Department of Chemistry,
University of New Orleans, New Orleans, Louisiana 70148

Highly functionalized 7-azabicyclo[2.2.1]heptadiene derivatives have been synthesized *via* a [4 + 2] cycloaddition reaction between *N*-acyl-3,4-disubstituted pyrroles and ethynyl *p*-tolyl sulfone 5.

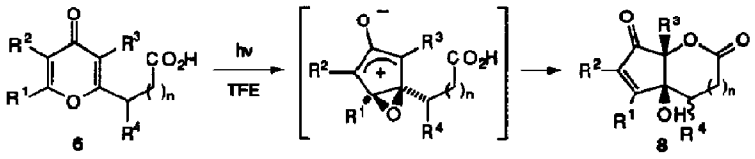


Tetrahedron Letters, **1994**, *35*, 9653

Intramolecular Carboxylic Acid Trapping of Pyran-4-one Derived Zwitterions: A Novel Synthesis of Fused Bicyclic Lactones

F. G. West, C. M. Amann and P. V. Fisher, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112*

Pyran-4-ones **6** bearing pendant carboxyl groups are photochemically converted to oxyallyl zwitterions, which then undergo intramolecular nucleophilic capture to give bicyclic lactones **8** in moderate to good yield.

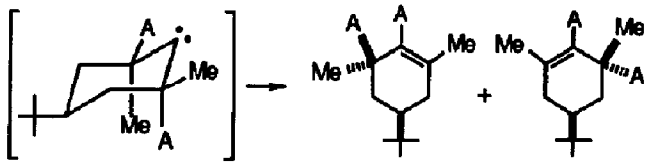


Tetrahedron Letters, **1994**, *35*, 9657

Axial and Equatorial Hydrogen Shifts in Methyl Substituted Cyclohexylidenes. Stereochemically-dependent Isotope Effects and Bystander Assistance.

James A. Kenar and Alex Nickon*
Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218-2685 USA

Products from carbenes **9a** and **9b** reveal that Me_{eq} assists H shift *ca.* 4.6 times better than does Me_{ax} and that the k_H/k_D isotope effect for H_{ax} migration is *ca.* 1.5 times larger than for H_{eq} migration.

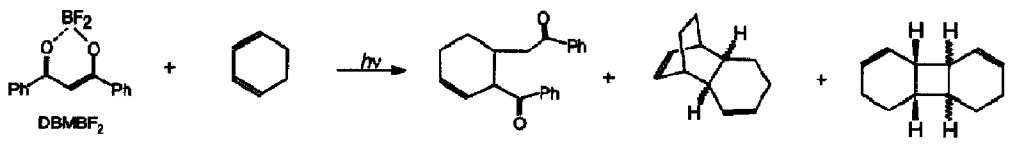


Tetrahedron Letters, **1994**, *35*, 9661

Solvent Effects on Photoreactions of Dibenzoylmethanatoboron Difluoride ($DBMBF_2$) with Cyclic Dienes

Yuan L. Chow* and Shi-Sen Wang, Department of Chemistry, Simon Fraser University, Burnaby, B. C., Canada V5A 1S6

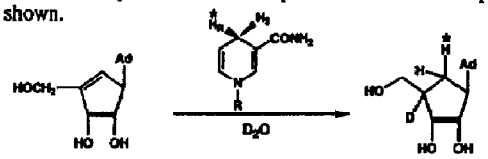
Different reaction patterns are observed for the photolysis of $DBMBF_2$ with cyclic dienes in a series of solvents.



Tetrahedron Letters, **1994**, *35*, 9665

THE BIOSYNTHESIS OF ARISTEROMYCIN. CONVERSION OF NEPLANOCIN A TO ARISTEROMYCIN BY A NOVEL ENZYMATIC REDUCTION. Ronald J. Parry* and Yijia Jiang , Department of Chemistry, Rice University, P. O. Box 1892, Houston, TX 77251 USA

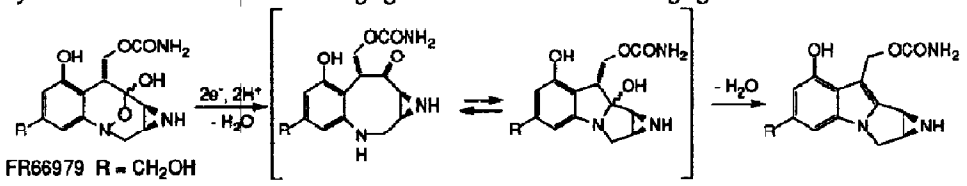
Partially purified extracts of the aristeromycin producer *S. citricolor* catalyze the NADPH-dependent reduction of neplanocin A to aristeromycin with the stereochemistry and regiochemistry shown.



