GRAPHICAL ABSTRACTS

THEORETICAL AND EXPERIMENTAL STUDIES OF THE 3-AZA-CLAISEN REARRANGE-MENT.

John C. Gilbert* and Kimberley R. Cousins, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712.

MNDO molecular orbital calculations support a spin-paired chair-like transition state for the 3-aza-Claisen rearrangement, and yield the prediction that an anionic substituent on the nitrogen t atom reduces the activation energy for the process. Attempted experimental demonstration of this prediction has been unsuccessful.
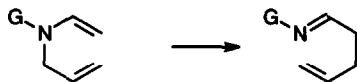

A FRIEDLANDER APPROACH TO NOVEL 1,10-PHENANTHROLINES AND THEIR USE AS LIGANDS FOR RU(II) AND CU(I) Chi-Ying Hung, Tie-Lin Wang, Zhiqiang Shi, and Randolph P. Thummel,* Department of Chemistry, University of Houston, Houston, Texas 77204-5641 USA

The six step synthesis of 8-amino-7-quinolinecarbaldehyde from 8-hydroxyquinoline and its subsequent Friedländer condensation with 2-acetylpyridine and cyclic 1,2-diketones is described. Complexes with Ru(II) & Cu(I) are prepared.
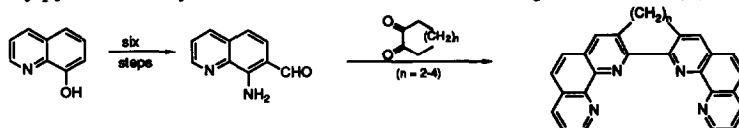

SYNTHESIS OF THE BICYCLOPROPENYLS

W. E. Billups* and Michael M. Haley
Department of Chemistry, Rice University, Houston, Texas 77251
Roland Boese* and Dieter Bläser
Institut für Anorganische Chemie, der Universität-GH Essen, Universitätsstr. 3-5, D-45117 Essen, Germany

Bicyclopropenyls 1-3 have been synthesized by the vacuum gas-phase elimination of β-halocyclopropylsilanes over solid fluoride.

1 **2** **3**
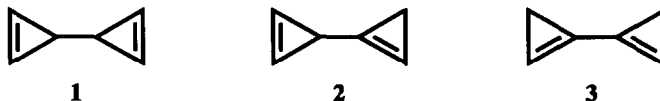
CHIRAL 1,4-DIAZEPINONES AND 1,4-THIAZEPINONES BY DIASTEREOSELECTIVE RING CHAIN TRANSFORMATION OF α, ß-UNSATURATED LACTONES OR LACTAMS

J. Bohrisch, H. Faltz, M. Pätzel, J. Liebscher*, Fachbereich Chemie, Humboldt-Universität Berlin, Hessische Str. 1-2, D-10115 Berlin
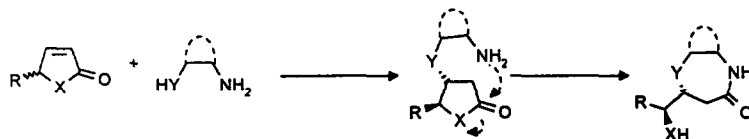
SYNTHESIS OF 13-ETHYL-11-METHYLENE-18,19-DINOR-17α-PREGN-4-EN-20-YN-17-OL (*DESOGESTREL*) AN ITS MAIN METABOLITE 3-OXO *DESOGESTREL*.

Sigfrid Schwarz*, Sven Ring, Gisela Weber, Gerhard Teichmüller, Hans-Joachim Palme, Carmen Pfeiffer, Bernd Undeutsch, Bernd Erhart, and Detlef Grawe, Division of Research and Development, Jenapharm GmbH, D-07745 Jena, Germany

Desogestrel 25 and 3-oxo desogestrel 28 have been synthesized from 18a-homo-estrane derivative 1.
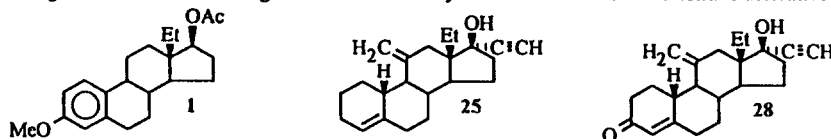
**GENERATION AND CHEMICAL REACTIONS OF QUINOXALINO-*O*-QUINODIMETHANE**

Ta-shue Chou* and Chung-Wen Ko
Institute of Chemistry, Academia Sinica, Taipei, Taiwan and
Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

