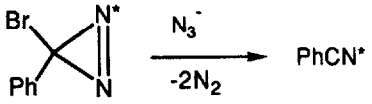
## GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30, 4901 (1989)

### ON THE MECHANISM OF THE DIAZIRINE EXCHANGE REACTION WITH AZIDE ANION

Kathleen E. Bainbridge and William P. Dailey*, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Treatment of isotopically labeled bromophenyldiazirine containing one $^{15}N$ atom with azide ion produces benzonitrile which contains 50% $^{15}N$.

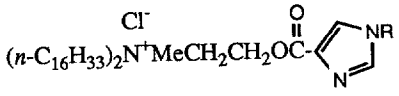



Tetrahedron Lett. 30, 4905 (1989)

### IMIDAZOLE MEDIATED ACYLATION OF CHOLESTEROL IN FUNCTIONAL VESICLES: A SIMPLE ANALOGUE OF LECITHIN:CHOLESTEROL ACYLTRANSFERASE

R. A. Moss, S. Bhattacharya, and Y. Okumura, Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903

Imidazole-functionalized surfactants (R=H) transfer acetyl groups from p-nitrophenyl acetate to cholesterol in vesicular coaggregates.

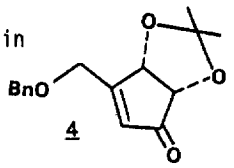



Tetrahedron Lett. 30, 4909 (1989)

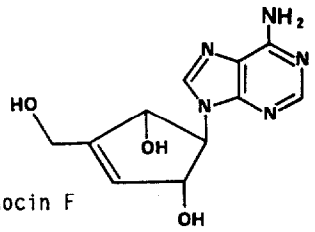
### TOTAL SYNTHESIS OF (±)-NEPLANOCIN F

Michael Bodenteich and Victor E. Marquez*
Laboratory of Medicinal Chemistry, DTP, DCT, National Cancer Institute, NIH, Bethesda, Maryland 20892

(±)-Neplanocin F was synthesized in 12 steps from 4.




4

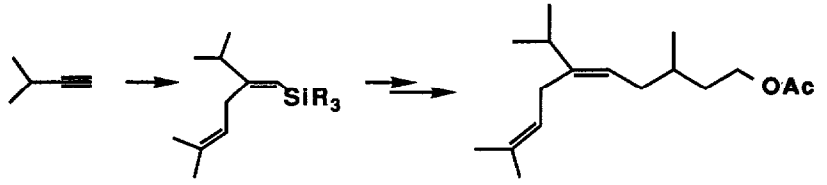



(±)-Neplanocin F

Tetrahedron Lett. 30, 4913 (1989)

### APPLICATION OF SILYLCUPRATION TO THE STEREO- AND REGIOSPECIFIC FORMATION OF TRISUBSTITUTED ALKENES. A SHORT SYNTHESIS OF YELLOW SCALE PHEROMONE.

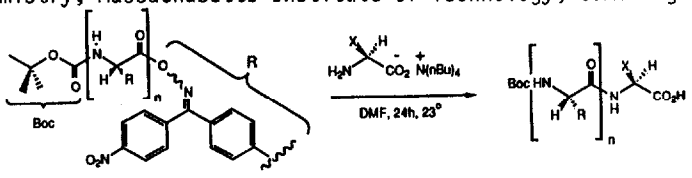
Jocelyn G. Millar, Dept of Entomology, University of California, Riverside CA 92521 USA



Tetrahedron Lett.30,4915(1989)

## A PRACTICAL METHOD FOR THE PREPARATION OF PROTECTED PEPTIDE FRAGMENTS USING THE KAISER OXIME RESIN

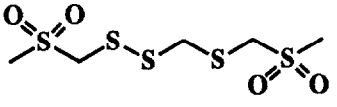
Peter T. Lansbury, Jr.*, Julia C. Hendrix, and Annemarie I. Coffman
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139




Tetrahedron Lett.30,4919(1989)

