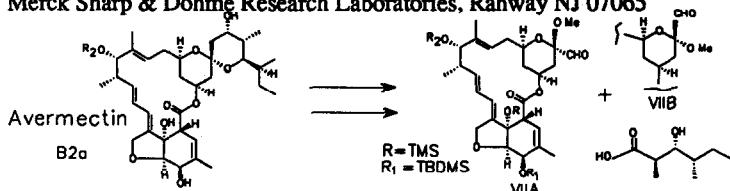


## GRAPHICAL ABSTRACTS

*Tetrahedron Lett.* 1990, 31, 3525

### CLEAVAGE OF THE SPIROKETAL PORTION OF AVERMECTIN B<sub>2a</sub>

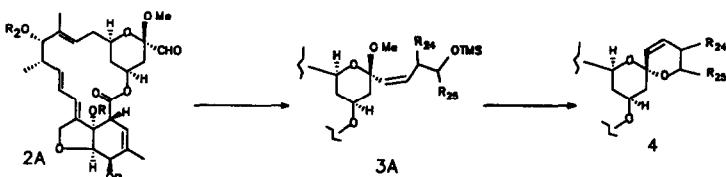
Thomas L. Shih\*, Helmut Mrozik, Mark A. Holmes, Michael H. Fisher  
Merck Sharp & Dohme Research Laboratories, Rahway NJ 07065



*Tetrahedron Lett.* 1990, 31, 3529

### A Wittig Approach to Novel C24 and C25-Substituted Avermectins

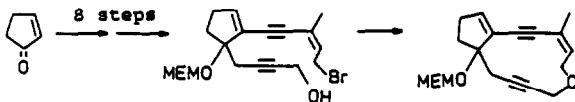
Thomas L. Shih\*, Helmut Mrozik, Mark A. Holmes, & Michael H. Fisher  
Merck Sharp & Dohme Research Laboratories, Rahway NJ 07065



*Tetrahedron Lett.* 1990, 31, 3533

### SYNTHESIS OF A BICYCLIC OXACYCLOALKENEDIYNE SYSTEM RELATED TO NEOCARZINOSTATIN CHROMOPHORE A

Adolf Krebs\*, Thomas Wehlage and Claus-Peter Kramer  
Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6,  
D 2000 Hamburg



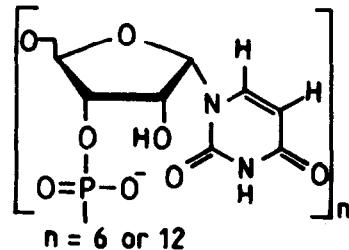
A novel bicyclic cycloalkenediyne system was synthesized starting from cyclopentenone.

*Tetrahedron Lett.* 1990, 31, 3537

### SUGAR MODIFIED OLIGONUCLEOTIDES : II. SOLID PHASE SYNTHESIS OF NUCLEASE-RESISTANT $\alpha$ -ANOMERIC URIDYLATES AS POTENTIAL ANTISENSE AGENTS

Françoise Debart, Bernard Rayner and Jean-louis Imbach  
Université de MONTPELLIER II Sciences et Techniques  
du Languedoc, Laboratoire de Chimie bio-organique  
U.R.A. 436 CNRS, Case 008, Place Eugène Bataillon,  
34095 MONTPELLIER Cedex 5, FRANCE.

For the first time, two  $\alpha$ -anomeric uridylates,  $\alpha$ -rU<sub>6</sub> and  $\alpha$ -rU<sub>12</sub>, have been synthesized. These non natural  $\alpha$ -oligonucleotides strongly resist to enzymatic degradation and bind to complementary RNA strand.

