GRAPHICAL ABSTRACTS

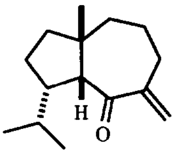
Tetrahedron, **1994**, *50*, 3065

FOUR SESQUITERPENES FROM THE SOUTH AFRICAN NUDIBRANCH *LEMINDA MILLECRA*

Jana Pika and D. John Faulkner*

Scripps Institution of Oceanography, University of California, San Diego,
La Jolla, CA 92093-0212

Leminda millecra was found to contain four new sesquiterpenes exemplified by millecrone A (1). The digestive glands of *L. millecra* contained spicules from soft corals.



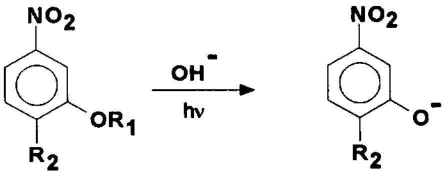
1

Tetrahedron, **1994**, *50*, 3071

Kinetic Studies of the Nucleophilic Quenching of Photoexcited Nitroaryl Ethers (NArE) by Bromide Ions in Cationic Micellar Solution

Antonio C. Tedesco, Rose M. Z. G.Naal, Julio C. Carreiro and João B.S. Bonilha.*

Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo
14040-901- Ribeirão Preto, SP - Brasil



$R_1 = CH_3$, $n\text{-}C_{10}H_{21}$

R_2 = H,Cl,Br

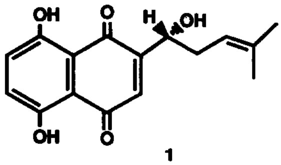
Tetrahedron, **1994**, *50*, 3081

Biotransformation of Shikonin by Human intestinal Bacteria

Meselhy R. Meselhy,[a] Shigetoshi Kadota,[a,*] Koji Tsubono,[b] Masao Hattori [a] and Tsuneo Namba[a]

Research Institute for Wakan-Yaku (Traditional Sino-Japanese Medicines),[a] Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama, 930-01, and Analytical Instruments Training and Application Center, JEOL Datum Ltd.,[b] Musashino, Akishima, Tokyo 196, Japan

The bacterial transformation of shikonin (1) in culture media has been investigated using humanintestinal bacteria. Of 24 anaerobes tested, *Bacteroides fragilis* subsp. *thetaotus* showed an ability to transform 1 extensively to ten metabolites, five monomers; anhydroalkannin, deoxyshikonin, cycloshikonin, metaboshikonin I and II, and five dimers; shikometabolins A, B, C, D and E, after anaerobic incubation for 3 days. The structures of these metabolites were determined mainly by 2D-NMR including the INADEQUATE experiment.

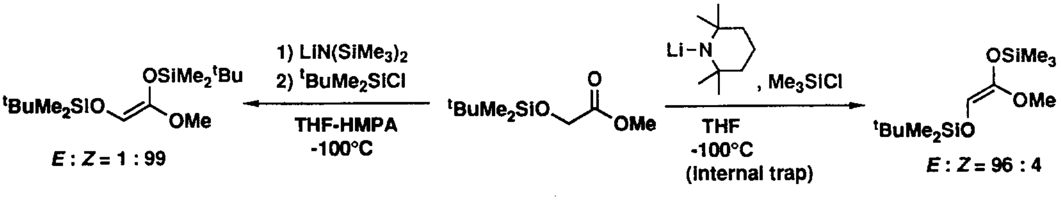


1

Tetrahedron, **1994**, *50*, 3099

Highly Selective Enolization Method for Heteroatom Substituted Esters; Its Application to the Ireland Ester Enolate Claisen Rearrangement

Kouji Hattori and Hisashi Yamamoto*
School of Engineering, Nagoya University, Chikusa, Nagoya 464-01, Japan

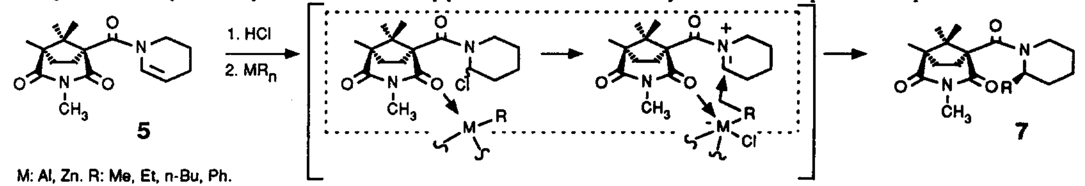


Asymmetric Electrophilic α-Amidoalkylation - 10:[1] A New Camphorimide Derived Chiral Auxiliary for the Asymmetric Synthesis with N-Acyliminium Ions - Preparation of Aracemic[2] 2-Substituted Piperidines.

