

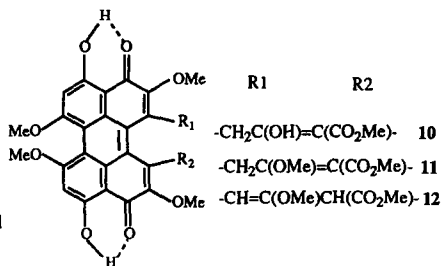
## GRAPHICAL ABSTRACTS

*Tetrahedron*, 1993, 49, 10785

### SYNTHETIC STUDIES IN NOVEL HYPOCRELLIN B DERIVATIVES

Jixiang Liu, Zhenjun Diwu and J. William Lown\*  
Department of Chemistry, University of Alberta, Edmonton,  
Alberta, Canada T6G 2G2

Three novel hypocrellin B (HB) derivatives required for their potential in photodynamic therapy have been synthesized. The possible reaction mechanisms and the properties of resulting HB derivatives are discussed



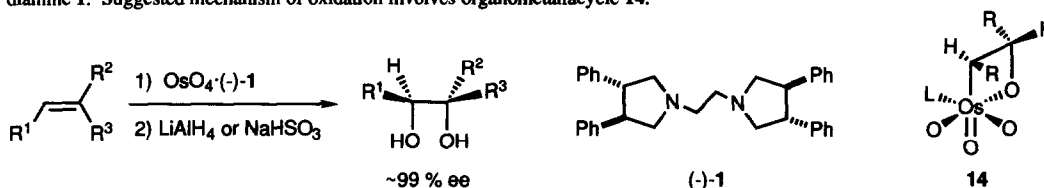
### HIGHLY ENANTIOSELECTIVE DIHYDROXYLATION OF OLEFINS BY OSMIUM TETROXIDE WITH CHIRAL DIAMINES

*Tetrahedron*, 1993, 49, 10793

Faculty of Pharmaceutical Sciences, University of Tokyo,  
Hongo, Bunkyo-ku, Tokyo 113, Japan

Makoto Nakajima, Kiyoshi Tomioka,\* Yoichi Iitaka, and Kenji Koga

Highly enantioselective dihydroxylation of mono-, *trans*-di-, and trisubstituted olefins was achieved by osmium tetroxide with chiral diamine **1**. Suggested mechanism of oxidation involves organometallacycle **14**.



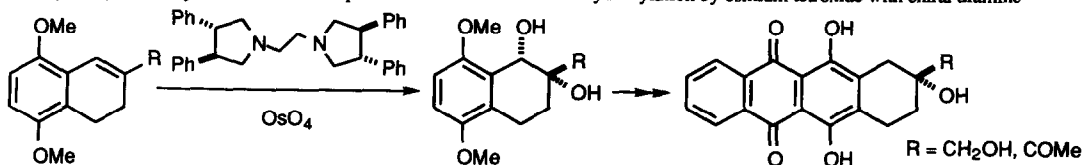
### SHORT-STEP ASYMMETRIC SYNTHESIS OF ANTHRACYCLINE ANTIBIOTICS VIA ENANTIOSELECTIVE DIHYDROXYLATION BY OSMIUM TETROXIDE WITH A CHIRAL DIAMINE

*Tetrahedron*, 1993, 49, 10807

Faculty of Pharmaceutical Sciences, University of Tokyo,  
Hongo, Bunkyo-ku, Tokyo 113, Japan

Makoto Nakajima, Kiyoshi Tomioka,\* and Kenji Koga

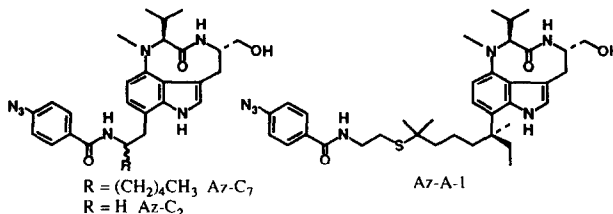
Short-step asymmetric syntheses of (+)-7-dehydroxy-4-demethoxydaunomycinone and (-)-9-deacetyl-7-dehydroxy-4-demethoxy-9-hydroxymethyl-daunomycinone were accomplished via enantioselective dihydroxylation by osmium tetroxide with chiral diamine



