Tetrahedron, **1991**, *47*, 9167

O-SULFINYLATION OF ALCOHOLS WITH METHANESULFONYL CYANIDE OR p-TOLUENESULFONYL CYANIDE.

Derek H. R Barton*, Joseph Cs. Jaszberenyi and Emmanouil A. Theodorakis,
Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

Primary, secondary and tertiary alcohols (2) have been O-sulfinylated with p-toluenesulfonyl cyanide or methanesulfonyl cyanide (1) in the presence of DBU or DABCO via sulfinyl cyanates (3) in 84-98% yield.

$$\underset{\mathbf{1}}{\mathrm{RSO_2CN}} \xrightarrow[\text{or DABCO}]{\text{DBU}} \left[\underset{\mathbf{3}}{\mathrm{R\overset{O}{\overset{\|}{S}}\text{-}OCN}}\right] \xrightarrow[\mathbf{2}]{\mathrm{R'OH}} \mathrm{R'O\text{-}\overset{O}{\overset{\|}{S}}\text{-}R}$$

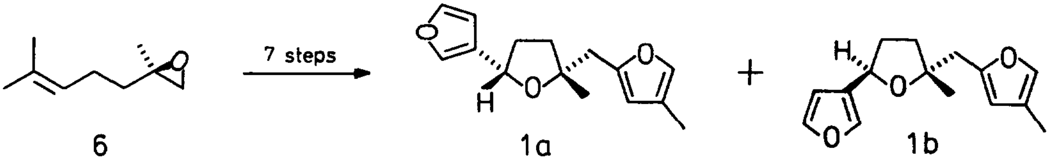
2 x 7 examples

Tetrahedron, **1991**, *47*, 9179

FIRST SYNTHESIS OF THE DIFURANSESQUITERPENE ATHANASIN AND THE ELUCIDATION OF ITS RELATIVE AND ABSOLUTE CONFIGURATION

Guido Bojack and Hans Bornowski*
Institut fur Organische Chemie der Technischen Universitat Berlin
Straße des 17 Juni 135, W-1000 Berlin 12

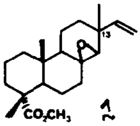
The chiral oxirane **6** is successively connected with suitable furan building blocks The resulting enantiomerically pure diastereomers **1a** and **1b** are separated and compared with the natural product



Tetrahedron, **1991**, *47*, 9187

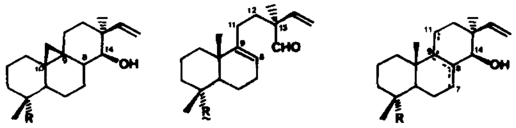
SYNTHESIS AND REARRANGEMENT OF METHYL-8,14β -EPOXYPIMARATE TO OBTAIN CASSANE DITERPENIC SKELETON

N SAM, B ARREGUY-SAN MIGUEL, M TARAN et B DELMOND
Institut du Pin - Laboratoire de Chimie Organique et Organométallique (UA 35) - Université Bordeaux 1 - 351, cours de la Libération 33405 TALENCE Cedex (France)



1

Epoxypimarate 1 is obtained from pimaric acid via stereocontroled epoxidation The rearrangement of this epoxide led to new diterpenic skeletons

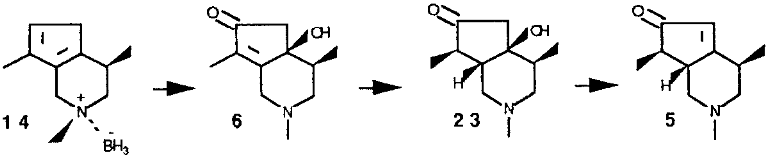


Tetrahedron, **1991**, *47*, 9195

ALCALOIDES MONOTERPÉNIQUES III : SYNTHESE STÉRÉOSPÉCIFIQUE DE LA (±) ÉPI-7,7a TÉCOMANINE[1]

Jean Pierre ALAZARD, Anne LEBOFF et Claude THAL
Institut de Chimie des Substances Naturelles, C N R S , 91198 GIF-SUR-YVETTE Cedex, France

The presence of a borane axial group in compound **14** induces a regio and stereospecific[1] O_2 cycloaddition This result allows a short and stereospecific synthesis of the (±) epi-7,7a tecomanine **5**