We have prepared the unsubstituted quinoxalino-3-sulfolene 7 *via* two convenient routes and discovered its unusual stability toward thermal extrusion of SO_2. The generation of the *o*-quinodimethane 14 from 7 was achieved at temperatures higher than 290 °C.
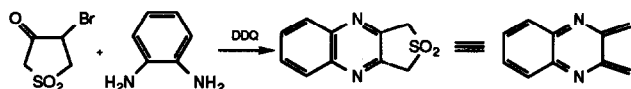
SYNTHETIC STUDY ON CHIRAL BUILDING BLOCK OF VICINAL DIOL CHIRON APPROACH TO THE PRECURSORS OF ALL SPHINGOSINE STEREOISOMERS

Yun-Long Li, Xiao-Ling Sun and Yu-Lin Wu*
State key Laboratory of Bio-organic and Natural Products Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, CHINA

Glucose, Xylose etc. ⟶

All four enantiomers
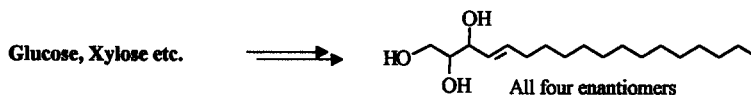
THE CHEMISTRY OF PSEUDOMONIC ACID PART 13[1]. MODIFICATIONS AT C12 TO C14

Andrew K. Forrest, Peter J. O'Hanlon, and Graham Walker*
SmithKline Beecham Pharmaceuticals, Brockham Park, Betchworth, Surrey, RH3 7AJ, UK

Semisynthetic analogues of pseudomonic acid have been prepared and tested as inhibitors of isoleucyl tRNA synthetase.


R = aryl, hydroxyalkyl, aminoalkyl
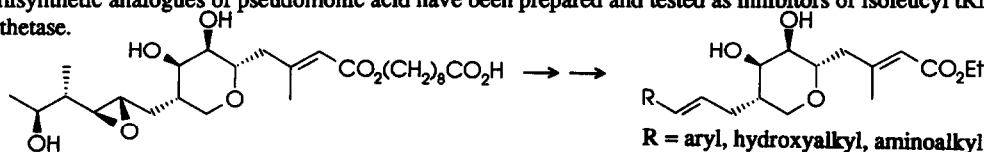
Comparison of the Enzymatic Activity of Commercial and Semipurified Lipase of *Candida cylindracea* in the Hydrolysis of the Esters of (R,S) 2-Aryl Propionic Acids. María J. Hernáiz, José M. Sánchez-Montéro and José V. Sinisterra[*]. Department of Organic and Pharmaceutical Chemistry. Facultad of Pharmacy. Universidad Complutense, 28040 Madrid (Spain). FAX(+34-1)3941822

Hydrolysis of (R,S) 2-Aryl Propionic Esters yield the (S) Acid and (R) Ester.
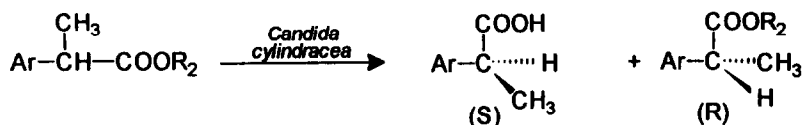
REARRANGEMENTS OF 14-MESYLOXY-*ent*-BEYER-15-ENES.

José Dueñas, Andrés García-Granados[*], Antonio Martínez and Andrés Parra.
Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Granada. 18071-Granada. (Spain).
Rearrangements of products (4) and (9), under several conditions, gave rearranged compounds 7 and 10 respectively.
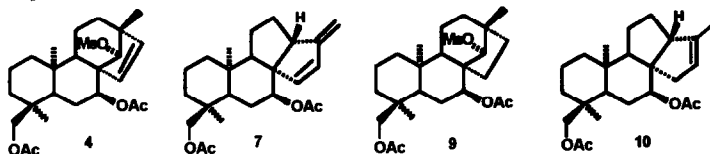
INTRAMOLECULAR AMIDOALKYLATION OF AROMATICS III. SYNTHESIS OF
CONFORMATIONALLY RESTRICTED BRIDGED PEPTIDE ANALOGUES OF PHE-GLY
  Amal Rabi-Barakay and Dov Ben-Ishai
Department of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel
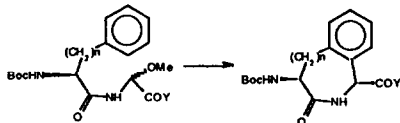
n = 1, 2
Y = OH, OMe, NH_2, $NHCH_2CH(CH_3)_2$,
Leu.OH, Lue.OMe, Leu.NH_2, Leu.Met.NH_2

Intramolecular amidoalkylation of *N*-Moc-S-Phe-α-OMe-GlyOMe and *N*-Moc-Homophe-α-OMe-GlyOMe leads to derivatives of benzazepin-3-one and benzazin-3-one as conformationally resrticted peptide analogues of Phe-Gly and Homophe-Gly.

