

GRAPHICAL ABSTRACTS

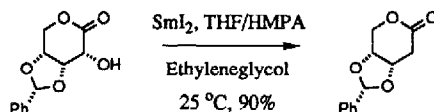
*Tetrahedron Lett.* 1992, 33, 573

**A PRACTICAL SYNTHESIS OF 2-DEOXY ALDONOLACTONES VIA A SMI<sub>2</sub>-MEDIATED α-DEOXYGENATION REACTION**

Stephen Hanessian\*, Christian Girard and Jose Luis Chiara;

Department of Chemistry, Université de Montréal, C.P. 6128, Succ. A, Montréal, QC, H3C 3J7, Canada

A one-step deoxygenation of 2-hydroxylactones or their acetates is possible using samarium diiodide as an electron-transfer reagent in conjunction with a proton source



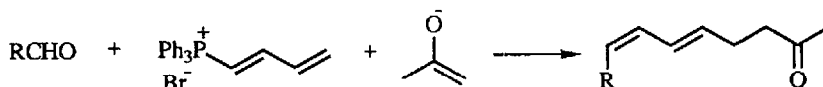
*Tetrahedron Lett.* 1992, 33, 577

**STEREOSELECTIVE SYNTHESIS OF E,Z-1,3-DIENES VIA TANDEM NUCLEOPHILE ADDITION TO A DIENYLPHOSPHONIUM SALT FOLLOWED BY WITTIG REACTION**

James D. White\* and Mark S. Jensen

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

E,Z-1,3-Dienes were synthesized in 43-77% yield with stereoselectivity varying from 2:1 to >20:1.



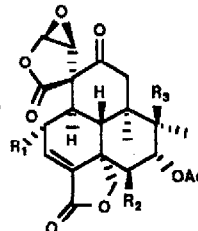
*Tetrahedron Lett.* 1992, 33, 581

**SALVILANGUIDULINES, FOUR NEW DITERPENOIDS ISOLATED FROM *Salvia languidula* WITH AN UNUSUAL EPOXY SPIRO γ-LACTONE**

Jorge Cárdenas, Thelma Pavón, Baldomero Esquivel, Alfredo Toscano and Lydia Rodríguez-Hahn\*

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510 México, D. F., México.

The structures of four new diterpenoids with a rearranged clerodane skeleton were elucidated by spectroscopic methods and by X-ray crystallographic analysis of one of them.



- 2a R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=H
- 2b R<sub>2</sub>=R<sub>3</sub>=H R<sub>1</sub>=OH
- 2c R<sub>1</sub>=R<sub>3</sub>=H R<sub>2</sub>=OH
- 2d R<sub>1</sub>=R<sub>2</sub>=H R<sub>3</sub>=OH

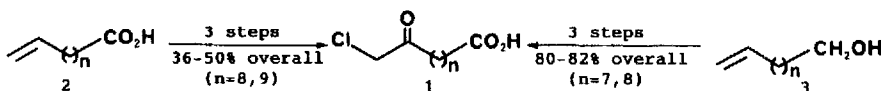
*Tetrahedron Lett.* 1992, 33, 585

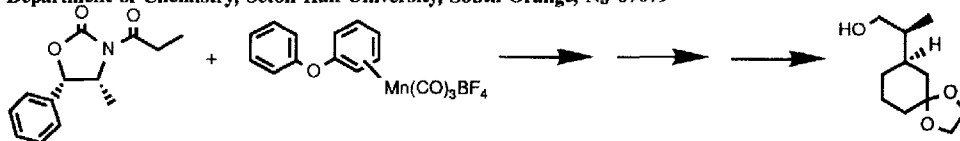
**A CONVENIENT AND EFFICIENT THREE-STEP SYNTHESIS OF α-CHLORO KETO ACIDS**

Ki-Byung Chai and Paul Sampson\*,

Department of Chemistry, Kent State University, Kent, Ohio 44242, U.S.A.

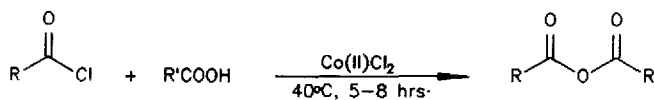
Efficient three-step (epoxidation/regioselective chloride-mediated epoxide ring opening/Jones oxidation) routes to α-chloro keto acids **1** are described.



