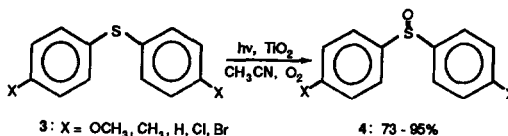


*Tetrahedron Lett.* 1990, 31, 4533

**Selectivity in the TiO<sub>2</sub>- Mediated Photocatalytic Oxidation of Thioethers**

Marye Anne Fox\* and A.A. Abdel-Wahab  
Department of Chemistry  
University of Texas at Austin  
Austin, TX 78712 USA

The TiO<sub>2</sub>-photocatalyzed oxidations of diaryl sulfides and dibenzyl sulfides proceed, via cation radical intermediates, to oxygenation and oxidative cleavage products, respectively.

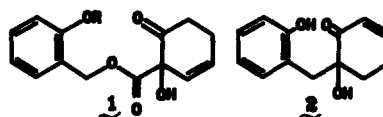


*Tetrahedron Lett.* 1990, 31, 4537

**AGLYCONE FRAGMENTATION ACCOMPANIES β-GLUCOSIDASE CATALYZED HYDROLYSIS OF SALICORTIN, A NATURALLY-OCCURRING PHENOL GLYCOSIDE**

Thomas P. Clausen, John W. Keller and Paul B. Reichardt\*  
Dept. of Chemistry, University of Alaska Fairbanks, Fairbanks,  
AK 99775-0520.

The aglycone of salicortin (1) undergoes an unusual fragmentation/recombination reaction to produce 2 via a proposed ortho-quinone methide pathway.

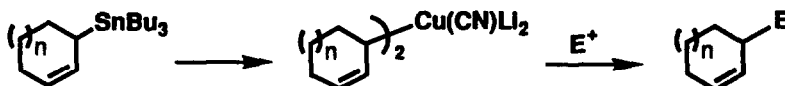


*Tetrahedron Lett.* 1990, 31, 4539

**PREPARATION AND REACTIONS OF CYCLIC ALLYLIC HIGHER ORDER CYANOCUPRATES**

Bruce H. Lipshutz,\* C. Ung, T.R. Elworthy, and D.C. Reuter  
Department of Chemistry, University of California, Santa Barbara, CA 93106

New cyclic allylic cuprates can be easily formed and utilized as a means of introducing a cycloalkenyl moiety into various organic substrates.

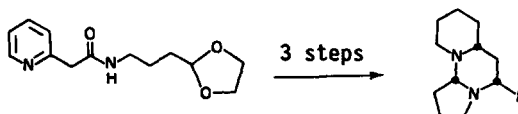


*Tetrahedron Lett.* 1990, 31, 4543

**A STEREOSELECTIVE SYNTHESIS OF THE (9Z,11Z) TETRAPONERINES T4 AND T8**

Tappey H. Jones  
Laboratory of Biophysical Chemistry  
National, Heart, Lung, and Blood Institute  
Bethesda, MD 20892

An efficient, stereoselective synthesis of the tetraponerines T4 and T8 (R= n-propyl and n-pentyl) is described.

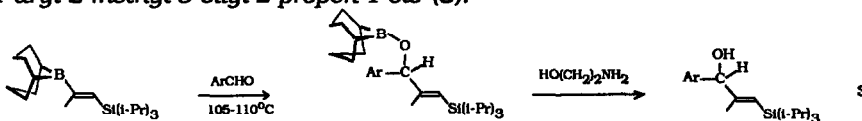


**E-3-SILYL ALLYL ALCOHOLS VIA ORGANOBORANES**

John A. Soderquist\* and Jaime Vaquer

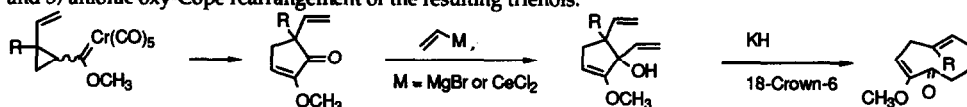
Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931

The Brown vinylation of aromatic aldehydes was developed to provide a simple, efficient route to pure E-1-aryl-2-methyl-3-silyl-2-propen-1-ols (**3**).