**Photolabile Derivatives of Indole Alkaloid Tumor Promoter Teleocidins:  
Synthesis, Biological Activities and Photoaffinity Labeling Studies**

Kazuhiro Irie<sup>a</sup>, Shigenori Okuno, Fumito Koizumi, Koichi Koshimizu, Hōyoku Nishino<sup>a</sup> and Akio Iwashima<sup>a</sup>  
Department of Food Science and Technology, Faculty of Agriculture, Kyoto University, Kyoto 606, Japan  
<sup>a</sup>Department of Biochemistry, Kyoto Prefectural University of Medicine, Kyoto 602, Japan

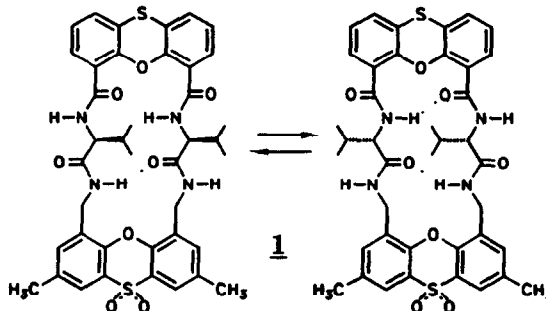
This paper describes the synthesis and biological activities of new photolabile teleocidin derivatives (Az-A-1, Az-C<sub>7</sub> and Az-C<sub>2</sub>). Photoaffinity labeling on the mouse epidermal particulate fraction, the target tissue of these tumor promoters, is also discussed



**Parallel  $\beta$ -Sheet Conformation in Macrocycles**

G. Wagner and M. Feigel<sup>\*</sup>, Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestr. 42, D-91054 Erlangen, Germany

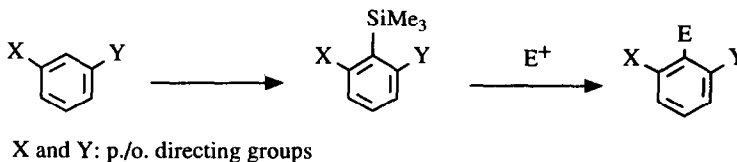
Two rigid phenoxathiin spacer molecules induce the conformation of a parallel  $\beta$ -sheet in peptidic macrocycles as **1**. The degenerate dynamic equilibrium is detected by NMR spectroscopy; MM3- and AM1-calculations support the conformation.



**REGIOSELECTIVE FUNCTIONALISATION IN 2 POSITION OF  
1,3-DISUBSTITUTED BENZENES**

Bernard Bennetau<sup>a</sup>, Florent Rajarison<sup>a</sup>, Pierre Babin<sup>b</sup> and Jacques Dunoguès<sup>a</sup>  
<sup>a</sup> Université Bordeaux I, France, <sup>b</sup> Université Bordeaux II, France

A regioselective functionalisation in 2 position of phenylsilanes 1,3-disubstituted by para-directing group is proposed according to:



**REACTIFS DE POLYVINYLLOGATION :**

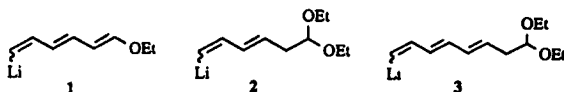
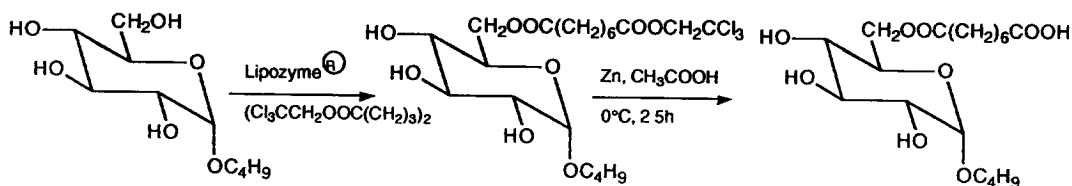
ACCES AISE ET RAPIDE A DES POLYENALS VARIES.