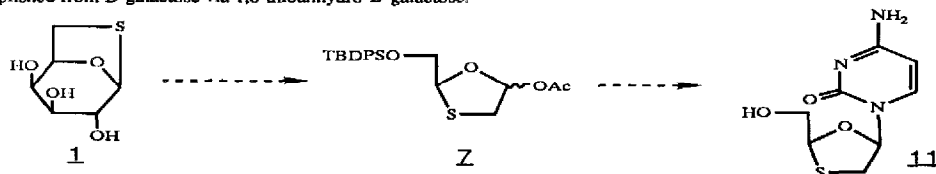
**A FORMAL SYNTHESIS OF (+)-JUVAIONE***Tetrahedron Lett.* 1992, 33, 589William H. Miles<sup>a</sup> and Herbert R. Brinkman<sup>b</sup><sup>a</sup>Department of Chemistry, Lafayette College, Easton, PA 18042<sup>b</sup>Department of Chemistry, Seton Hall University, South Orange, NJ 07079**COBALT(II) CHLORIDE CATALYZED SYNTHESIS OF ACID ANHYDRIDES FROM ACID CHLORIDES***Tetrahedron Lett.* 1992, 33, 593R. R. Srivastava and G. W. Kabalka<sup>\*</sup>,

Departments of Chemistry and Radiology, University of Tennessee, Knoxville, TN. 37996-1600

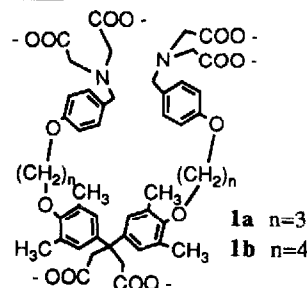
Acid anhydrides were synthesized from acid chlorides and carboxylic acids using cobalt(II) chloride as a catalyst.

**AN EFFICIENT SYNTHESIS OF ENANTIOMERICALLY PURE (+)-(2S,5R)-1-[2-(HYDROXYMETHYL)-1,3-OXATHIOLAN-5-YL]CYTOSINE [(+)-BCH-189] FROM D-GALACTOSE.***Tetrahedron Lett.* 1992, 33, 595

Lak S. Jeong, Antonio J. Alves, Sean W. Carrigan, Hea O. Kim, J. Warren Beach and Chung K. Chu<sup>\*</sup>. Department of Medicinal Chemistry, College of Pharmacy, The University of Georgia, Athens, GA 30602. An efficient and short synthesis of enantiomerically pure (+)-BCH-189 has been accomplished from D-galactose via 1,6-thioanhydro-D-galactose.

**A New Water Soluble Cyclophane Host That Is Organized by Calcium Binding**Kathryn L. Cole, M. Angeles Farran, and Kurt Deshayes<sup>\*</sup>  
Department of Chemistry and Center for Photochemical Sciences  
Bowling Green State University  
Bowling Green, OH 43403

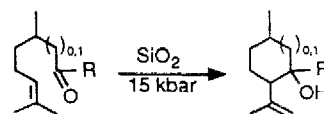
Two new water soluble cyclophanes **1a** and **1b** were synthesized. The allosteric regulation of the host-guest interactions was studied by fluorescence spectroscopy.

*Tetrahedron Lett.* 1992, 33, 599

### THE ACID CATALYZED CYCLIZATIONS OF UNSATURATED CARBONYL COMPOUNDS UTILIZING SILICA GEL AT HIGH PRESSURE

William G. Dauben<sup>\*</sup> and Robert T. Hendricks  
Department of Chemistry, University of California, Berkeley, CA 94720

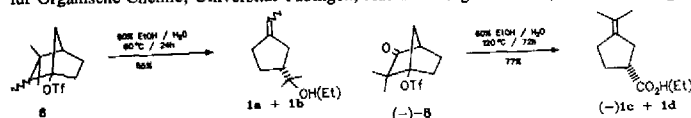
The ene-like cyclizations of a series of unsaturated carbonyl compounds have been studied using silica gel at high pressure (15 kbar) as a new catalytic system. This new method is general for the formation of 5- and 6-membered ring carbocycles. The mildness of this method was demonstrated by the successful cyclization of a vinyl cyclopropyl aldehyde.