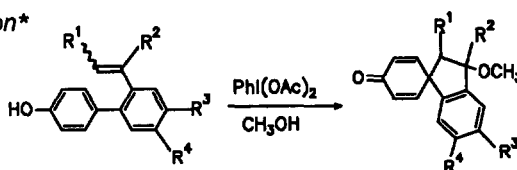
**Sequential Vinylcyclopropylcarbene and Anionic Oxy-Cope Rearrangements: An Expedient Synthesis of Nine-Membered Rings.**

James W. Herndon\*, Leonard A. McMullen, and Charles E. Daitch, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA

A variety of nine-membered ring-derivatives can easily be prepared by the following sequence of reactions: 1) thermolysis of 2-vinylcyclopropylcarbene-chromium complexes; 2) vinyl anion addition to the resulting 5-alkenyl-2-cyclopentenone; and 3) anionic oxy-Cope rearrangement of the resulting trienols.

**SPIRO-ANNULATED 2,5-CYCLOHEXADIENONES VIA OXIDATION OF 2'-ALKENYL-p-PHENYL PHENOLS WITH IODOBENZENE DIACETATE**A. Callinan, Y. Chen, G. W. Morrow, and J. S. Swenton\*  
Department of Chemistry, The Ohio State University,  
Columbus, Ohio 43210

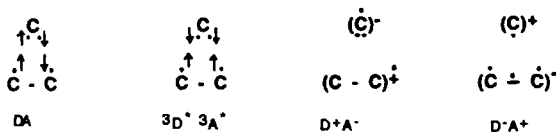
The oxidation of 2'-alkenyl-substituted p-phenyl phenols via iodobenzene diacetate gives spiro-annulated-2,5-cyclohexadienones.

**A CURVE CROSSING APPROACH TO CARBENIC REACTIVITY**

Addy Pross and Robert A. Moss, Wright and Rieman Laboratories,

Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903

The barrier to singlet carbene addition is generated from the configuration mixing of  $DA$ ,  ${}^3D^*3A^*$ ,  $D^+A^-$ , and  $D^-A^+$  configurations.

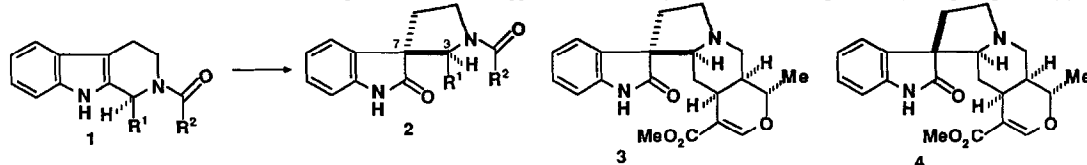


**NEW METHODS FOR THE SYNTHESIS OF OXINDOLE ALKALOIDS.  
TOTAL SYNTHESSES OF ISOPTEROPODINE AND PTEROPODINE.**

Stephen F. Martin\* and Michael Mortimore

Department of Chemistry, The University of Texas, Austin, TX 78712

A new protocol to effect oxidation/rearrangement 1 → 2 was applied to the total syntheses of isopteropodine (3) and pteropodine (4).



**IMPROVED COUPLING OF PROTECTED PEPTIDES ON THE KAISER  
OXIME RESIN USING BOP ACTIVATION**

Joseph T. Jarrett and Peter T. Lansbury, Jr.\*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

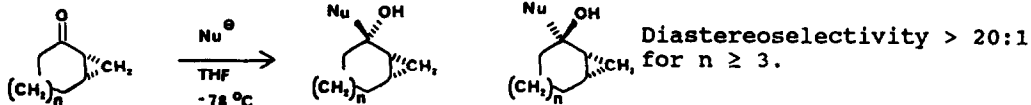
Protected peptides and amino acids can be coupled to resin-bound amine in high yield with low levels of racemization using BOP activation. The synthesis of the 16 amino acid protected peptide VI derived from the ice nucleation protein is described and experimental procedures for these couplings are provided.