## DYSOXYSULFONE, A SULFUR RICH METABOLITE FROM THE FIJIAN MEDICINAL PLANT DYSOXYLUM RICHII

Madhu K. Jogia[1], Raymond J. Andersen*[1], Ellen K. Mantus[2] and Jon Clardy*[2].
[1]Departments of Chemistry and Oceanography, UBC, Vancouver, B.C., Canada V6T 1W5
[2]Department of Chemistry-Baker Laboratory, Cornell University, Ithaca, N.Y., USA 14853

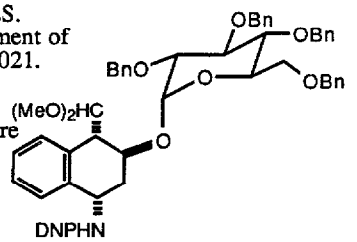


Tetrahedron Lett.30,4921(1989)

## CYCLOADDITION OF ISOQUINOLINIUM SALTS: HOMOCHIRAL TETRALINS VIA DIENOPHILES BEARING CHIRAL AUXILIARIES.

Anusuya Choudhury, Richard W. Franck* and Ram B. Gupta, Department of Chemistry, Hunter College/CUNY, 695 Park Ave., New York, NY 10021.

Inverse electron demand cycloaddition of isoquinolinium salts to dienophiles bearing chiral auxiliaries to produce homochiral tetralins are described. The optical purity of the product ranges from 5% to 95+% depending on the chiral auxiliary.




Tetrahedron Lett.30,4925(1989)

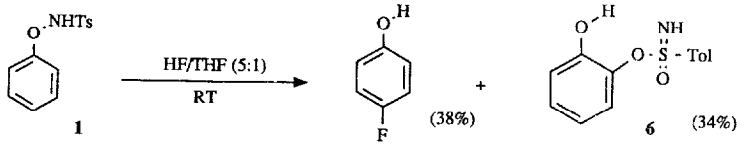
## CONTROLLED BETA-HYDRIDE ELIMINATION DURING TETRAHYDROPYRAN FORMATION WITH Pd(II); DIASTEREOSELECTIVE FORMATION OF THE TETRAHYDROPYRAN RING OF TETRONOMYCIN

M. F. Semmelhack*, Chung Ryeol Kim, Walter Dobler, and Michael Meier
Department of Chemistry, Princeton University, Princeton, NJ 08544.

In the intramolecular alkoxy-palladation of alkenes, the use of DMSO as solvent leads to specific β-hydride elimination and formation of a *trans* 2-vinyl substituent. An example is the model(1) for the tetrahydropryan ring of tetronomycin.

Tetrahedron Lett. 30, 4929 (1989)

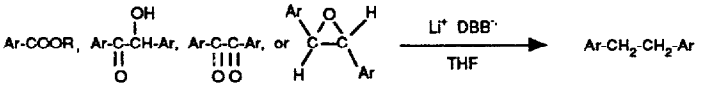
FLUORINATION REACTIONS WITH HF/THF MEDIUM SOLVOLYSIS OF N-TOSYL-O-PHENYLHYDROXYLAMINE. William R. Dolbier, Jr., Lech Celewicz and Keiichi Ohnishi; Department of Chemistry; University of Florida 32611.




Tetrahedron Lett. 30, 4931 (1989)

## DEOXIDATION/REDUCTION OF AROMATIC ESTERS, α-DIKETONES, ACYLOINS, AND EPOXIDES TO THE CORRESPONDING BIBENZYL PRODUCTS WITH LITHIUM 4,4′-DI-*T*-BUTYLBIPHENYL RADICAL ANION

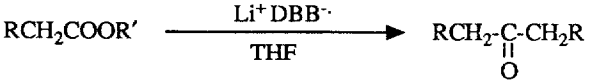
Rafik Karaman and James L. Fry
Bowman-Oddy Laboratories, Department of Chemistry
The University of Toledo, Toledo, OH 43606-3390




Tetrahedron Lett. 30, 4935 (1989)