Y. RAMONDENC et G. PLE \*

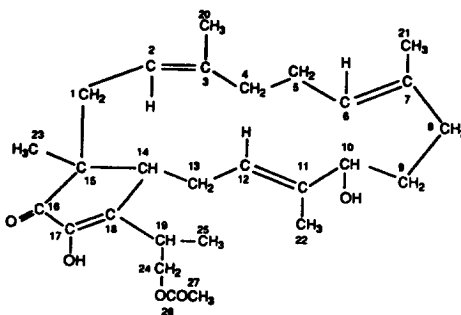
IRCOF et Université de Rouen, Laboratoire de Chimie Organique. URA DO 464 CNRS.

UFR des Sciences et Techniques de Rouen. 76821 Mont-Saint-Aignan Cédex, France.

The synthesis and the reactivity of three reagents of polyvinyllogation, leading to polyenals is described.

**VERSATILE ENZYMATIC DIACID ESTER SYNTHESIS OF BUTYL** **$\alpha$ -D-GLUCOPYRANOSIDE.** Jean FABRE, Didier BETBEDER, François PAUL \* ,Pierre MONSAN, Jacques PERIE<sup>†</sup>. BioEurope, BP 4196 4 impasse Didier Daurat, 31031 Toulouse, FRANCE, <sup>†</sup>Laboratoire de Chimie Organique Biologique, U.R.A. C.N.R.S. 470, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex FRANCE. Enzymatic transesterification of an activated diacid with butyl  $\alpha$ -D-glucopyranoside was achieved, followed by selective chemical hydrolysis, yielding the acid's 6-O-diacyl derivative in a regiospecific manner.**PROLIFERIN, A NEW SESTERTERPENE FROM FUSARIUM PROLIFERATUM**Giacomino Randazzo<sup>a</sup>, Vincenzo Fogliano<sup>a</sup>, Alberto Ritieni<sup>a</sup>, Luisa Mannina<sup>b</sup>, Enrico Rossi<sup>b</sup>, Angela Scarallo<sup>c</sup> and Anna Laura Segre<sup>b</sup>.<sup>a</sup>Istituto di Industrie Agrarie dell'Università degli Studi di Napoli "Federico II"; <sup>b</sup>Istituto di Strutturistica Chimica C.N.R., Roma; <sup>c</sup>CO.E.PO.

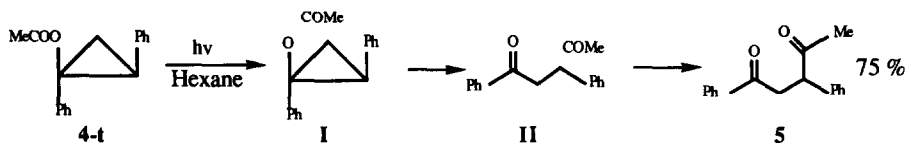
A new compound was identified using 2D-NMR strategies .



**PHOTOREARRANGEMENT AND ELECTRON TRANSFER PHOTO-OXIDATION OF 1-ACETOXY-1,2-DIPHENYLCYCLOPROPANE**

Felipe Algarra, María V. Baldoví, Hermenegildo García,\* Miguel A. Miranda,\* Jaime Primo

Departamento de Química/Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Apartado 22012, E-46071-Valencia (Spain)



Other conditions:

Methanol: Polar addition (cationic intermediate). Photosensitization by acetone: *Trans/cis* isomerization (1,3-dradical).  
ET-activation:  $\beta$ -functionalized ketones or enones (1,3-radical cation).

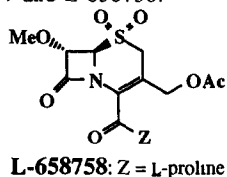
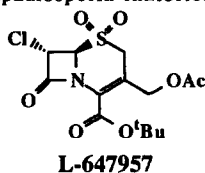
**AN INVESTIGATION INTO THE MECHANISM OF ELASTASE**

**INHIBITION BY CEPHALOSPORIN USING ELECTROSPRAY IONISATION MASS SPECTROMETRY**

Robin T. Aplin, Carol V. Robinson, Christopher J. Schofield and Nicholas J. Westwood,

The Dyson Perrins Laboratory and Oxford Centre for Molecular Sciences, South Parks Road, Oxford, OX1 3QY.