**DIASTEREOSELECTIVE MANIPULATIONS OF CONFORMATIONALLY  
RESTRICTED ENANTIOMERICALLY PURE  
BICYCLO[m.1.0]ALKANES. 1. NUCLEOPHILIC ADDITIONS  
TO THE CARBONYL CARBONS OF BICYCLO[m.1.0]ALKAN-2-ONES**

Eugene A. Mash\*, Michelle A. Kaczynski, and Daniel P. Dolata

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

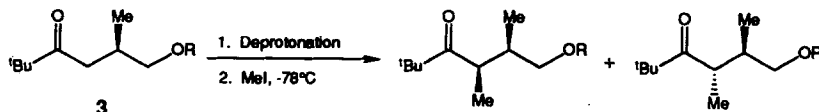


**THE DIASTEREOSELECTIVE INFLUENCES OF REMOTE  
SUBSTITUENTS ON ENOLATE ALKYLATIONS**

Glenn J. McGarvey\* and Marc W. Andersen

University of Virginia, Department of Chemistry, Charlottesville, Virginia 22901

The stereodirecting influences of a variety of R groups upon the methylation of the enolate derived from ketone 3 have been examined.

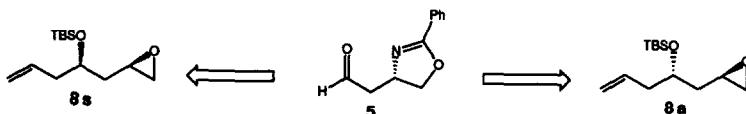


## STUDIES TOWARD THE APPLICATION OF OXAZOLINE-EPOXIDE EQUIVALENCY IN 1,3-ASYMMETRIC INDUCTION

Kenneth R. Overly, J. Michael Williams, and Glenn J. McGarvey\*

University of Virginia, Department of Chemistry, Charlottesville, Virginia, 22901

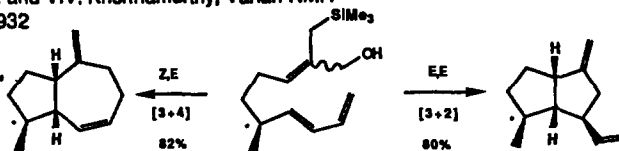
Synthetically versatile epoxy alcohols **8a** and **8b** have been prepared from a common intermediate, chiral aldehyde **5**, through a sequence involving diastereoselective allylation followed by stereospecific transformation of the oxazoline to an epoxide.



## DIASTEREOSELECTIVITY AND REGIOCONTROL IN INTRAMOLECULAR ALLYL CATION CYCLOADDITIONS: SELECTIVE FORMATION OF [3 + 2] OR [3 + 4] CYCLOADDUCTS

Raymond J. Giguere,\* Susan M. Tassely, Michael I. Rose, Department of Chemistry, Skidmore College, Saratoga Springs, New York 12866-1632 and V.V. Krishnamurthy, Varian NMR Instrument Division, Florham Park, New Jersey 07932

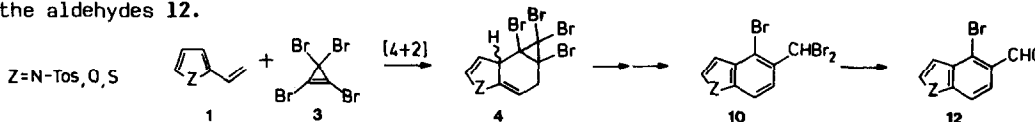
Intramolecular Hoffmann-Noyori reactions of chiral, diastereomeric trienols **1a** and **1b** demonstrate site-selectivity control to form either [3+4] or [3+2] cycloadducts **2a** and **2b**, respectively.