Tetrahedron Letters, **1994**, *35*, 9669

FR66979 Requires Reductive Activation to Cross-Link DNA Efficiently. Huifang Huang[a], Scott R. Rajski[b], Robert M. Williams[b]*, and Paul B. Hopkins[a]*, [a]Department of Chemistry, University of Washington, Seattle WA 98195 USA and [b]Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

The activity of FR66979 as a DNA cross-linking agent in the absence of reducing agents was re-examined.

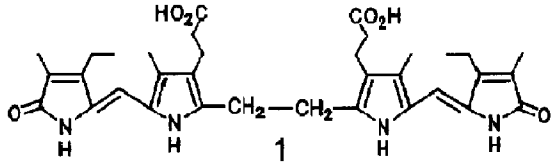


FR66979 R = CH_2OH

Tetrahedron Letters, **1994**, *35*, 9673

HOMORUBIN. A CENTRALLY HOMOLOGATED BILIRUBIN William P. Pfeiffer and David A. Lightner,*
Department of Chemistry, University of Nevada, Reno, NV 89557 USA

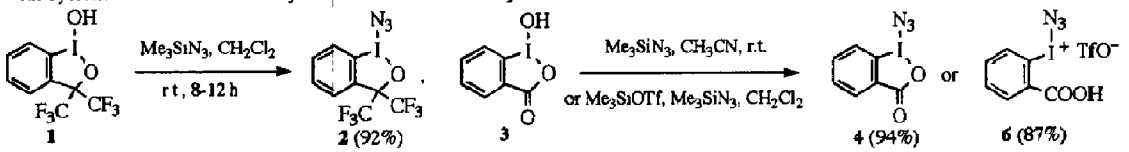
Homorubin (1) was synthesized from monopyrrole precursors in 5 steps. It has UV-vis and NMR spectroscopic properties similar to its parent, mesobilirubin-XIIIα but adopts a different hydrogen-bonded conformation.



Tetrahedron Letters, **1994**, *35*, 9677

PREPARATION AND CHEMISTRY OF STABLE AZIDOIODINANES: 1-AZIDO-3,3-BIS(TRIFLUOROMETHYL)-3-(1*H*)-1,2-BENZIODOXOL AND 1-AZIDO-1,2-BENZIODOXOL-3-(1*H*)-ONE. Viktor V. Zhdankin*, Chris J. Kuehl, Alexei P. Krasutsky, Mark S. Formaneck, Jason T. Bolz
Chemistry Department, University of Minnesota-Duluth, Duluth, Minnesota 55812 USA

Azidoiodinanes **2,4,6** can be prepared from benziodoxols **1,3** and trimethylsilyl azide in the form of stable, crystalline compounds. These compounds are potentially useful reagents for electrophilic azidonation of organic substrates For example, reaction of azide **6** with cyclohexene affords 2-azidocyclohexanone in moderate yield.

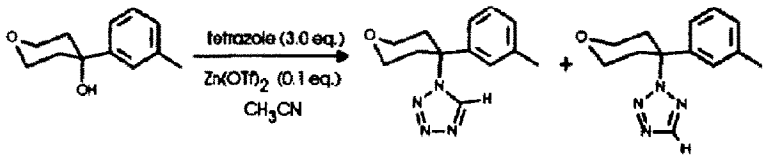


Tetrahedron Letters, **1994**, *35*, 9681

New Preparation of N(1)- and N(2)-Alkylated Tetrazoles via Displacement of Activated Alcohols.

Réjean Fortin* and Christian Brochu
Merck Frosst Centre for Therapeutic Research. P.O. Box 1005, Pointe-Claire Dorval, Québec, Canada H9R4P8.

A facile and convenient synthesis of *N*(1)- and *N*(2)-alkyltetrazoles is described. Tetrazole in the presence of zinc triflate reacts smoothly with activated alcohols to give the corresponding alkyltetrazole in high yield.

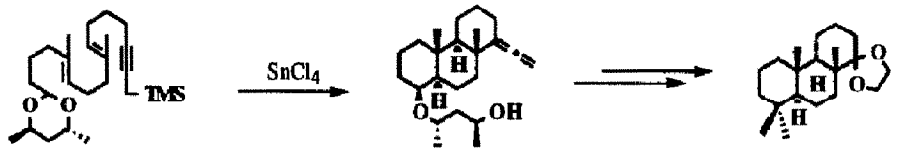


Tetrahedron Letters, **1994**, *35*, 9685

TOWARDS OLEANANES: GEMINAL DIMETHYLATION AT C-4.