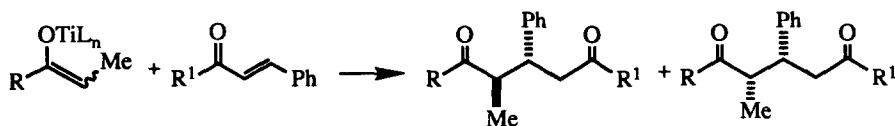
Electrospray ionisation mass spectrometry has been used to study the mechanism of inhibition of porcine pancreatic elastase by two cephalosporin inhibitors L-647957 and L-658758.



**ACCELERATION OF THE CONJUGATE ADDITION OF TI "ATE" ENOLATES VIA LEWIS ACID CATALYSIS.**

A. Bernardi, M. Cavicchioli, and C. Scolastico; Dipartimento di Chimica Organica e Industriale, e Centro CNR per lo Studio delle Sostanze Organiche Naturali, via Venezian 21, 20133 Milano- Italy.

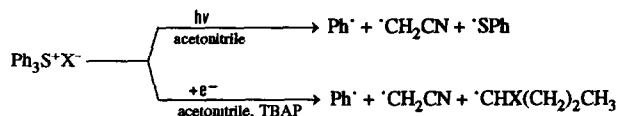
The conjugate addition of Ti "ate" complexes of ketone enolates to  $\alpha,\beta$ -unsaturated ketones can be accelerated via complexation with Lewis acids, such as TBDMSCl or trityl triflate.



**PHOTOCHEMICALLY AND ELECTROCHEMICALLY INITIATED  
RADICAL DECOMPOSITION OF SULFONIUM SALTS  
(A SPIN TRAP STUDY)**

A. Staško<sup>a\*</sup>, P. Rapta<sup>a</sup>, V. Brezová<sup>a</sup>, O. Nuyken<sup>b</sup> and R. Vogel<sup>b</sup>; <sup>a</sup>Slovak Technical University, SK-812 37 Bratislava (Slovakia), <sup>b</sup>University Bayreuth, D-8580 Bayreuth (Germany)

Using spin traps 5,5-dimethylpyrroline-N-oxide, nitrosodurene and <sup>t</sup>BuNO, following radicals were identified in the photochemically and electrochemically initiated decomposition of sulfonium salts:

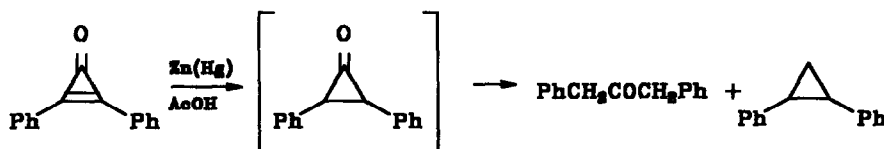


**ZINC-PROMOTED REACTIONS. 6. THE REDUCTION OF  
DIPHENYLCYCLOPROPENONE IN ACIDIC MEDIA.**

Maria Luisa Di Vona and Vittorio Rosnati

Dip di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Roma, Italy

Different product distributions were obtained in the Zn(Hg)/AcOH reduction in the presence of LiCl, HCl, TFA and in the Clemmensen reduction. The reactions were interpreted according to a general mechanism

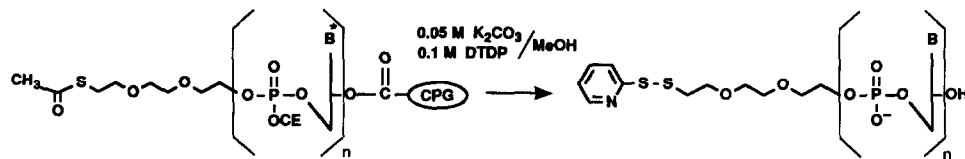


**A NEW STRATEGY FOR THE SOLID-PHASE SYNTHESIS OF  
5'-THIOLATED OLIGODEOXYNUCLEOTIDES.**

Will H.A. Kuijpers and Constant A.A. van Boeckel

Organon International B.V., Scientific Development Group P.O. Box 20, 5340 BH Oss, The Netherlands.