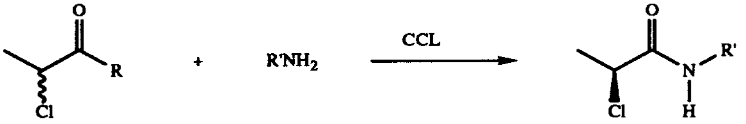


Tetrahedron, **1991**, *47*, 9207

ENZYMATIC AMINOLYSIS AND TRANSAMIDATION REACTIONS

Vicente Gotor*, Rosario Brieva, Carmen González and Francisca Rebolledo
Departamento de Química Organometálica. Facultad de Química Universidad de Oviedo 33071 Oviedo Spain

(*S*)-(-)-2-Chloropropionamides are obtained by *Candida cylindracea* lipase catalyzed aminolysis of (±)-2-chloropropionate ester or transamidation of (±)-N-(2,2,2-trifluoroethyl)-2-chloropropionamide The aminolysis of ethyl (±)-2-methylbutyrate is carried out using CC and PS lipases as catalysts



1a, R= $O\text{-}CH_2\text{-}CH_3$
1b, R= $O\text{-}CH_3$
1c, R= $O\text{-}CH_2\text{-}CCl_3$
4, R= $NH\text{-}CH_2\text{-}CF_3$

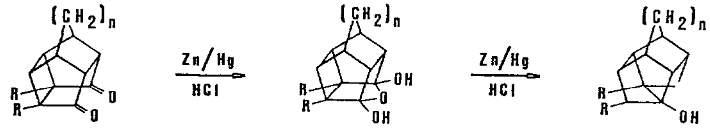
2

3

Tetrahedron, **1991**, *47*, 9215

THE INFLUENCE OF HYDRATE FORMATION ON THE CLEMMENSEN REDUCTION OF PENTACYCLO[5.4.0 $0^{2,6}.0^{3,10}.0^{5,9}$]UNDECANE-8,11-DIONE AND PENTACYCLO [6.4.0.$0^{2,7}$ $0^{3,11}.0^{6,10}$]-DODECANE-9,12-DIONE

Frans J C. Martins*, Agatha M. Viljoen, Marinda Coetzee, Louis Fourie and Philiphus L. Wessels.
Department of Chemistry, Potchefstroom University for CHE, Potchefstroom 2520, South Africa



1 n=1, R=CH_3
2 n=2, R=H

3 n=1, R=CH_3
4 n=2, R=H

5 n=1, R=CH_3
6 n=2, R=H

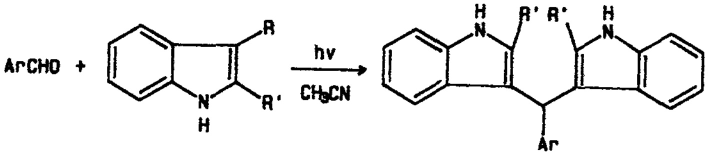
Tetrahedron, **1991**, *47*, 9225

PHOTOCHEMICAL SYNTHESIS OF DIINDOLYLMETHANES

Maurizio D'Auria

Centro CNR per lo Studio della Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro, 2, 00185 Roma Italy

Photochemical coupling of aromatic aldehydes and indole to give title compounds is described.

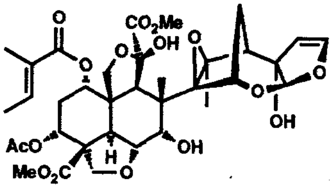


Tetrahedron, **1991**, *47*, 9231

CHEMISTRY OF INSECT ANTIFEEDANTS FROM *AZADIRACHTA INDICA* (PART 11): CHARACTERISATION AND STRUCTURE ACTIVITY RELATIONSHIPS OF SOME NOVEL REARRANGED AZADIRACHTINS.

Steven V. Ley,* James C. Anderson, Wally M. Blaney, E. David Morgan,
Richard N. Sheppard, Monique S.J. Simmonds, Alexandra M.Z. Slawin,
Stephen C. Smith, David J. Williams, and Anthony Wood.

Several novel rearrangment reactions of the natural product azadirachtin and related derivatives have been characterised using a combination of x-ray crystallographic and high field nmr techniques. The insect antifeedant properties of these and a number of C7 modified compounds have been investigated.