Garth S. Jones,
Department of Chemistry, Stanford University, Stanford, CA. 94305, USA

A tricyclic model of the ABC rings of oleanane has been synthesized by biomimetic polyene cyclication and successfully dimethylated at the sterically hindered C-4 position.

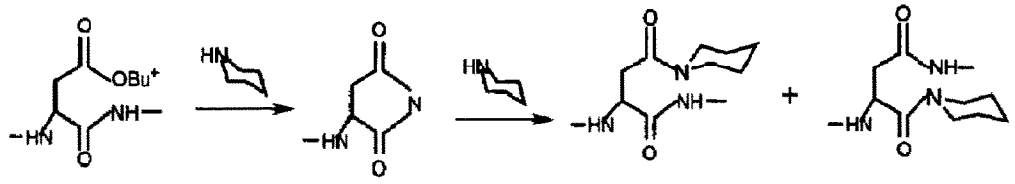


Tetrahedron Letters, **1994**, *35*, 9689

ASPARTIMIDE FORMATION IN BASE-DRIVEN 9-FLUORENYL-METHOXYCARBONYL CHEMISTRY.

Yan Yang[1], Willam V. Sweeney[1], Klaus Schneider[2], Susanna Thornqvist[2], Brian T. Chait[2], and James T. Tam[3]* 1. Dept. of Chem., Hunter College of CUNY, New York, NY 10021, USA. 2. Lab. for Mass Spectrom. and Gaseous Ion Chem.,The Rockefeller Univ., New York, NY 10021, USA. 3. Dept. of Microbiol. and Immun., Vanderbilt Univ., Nashville, TN 37232, USA.

Aspartimide and its piperidine adduct formed between -Asp-Asn- or -Asp-Gly- have been found.



Tetrahedron Letters, **1994**, *35*, 9693

Synthesis of P1 Aspartate-Based Peptide Acyloxymethyl and Fluoromethyl Ketones as Inhibitors of Interleukin-1β-Converting Enzyme

Laszlo Revesz*, Chantal Briswalter, Richard Heng, Albert Leutwiler, Rudolf Mueller und Hans-Juerg Wuethrich
Sandoz Research Institute Berne Ltd., CH-3001 Berne, Switzerland

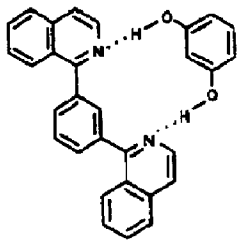
Improved procedures have been developed for the synthesis of dichlorobenzoyloxymethyl ketone **1** and fluoromethyl ketone **2**, the prodrugs of two potent ICE-inhibitors:

Tetrahedron Letters, **1994**, *35*, 9697

Isoquinolines as Receptors for Resorcinol

Gerald Dyker*, Matthias Gabler, Mahmoud Nouroozian and Petra Schulz, Institut für Organische Chemie der TU, Hagenring 30, D-38106 Braunschweig, FRG

Host-guest interaction of isoquinolines with resorcinol is studied by NMR spectroscopy including NOE experiments.

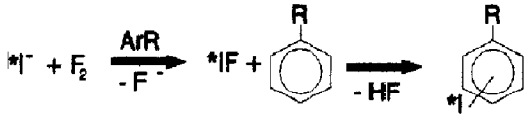


Tetrahedron Letters, **1994**, *35*, 9701

REACTIVITY OF IODINE MONOFLUORIDE ON SUB-MICROMOLAR SCALE WITH ARENES.

Oliver Thimm, Klaus Dutschka, *Heinz H. Coenen
AG Nuklearchemie und Radiopharmazie, Universitätsklinikum Essen, Hufelandstr. 55, D-45122 Essen, Germany.

Reaction of *in situ* generated iodine monofluoride; its reactivity and selectivity studied by the radiotracer method with [^{123,131}I]iodine.

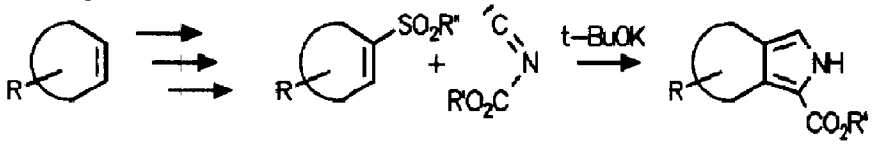


Tetrahedron Letters, **1994**, *35*, 9703

A useful Preparation of Pyrroles from α,β-unsaturated Sulfones

Gerold Haake, Daria Struve, Franz-Peter Montforts*
Institut für Organische Chemie FB 2, Universität Bremen, Leobener Str. NW 2, D-28359 Bremen, Germany

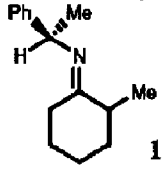
Abstract: The addition of alkyl isocyanoacetate to easily accessible α,β-unsaturated sulfones affords a convenient route to pyrroles with unusual substitution patterns.