## ELECTRON TRANSFER REACTIONS OF ALIPHATIC ESTERS TO THE CORRESPONDING ALIPHATIC KETONES BY LITHIUM 4,4′-DI-*T*-BUTYLBIPHENYL RADICAL ANION

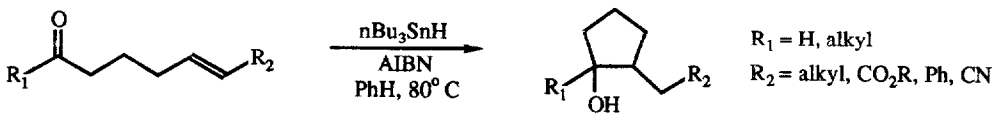
Rafik Karaman and James L. Fry
Bowman-Oddy Laboratories, Department of Chemistry
The University of Toledo, Toledo, OH 43606-3390




Tetrahedron Lett. 30, 4939 (1989)

## TRIBUTYLTIN HYDRIDE-INDUCED O-STANNYL KETYLS IN THE CYCLIZATION OF ALDEHYDES AND KETONES WITH ALKENES

Eric J. Enholm* and Girija Prasad
Department of Chemistry, University of Florida, Gainesville, Florida 32611

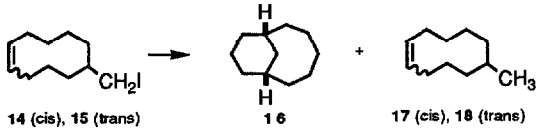


Tetrahedron Lett. 30, 4943 (1989)

## TEN-MEMBERED RING TEMPLATES FOR STEREOSELECTIVE RADICAL CYCLIZATIONS

Jeffrey D. Winkler*, V. Sridar and Miles G. Siegel
Searle Chemical Laboratories, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Transannular cyclization of the radicals derived from **14** and **15** both lead to the regio- and stereoselective formation of cis-bicyclo[5.3.1]undecane, **16**, an important structural feature of the taxane diterpenes. The ratio of cyclization to reduction depends critically on the alkene geometry.




**14** (cis), **15** (trans) **16** **17** (cis), **18** (trans)

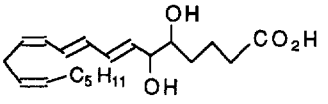
Tetrahedron Lett. 30, 4947 (1989)

## STEREOSPECIFIC TOTAL SYNTHESIS OF (5.6)-DIHETE ISOMERS

C. KUGEL , J. P. LELLOUCHE, J. P. BEAUCOURT, G. NIEL* , J.P. GIRARD*, J.C. ROSSI* .

C.E.N. Saclay, Service des Molécules Marquées, Bât 547, F-91191 GIF sur YVETTE.* U.R.A 1.111 C.N.R.S., Université Montpellier I, Faculté de Pharmacie; 15, Avenue Charles Flahault, F-34O6O MONTPELLIER.

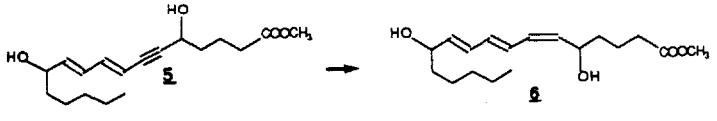
The first highly practical stereocontrolled synthesis of the four diastereoisomeric (5,6)-DiHETEs is described using the acetonides of D-and L-glyceraldehyde as a source of chirality.




Tetrahedron Lett. 30, 4951 (1989)

## IMPROVED STEREOSELECTIVE REDUCTION OF A E,E,CONJUGATED DIENYNE TO A E,E,Z,CONJUGATED TRIENE

M.Avignon-Tropis* and J.R.Pougny
Centre de Recherche de Biochimie et de Génétique Cellulaires CNRS
118 Route de Narbonne, 31062 Toulouse cedex. France.