Tetrahedron, **1994**, *50*, 3113

Klaus Th. Wanner* and Franz F. Paintner, Institut für Pharmazie der Freien Universität Berlin, Königin-Luise-Str. 2 + 4, D-14195 Berlin, Germany

A new reagent **5** for the asymmetric synthesis of 2-substituted piperidines with a chiral auxiliary derived from camphoric acid is presented.

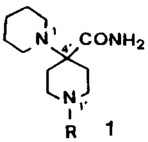


M: Al, Zn. R: Me, Et, n-Bu, Ph.

FUNCTIONALIZED CHLOROENAMINES IN AMINOCYCLOPROPANE SYNTHESIS - XV. SYNTHESIS OF CONFORMATIONALLY RIGID ANALOGUES OF [1,4'-BIPIPERIDINE]-4'-CARBOXAMIDE - A COMMON PHARMACOPHORIC GROUP

Tetrahedron, **1994**, *50*, 3123

Wolf-Rüdiger Schlag, Elmar Vilsmaier* and Gerhard Maas, Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany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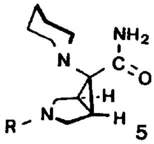
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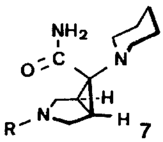

7

Diastereomeric carboxamides **5**/**7** are prepared with high stereoselectivity. These compounds represent conformationally rigid analogues of [1,4'-bipiperidine]-4'-carboxamide **1**, a common pharmacophoric group (**1**, **5**, **7**: R = H).

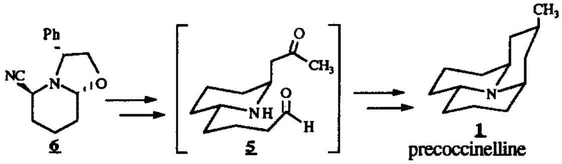
A NEW STEREOSELECTIVE SYNTHESIS OF LADYBUG DEFENCE ALKALOID PRECOCCINELLINE

Tetrahedron, **1994**, *50*, 3139

Chongwei Yue, Jean-François Nicolay, Jacques Royer* and Henri-Philippe Husson

Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France

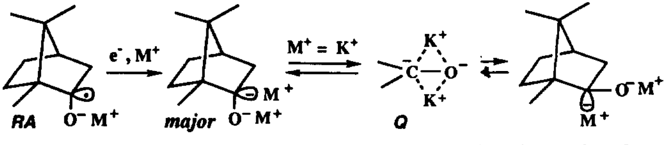
A new stereoselective synthesis of precoccinelline **1** in six steps from the chiral synthon **6** with a overall yield of 31 % is reported.



COUNTERION EFFECT ON STEREOCHEMISTRY OF REDUCTION OF CYCLOALKANONES BY ALKALI METALS IN AMMONIA

Tetrahedron, **1994**, *50*, 3149

Suresh K. Pradhan and Ramanathan Sankaran
Bombay University Department of Chemical Technology, Matunga Road, Bombay 400 019, India.



Explanation given why major epimer is endo with Li^+ and exo with K^+

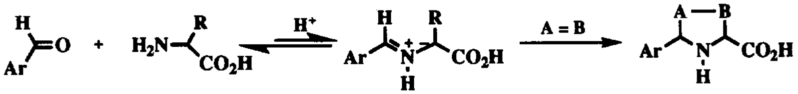
Pyramidalisation in **RA** determines stereochemistry in former. Rapid dianion interconversion in latter via **Q** shifts stereochemistry control to transition state energies for protonation. Concept applied to many cases.

Tetrahedron, **1994**, *50*, 3159

NON-DECARBOXYLATIVE 1,3-DIPOLAR CYCLOADDITIONS OF α-AMINO ACIDS AS ROUTE TO PROLINE DERIVATIVES.

Moustafa F. Aly,[*a] **Mansour I. Younes**[a] **and Saoud A.M. Metwally**[b].
a. Chemistry Department, Faculty of Science at Qena, Assiut University, Egypt, b. Chemistry of Chemistry, Faculty of Science, UAE University, P.O.17551, Al-Ain,The United Arab Emirates.

Synthesis of some proline drivatives via a non-decarboxylative 1,3-dipolar cycloaddition process.