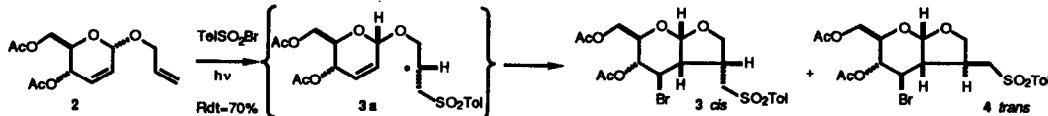


**Stereoselective Free-Radical Cyclization on Sugar Template. The Sulphonyl Radical as a Synthetic Tool for Functionalized Glycosides**

*Tetrahedron Lett.* 1990, 31, 3541

Robert NOUGUIER, Catherine LESUEUR, Enzo De RIGGI, Michèle Paula BERTRAND *Laboratoire de Chimie Organique B - Associé au CNRS - Faculté des Sciences Saint Jérôme, Av. Normandie Niemen - 13397 Marseille Cedex 13 - France.*  
Albert VIRGILI *Departament de Química Orgànica Universitat Autònoma de Barcelona, Bellaterra - Spain.*

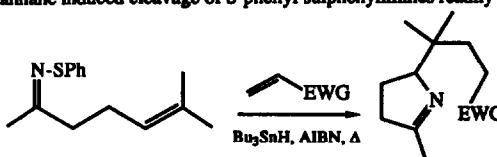
The addition of a sulphonyl radical to the external double bond of 2 generates the prochiral radical 2a which adds to the glycal double bond and leads with high stereoselectivity to a 7/1 mixture of 3+4.



*Tetrahedron Lett.* 1990, 31, 3545

**MULTIPLE RADICAL ADDITIONS STARTING WITH IMINYL RADICALS DERIVED FROM SULPHENYLLIMINES.** Jean Boivin, Eric Fouquet, and Samir Z. Zard. *Laboratoire de Synthèse Organique, Ecole Polytechnique, 91128 Palaiseau, France.*

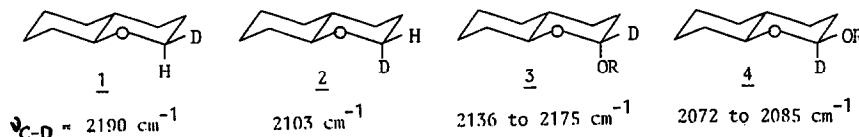
Iminyl radicals obtained by tri-n-butylstannane induced cleavage of S-phenyl sulphenylimines readily cyclise onto suitably located double bonds. The intermediate carbon centered radical can be trapped by a variety of electron-poor olefins.



*Tetrahedron Lett.* 1990, 31, 3549

**ANOMERIC EFFECT AND INFRA-RED  $\nu_{\text{C}-\text{D}}$  STRETCHING FREQUENCY IN TETRAHYDROPYRAN COMPOUNDS**

E. Touhoui\* and G. Dana  
*Laboratoire de Stéréochimie Réactionnelle, Bât. F., Université Pierre et Marie Curie, 4, Place Jussieu, 75252 PARIS Cedex 05, FRANCE*

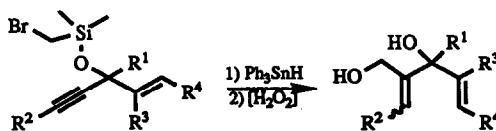


*Tetrahedron Lett.* 1990, 31, 3555

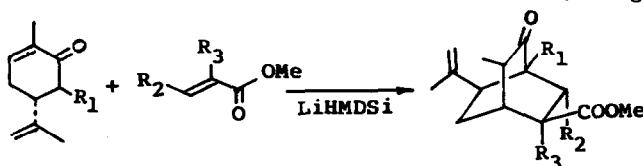
**CHEMOSELECTIVITY OF THE INTRAMOLECULAR RADICAL ADDITION BETWEEN TRIPLE AND DOUBLE BOND.**

Gilbert AGNEL and Max MALACRIA\*  
*Université P. et M. Curie, Laboratoire de Chimie Organique de Synthèse, URA 408, 4 Place Jussieu, 75252 Paris cédex 05, FRANCE.*

Radical cyclization of (bromomethyl) dimethylsilyl propargyl ethers is chemoselective at the triple bond.