## [4+2]-CYCLOADDITIONEN MIT TETRABROMCYCLOPROPEN: EIN NEUER SYNTHESEWEG ZU POLYFUNKTIONALISIERTEN INDOLEN, BENZOFURANEN UND BENZOTHIOPHENEN.

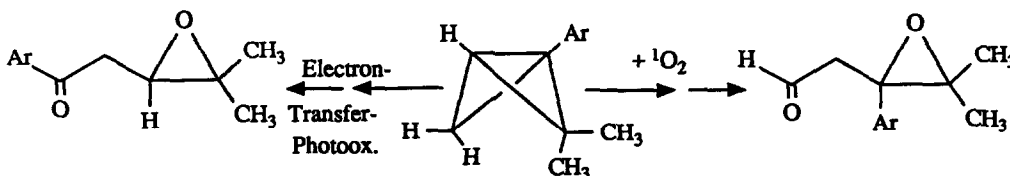
J.-M. Keil, T. Kämpchen und G. Seitz\*, Pharmazeutisch-Chemisches der Philipps-Universität, Marbacher Weg 6, D-3550 Marburg/Lahn 1 (FRG)

[4+2]-Cycloaddition of **1** with **3** leads via **4** to the 10-hetarenes **10**, which can be converted to the aldehydes **12**.



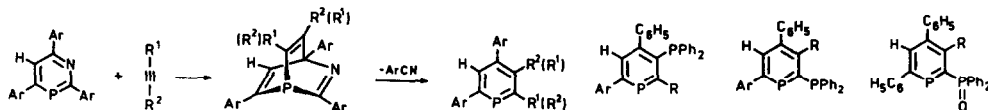
## PHOTOXYGENIERUNG VON 1-ARYL-2,2-DIMETHYLBICYCLO[1.1.0]BUTANEN

Klaus Gollnick und Maria Weber, Institut für Organische Chemie der Universität München, D-8000 München 2, Bundesrepublik Deutschland



**(4+2)-CYCLOADDITIONEN VON 1,3,3'-AZAPHOSPHINEN  
MIT ALKINYLPHOSPHANEN BEI HOHEN DRUCKEN.**

G. Märkl, Ch. Dörger, Th. Riedl, Institut für Organische Chemie der Universität, Universitätsstr. 31, D-8400 Regensburg;  
F.-G. Klärner, C. Ledwig, Fakultät für Chemie der Ruhr-Universität, Universitätsstr. 150, D-4630 Bochum.

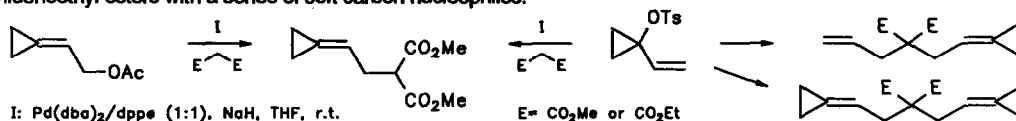
**PALLADIUM(0) CATALYZED SUBSTITUTION REACTIONS OF CYCLO-  
PROPYL GROUP CONTAINING ALLYLIC ESTERS**

Andreas Stolle,<sup>a,b</sup> Jacques Salaün<sup>a,b</sup> and Armin de Meijere<sup>a\*</sup>

Institut für Organische Chemie der Universität<sup>a</sup> D-2000 Hamburg 13, FR Germany

Laboratoire des Carbocycles Associé au CNRS,<sup>b</sup> Université de Paris-Sud, F-91405 Orsay, France

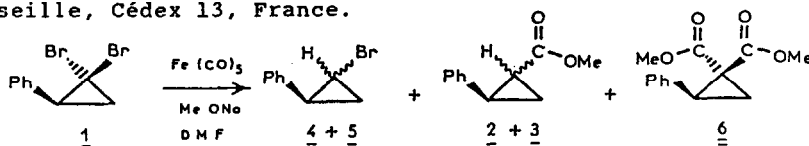
Complete regioselectivity is observed in palladium(0) catalyzed allylic substitution reactions of 1-vinylcyclopropyl and cyclopropylideneethyl esters with a series of soft carbon nucleophiles.