The preparation of a thioacetyl linker phosphoramidite is described which enables the introduction of a pyridyldisulfide function at the 5'-terminus of oligodeoxynucleotides.



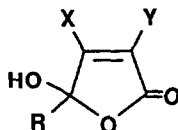
DTDP: 2,2'-Dithiodipyridine, CE: 2-Cyanoethyl, CPG: Controlled-pore glass

**SYNTHETIC APPROACHES TO CHLORINATED 5-HYDROXY-5-METHYL-2-FURANONES**

Robert Franzén and Leif Kronberg\*

Department of Organic Chemistry, Åbo Akademi University, Akademigatan 1, SF-20500, Turku/Åbo, Finland.

The syntheses of chlorinated hydroxyfuranones with a mono-, di-, and trichloromethylgroup at C-5 are described.



- 1a** X = Y = H, R = CH<sub>2</sub>Cl  
**1b** X = Cl, Y = H, R = CH<sub>2</sub>Cl  
**2a** X = Y = H, R = CHCl<sub>2</sub>  
**2b** X = H, Y = Cl, R = CHCl<sub>2</sub>  
**2c** X = Cl, Y = Cl, R = CHCl<sub>2</sub>  
**3a** X = Y = H, R = CCl<sub>3</sub>  
**3b** X = H, Y = Cl, R = CCl<sub>3</sub>  
**3c** X = Cl, Y = Cl, R = CCl<sub>3</sub>

**ORGANIC REACTIONS IN A SOLID MATRIX-VII**

**SODIUM ON ALUMINA : A CONVENIENT REAGENT FOR REDUCTION OF KETONES, ESTERS AND OXIMES**

Satendra Singh and Sukh Dev

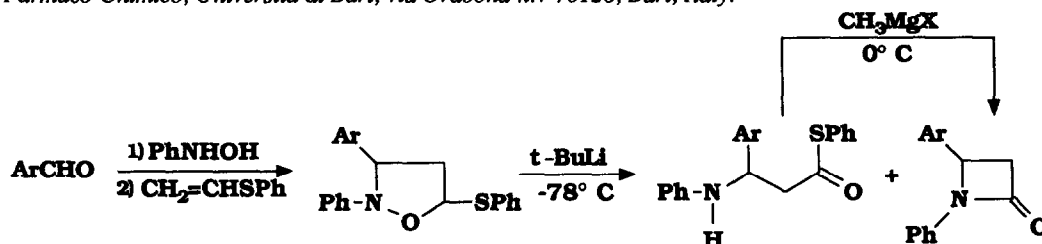
Multi-Chem Research Centre, Nandesari, Vadodara, India

Sodium dispersed on alumina is described and evaluated as a convenient off-the-shelf reagent (in a wax-coated form) for reduction of ketones, esters and oximes. Stereochemical outcome of ketone reductions is essentially the same as results from traditional mode reductions.

**A NEW SYNTHESIS OF β-PHENYLAMINOTHIOESTERS**

**AND β-LACTAMS VIA BASE-INDUCED RING-OPENING**

**OF 2-PHENYL-3-ARYL-5-PHENYLTHIOISOXAZOLIDINES.** Leonardo Di Nunno<sup>a,b</sup> and Antonio Scilimati<sup>b</sup>, (a) *Centro CNR di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica, Università di Bari, via Amendola n.173-70126 Bari, Italy;* (b) *Dipartimento Farmaco-Chimico, Università di Bari, via Orabona n.4-70126, Bari, Italy.*