## DOUBLE MICHAEL REACTION OF CARVONE AND ITS DERIVATIVES

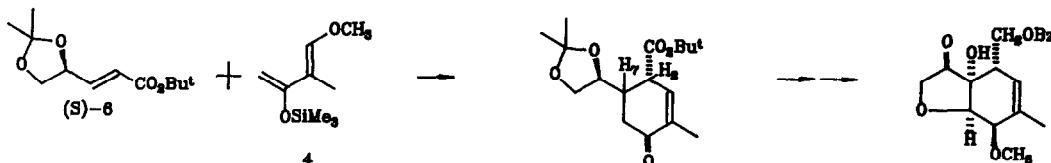
Rong-Bao Zhao<sup>a</sup>, Yu-Fen Zhao<sup>a</sup>, Guo-Qiang Song<sup>b</sup>, Yu-Lin Wu<sup>\*</sup><sup>a</sup>, Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai 200032, CHINA<sup>b</sup>, Shanghai Institute of Materia Medica, Academia Sinica, Shanghai 200031, CHINA

## ENANTIOSELECTIVE SYNTHESIS OF THE HEXAHYDROBENZOFURAN SUBUNIT OF THE avermectins AND THE MILBEVYCINS

Kwang-Chung Lee, Jackson C. C. Wu, Kuang-Fu Yen, Bling-Jiun Uang\*

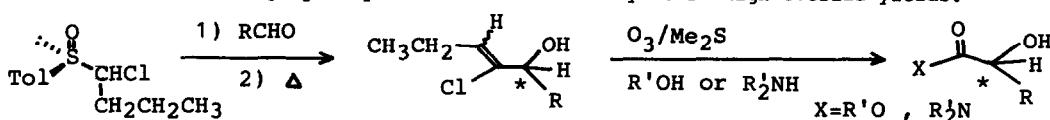
Department of Chemistry, National Tsing Hua University,

Hsinchu, Taiwan 30043, Republic of China

A NOVEL SYNTHESIS OF BOTH ENANTIOMERS OF  $\alpha$ -HYDROXYCARBOXY-YLIC ESTERS AND AMIDES FROM (-)-1-CHLOROBUTYL P-TOLYL SULFOXIDE

Tsuyoshi Satoh, Ken-Ichi Onda, and Koji Yamakawa\*

Faculty of Pharmaceutical Sciences, Science Univ. of Tokyo, Shijuku-ku, Tokyo, Japan

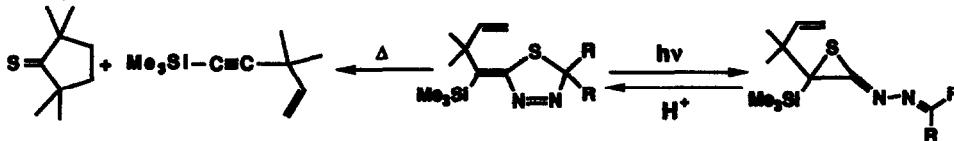
Both enantiomers of  $\alpha$ -hydroxycarboxylic esters and amides are synthesized from optically active (-)-1-chlorobutyl p-tolyl sulfoxide and aldehydes in high overall yields.

## NOVEL RING TRANSFORMATION IN THE REACTIONS OF 2-ALKYLDENE-1,3,4-THIADIAZOLINES AND THEIR SELENIUM ANALOGUES

Norihiko Tokotoh, Nam Choi, and Wataru Ando\*

Department of Chemistry, University of Tsukuba,

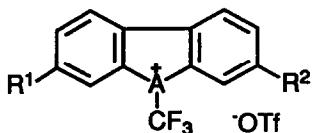
Tsukuba, Ibaraki 305, JAPAN



SECONDARY  $\alpha$ -DEUTERIUM KINETIC ISOTOPE EFFECTS FOR ADDITION OF PHENYL RADICAL TO BENZYL ISOCYANIDES:  
AN EVIDENCE OF CONCERTED MECHANISM.