**Reduction and carbonylation of gem dihalogeno  
cyclopropanes with iron pentacarbonyl**

by F.Reyne, P.Brun et B.Waegell

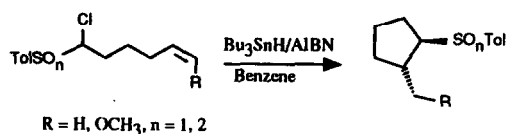
Laboratoire de Stéréochimie, associé au  
Marseille, Faculté des Sciences, Avenue  
532, 13397 Marseille, Cédex 13, France.

CNRS, LASCO, Université l'Aix-  
Escadrille Normandie-Niemen, case

**ADDITION OF SULFINYLATED AND SULFONYLATED CARBON  
CENTERED RADICALS TO ALKENES AND ENOLETHERS**

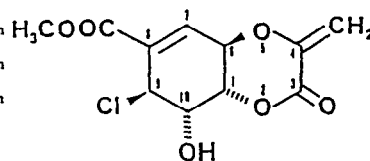
Philippe Renaud, Université de Lausanne, Institut de Chimie Organique,  
Rue de la Barre 2, CH-1005 Lausanne (Switzerland)

Inter- and intramolecular addition reactions to electron rich  
alkenes are described. Cyclizations have been shown to  
proceed with high diastereoselectivity.



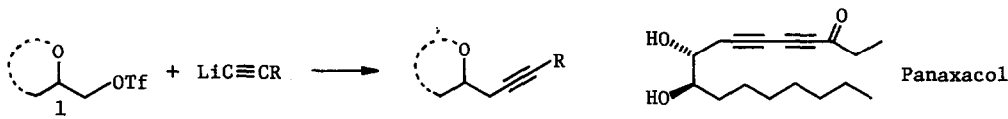
(1R,6R,9S,10S)-9-CHLORO-10-HYDROXY-8-METHOXYCARBONYL-4-METHYLENE-2,5-DIOXA-BICYCLO[4.4.0]DEC-3-ONE-7-ENE, A FIRST CHLORINE-CONTAINING SHIKIMATE-RELATED METABOLITE FROM FUNGI

Eiji Kitamura, Akira Hirota, Masahira Nakagawa, Mitsuru Nakayama\*  
Department of Agricultural Chemistry, University of Osaka Prefecture, Osaka 591, Japan  
Hiroshi Nozaki  
Department of Biological Chemistry, Okayama University of Science, Okayama 700, Japan  
Toshiji Tada  
Analytical Research Laboratories, Fujisawa Pharmaceutical Co., Ltd., Osaka 532, Japan  
Manabu Nukina\*  
Department of Agricultural Chemistry, Yamagata University, Tsuruoka 997, Japan  
Hiroshi Hirota  
Department of Chemistry, The University of Tokyo, Tokyo 113, Japan



AN EFFICIENT METHOD FOR THE ALKYLATION OF CHIRAL TRIFLATES WITH ALKYNYL LITHIUM REAGENTS. A HIGHLY CONCISE TOTAL SYNTHESIS OF (+)-PANAXACOL

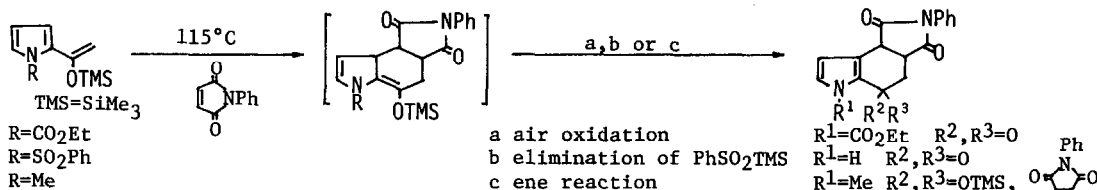
Hiyoshizo Kotsuki,\* Isao Kadota, Masamitsu Ochi  
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan  
Usefulness of the chiral triflate 1 was demonstrated in the total synthesis of panaxacol.