### ESTERASE CATALYZED REGIOSELECTIVE HYDROLYSES OF ACETYLATED MONOSACCHARIDES

Srdanka Tomić<sup>1\*</sup>, Đurđica Ljevaković and Jelka Tomašić

<sup>1</sup>Department of Chemistry, Faculty of Science, University of Zagreb, 41000 Zagreb, Strossmayerov trg 14, Croatia  
Institute of Immunology, Rockefellerova 10, 41000 Zagreb, Croatia

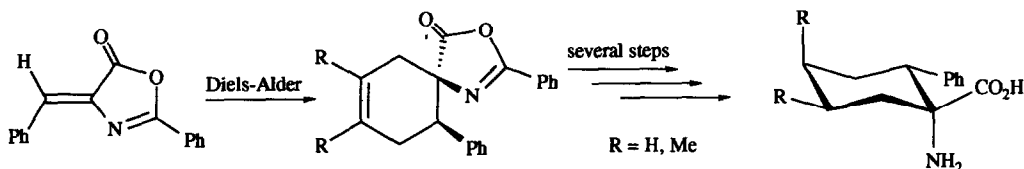
Regioselective deacylations of the presented fully acylated monosaccharides catalyzed by rabbit serum or the esterase isolated from rabbit serum were investigated. Intramolecular migration of acetyls in partially protected substrates was observed



### SYNTHESIS OF NEW CONFORMATIONALLY RIGID PHENYLALANINE ANALOGUES.

Carlos Cativiela\* and María D. Díaz-de-Villegas. Department of Organic Chemistry, Instituto de Ciencia de Materiales de Aragón. Universidad de Zaragoza-CSIC. 50009 Zaragoza, Spain. Alberto Avenzoa and Jesús M. Peregrina. Department of Chemistry (Organic Chemistry), Edificio Científico-Técnico, Sección Ciencias, Universidad de La Rioja, 26001 Logroño, Spain.

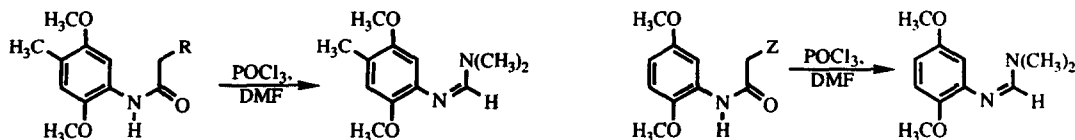
This present report describes the synthesis and the structural assignment of two conformationally restricted cyclic analogues of phenylalanine, 1-amino-*c*-4,*c*-5-dimethyl-*r*-2-phenyl-*r*-1-cyclohexanecarboxylic acid and *cis*-1-amino-2-phenylcyclohexanecarboxylic acid, starting from easily available (*Z*)-2-phenyl-4-benzylidene-5(4H)-oxazolone



### NEW FINDINGS ON THE VILSMEIER-HAACK APPROACH TO QUINOLINE DERIVATIVES

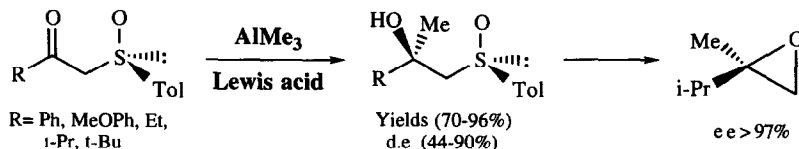
Miguel Ángel Alonso, J. Ignacio Úbeda, Carmen Avendaño, J. Carlos Menéndez, and Mercedes Villacampa  
Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain.

4-Methyl-2,5-dimethoxyanilides or anilides bearing  $\pi$ -donor groups on the  $\alpha$  position of the side chain do not yield quinoline derivatives under Vilsmeier-Haack conditions, as expected, but *Z*-formamidines. The stability of these compounds is studied.



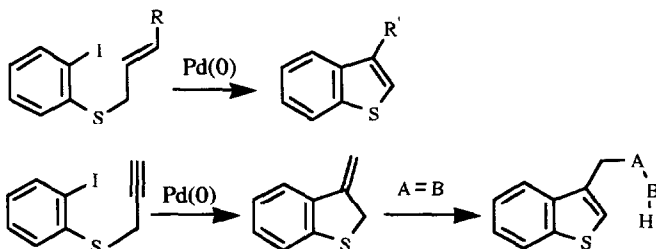
### STERESELECTIVE REACTIONS OF $\text{AlMe}_3$ WITH CHIRAL ACYCLIC $\beta$ -KETOSULFOXIDES.