Sung Soo Kim, Ki Seung Lee, Soo Bong Hwang, and Hee Jin Kim  
 Department of Chemistry, Inha University, Incheon 402-751, South Korea  
 $\text{YC}_6\text{H}_4\text{-CH}_2$  (or  $-\text{CD}_2$ )-N=C: + Ph-  $\xrightarrow{k_{\text{H}}(\text{or D})}$   $\text{YC}_6\text{H}_4\text{-CH}_2$  (or  $-\text{CD}_2$ )- + PhC≡N:  
 Hammett  $\rho = 0.26$ ;  $k_{\text{H}}/k_{\text{D}} = 1.289, 1.075$ , and  $1.251$  for Y=  $p\text{-OCH}_3$ , H, and  $p\text{-CN}$ , respectively; Concerted mechanism with polar transition states.

POWER-VARIABLE TRIFLUOROMETHYLATING AGENTS, (TRIFLUOROMETHYL)DIBENZOTHO- AND -SELENOPHENIUM SALT SYSTEM. Teruo Umemoto\* and Sumi Ishihara, Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

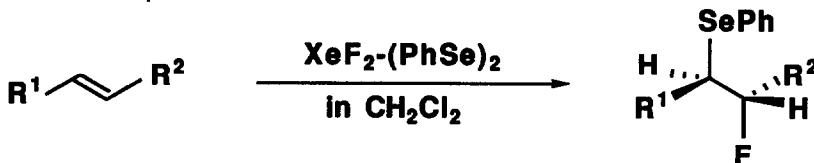


- 1; A=S, R<sup>1</sup>=R<sup>2</sup>=H  
 2; A=Se, R<sup>1</sup>=R<sup>2</sup>=H  
 3; A=S, R<sup>1</sup>=H, R<sup>2</sup>=NO<sub>2</sub>  
 4; A=S, R<sup>1</sup>=R<sup>2</sup>=NO<sub>2</sub>  
 5; A=Se, R<sup>1</sup>=R<sup>2</sup>=NO<sub>2</sub>

Power order  
 $2 < 1 < 3 < 5 < 4$

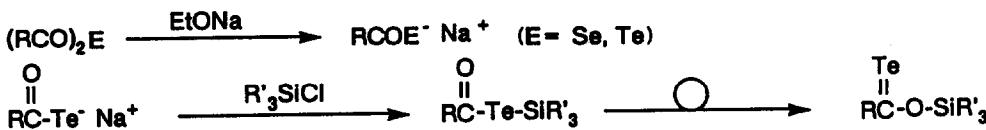
BENZENESELENENYL FLUORIDE EQUIVALENT IN SITU GENERATED WITH XeF<sub>2</sub>-(PhSe)<sub>2</sub> IN CH<sub>2</sub>Cl<sub>2</sub> FOR FLUOROSELENENYLATION OF OLEFINS

Kenji Uneyama\* and Masatomi Kanai  
 Department of Applied Chemistry, Faculty of Engineering, Okayama University,  
 Okayama 700, Japan



Crystalline Sodium Seleno- and Tellurocarboxylates: Localization of Negative Charge on Electropositive Chalcogeno Atoms

Shinzi Kato,\* Hideki Kageyama, Takahiro Kanda, Toshiaki Murai  
 and Takashi Kawamura  
 Department of Chemistry, Gifu University, Yanagido, Gifu 501-11, Japan

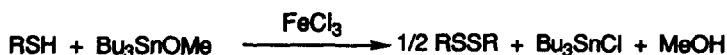


**ACTIVATION AND SYNTHETIC APPLICATIONS OF  
THIOTANNANES. EFFICIENT CONVERSION OF THIOLS INTO DISULFIDES**

Tsuneo Sato, Tatsushi Tada, Junzo Otera,\* and Hitosi Nozaki

Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, JAPAN

Thiols are converted into disulfides efficiently with alkoxystannane-ferric chloride.

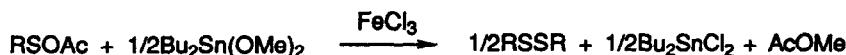


**ACTIVATION AND SYNTHETIC APPLICATIONS OF  
THIOTANNANES. EFFICIENT CONVERSION OF THIOL ACETATES INTO DISULFIDES**

Tsuneo Sato, Junzo Otera,\* and Hitosi Nozaki

Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan

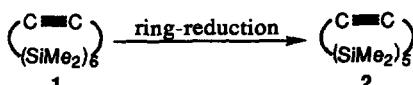
Thiol acetates are converted into disulfides efficiently with alkoxystannane-ferric chloride.