DIVERSE PROCESS IN [4+2]CYCLOADDITION REACTION OF SILYL ENOL ETHERS OF *N*-SUBSTITUTED 2-ACETILPYRROLES TO

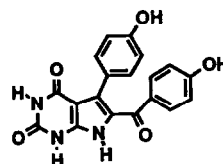
A INDOLE SKELETON M. Ohno, S. Shimizu, and S. Eguchi\*

(Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan)



RIGIDIN, A NOVEL ALKALOID WITH CALMODULIN ANTAGONISTIC ACTIVITY FROM THE OKINAWAN MARINE TUNICATE *EUDISTOMA* CF. *RIGIDA*

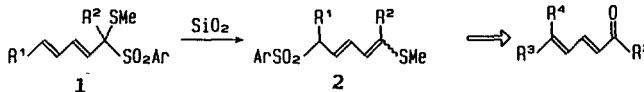
Jun'ichi Kobayashi,\* Jie-fei Cheng,<sup>a</sup> Yumiko Kikuchi, Masami Ishibashi, Shosuke Yamamura,<sup>a</sup> Yasushi Ohizumi,<sup>b</sup> Tomihisa Ohta,<sup>c</sup> and Shigeo Nozoe<sup>c</sup>  
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan,  
<sup>a</sup>Faculty of Science and Technology, Keio University, Yokohama 223, Japan,  
<sup>b</sup>Mitsubishi Kasei Institute of Life Sciences, Machida, Tokyo 194, Japan, and  
<sup>c</sup>Pharmaceutical Institute, Tohoku University, Sendai 980, Japan



**A Novel 1,5-Rearrangement of a Sulfonyl Group  
in a 1-Sulfonylated 2,4-Alkadiene**

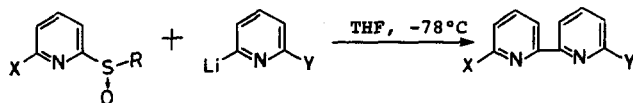
Katsuyuki Ogura, Nobuhiro Yahata, Taketoshi Fujimori, and Makoto Fujita  
Department of Synthetic Chemistry, Faculty of Engineering and Graduate School of  
Science and Technology, Chiba University, 1-33 Yayoicho, Chiba 260, Japan

A smooth 1,5-rearrangement of a sulfonyl group occurred on SiO<sub>2</sub> treatment of 1 to give 2, which was also shown to be an important precursor for a variety of conjugated dienones.

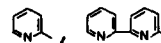


**Ipsso Substitution of 2-Alkylsulfinylpyridine by 2-Pyridyllithium;  
A New Preparation of Oligopyridine and Their Bromomethyl Derivatives**

Junichi Uenishi, Takakazu Tanaka, Shoji Wakabayashi and Shigeru Oae, Department of Chemistry,  
Okayama University of Science, Okayama, 700 Japan  
Hiroshi Tsukube, Department of Chemistry and Liberal Arts & Science, Okayama University, Okayama, 700 Japan



X: H<sub>3</sub>C, EtS, TBSOCH<sub>2</sub>, Cl

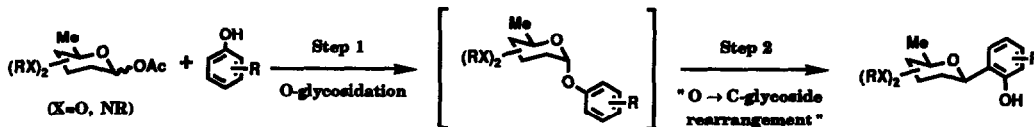


Y: H, Br, TBSOCH<sub>2</sub>

R: H<sub>3</sub>C, Et

**Improvement in O → C-Glycoside Rearrangement Approach to  
C-Aryl Glycosides: Use of 1-O-Acetyl Sugar as Stable but Efficient Glycosyl Donor**