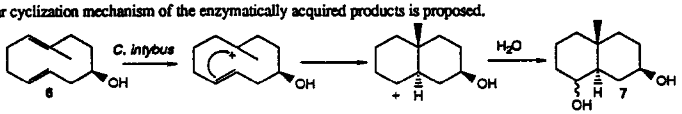
Tetrahedron, **1994**, *50*, 3169

SYNTHESIS OF 8-METHYL-*TRANS,TRANS*-CYCLODECA-3,7-DIEN-1β-OL AND BIOTRANSFORMATION INTO 4aβ-METHYL-1,2,3,4,4a,5,6,7,8,8aα-DECAHYDRONAPHTHALENE-1,7β-DIOL BY *CICHORIUM INTYBUS*

Dennis P. Piet, Maurice C.R. Franssen and Aede de Groot.

Department of Organic Chemistry, Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands.

The biotransformation of 8-methyl-*trans,trans*-cyclodeca-3,7-dien-1β-ol (6) into *trans*-decaline 7 by a suspension of fresh chicory root (*Cichorium intybus*) was investigated. In this paper, the synthesis of 6 as well as its enzymatic transfomation into 7, is presented. A transannular cyclization mechanism of the enzymatically acquired products is proposed.



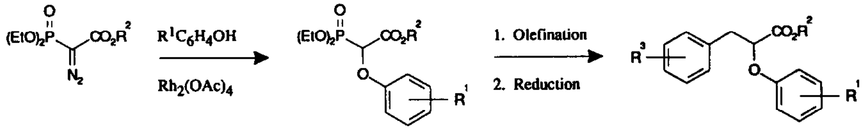
Tetrahedron, **1994**, *50*, 3177

RHODIUM CARBENOID O-H INSERTION REACTIONS WITH PHENOLS; A FACILE METHOD FOR THE SYNTHESIS OF TRIALKYL 2-ARYLOXYPHOSPHONOACETATES AND THEIR USE IN THE PREPARATION OF 2-ARYLOXY-3-PHENYLPROPANOATES.

David Haigh

SmithKline Beecham Pharmaceuticals, Great Burgh, Yew Tree Bottom Road, Epsom, Surrey KT18 5XQ, UK.

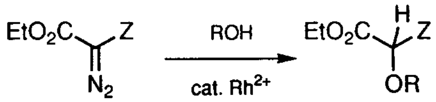
Rhodium(II) acetate catalysed decomposition of trialkyl 2-diazophosphonoacetates in the presence of phenols affords trialkyl 2-aryloxyphosphonoacetates by O-H insertion. Subsequent Wadsworth-Emmons olefination with benzaldehydes followed by reduction affords 2-aryloxy-3-phenylpropanoates.



Tetrahedron, **1994**, *50*, 3195

RHODIUM-CARBENOID MEDIATED O-H INSERTION REACTIONS. O-H INSERTION vs. H-ABSTRACTION AND EFFECT OF CATALYST

G. G. Cox, D. J. Miller, C. J. Moody and E.-R. H. B. Sie, Department of Chemistry, Loughborough University of Technology, Loughborough, Leics, LE11 3TU, U. K.
J. J. Kulagowski, Merck, Sharp and Dohme Research Laboratories, Terlings Park, Harlow, Essex, CM20 2QR, U.K.



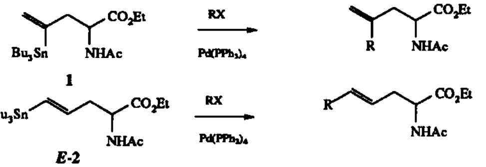
The synthesis and rhodium mediated O-H insertion reactions of a wide range of diazo compounds are described. The rate at which the diazo compounds decompose in the presence of 2-propanol and the rhodium catalyst is strongly dependent on the electron withdrawing group(s) attached to the diazo carbon, with diazophosphonates being the least reactive. Insertion into the O-H bond of methanol, t-butanol and phenols was also investigated, as well as the effect of catalyst. In some cases 'reduction' of the diazo group to the corresponding CH_2 group competes with O-H insertion, although this is highly catalyst and substrate dependent. Of the catalysts used, rhodium(II) trifluoroacetamide is the most effective for O-H insertion reactions.