**SYNTHESIS AND STRUCTURE OF  
PENTASILACYCLOHEPTYNE**

Wataru Ando,\* Nobuko Nakayama, Yoshio Kabe, and Toshio Shimizu  
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Pentasilacycloheptyne (2) was synthesized by ring-reduction of hexasilacyclooctyne (1) and the molecular structure of 2 was determined by X-ray analysis.



**KALIHNENE AND ISOKALIHNOL B, CYTOTOXIC DITERPENE ISONITRILES  
FROM THE MARINE SPONGE *ACANTHELLA KLETHRA***

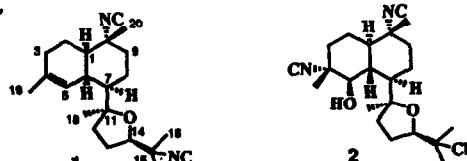
N. Fusetani,\* K. Yasumuro, H. Kawai,<sup>†</sup> T. Natori,<sup>†</sup> L. Brinen,<sup>††</sup> and J. Clardy<sup>††\*</sup>

Laboratory of Marine Biochemistry, Faculty of Agriculture,  
The University of Tokyo, Bunkyo-ku, Tokyo 113 (Japan)

<sup>†</sup>Kirin Brewery Co., Ltd, Pharmaceutical Laboratory,  
Takasaki-shi, Gunma 370-12 (Japan)

<sup>††</sup>Baker Laboratory, Department of Chemistry, Cornell  
University, Ithaca, New York 14853-1301 (U.S.A.)

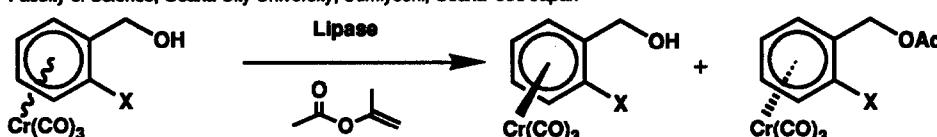
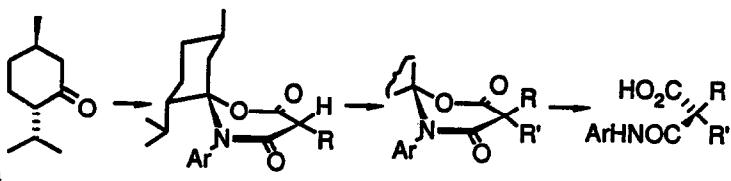
Two cytotoxic diterpene isonitriles, kalihinene (1) and isokalihinol B (2), have been isolated from the marine sponge *Acanthella klethra*.



KINETIC RESOLUTION OF ( $\eta^6$ -ARENE)CHROMIUM COMPLEXES BY A LIPASE

Kaoru NAKAMURA,\* Kohji ISHIHARA, Atsuyoshi OHNO, Motokazu UEMURA,  
Hikaru NISHIMURA, and Yuji HAYASHI

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 Japan and Department of Chemistry,  
Faculty of Science, Osaka City University, Sumiyoshi, Osaka 558 Japan

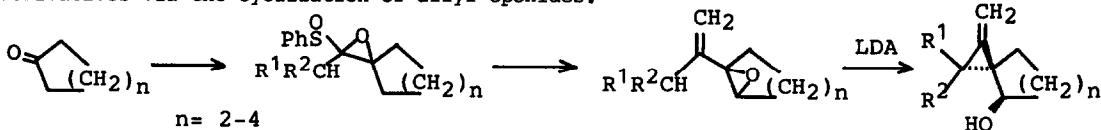
CHIRAL SPIROCYCLIC 1,3-OXAZINE-4,6-DIONES AS NOVEL SYNTHONS OF ENANTIOMERICALLY PURE COMPOUNDS: Masayuki Sato<sup>a,\*</sup>, Hiroyuki Hisamichi<sup>a</sup>, Noritaka Kitazawa<sup>a</sup>, Chikara Kaneko<sup>a,\*</sup>, Pharmaceutical Institute, Tohoku Univ., Sendai 980, Japan: Toshio Furuya<sup>b</sup>, Naoko Suzuki<sup>b</sup>, and Noriyoshi Inukai<sup>b</sup> Research Lab., Yamanouchi Pharmaceutical Co., Ltd., Tsukuba, Ibaragi 305, Japan