### ENANTIOSPECIFIC SYNTHESIS OF 3-SUBSTITUTED ALKYLIDINECYCLOPENTANES

A. García Martínez,<sup>\*a</sup> E. Teso Vilar,<sup>b</sup> J. Osfo Barcina,<sup>a1</sup> Manrique Alonso,<sup>a</sup> E. Rodríguez Herrero,<sup>a</sup>  
M. Hanack<sup>\*c</sup> and L.R. Subramanian<sup>c</sup>

<sup>\*a</sup>Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid, Spain; <sup>\*b</sup>Departamento de Química Orgánica, Facultad de Ciencias, UNED, Ciudad, E-28040 Madrid, Spain; <sup>\*c</sup>Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany



### ALKYLATION OF AZAGLYCINE AMIDE CONTAINING PEPTIDES.

Patrice Talaga<sup>#</sup>, Wolfgang König<sup>\*</sup>

Hoechst AG, D-6230 Frankfurt am Main 80 (Germany)

<sup>#</sup>Present Address: UCB S.A., Chemin du Foriest, B-1420 Braine l'Alleud (Belgium)

1) PPh<sub>3</sub>, DEAD  
ROH, THF

X-NH-Phe-CO-NH-NH-CO-NH<sub>2</sub>

HCl<sub>2</sub>HN-Phe-CO-N(R)-NH-CO-NH<sub>2</sub>

2) Deprotection

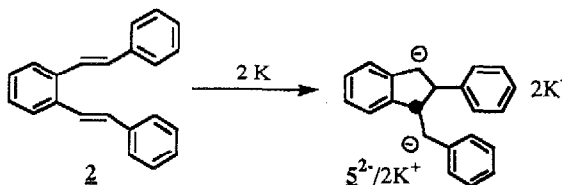
X = Boc, Fmoc or Z.

### ELECTRON-TRANSFER INDUCED VALENCE ISOMERIZATION OF 1,2-DISTYRYLBENZENE

Arno Böhm and Klaus Müllen<sup>\*</sup>

Max-Planck-Institut für Polymerforschung,  
Ackermannweg 10, D - 6500 Mainz, FRG

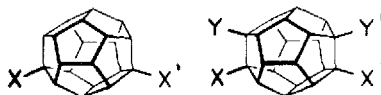
The electron-transfer induced rearrangement of 1,2-distyrylbenzene **2** leads to the indane frame.



### THE PAGODANE ROUTE TO DODECAHEDRANES - FUNCTIONAL GROUP MANIPULATIONS ON THE DODECAHEDRANE SPHERE

Klaus Scheumann, Fabian Wahl, and Horst Prinzbach\*  
Chemisches Laboratorium der Universität Freiburg i. Br.,

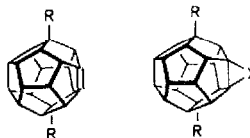
Reductive and halo decarboxylations of thiohydroxamic esters allow expeditious functional group manipulations on the dodecahedrane sphere.



### THE PAGODANE ROUTE TO DODECAHEDRANES - UNSATURATED DODECAHEDRANES, PROTECTION AND DEPROTECTION

Klaus Weber, Hans Fritz, and Horst Prinzbach\*  
Chemisches Laboratorium der Universität Freiburg i. Br.,

Highly pyramidalized ( $\psi = 46.5^\circ$ ) dodecahedrenes are isolable. Various ways for their protection/deprotection are explored.

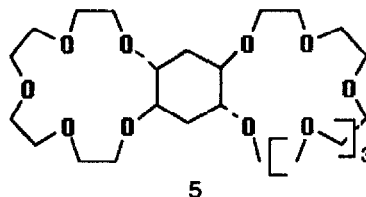


### INFLUENCE OF NEGATIVE ALLOSTERIC COOPERATIVITY IN CATION TRANSPORT

A.M. Costero\* and S. Rodríguez

Dpt.de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Spain

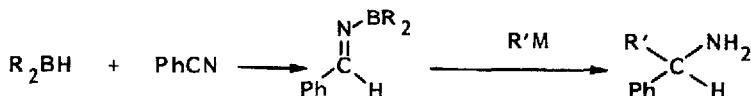
We have prepared a system, **5**, which seems to show negative allosteric cooperativity. In this kind of system the single subunit crown ether complex formation forces the two oxygens to remain in the diequatorial conformation. This conformation is transmitted through the cyclohexane to the second ether subunit