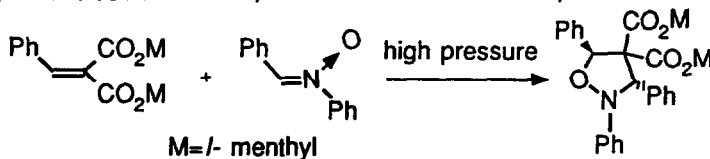
Takashi Matsumoto, Takamitsu Hosoya, and Keisuke Suzuki\*  
Department of Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan



Application to a few 2-deoxy sugars, including an amino sugar, was investigated.

**1,3-DIPOLAR CYCLOADDITION OF DI-1-MENTHYL  
BENZYLIDENEMALONATE TO (Z)-N,α-DIPHENYL-**

**NITRONE: EXPLANATION FOR DIASTEREOSELECTIVITY:** Nobuya Katagiri,<sup>a,\*</sup> Nobuhisa Watanabe,<sup>a</sup> Jun-ichi Sakaki,<sup>a</sup> Takatoshi Kawai,<sup>b</sup> and Chikara Kaneko,<sup>a,\*</sup> <sup>a</sup> Pharmaceutical Institute, Tohoku Univ., Sendai 980, Japan and <sup>b</sup> Tsukuba Research Lab., Eisai Co., Ltd., Tsukuba, Ibaraki 300-26, Japan



M = /- menthyl

Asymmetric induction is caused by pyramidarization.

PROTEIN ENGINEERING OF HIV PROTEINS BY TOTAL CHEMICAL SYNTHESIS: THE C-TERMINAL 104 RESIDUE FROM GAG p24  
 Paolo Mascagni<sup>1</sup>, Dwo Y. Sia<sup>2</sup>, Anthony RM Coates<sup>2</sup>  
 and William A Gibbons<sup>1</sup>

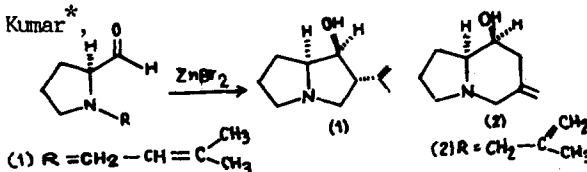
- 1) The School of Pharmacy, University of London, UK
- 2) The London Hospital, London, UK

The chemical synthesis of the 104 residue peptide from HIV-1 gag p24 protein has been performed using BOC-amino acid chemistry. 15-20% (w/w) of homogeneous peptide was purified from about 2g of crude material. Rigorous quality control was used to assess the chemical integrity of the peptide. This was found to be immunogenic in its free form.

DIASTEREOSELECTIVE SYNTHESIS OF OPTICALLY ACTIVE  
 PYRROLIZIDINE AND INDOLIZIDINE RING SYSTEMS THROUGH  
 INTRAMOLECULAR ENE REACTION.

Suneel Y. Dike<sup>\*</sup>, Murli Mahalingam and Ashok Kumar<sup>\*</sup>,  
 Alchemie Research Centre, P.O.Box 155,  
 Thane-Belapur Road, THANE 400601, INDIA.

Optically active hydroxy pyrro-  
 lidine and indolizidine are  
 prepared by ZnBr<sub>2</sub> induced intra-  
 molecular ene reaction.