## A NOVEL SYNTHESIS OF CARBOCYCLIC SPIRO-TYPE METHYLENECYCLOPROPANE DERIVATIVES

Tsuyoshi Sato<sup>a</sup>, Yasushi Kawase, and Koji Yamakawa\*

Faculty of Pharmaceutical Sciences, Science Univ. of Tokyo, Shinjuku-ku, Tokyo 162, Japan

A novel method is described for the synthesis of carbocyclic spiro-type methylenecyclopropane derivatives via the cyclization of allyl epoxides.

FAILURE OF THE LINEAR CORRELATION OF  $\log k$  WITH  $\gamma_{\text{AdCl}}$  IN THE SOLVOLYSIS OF TERTIARY BENZYLIC CHLORIDES.

THE ESTABLISHMENT OF A NEW  $\gamma$  SCALE BASED ON 2-ARYL-2-CHLOROADAMANTANES

Kwang-Ting Liu,\* Hun-Chang Sheu, Hung-I Chen, Pao-Feng Chiu, and Chia-Ruei Hu  
Department of Chemistry, National Taiwan University, Taipei 10764, Taiwan,  
Republic of China

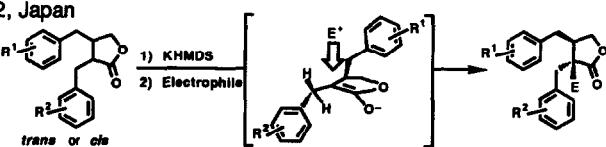
A new  $\gamma$  scale,  $\gamma_{\text{BnCl}}$ , based on 2-aryl-2-chloroadamantanes is developed for the correlation of solvolysis rates of benzylic chlorides, in which the solvation on the delocalized transition state is significant.

A SYNTHESIS OF  $\alpha$ -SUBSTITUTED *trans*- $\alpha$ ,  $\beta$ -DIBENZYL- $\gamma$ -BUTYROLACTONES: DIASTEROEOFACIAL DIFFERENTIATION

IN THE ELECTROPHILIC ATTACK ON THE METAL ENOLATES OF  $\alpha$ ,  $\beta$ -DIBENZYL- $\gamma$ -BUTYROLACTONES  
Yasunori Moritani, Tatsuzo Ukitai, Takashi Nishitani, Masahiko Seki, and Tameo Iwasaki\*

Department of Synthetic Chemistry, Research Laboratory of Applied Biochemistry,  
Tanabe Seiyaku Co., Ltd., Yodogawa, Osaka 532, Japan

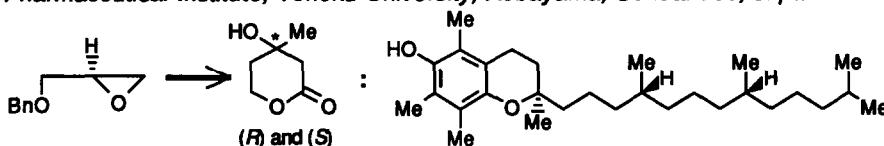
$\alpha$ -Substituted *trans*- $\alpha$ ,  $\beta$ -dibenzyl- $\gamma$ -butyrolactones were synthesized in a diastereoselective manner by the reaction of the potassium enolates of  $\alpha$ ,  $\beta$ -dibenzyl- $\gamma$ -butyrolactones with electrophiles.