### SYNTHESIS OF SECONDARY CARBINAMINE VIA N-BORYL IMINES GENERATED FROM NITRILES AND ALKYL BORANES

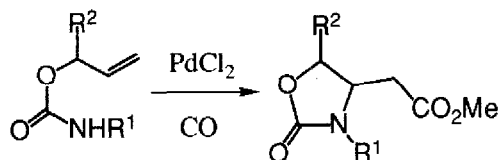
S. Itsuno, C. Hachisuka, K. Kitano, and K. Ito

Department of Materials Science, Toyohashi University of Technology, Tempaku-cho Toyohashi 441 Japan

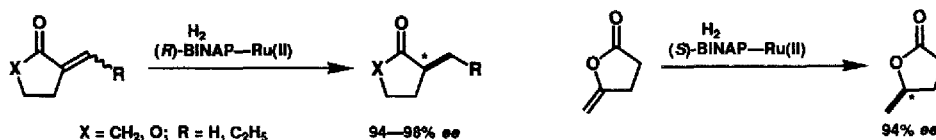


**Palladium(II)-catalyzed Oxidative Aminocarbonylation of Unsaturated Carbamates**

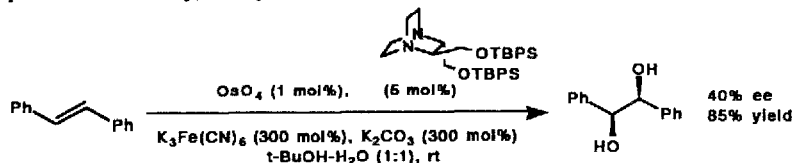
Yoshinao Tamaru, Hiraki Tanigawa, Souko Itoh, Masanari Kimura, Shuji Tanaka, and Keigo Fugami  
 Department of Applied Chemistry, Faculty of Engineering,  
 Nagasaki University, Bunkyo, Nagasaki 852, Japan  
 Takaaki Sekiyama and Zen-ichi Yoshida  
 Department of Synthetic Chemistry, Faculty of  
 Engineering, Kyoto University, Sakyo, Kyoto 606,  
 Japan


**ASYMMETRIC HYDROGENATION OF UNSATURATED CARBONYL COMPOUNDS CATALYZED BY BINAP—Ru(II) COMPLEXES. ENANTIO-SELECTIVE SYNTHESIS OF  $\gamma$ -BUTYROLACTONES AND CYCLOPENTANONES**

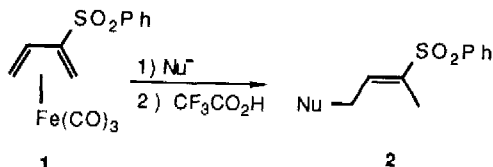
Tetsuo Ohta, Tsutomu Miyake, Nobuo Seido,<sup>†</sup> Hidenori Kumobayashi,<sup>†</sup> Susumu Akutagawa,<sup>†</sup> and Hidemasa Takaya  
 Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan  
<sup>†</sup> Takasago Research Institute, Inc., Kamata, Ohta-ku, Tokyo 144, Japan


**Synthesis of Chiral 2,3-Disubstituted 1,4-Diazabicyclo[2.2.2]octane. New Ligand for the Osmium-Catalyzed Asymmetric Dihydroxylation of Olefins**

Tohru Oishi and Masahiro Hiramata\*  
 Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan.

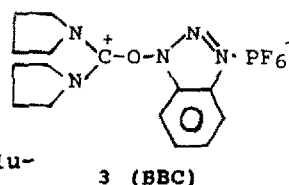

**Novel Nucleophilic Additions to  $[\eta^4$ -2-(phenylsulfonyl)-1,3-butadiene]tricarbonyliron(0) Complex**

Shang-Shing P. Chou, Chien-Hung Hsu,  
 Department of Chemistry, Fu Jen Catholic  
 University, Taipei, Taiwan 242,  
 Ming-Chang P. Yeh, Department of Chemistry  
 Taipei, Taiwan 117, Republic of China



**A NEW COUPLING REAGENT FOR PEPTIDE SYNTHESIS. BENZOTRIAZOLYLOXY-BIS(PYRROLIDINO)-CARBONIUM HEXAFLUOROPHOSPHATE (BBC)**

Shaoqing Chen and Jiecheng Xu  
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Road, Shanghai 200032, China  
Benzotriazolyloxy-bis(pyrrolidino)-carbonium hexafluorophosphate (BBC) prepared and found to be a new efficient coupling reagent in both the solution and the solid phase peptide synthesis.