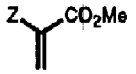
Tetrahedron Letters, **1994**, *35*, 9705

THE ASYMMETRIC MICHAEL REACTION USING CHIRAL IMINES UNDER NEUTRAL CONDITIONS: STEREOCHEMICAL EVIDENCES IN SUPPORT OF A CYCLIC TRANSITION STATE

Lydia Ambroise, Didier Desmaële, Jacqueline Mahuteau, Jean d'Angelo*
Unité de Chimie Organique, Centre d'Etudes Pharmaceutiques, 5, rue J.- B. Clément, 92296 Châtenay-Malabry.

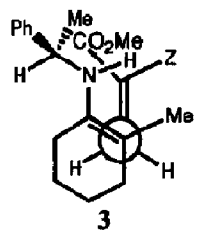


1



2

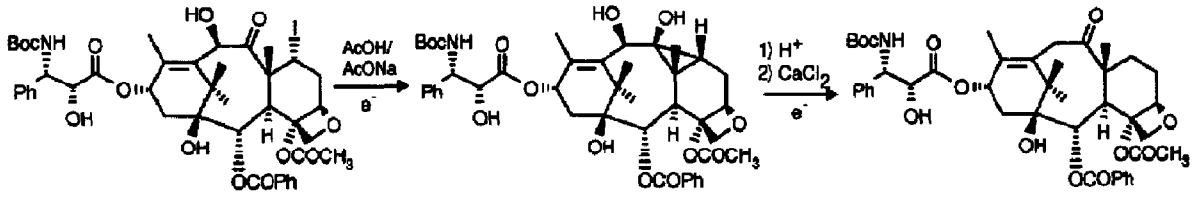
The stereochemical course of the Michael addition of imine 1 to α-substituted acrylates 2 (Z = OAc, D) is rationalized by evoking the compact approach 3.



3

PREPARATION OF 7-MODIFIED DOCETAXEL ANALOGS USING ELECTROCHEMISTRY. J-P. Pulicani, H. Bouchard, J-D. Bourzat and A. Commerçon*, Rhône-Poulenc Rorer S.A., CRVA, 13 Quai Jules Guesde , BP14, 94403 Vitry-sur-Seine (France)

Tetrahedron Letters, **1994**, *35*, 9709

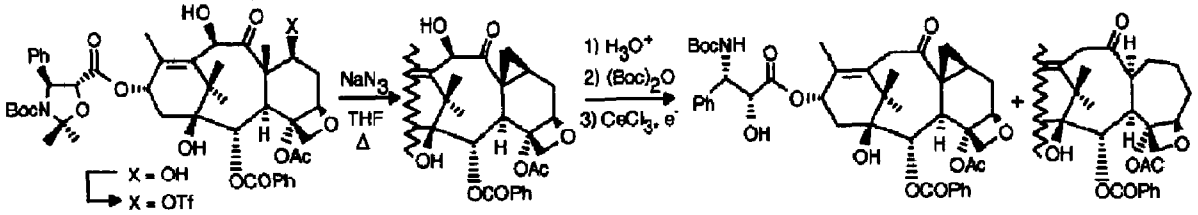


7-deoxy-7α-iodo-docetaxel

7,10-dideoxy-docetaxel

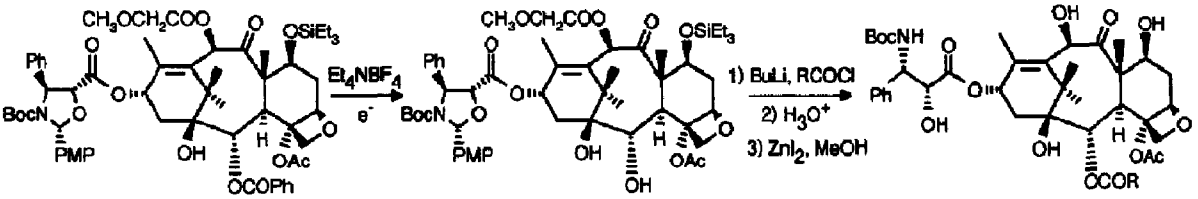
IMPROVED ACCESS TO 19-NOR-7β,8β-METHYLENE-TAXOIDS AND FORMATION OF A 7-MEMBERED C-RING ANALOG OF DOCETAXEL BY ELECTROCHEMISTRY. H. Bouchard, J-P. Pulicani, M. Vuilhorgne, J-D. Bourzat and A. Commerçon*, Rhône-Poulenc Rorer S.A., CRVA, 13 Quai Jules Guesde, BP14, 94403 Vitry-sur-Seine (France)