A CONVENIENT ENANTIOCONTROLLED ROUTE TO MEVALONOLACTONE AND VITAMIN E FROM (S)-O-BENZYLGLYCIDOL

S. Takano,\* Y. Shimazaki, Y. Iwabuchi, and K. Ogasawara

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

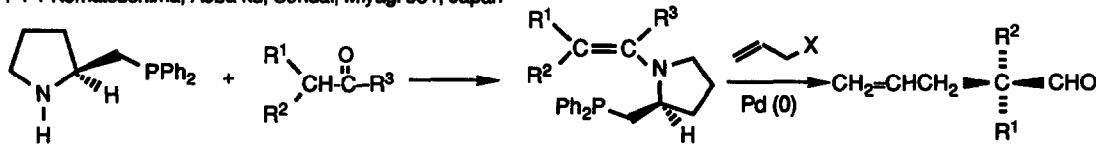


PALLADIUM-CATALYZED ASYMMETRIC ALLYLATIONS OF CHIRAL ENAMINES BEARING PHOSPHINE FUNCTIONALITY.

EFFECTS OF ANIONIC COUNTERPARTS OF ALLYLATING REAGENTS ON ASYMMETRIC INDUCTION

Kunio Hiroi\* and Jun Abe

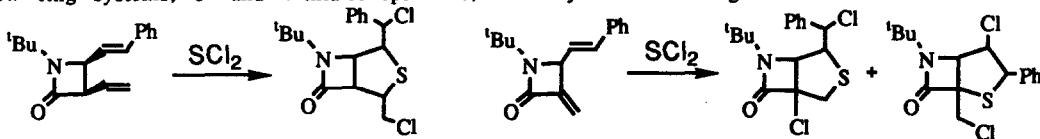
Department of Synthetic Organic Chemistry, Tohoku College of Pharmacy,  
4-4-1 Komatsushima, Aoba-ku, Sendai, Miyagi 981, Japan



NOVEL SYNTHESIS OF SULFUR-CONTAINING BICYCLIC  $\beta$ -LACTAMS (THIAISOALKANAMS) USING SULFUR DICHLORIDE AS A SULFUR TRANSFER REAGENT

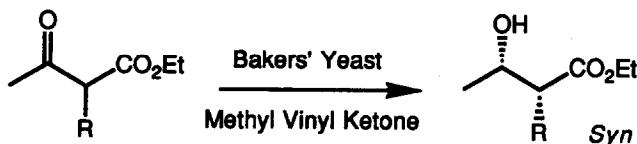
Mitsuo Komatsu,\* Hirosumi Ogawa, Masaaki Mohri, and Yoshiki Ohshiro,\* Department of Applied Chemistry, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

New ring systems, 6- and 7-thiaisoheptanams, were synthesized using sulfur dichloride.



STEREOCHEMICAL CONTROL IN DIASTEREORESELECTIVE  
REDUCTION WITH BAKERS' YEAST

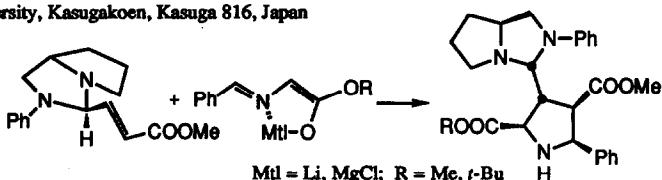
Kaoru NAKAMURA,\* Yasushi KAWAI, Takehiko MIYAI, and Atsuyoshi OHNO  
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 Japan



ASYMMETRIC 1,3-DIPOLAR CYCLOADDITIONS OF AZOMETHINE YLIDE  
WITH A CHIRAL ELECTRON-DEFICIENT OLEFINIC DIPOLAROPHILE

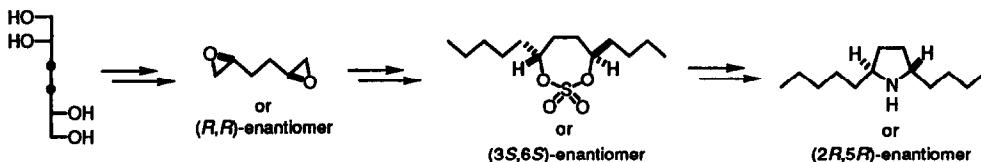
Shuji Kanemasa and Hidetoshi Yamamoto  
Institute of Advanced Material Study, Kyushu University, Kasugakoen, Kasuga 816, Japan

The first efficient asymmetric 1,3-dipolar cycloaddition of azomethine ylide is presented by use of *N*-metalated ylides and the acrylate bearing a perhydropyrido[1,2-*c*]imidazol-3-yl chiral controller at the  $\beta$ -position.