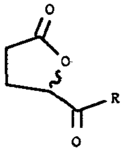


Tetrahedron, **1991**, *47*, 9247

ON THE MODE OF BAKER'S YEAST REDUCTION OF ENANTIOMERIC 4-ACYL BUTANOLIDES

Giovanni Fronza, Claudio Fuganti*, Piero Grasselli, Rosalino Pulido-Fernandez[#], Stefano Servi, Auro Tagliani and Marco Terreni. Dipartimento di Chimica, Politecnico di Milano. 20133 Milano, ITALY and [#]Departamento de Quimica Organometallica, Universidad de Oviedo, SPAIN

The baker's yeast reduction of homochiral and racemic ketones 1 is reported.

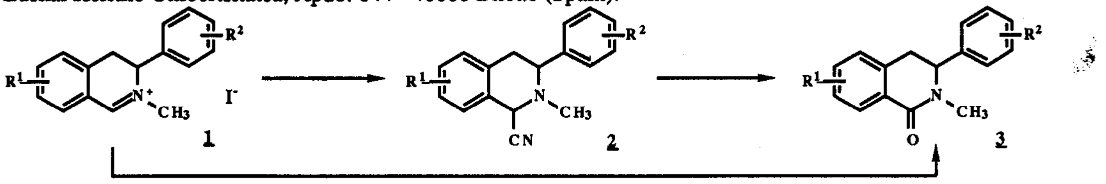


1

Tetrahedron, **1991**, *47*, 9253

ON THE PREPARATION AND STRUCTURAL DETERMINATION OF 3-ARYLISOQUINOLINONES

E. Domínguez, E. Martínez de Marigorta, L. Carrillo and R. Fañanás
Departamento de Química Orgánica, Facultad de Ciencias, Universidad del País Vasco
Euskal Herriko Unibertsitatea, Apdo. 644 - 48080 Bilbao (Spain).

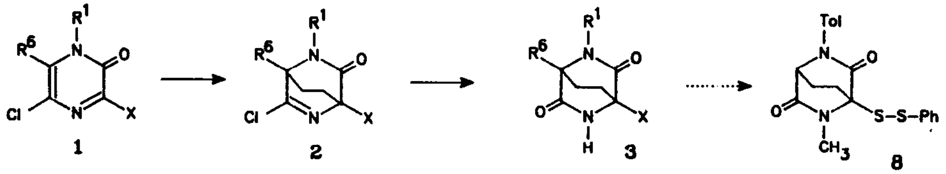


Tetrahedron, **1991**, *47*, 9259

CYCLOADDUCTS OF ETHENE WITH 2(1*H*)-PYRAZINONES AND THEIR CONVERSION INTO 2,5-DIAZABICYCLO[2.2.2]OCTANE-3,6-DIONES.

P. Loosen, M. Tutonda, M. Khorasani, F. Compernolle and G. Hoornaert*, Laboratorium voor Organische Synthese, Department of Chemistry, K.U.Leuven, Celestijnenlaan 200F, B-3001 Leuven (Belgium).

Cycloaddition of variously substituted 2(1*H*)-pyrazinones **1** with ethene and subsequent hydrolysis of the adducts **2** provides a general and efficient route to the title compounds **3**. Compound **8** was prepared as a structural analogue of gliotoxin.

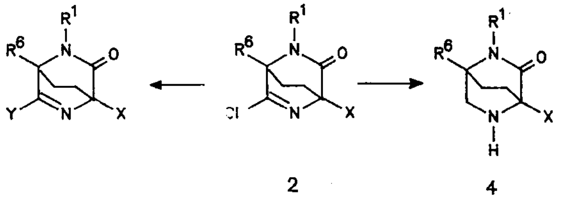


Tetrahedron, **1991**, *47*, 9269

CYCLOADDUCTS OF ETHENE WITH 2(1*H*)-PYRAZINONES FUNCTIONALISATION AND REDUCTION TO 2,5-DIAZABICYCLO[2.2.2]OCTAN-3-ONES.

P. Loosen, M. Khorasani, S. Toppet and G. Hoornaert*, Laboratorium voor Organische Synthese, Department of Chemistry, K.U.Leuven, Celestijnenlaan 200F, B-3001 Leuven (Belgium).

The title compounds **4** were prepared via Diels-Alder reaction of 3,5-dichloro-2(1*H*)-pyrazinones 1 with ethene, followed by catalytic reduction of the iminochloride group generated in the cycloadducts **2**. Substitution of the chlorimino group with various nucleophiles afforded the 6-functionalised analogues of **2**. Their reduction can lead to 6-substituted derivatives of compound **4**. One example is given.