Tetrahedron Letters, **1994**, *35*, 9713



DIRECT ACCESS TO 2-DEBENZOYL TAXOIDS BY ELECTROCHEMISTRY, SYNTHESIS OF 2-MODIFIED DOCETAXEL ANALOGS. J-P. Pulicani, D. Bézard, J-D. Bourzat, H. Bouchard, M. Zucco, D. Deprez and A. Commerçon*, Rhône-Poulenc Rorer S.A., CRVA, 13 Quai Jules Guesde, BP14, 94403 Vitry-sur-Seine (France)

Tetrahedron Letters, **1994**, *35*, 9717

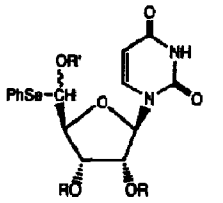


DIASTEREOFACE SELECTIVITY IN RADICAL-MEDIATED C-C BOND FORMATION OF URIDINE 5'-MONOSELENOACETALS

Tetrahedron Letters, **1994**, *35*, 9721

Kazuhiro Haraguchi, Hiromichi Tanaka,* Shigeru Saito, Kentaro Yamaguchi, and Tadashi Miyasaka
School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo 142

Radical reactions of uridine 5'-monoselenoacetals, both intramolecular and intermolecular, have been shown to proceed with preferential anti-Cram diastereoface selection.



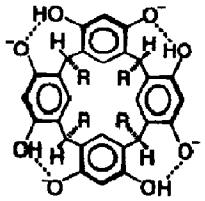
R= isopropylidene, Ac, or TBDMS
R'= Ac or COPh

Tetrahedron Letters, **1994**, *35*, 9725

ENHANCED SUGAR-BINDING ABILITY OF DEPROTONATED CALIX[4]RESORCARENE IN WATER: BALANCE OF CH–π INTERACTION AND HYDROPHOBIC EFFECT

Ryoji Yanagihara and Yasuhiro Aoyama*
Section of Biofunctional Chemistry, Department of BioEngineering, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan

The complexation of calix[4]resorcarene and sugar (fucose) in water can be significantly facilitated upon deprotonation of the OH groups of the host, as a result of a better sugar–host CH–π interaction.

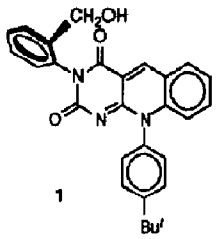


Tetrahedron Letters, **1994**, *35*, 9729

VARIATION OF REACTION CHANNEL IN A FLAVOENZYME MODEL WITH A MODIFIED PYRIMIDINE RING

Atsuyoshi Ohno[1], Jun Kunitomo[1], Tetsuji Kawamoto[2], Masaki Tomishima[2], Kiyoshi Bessho[2] and Fumio Yoneda[2]
[1] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
[2] Faculty of Pharmaceutical Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

A novel 5-deazaflavin derivative **1** with axial chirality has been synthesized. The hydroxy group of **1** has significant effects on both reactivity and stereochemistry of its reaction.

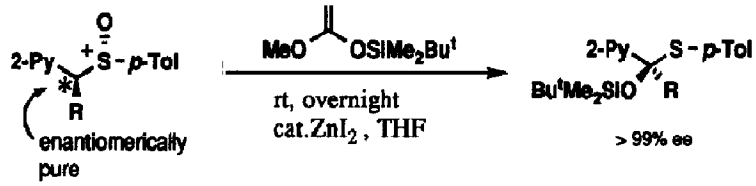


1

Tetrahedron Letters, **1994**, *35*, 9733

ENANTIOSELECTIVE PUMMERER-TYPE REARRANGEMENT BY REACTION OF O-SILYLATED KETENE ACETAL WITH ENANTIOPURE α-SUBSTITUTED SULFOXIDES

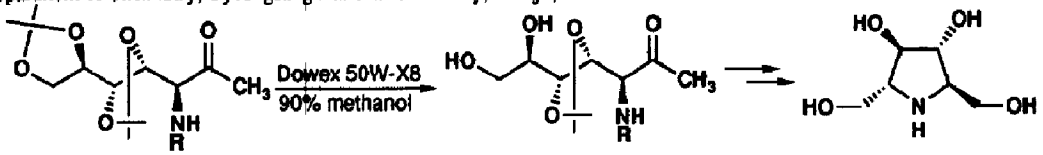
Yasuyuki Kita*, Norio Shibata, Seiji Fukui, and Shigekazu Fujita
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-oka, Suita, Osaka 565, Japan



Tetrahedron Letters, **1994**, *35*, 9737

Efficient Cleavage of Terminal Acetonide group: Chirospecific Synthesis of 2,5-Dideoxy-2,5-Imino-D-Mannitol.