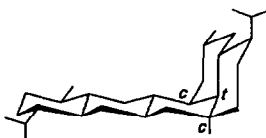


*CIS-CIS-TRANS-BICADINANE*, A NOVEL MEMBER OF AN UN-  
 COMMON TRITERPANE FAMILY ISOLATED FROM CRUDE OILS

B.G.K. van Aarssen<sup>a\*</sup>, C. Kruk<sup>b</sup>, J.K.C. Hessels<sup>a</sup>, and J.W. de Leeuw<sup>a</sup>

<sup>a</sup>Delft University of Technology, Faculty of Chemical Technology and Materials' Science, Organic Geochemistry Unit, De Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands. <sup>b</sup>University of Amsterdam, Faculty of Chemistry, Organic Chemistry Unit, Nieuwe Achtergracht 129, 1018 WS, Amsterdam, The Netherlands

*Cis-cis-trans-bicadinane*, an uncommon  
 triterpane present in South East Asian crude  
 oils has been isolated and its structure has  
 been revealed by NMR-spectroscopic  
 methods.

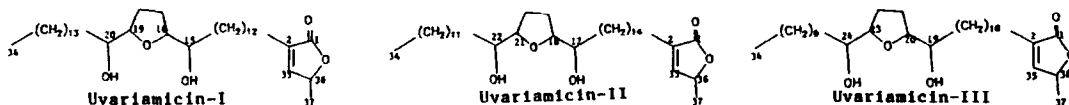


UVARIAMICIN-I, II AND III: THREE NOVEL ACETOGENINS FROM  
*UVARIA NARUM*

A. Hisham<sup>1</sup>, L.A.C. Pieters<sup>1</sup>, M. Claeys<sup>1</sup>, E. Esmans<sup>2</sup>, R.  
 Domnisse<sup>2</sup>, and A.J. Vlietinck<sup>1</sup>

<sup>1</sup>Department of Pharmaceutical Sciences, University of Antwerp  
 (UIA), B-2610 Antwerp, Belgium

<sup>2</sup>Department of Organic Chemistry, University of Antwerp  
 (RUCA), B-2020 Antwerp, Belgium

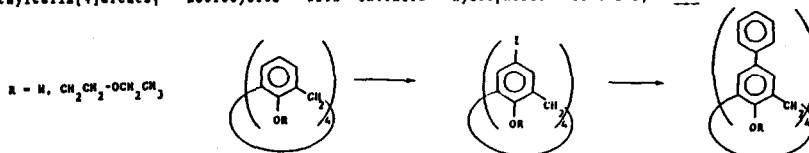




A NOVEL SYNTHESIS OF *p*-PHENYLCALIX[4]ARENES VIA TETRATOLO DERIVATIVES

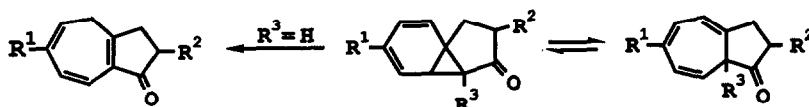
A. Arduini,<sup>2</sup> A. Pochini, A. Rizzi, A.R. Sicuri, R. Ungaro  
 Istituto di Chimica Organica dell'Università, Viale delle Scienze, I-43100 Parma, Italy

The synthesis of *p*-phenylcalix[4]arenes, macrocycles with extended hydrophobic cavities, via iodo derivative is described.



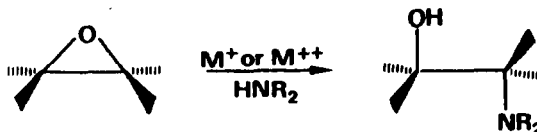
7-METHYL-TRICYCLO[5.3.0.0.<sup>1,6</sup>]DECA-2,4-DIEN-8-ONES:  
 THE FIRST EXAMPLES OF TRICYCLONORCARADIENONES IN TAUTOMERIC  
 EQUILIBRIUM WITH THE 7-METHYL-BICYCLO[5.3.0]1,3,5-DECATRIEN-8-ONES.

Antonio Saba  
 Dipartimento di Chimica, Via Vienna, 2 1-07100 Sassari Italy



METAL SALTS AS NEW CATALYSTS FOR MILD AND  
 EFFICIENT AMINOLYSIS OF OXIRANES

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A new simple, efficient, inexpensive, anti stereoselective, highly regioselective method for aminolysis of 1,2-epoxides, by means of metal salts, is described.