ENANTIODIVERGENT TOTAL SYNTHESIS OF  
NATURALLY OCCURRING *trans*-2-BUTYL-5-PENTYL PYRROLIDINE

Nobuo Machinaga and Chihiro Kibayashi\*  
Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

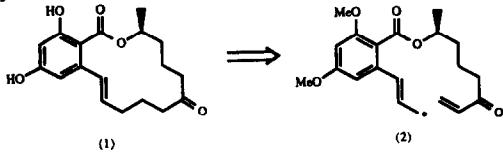


SYNTHESIS OF MACROCYCLES VIA ALLYLIC RADICAL INTERMEDIATES.  
A TOTAL SYNTHESIS OF (-)-ZEARALENONE

Stephen A. Hitchcock and Gerald Pattenden\*

Department of Chemistry, The University, Nottingham NG7 2RD

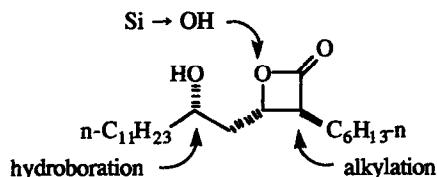
A 14-*endo* trig cyclisation from the allylic radical (2) forms the basis of a new and concise synthesis of (-)-zearalenone (1).



A SYNTHESIS OF (-)-TETRAHYDROLIPSTATIN IN WHICH THE RELATIVE STEREOCHEMISTRY IS CONTROLLED BY A PHENYLDIMETHYLSILYL GROUP

Ian Fleming\* and Nicholas J. Lawrence (University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK)

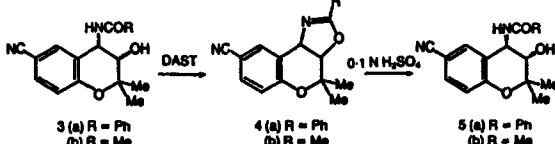
The alkylation of a  $\beta$ -silylenolate and the hydroboration of an allylsilane successively control the relative stereochemistry of the three stereogenic centres on the carbon backbone in a synthesis of the esterase inhibitor tetrahydrolipstatin.



THE ACTION OF DIETHYLAМИNOSULPHUR TRIFLUORIDE (DAST) ON TRANS 4-AMIDO-3-CHROMANOLS : PREPARATION OF CIS-AMIDO-CHROMANOLS VIA OXAZOLINES

Gordon Burrell, John M. Evans, Graham E. Jones and Geoffrey Stemp, Beecham Pharmaceuticals Research Division, Medicinal Research Centre, The Pinnacles, Harlow, Essex CM19 5AD, England.

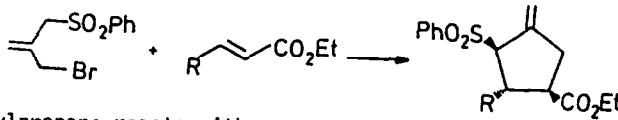
Trans 4-amido-3-chromanols are epimerised at the 3-carbon via formation of oxazolines



A NEW DIASTEROSELECTIVE 3+2 ANNULATION APPROACH TO FIVE-MEMBERED CARBOCYCLES.

Eugene Ghera\*, Tamar Yechezkel and Alfred Hassner\*

Department of Chemistry  
Bar-Ilan University  
Ramat Gan 52100, Israel



1-Bromo-methylene-3-phenylsulfonylpropane reacts with unsaturated esters to afford cyclopentane derivatives with complete diastereoselectivity.