KI Hun Park, Yong Jin Yoon and Sang Gyeong Lee*
Department of Chemistry, Gyeongsang National University, Chinju, Korea 660-701.



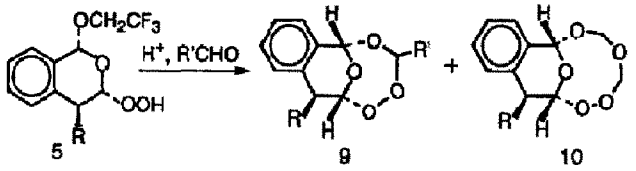
Dowex 50W-X8 was efficient catalyst for selective cleavage of terminal acetonide having acid-sensitive groups

Tetrahedron Letters, **1994**, *35*, 9741

Transformation of Solvent-Derived Ozonolysis Products to Bicyclic Peroxides: Isolation and Characterisation of Novel Pentoxonane Derivatives.

Yoshihiro Ushigoe,[a] Shogo Tanaka,[a] Masatomo Nojima,[a] and Kevin J. McCullough,[b]
[a] Department of Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan
[b] Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland

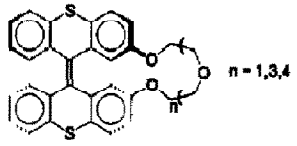
α-Hydroperoxyisochroman derivatives **5** react with formaldehyde under acidic conditions to produce mixtures of bicyclic 1,2,4,6-tetroxepane **9** and 1,2,4,6,8-pentoxonane **10** derivatives. With acetaldehyde (R' = CH_3), only the corresponding 1,2,4,6-tetroxepanes **9** were obtained.



Tetrahedron Letters, **1994**, *35*, 9745

SYNTHESIS AND ^{1}H-NMR COMPLEXATION STUDIES OF ALKALI METAL BITHIOXANTHYLIDENE CROWN ETHER COMPLEXES

Anne Marie Schoevaars, Ron Hulst and Ben L. Feringa* Department of Organic and Molecular Inorganic Chemistry, Groningen Center of Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

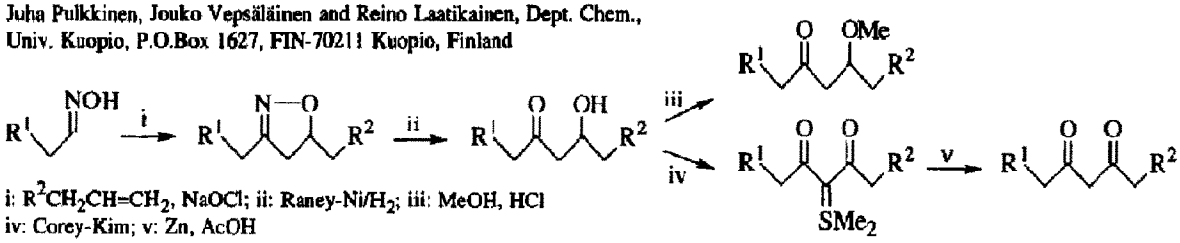


Bithioxanthylidene crown ethers were synthesized and subjected to ^{1}H NMR (T_1) complexation studies with alkalimetal cations.

Tetrahedron Letters, **1994**, *35*, 9749

A GENERAL ROUTE TO 3-UNSUBSTITUTED 1,5-DIARYL-2,4-PENTANEDIONES AND -4-METHOXY-2-PENTANONES.

Juha Pulkkinen, Jouko Vepsäläinen and Reino Laatikainen, Dept. Chem., Univ. Kuopio, P.O.Box 1627, FIN-70211 Kuopio, Finland



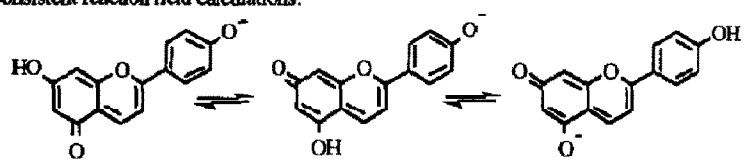
i: $R^2CH_2CH{=}CH_2$, NaOCl; ii: Raney-Ni/H_2; iii: MeOH, HCl
iv: Corey-Kim; v: Zn, AcOH

Tetrahedron Letters, **1994**, *35*, 9751

SOLVENT EFFECTS ON THE TAUTOMERISM OF APIGENINIDIN

Giulio Rastelli,* Luca Costantino, Albano Albasini
Dipartimento di Scienze Farmaceutiche, Università di Modena, Via G. Campi 183 41100 Modena (Italy)