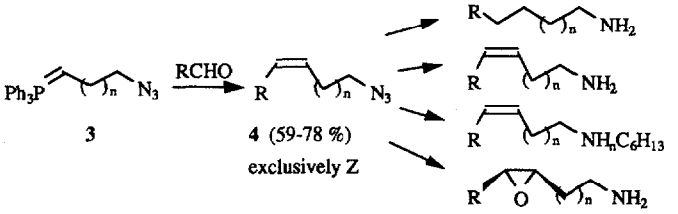

The stereoselective reduction of the functionalised E,E conjugated dienyne **5** with Zn(Cu/Ag) in aqueous methanol produces the E,E,Z conjugated triene **6**.

Tetrahedron Lett. 30, 4953 (1989)

## ω-azidoalkylidenetriphenylphosphoranes for the stereospecific synthesis of Z olefins bearing an ω-azido group.

A. Chhen, M. Vaultier * and R. Carrié
Groupe de Physicochimie Structurale associé au C.N.R.S., Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cédex, France.

Ylids **3** are stable at low temperature and react with aldehydes to give Z-**4** in good yields. **4** are the precursors of a number of primary or secondary amino derivatives.



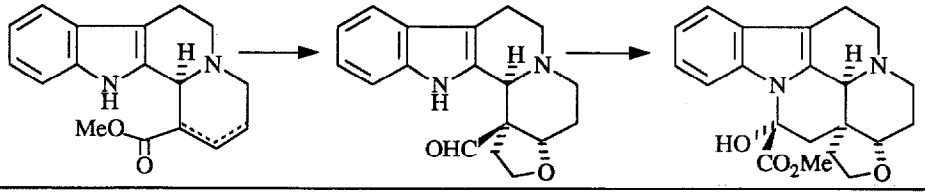

**3** **4** (59-78 %) exclusively Z

## A SHORT STEREOSELECTIVE SYNTHESIS OF (±) 12-DESMETHOXY CUANZINE.

Tetrahedron Lett. 30, 4957 (1989)

J-C. Ortuno, N. Langlois and Y. Langlois*.
Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif s/Yvette Cedex, France.

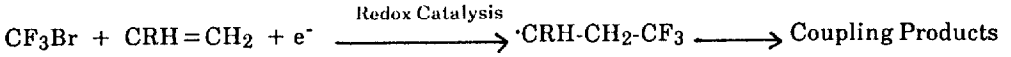
A stereoselective synthesis of 12-desmethoxy cuanzine was achieved in eleven steps.




## UNUSUAL REACTIONS RESULTING FROM THE ADDITION ON OLEFINS OF TRIFLUOROMETHYL RADICALS OBTAINED FROM DISSOCIATIVE ELECTRON TRANSFER BETWEEN ELECTRO-CHEMICALLY GENERATED AROMATIC ANION RADICALS AND TRIFLUOROMETHYL BROMIDE

Tetrahedron Lett. 30, 4961 (1989)

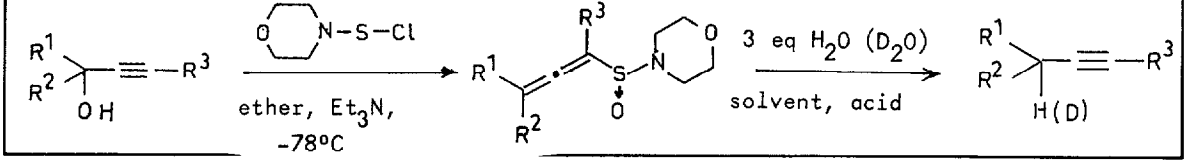
C.P. ANDRIEUX, L. GELIS and J.M. SAVEANT, Laboratoire d'Electrochimie Moléculaire de l'Université Paris 7.




## SUBSTITUTED 4-(1',2'-ALKADIENESULPHINYL)-MORPHOLINES; PREPARATION AND HYDROLYTIC DESULPHINYLATION INTO THE CORRESPONDING ALKYNES.

Tetrahedron Lett. 30, 4965 (1989)

Jean-Bernard Baudin, Sylvestre A. Julia, Yuan Wang, Laboratoire de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France.