Tetrahedron, 1994, 50, 3213

Elaboration of the Side Chain of α–Amino Acids by Palladium-Catalysed Stille Couplings

Geoffrey T. Crisp* and Peter T. Glink
Department of Chemistry, University of Adelaide, Adelaide, South Australia, Australia 5005

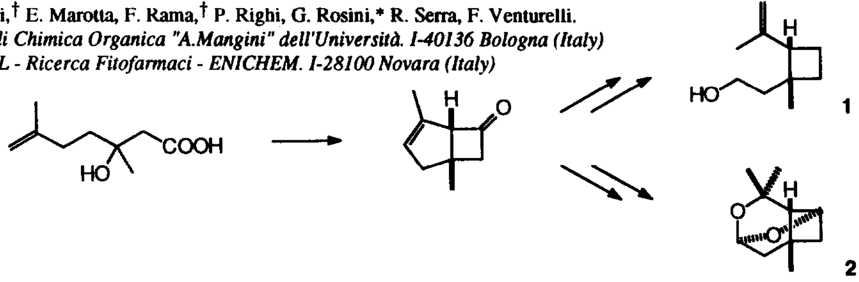
The palladium-catalysed couplings of a γ-tri-*n*-butylstannylallylglycine derivative and an *E*-δ-tri-*n*-butylstannylallylglycine derivative with various organic electrophiles are described.



Tetrahedron, 1994, 50, 3235

PRACTICAL PREPARATION OF BICYCLO[3.2.0]HEPT-3-EN-6-ONES AND ITS UTILIZATION IN STEREOSELECTIVE TOTAL SYNTHESIS OF GRANDISOL AND LINEATIN *VIA* A VERSATILE INTERMEDIATE.

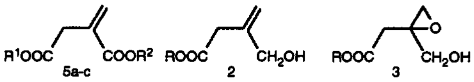
G. Confalonieri,† E. Marotta, F. Rama,† P. Righi, G. Rosini,* R. Serra, F. Venturelli.
Dipartimento di Chimica Organica "A.Mangini" dell'Università. I-40136 Bologna (Italy)
† ISAGRO S.r.L - Ricerca Fitofarmaci - ENICHEM. I-28100 Novara (Italy)



Tetrahedron, 1994, 50, 3251

SELECTIVE ENZYMATIC TRANSFORMATIONS OF ITACONIC ACID DERIVATIVES: AN ACCESS TO POTENTIALLY USEFUL BUILDING BLOCKS.

*P. Ferraboschi, S. Casati, P. Grisenti, E. Santaniello**
Dipartimento di Chimica e Biochimica Medica, Universita' di Milano.



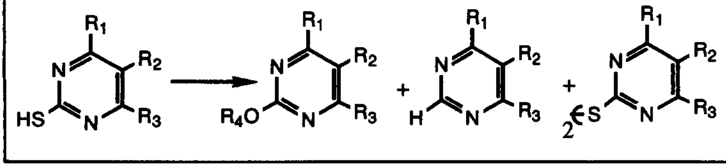
The monoesters **5b** (R^1=Et, R^2=H) and **5c** (R^1=H, R^2=Et) are prepared by enzymatic methods starting from diethyl itaconate **5a** (R^1=R^2=Et) and itaconic anhydride. The ester **5b** is reduced to **2**, in turn converted into the epoxide **3**, which is enantioselectively resolved by a PFL-catalyzed transesterification.

Tetrahedron, 1994, 50, 3259

OXIDATION OF SUBSTITUTED 2-THIOURACILS AND PYRIMIDINE-2-THIONE WITH OZONE AND 3,3-DIMETHYL-1,2-DIOXIRANE.

C. Crestini[a], R. Nicoletti[a], R. Saladino[b], E. Mincione[b]. a Università degli studi "La Sapienza", Roma (Italy), b Università degli studi "La Tuscia", Viterbo (Italy).

The reactions of title compounds with ozone and 3,3-dimethyl-1,2-dioxirane are reported.

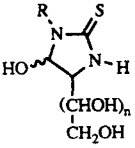


CONDENSATION OF 2-AMINO-2-DEOXY SUGARS WITH ISOTHIOCYANATES. SYNTHESIS OF *cis*-1,2-FUSED GLYCOPYRANO HETEROCYCLES.

Tetrahedron, **1994**, *50*, 3273

Martín Avalos, Reyes Babiano, Pedro Cintas, José L. Jiménez, Juan C. Palacios, and Concepción Valencia.
Departamento de Química Orgánica. Facultad de Ciencias. Universidad de Extremadura. 06071-Badajoz, Spain

Compounds **1**-**4** were synthesised and their mechanism of formation was discussed.



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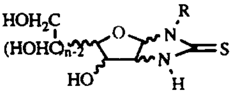

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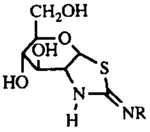

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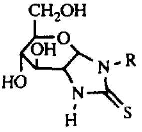

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