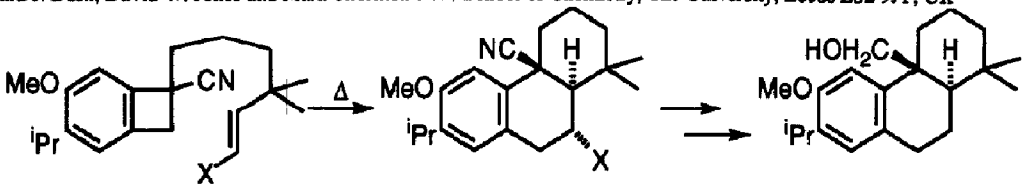
Tautomerism of apigeninidin in water solution is examined by means of free energy perturbation/molecular dynamics simulations and self-consistent reaction field calculations.



Tetrahedron Letters, **1994**, *35*, 9755

SYNTHESIS OF PISIFEROL REVISITED; CONTROL OF STEREO-CHEMISTRY IN AN INTRAMOLECULAR DIELS-ALDER REACTION.

Edward J. Bush, David W. Jones and Mark Thornton-Pett, School of Chemistry, The University, Leeds LS2 9JT, UK

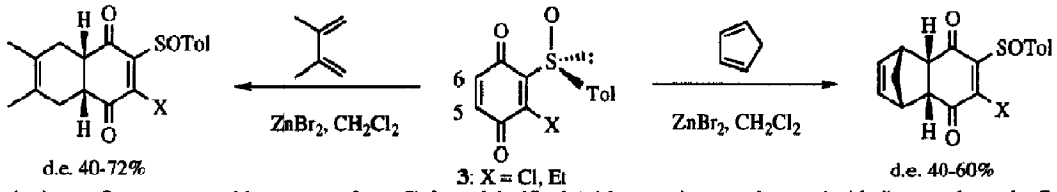


Unlike the system with X=H that with X=SO_2Ph gives mostly the product of *endo*-SO_2Ph (*exo*-tether) addition. Thich is readily converted into pisiferol.

Tetrahedron Letters, **1994**, *35*, 9759

SYNTHESIS AND DIELS-ALDER REACTIONS OF (S)-3-CHLORO AND (S)-3-ETHYL-2-p-TOLYLSULFINYL-1,4-BENZOQUINONES.

M.C. Carreño, J.L. García Ruano, M.A. Toledo and A. Urbano. Dpto de Química (C-I). Universidad Autónoma de Madrid. Spain.



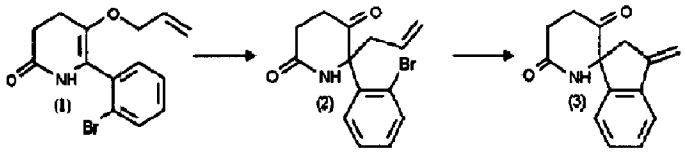
d.e. 40-72% — **3**: X = Cl, Et — d.e. 40-60%

Sulfinylquinones **3** were prepared in two steps from (S)-2-p-tolylsulfinyl-1,4-benzoquinone and reacted with dienes only on the C_5-C_6 unsubstituted double bond.

Tetrahedron Letters, **1994**, *35*, 9763

A NOVEL PALLADIUM(0) CATALYSED TANDEM 1,3-ALLYL SHIFT AND HECK ARYLATION: Stephen P.Watson, Graham R. Knox and Nicola M. Heron

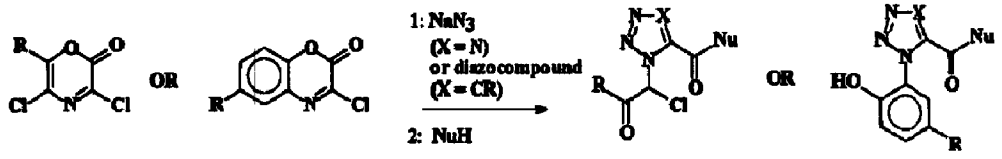
On treatment with $Pd(PPh_3)_4$ allyl vinyl ether (1) undergoes a Pd(0) catalysed 1,3 oxygen to carbon allyl shift to afford ketone (2). On treatment with $Pd(PPh_3)_4$ and base (1) undergoes a Pd(0) catalysed tandem 1,3 allyl shift and intramolecular Heck arylation to give spiro indane (3). Mechanistic investigations suggest that the 1,3-allyl shift involves a π-allyl palladium intermediate.