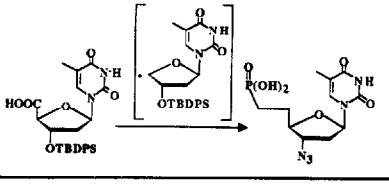



## STEREOSELECTIVITY IN RADICAL REACTIONS OF 2'-DEOXYNUCLEOSIDES. A SYNTHESIS OF AN ISOSTERE OF 3'-AZIDO-3'-DEOXYTHYMIDINE-5'-MONOPHOSPHATE. (AZT-5'-MONOPHOSPHATE)

Tetrahedron Lett. 30, 4969 (1989)

Derek H.R. Barton,[a] Stephan D. Géro,[b] Béatrice Quiclet-Sire,[b] and Mohammad Samadi*[b]
[a]Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.
[b]Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France.

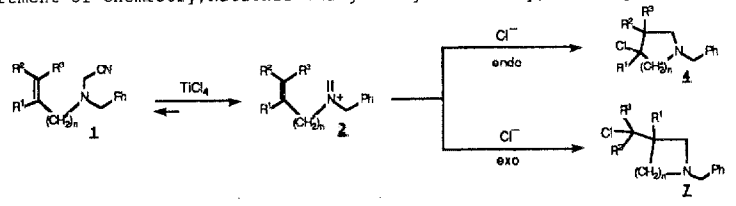
An isosteric phosphonate of AZT 5'-monophosphate has been synthesised by a stereoselective addition of diethylvinylphosphonate on a radical generated from an acid derivative of thymidine.



Tetrahedron Lett.30,4973(1989)

## TICL4 INDUCED IMINIUM ION CYCLIZATIONS OF α-CYANOAMINES

Teng-Kuei Yang*, Shun-Ming Hung,
Dong-Sheng Lee, An-Way Hong, Chan-Chun Cheng
Department of Chemistry, National Chung-Hsing University, Taichung, Taiwan 40227, R.O.C.

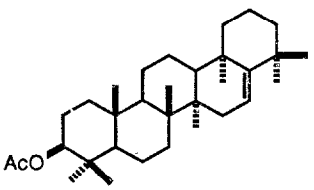


Tetrahedron Lett.30,4977(1989)

## COMPOSITE CONSTITUENTS: THREE GAMMACER-16-ENE DERIVATIVES, NOVEL TRITERPENOIDS, ISOLATED FROM ROOTS OF *PICRIS HIERACIOIDES* SUBSP. *JAPONICA*

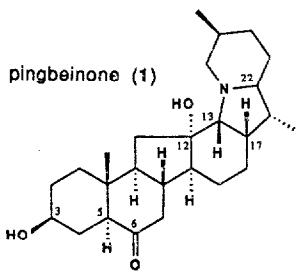
Kenji Shiojima, Kazuo Masuda, Tokuhide Lin and Hiroyuki Ageta*, *Showa College of Pharmaceutical Sciences, 5-1-8 Tsurumaki, Setagaya-ku, Tokyo 154, JAPAN*
Masatoshi Inoue and Toshimasa Ishida, *Osaka University of Pharmaceutical Sciences, 2-10-65 Kawai, Matsubara, Osaka 580, JAPAN*

New triterpenoids, gammacer-16-en-3β-yl acetate and its 3β-, 3α-ols were isolated from *Picris hieracioides* subsp. *japonica*. Their structures were established by chemical, spectral and X-ray methods.




Tetrahedron Lett.30,4981(1989)

pingbeinone (1)




## Pingbeinone, A Novel Steroidal Alkaloid having C-18 nor Cevane Skeleton from *Fritillaria ussuriensis* Maxim.

Yukie Kitamura, Makoto Nishizawa, Koh Kaneko*, Motoo Shiro, Yuh-Pan Chen and Hong-Yen Hsu, *Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

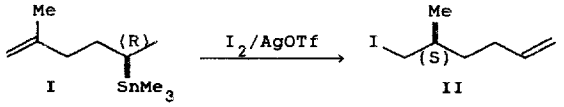
The structure of pingbeinone (1) was established by X-ray crystallographic analysis, and 1 was shown to have a novel C-18 nor cevane skeleton.