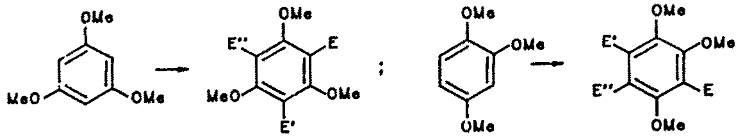


Tetrahedron, **1991**, *47*, 9279

METALATION REACTIONS. XVI. POLYLITHIATION OF 1,3,5- AND 1,2,4-TRIMETHOXYBENZENE

Salvatore Cabiddu*, Liliana Contini, Claudia Fattuoni, Costantino Floris and Gioanna Gelli
Dipartimento di Scienze Chimiche, Università, Via Ospedale, 72, I-09124 Cagliari, Italy

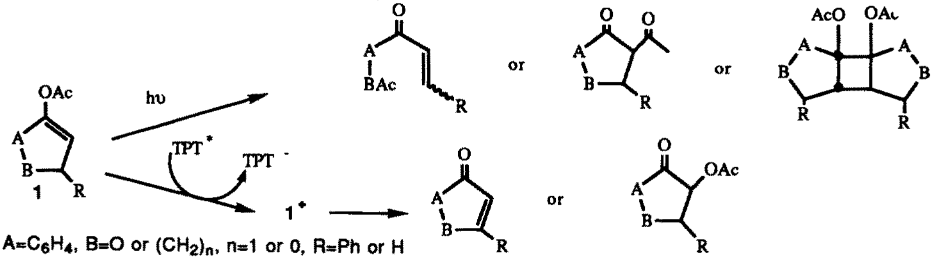
Steric limits in the preparation of hexasubstituted benzenes by one-pot sequence of bimetalation/monometalation, or monometalation/bimetalation or three consecutive monometalations were investigated.



Tetrahedron, **1991**, *47*, 9289

PHOTOLYSIS OF CYCLIC ENOL ESTERS IN THE PRESENCE OR ABSENCE OF A SINGLE ELECTRON TRANSFER PHOTOSENSITIZER

M J Climent , H García, S Iborra, M.A Miranda* and J Primo
Universidad Politécnica de Valencia, Spain



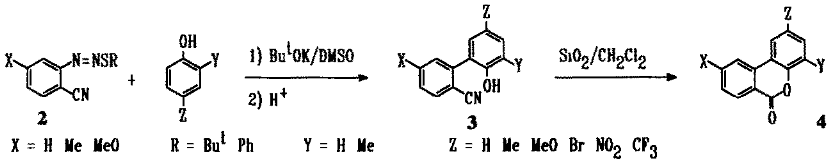
A=C_6H_4, B=O or $(CH_2)_n$, n=1 or 0, R=Ph or H

Tetrahedron, **1991**, *47*, 9297

$S_{RN}1$ C-ARYLATION OF PHENOLS BY AZOSULFIDES: A NOVEL SYNTHESIS OF DIBENZO[*b,d*]PYRAN-6-ONES

Giovanni Petrillo,* Marino Novi, Carlo Dell'Erba, and Cinzia Tavani
Istituto di Chimica Organica dell'Università and C N R Centro di Studio sui Diariloidi, Genova, Italy

A simple access to **4** is achieved *via* arylation of a phenol by a (2-cyanoaryl)azo *t*-butyl (or phenyl) sulfide **2**, followed by lactonisation of the non-isolated biaryl **3** on silica-gel.

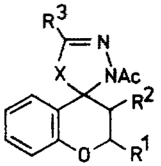


X = H Me MeO   R = Bu^t Ph   Y = H Me   Z = H Me MeO Br NO_2 CF_3

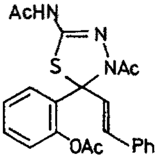
Tetrahedron, **1991**, *47*, 9305

REACTIONS OF FLAVONOID THIOSEMICARBAZONES UNDER ACETYLATING CONDITIONS

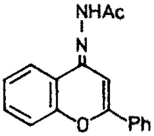
L. Somogyi; Research Group for Antibiotics (Hungary)



A



B



C

X = S, O
R^1 = H, Ph
R^2 = H, OAc
R^3 = AcHN, Ac_2N, Me

Upon acetylation, dihydrobenzopyrone and chalcone thiosemicarbazones transform into thiadiazolines (A, B), but acetylhydrazone C was obtained from flavone thiosemicarbazone under analogous conditions.