Tetrahedron Letters, **1994**, *35*, 9767

SYNTHESIS OF NEW [1,2,3]TRIAZOLES AND 1*H*-TETRAZOLES *VIA* REACTIONS OF 3,(5)-(DI)CHLORO-2*H*-1,4-(BENZ)OXAZIN-2-ONES WITH DIAZOCOMPOUNDS OR SODIUM AZIDE. **Georges Hoornaert*, Bart Medaer, Koen Van Aken, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.**

Sodium azide and diazocompounds react with (benz)oxazinones to give specifically substituted [1,2,3]triazoles and 1*H*-tetrazoles after lactone cleavage with various nucleophiles.

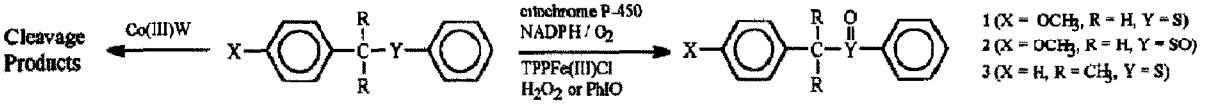


Tetrahedron Letters, **1994**, *35*, 9771

THE MECHANISM OF ENZYMATIC AND BIOMIMETIC OXIDATIONS OF AROMATIC SULFIDES AND SULFOXIDES

Enrico Baciocchi*, Osvaldo Lanzalunga, Francesco Marconi.
Dipartimento di Chimica and Centro CNR di Studio sui Meccanismi di Reazione, Università "La Sapienza", P.le A. Moro 5, 00185 Rome (Italy)

Biomimetic and enzymatic oxidations of **1-3** lead to products (sulfoxides or sulfones) different from those obtained in the electron transfer oxidations (products of C-H and/or C-S bond cleavage), which suggest an oxygen transfer mechanism.

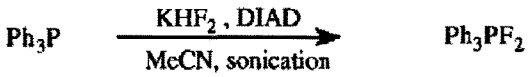


Tetrahedron Letters, **1994**, *35*, 9775

Synthesis of Fluorophosphoranes via The Mitsunobu Reaction

Peta J. Harvey and Ian D. Jenkins*
Faculty of Science and Technology, Griffith University, Nathan, Qld. 4111, Australia

Treatment of triphenylphosphine with potassium hydrogen fluoride and diisopropyl azodicarboxylate, results in the formation of difluorotriphenylphosphorane.

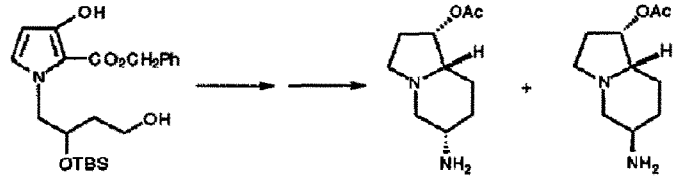


Tetrahedron Letters, **1994**, *35*, 9779

THE CHEMISTRY OF VICINAL TRICARBONYLS. A SYNTHESIS OF (±)-SLAFRAMINE AND (±)-6-EPI-SLAFRAMINE.

Harry H. Wasserman,* and Chi B. Vu, Department of Chemistry, Yale University, New Haven, CT 06520-8107 USA

A synthesis of (±)-slaframine and (±)-6-epi-slaframine is described. The approach makes use of the intramolecular alkylation of an N-substituted 3-hydroxypyrrole-2-carboxylate ester.

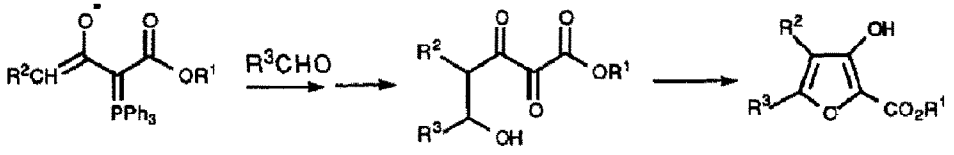


Tetrahedron Letters, **1994**, *35*, 9783

THE CHEMISTRY OF VICINAL TRICARBONYLS. A NEW SYNTHESIS OF SUBSTITUTED FURANS.

Harry H. Wasserman* and Gary M. Lee, Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107 USA

Enolates of acyl phosphoranylidine carboxylates react with aldehydes to form alcohols which undergo intramolecular addition to a vicinal tricarbonyl unit, leading to substituted furans.



Tetrahedron Letters, **1994**, *35*, 9787

THE CHEMISTRY OF VICINAL TRICARBONYLS. USE OF VINYL AND ACETYLENIC DERIVATIVES IN THE SYNTHESIS OF SUBSTITUTED INDOLES.

Harry H. Wasserman* and Charles A. Blum, Department of Chemistry, Yale University, New Haven, CT 06520-8107 USA

Vinyl and acetylenic vicinal tricarbonyl derivatives take part as dienophiles in Diels-Alder reactions, leading to substituted indoles as well as to their dihydro and tetrahydro derivatives.