Tetrahedron Lett.30,4983(1989)

## CHIRALITY TRANSFER IN THE 1,5-HYDRIDE SHIFT OF A STANNYL COMPOUND HAVING CATIONIC CENTER AT δ-POSITION

Tadashi Sato,* Masayuki Haramura, and Naoki Taka. Department of Applied Chemistry, Waseda University, Ookubo 3, Shinjuku-ku, Tokyo 169, Japan

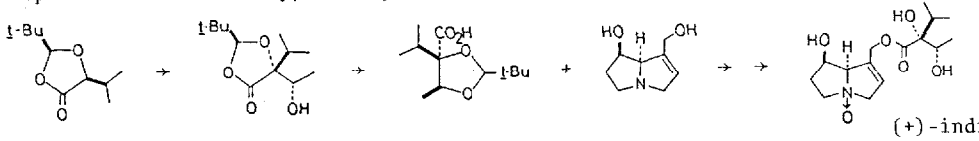
Chirality transfer with 7 : 1 selectivity was realized in the $I_2$-AgOTf-induced 1,5-hydride shift of I to II.



Tetrahedron Lett. 30, 4985 (1989)

## AN EFFICIENT ENANTIOSELECTIVE SYNTHESIS OF (+)-INDICINE N-OXIDE, AN ANTITUMOR PYRROLIZIDINE ALKALOID

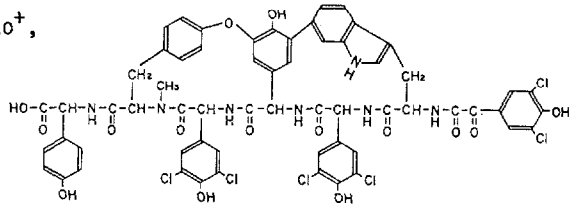
Haruki Niwa,* Takeshi Ogawa, and Kiyoyuki Yamada
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan




Tetrahedron Lett. 30, 4987 (1989)

## STRUCTURE OF COMPLESTATIN, A VERY STRONG INHIBITOR OF PROTEASE ACTIVITY OF COMPLEMENT IN THE HUMAN COMPLEMENT SYSTEM

H. Seto, T. Fujioka, K. Furihata, I. Kaneko+, S. Takahashi++ Institute of Applied Microbiology, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan , +Bioscience Research Laboratories, ++Fermentation Research Laboratories, Sankyo Co. Ltd., Hiromachi, Shinagawa-ku, Tokyo 114, Japan

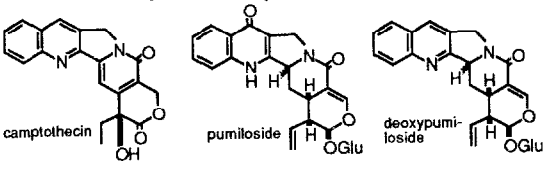


Tetrahedron Lett. 30, 4991 (1989)

## PUMILOSIDE AND DEOXYPUMILOSIDE; PLAUSIBLE INTERMEDIATES OF CAMOTOTHECIN BIOSYNTHESIS

N. Aimi, M. Nishimura, A. Miwa, H. Hoshino, S. Sakai , and J. Haginiwa
Faculty of Pharmaceutical Sciences, Chiba University, 1-33 Yayoi-cho, Chiba 260, Japan

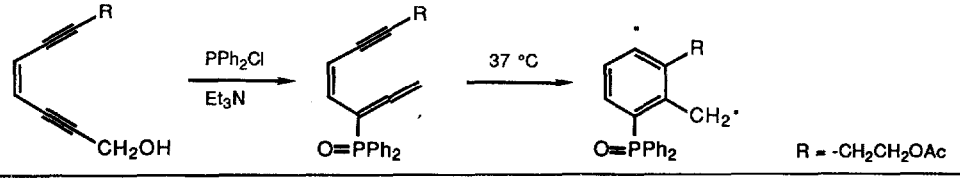
Long-postulated poststrictosamide intermediates of camptothecin biosynthesis were found in nature.