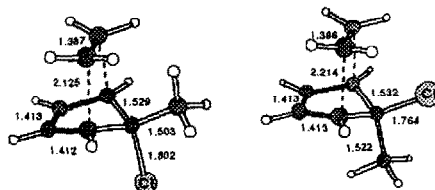


**THE "CIEPLAK EFFECT": HYPERCONJUGATIVE INTERACTIONS IN DIELS ALDER REACTIONS**

James M. Coxon and D. Quentin McDonald  
Department of Chemistry, University of Canterbury, Christchurch, NZ.

AM1 calculations for the reaction of **1a-e** with ethylene show a lengthening of the C-X or C-Me bond for anti addition consistent with hyperconjugative stabilization from the  $\sigma$ -bond of the *anti* substituent to the forming  $\sigma^*$ -orbital being important in determining facial selection.

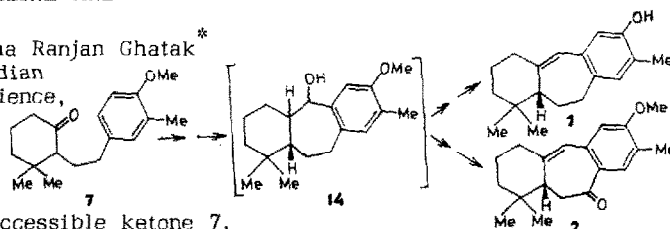
- 1 a X = Me  
b X = Cl  
c X = OH  
d X = OMe  
e X = SMe



**FIRST TOTAL SYNTHESIS OF THE NOVEL CYTOTOXIC BENZOCYCLOHEPTENES ( $\pm$ )-DEOXOFAVELINE AND ( $\pm$ )-FAVELINE METHYL ETHER**

Ajit K. Ghosh, Chhanda Ray and Usha Ranjan Ghatak\*  
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India.

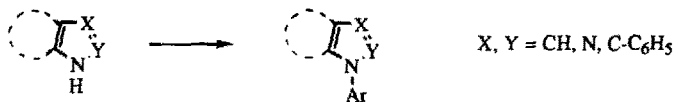
First and efficient total syntheses of ( $\pm$ )-deoxofaveline (**1**) and ( $\pm$ )-faveline methyl ether (**2**) are described starting from the easily accessible ketone **7**.



**N-ARYLATION OF AZOLES AND THEIR BENZO DERIVATIVES BY *p*-TOLYLLEAD TRIACETATE.**

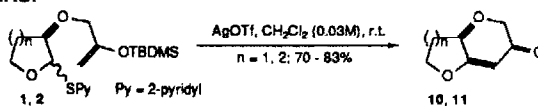
Pilar López-Alvarado, Carmen Avendaño and J. Carlos Menéndez. Departamento de Química Orgánica y Farmacéutica. Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain.

Azoles and their benzo derivatives are efficiently arylated by *p*-tolyllead triacetate in the presence of copper II.



**STEREOSELECTIVE TEMPLATE-DIRECTED C-GLYCOSIDATION. SILVER(I)-MEDIATED INTRAMOLECULAR REACTIONS OF (2-PYRIDYLTHIO)GLYCOSIDIC SILYL ENOL ETHERS.**

Donald Craig\* and V. Ranjit N. Munasinghe  
Department of Chemistry, Imperial College of Science,  
Technology and Medicine, London SW7 2AY, U.K.



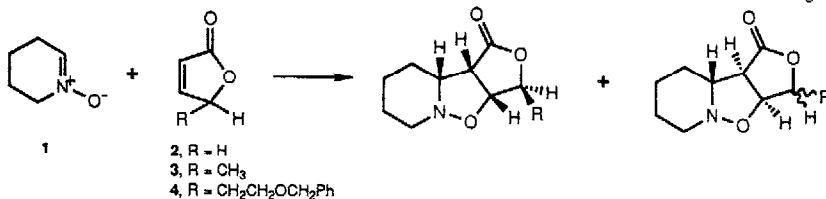
(2-Pyridylthio)glycosidic silyl enol ethers **1** ( $n = 1$ ) and **2** ( $n = 2$ ) undergo highly stereoselective silver-induced cation-mediated cyclization reactions upon treatment with AgOTf to give bicyclic C-glycosides **10** ( $n = 1$ ) and **11** ( $n = 2$ ).