M. Carmen Carreño,\* José L. García Ruano,\* M. Carmen Maestro and Manuel Pérez González  
 Departamento de Química (C-I), Fac. de Ciencias, Universidad Autónoma. Cantoblanco 28049-Madrid, Spain.  
 Ana B. Bueno and Jean Fischer  
 Laboratoire de Cristalochimie, UA 424, Université Louis Pasteur 67070-Strasbourg, France



### PREPARATION OF BENZO(b)THIOPHENES BY Pd(0)-CATALYZED INTRAMOLECULAR CYCLIZATION OF ALLYL (AND PROPARGYL) o-IODOPHENYL SULFIDES.

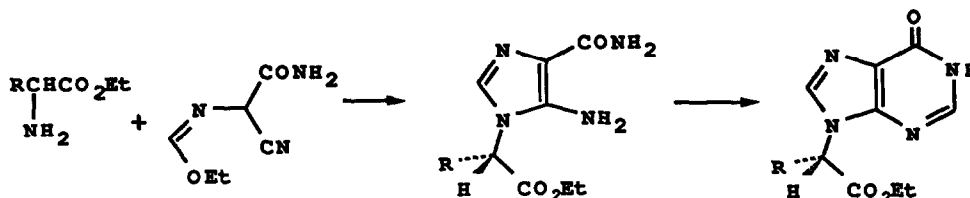
N. Arnau, M. Moreno-Mañas and R. Pleixats  
 Department of Chemistry, Universitat Autònoma de Barcelona, Bellaterra, 08193-Barcelona, Spain



### SYNTHESIS OF OPTICALLY ACTIVE $\alpha$ -(IMIDAZOL-1-YL, PURIN-9-YL OR URACIL-1-YL) PROPANOIC AND SUCCINIC ACID DERIVATIVES

Paul R. Birkett and Hazel King, Humberstone University, Cottingham Road, Hull HU6 7RT.  
 Christopher B. Chapleo, Department of Medicinal Chemistry, Reckitt and Colman Products, Dansom Lane, Hull HU8 7DS.  
 David F. Ewing and Grahame Mackenzie\*, School of Chemistry, University of Hull, Cottingham Road, Hull HU6 7RX

Simple organic esters, substituted in the  $\alpha$ -position with a purine or pyrimidine base are synthesised in enantiomerically pure form.

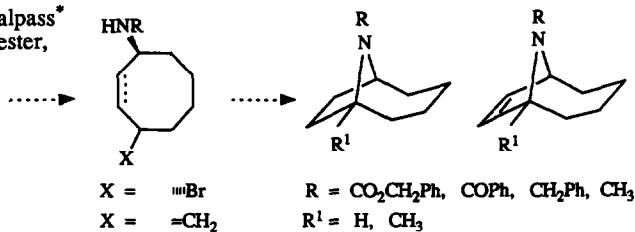




**SYNTHETIC APPROACHES TO HOMOTROPANES AND HOMOTROP-7-ENES USING INTRAMOLECULAR DISPLACEMENT AND AMIDOMERCURATION STRATEGIES**

Craig R. Smith, David Justice and John R. Malpass\*  
Department of Chemistry, University of Leicester,  
Leicester LE1 7RH, U.K.

The synthesis of homotropanes, homotrop-7-enes and 1-methyl derivatives from cycloocta-1,3-diene is described.



**PEPTIDES CONTAINING THE NOVEL METHYLPHOSPHINAMIDE TRANSITION-STATE ISOSTERE**

Wilna J. Moree, Gijs A. van der Marel, Jacques H. van Boom and Rob M. J. Liskamp\*;  
Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

A methylphosphinamide transition-state isostere is incorporated in peptides by coupling of a methylphosphinic chloride with an amino acid or peptide.