Tetrahedron Lett. 30, 4995 (1989)

## BIRADICAL FORMATION FROM ACYCLIC CONJUGATED ENEYNE-ALLENE SYSTEM RELATED TO NEOCARZINOSTATIN AND ESPERAMICIN-CALICHEMICIN

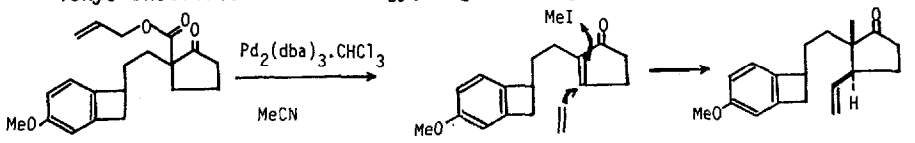
Ryu Nagata, Hidenori Yamanaka, Eiichi Okazaki, and Isao Saito*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan



Tetrahedron Lett.30,4999(1989)

EFFICIENT APPROACH TO THE OPPOLZER-KAMETANI INTERMEDIATE FOR ESTRONE METHYL ETHER USING THE CONJUGATE ADDITION-METHYLATION OF THE CYCLOPENTENONE CONTAINING AN α-APPENDED BENZOCYCLOBUTANE MOIETY.

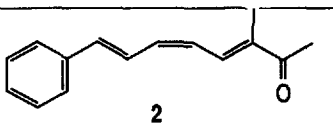
Takashi Takahashi*, Katsuya Shimizu, Takayuki Doi, Jiro Tsuji and Keiji Yamamoto
Tokyo Institute of Technology, Meguro, Tokyo 152, JAPAN



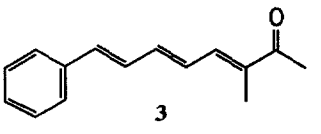

Tetrahedron Lett.30,5003(1989)

POTENTIAL ALARM PHEROMONES FROM THE MEDITERRANEAN OPISTHOBRANCH *S. LIGNARIUS*

G. Cimino◊, A. Spinella◊* and G. Sodano#
◊Istituto per la Chimica di Molecole di Interesse Biologico del CNR. Arco Felice, Napoli, Italy.
#Istituto di Chimica, Università della Basilicata. Potenza, Italy.




2




3

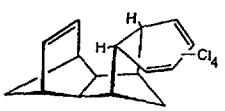
Two new ω-phenyl conjugated trienones, lignarenone-A (2) and lignarenone-B (3), are the main metabolites present in the mantle of *Scaphander lignarius*. Their structures are closely related to those of the alarm pheromones of *Navanax inermis*.

Tetrahedron Lett.30,5005(1989)

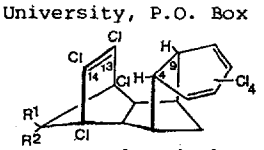
On Intramolecular Dyotropy: Structural Effects on Reaction Rates and X-ray Crystal Structure - Molecular Mechanics Correlations.

Judith A.K. Howard, Kenneth Mackenzie, Robert E. Johnson (School of Chemistry, The University, Bristol BS8 1TS, U.K.) and K. Brian Astin (Department of Chemistry, The University, P.O. Box 32038, Bahrain).

Abstract: Differential kinetic behaviour in thermal dyotropic isomerisation of pentacyclic trienes e.g. norbornene-unsubstituted compound T and substituted analogues 9, 13 is discussed.




T



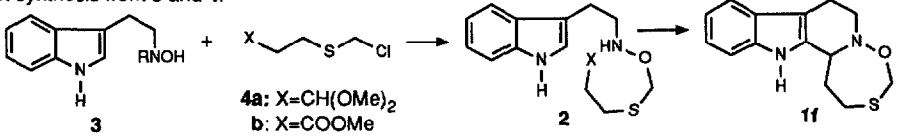

9 $R^1=R^2=H$
13 $R^1=R^2=Cl$

Tetrahedron Lett.30,5009(1989)

**Intramolecular Pictet-Spengler reaction of N-alkoxytryptamines.Synthesis of (±)-deamino-debromo-Eudistomin L**

Pedro H.H.Hermkens, Jan H.v.Maarseveen, Chris G.Kruse, Hans W.Scheeren
Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

The Eudistomin analogue **11** was obtained by an intramolecular Pictet-Spengler reaction of **2**. The latter has been synthesized in an one-pot synthesis from **3** and **4**.