**STEREOCHEMICAL STUDIES ON THE 1,3-DIPOLAR CYCLOADDITION OF 3,4,5,6-Tetrahydropyridine 1-oxide TO 2(SH)-FURANONES**

Pau Cid, Pedro de March,\* Marta Figueredo,\* Josep Font, Sergio Milán

Unitat de Química Orgànica, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain.

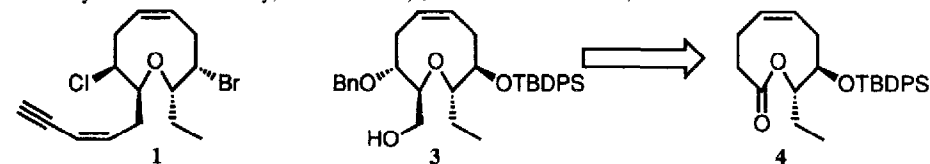
The 1,3-dipolar cycloaddition of 3,4,5,6-tetrahydropyridine 1-oxide, **1**, to 2(*SH*)-furanones **2**, **3**, and **4** is investigated.



**STUDIES TOWARDS THE SYNTHESIS OF OBTUSENYNE. SYNTHESIS OF THE HEXAHYDROOXONIN NUCLEUS.**

Neil R. Curtis, Andrew B. Holmes,\* and Mark G. Looney

University Chemical Laboratory, Lensfield Road, CAMBRIDGE CB2 1EW, U.K.

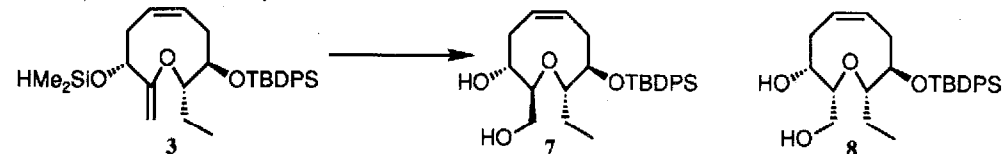


Stereoselective enolate hydroxylation of **4** and a hydroxyl-directed intramolecular hydrosilylation afforded the 2,3,4,7,8,9-hexahydrooxonin **3**, which is an advanced precursor for the *Laurencia*-derived natural product obtusenyne **1**.

**AN INTRAMOLECULAR HYDROSILATION APPROACH TO HEXAHYDROOXONINS RELATED TO OBTUSENYNE. EFFECT OF CATALYST AND CONDITIONS ON STEREOSELECTIVITY**

Neil R. Curtis and Andrew B. Holmes\*

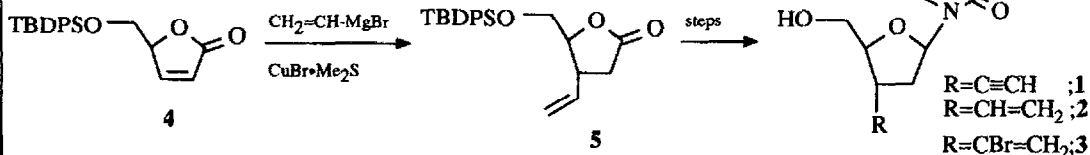
University Chemical Laboratory, Lensfield Road, CAMBRIDGE CB2 1EW, U.K.



The stereoselective intramolecular hydrosilylation of enol ether **3**, to afford either hexahydrooxonin diol **7** or **8**, was found to be dependent upon catalyst and conditions employed.