# SYNTHESIS OF δ-LACTAMS FROM PENTA-CYCLO[5.4.0.0^{2,6}0^{3,10}.0^{5,9}]UNDECANE-8,11-DIONE

F.J.C. Martins, A.M. Viljoen, H.G. Kruger, J.A. Joubert and P.L. Wessels, Department of Chemistry, Potchefstroom University for CHE, Potchefstroom 2520, South Africa.

2; R = OH
3; R = CN
4; R = NH_2

5; R = CN
6; R = COOH
7; R = $CONH_2$
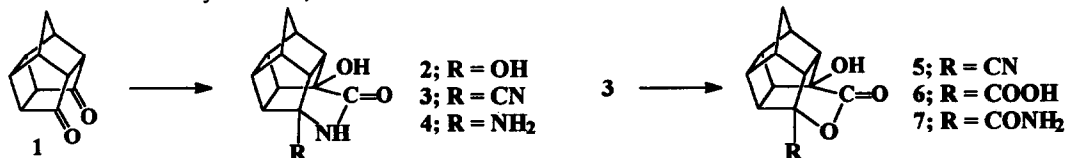
RING–A FUNCTIONALIZED *NEO*–CLERODANE DITERPENOIDS FROM*CISTUS POPULIFOLIUS*. Julio G. Urones*, Pilar Basabe, Isidro S. Marcos, Alicia Jiménez, Anna M. Lithgow, Margarita López, Rosalina F. Moro and Antonio Gómez. Dpto. Química Orgánica, Pza. de los Caídos 1–5, 37008, Salamanca, Spain
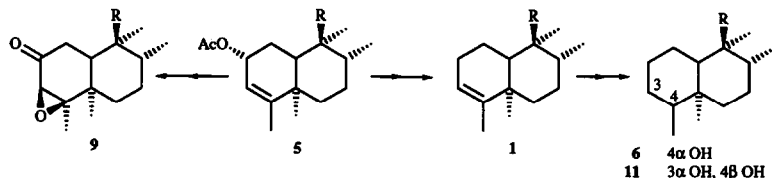
Some of the *neo*–clerodane isolated from *C. populifolius* showed a moderate antifeedant activity. The structure and stereochemistry of **9**, **6** and **11** were determined unequivocally by hemisynthesis.

R = (CH$_2$)$_2$CH(CH$_3$)CH$_2$CO$_2$Me

6   4α OH
11   3α OH, 4β OH

SYNTHESIS OF INDOLYLQUINOLINES UNDER FRIEDEL-CRAFTS CONDITIONS

Shashi B. Mahato[*a], Nirup B. Mandal[a], Sukanya Chattopadhyay[a], Gopa Nandi[a], Peter Luger[b], and Manuela Weber[b]

[a]Indian Institute of Chemical Biology, 4 Raja S.C.Mullick Road, Calcutta-700032, India, [b]Institut für Kristallographie, Freie Universität Berlin, Takustr.6, D-14195 Berlin, Germany.

A one-pot synthesis of some novel indolylquinolines 2a-2e using indole or its 5-substituted derivatives as substrates under Friedel-Crafts acylation conditions is reported.
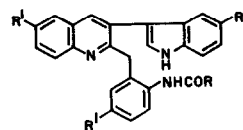

2a: R=CHCl$_2$, R'=H   2b: R=CH$_2$Cl, R'=H
2c: R=CH$_3$, R'=H 2d: R=CHCl$_2$, R'=OCH$_3$
2e: R=CHCl$_2$, R'=Br

ON THE ORIGIN OF TRANSANNULAR INTERACTIONS IN DIKETONES AND METHYLENE–KETONES, AS DETECTED BY [13]C N.M.R. SPECTROSCOPY: AN *AB INITIO* MO STUDY

Michael N. Paddon–Row
School of Chemistry, University of New South Wales, PO Box 1, Kensington, NSW, 2033, Australia

Transannular interactions responsible for [13]C n.m.r. chemical shift changes in 1 and 2 have been investigated using natural population analysis (HF/6–31G(d) level). The results indicate that electrostatic effects are the prime cause of the n.m.r. shifts.

1: X = O;   2: X = CH$_2$
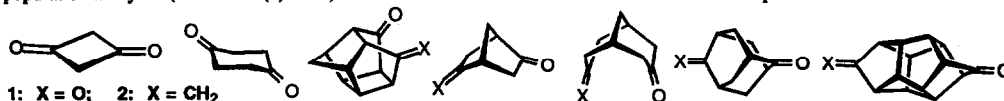
THE ASYMMETRIC SYNTHESIS OF AN ISOMER OF PODOPHYLLOTOXIN
By Andrew Pelter, Robert S. Ward and Neil P. Storer
(Chemistry Department, University of Wales, Swansea, Singleton Park, Swansea, SA2 8PP, U.K.)

A chiral isomer of podophyllotoxin has been synthesised by a route involving tandem conjugate addition by an O-silylcyanohydrin derived carbanion.