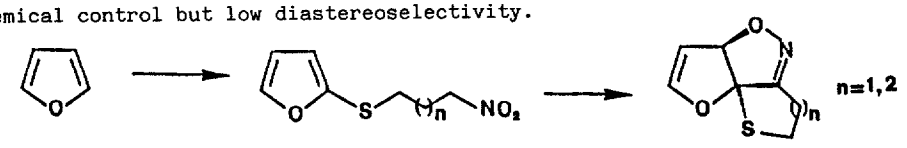


Tetrahedron Lett.30,5013(1989)

Regio- and Stereoselectivity of Intramolecular Nitrile Oxide Cycloaddition to Furan.

R.Annunziata, M.Cinquini, F.Cozzi and L.Raimondi
Dipartimento di Chimica Organica e Industriale, Via Golgi 19, I-20133 Milano, Italy.

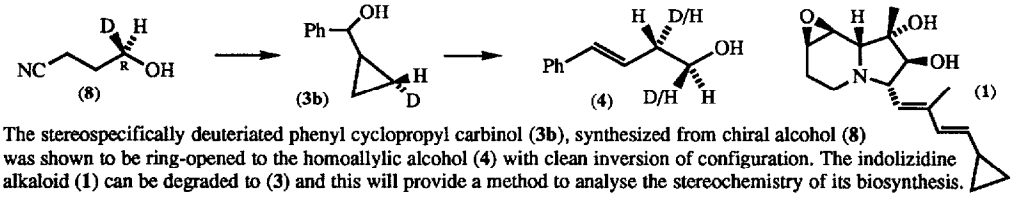
Intramolecular nitrile oxide cycloaddition to functionalized furans occurs with complete regiochemical control but low diastereoselectivity.




Tetrahedron Lett.30,5017(1989)

STEREOSPECIFIC NUCLEOPHILIC RING-OPENING OF A DEUTERIATED CYCLOPROPYLCARBINOL

F. J. Leeper and P. Padmanabhan, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.



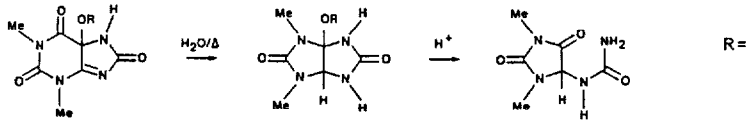

The stereospecifically deuteriated phenyl cyclopropyl carbinol (**3b**), synthesized from chiral alcohol (**8**) was shown to be ring-opened to the homoallylic alcohol (**4**) with clean inversion of configuration. The indolizidine alkaloid (**1**) can be degraded to (**3**) and this will provide a method to analyse the stereochemistry of its biosynthesis.

Tetrahedron Lett.30,5021(1989)

SYNTHESIS OF OPTICALLY ACTIVE 1,3-DIMETHYLALLANTOINS VIA (-)-MENTHYL ETHERS OF THEIR BICYCLIC TAUTOMERS

N.Modrić,[a] A.F.Drake,[b] and M.Poje,[a]* [a]Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, P. O. Box 153, 41001 Zagreb, Yugoslavia, and [b]Department of Chemistry, Birkbeck College, University of London, London WC1H OAJ, U.K.

The easy availability of both diastereomers of **5** allowed the first synthesis of both enantiomers of **6**.




Tetrahedron Lett.30,5025(1989)

THE REGIOCHEMISTRY OF THE (ETHOXYCARBONYL)NITRENE ADDITION REACTION TO SILOXYDIENES

M. Antonietta Loreto, Lucio Pellacani, P. A. Tardella
Dipartimento di Chimica, Università "La Sapienza",
P.le Aldo Moro 2, I-00185 Roma, Italy