**SYNTHESIS OF 3'-ETHYNYLTHYMIDINE, 3'-VINYLTHYMIDINE  
AND 3'-BROMOVINYLTHTYMIDINE AS POTENTIAL ANTIVIRAL AGENTS**

Christer Sahlberg  
Medivir AB, Lunastigen 7, S-141 44 Huddinge, Sweden

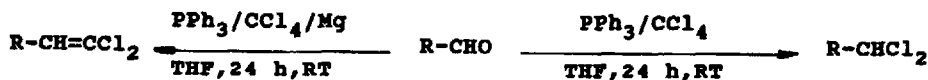


**CHEMISTRY OF THE WITTIG REACTION, IV.  
SIMPLE CONVERSION OF ALDEHYDES TO 1,1-DICHLOROALKANE AND 1,1-DICHLORO-  
-1-ALKENE DERIVATIVES, USEFUL INTERMEDIATES FOR THE SYNTHESIS OF  
ACETYLENIC COMPOUNDS**

P.Vinczer<sup>a,\*</sup>, Sz.Sztruhar<sup>a</sup>, L.Novak<sup>b</sup> and Cs.Szantay<sup>a,b,\*</sup>

<sup>a</sup>Cent. Res. Inst. Chem.; P.O. Box 17., 1525 Budapest, HUNGARY

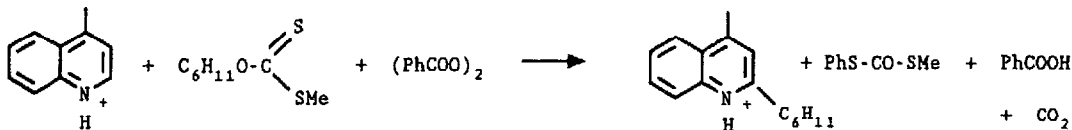
<sup>b</sup>Inst. for Org. Chem., Technical Univ.; P.O. Box 91., 1521 Budapest, HUNGARY



**A NOVEL RADICAL REACTION OF ALKYL XANTATES, USEFUL FOR  
THE SELECTIVE SUBSTITUTION OF HETEROAROMATIC BASES .**

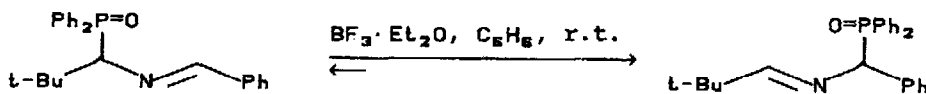
Fausta Coppa, Francesca Fontana, Francesco Minisci, Giuseppe Pianese, Paola Tortoreto, Lihua Zhao  
Dipartimento di Chimica del Politecnico - piazza Leonardo da Vinci, 32 - 20133 Milano, Italy.

Cyclohexyl radical from cyclohexyldithiocarbonate and benzoyl peroxide is utilized for heteroaromatic substitution.



**BORON TRIFLUORIDE ETHERATE - AN EFFECTIVE  
CATALYST OF 1,3-PHOSPHOTROPIC MIGRATION  
IN C=N-C TRIAD**

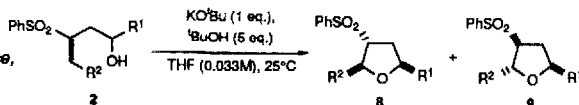
P.P.Onys'ko, T.V.Kim, E.I.Kiseleva, A.D.Sinita; Institute of Organic  
Chemistry, Academy of Sciences of Ukraine, Kiev 253660





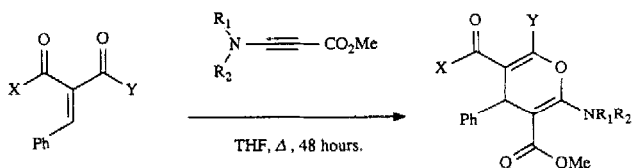
**STEREOSELECTIVE SYNTHESIS OF 3-(PHENYLSULPHONYL)-2,5-DISUBSTITUTED TETRAHYDROFURANS VIA 5-ENDO-TRIG RING-CLOSURE REACTIONS**

Donald Craig\* and Alison M. Smith  
 Department of Chemistry, Imperial College of Science,  
 Technology and Medicine, London SW7 2AY, U.K.



Sulphonyl-substituted homoallylic alcohols **2** undergo stereoselective 5-endo-trig cyclization reactions upon treatment with base to give substituted tetrahydrofurans **8** and **9**.

**STERIC CONTROL OF CHEMOSELECTIVITY IN THE REACTION OF YNAMINE ESTERS WITH HETERODIENES.** Colin P. Dell, Lilly Research Centre, Erl Wood Manor, Windlesham, Surrey, GU20 6PH, U.K.



The reaction of ynamine esters with unsaturated dicarbonyl compounds provides a regio- and chemoselective approach to multiply functionalised pyrans.