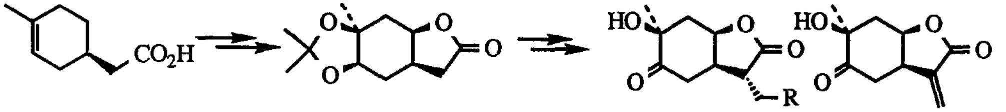
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1990**, *31*, 5973

EREOSELECTIVE SYNTHESIS OF THE PAEONILACTONES A, B AND C

David P. Richardson,* Thomas E. Smith, William W. Lin, Cynthia N. Kiser,
and Brian R. Mahon. Department of Chemistry, Williams College
Williamstown, Massachusetts 01267

The first syntheses of the title monoterpenes 2, 3 and 4 are reported. Synthesis begins with 7 and proceeds via 6.

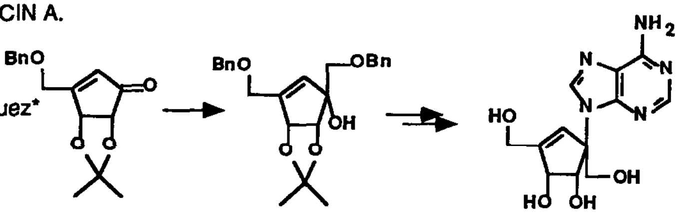


7 6 2 R=H; 4 R=$C_6H_5CO_2$ 3

Tetrahedron Lett. **1990**, *31*, 5977

SYNTHESIS OF (±)- PSICOPLANOCIN A. A CARBOCYCLIC NUCLEOSIDE COMBINING THE STRUCTURAL FEATURES OF PSICOFURANINE AND NEPLANOCIN A.

Michael Bodenteich and Victor E. Marquez*
Laboratory of Medicinal Chemistry, NCI
National Institutes of Health,
Bethesda, Maryland 20892

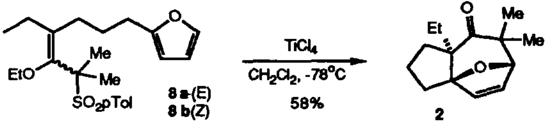


Tetrahedron Lett. **1990**, *31*, 5981

ALLYL CATION STEREOCHEMISTRY IN THE INTRAMOLECULAR 4+3 CYCLOADDITION REACTION

Michael Harmata*, Chandra B. Gamlath and Charles L. Barnes
Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

Summary: Initial allyl cation geometry appears to be irrelevant with respect to the stereochemistry of cycloadducts in the intramolecular 4+3 cycloaddition of alkoxyallylic cations derived from alkoxyallylic sulfones.

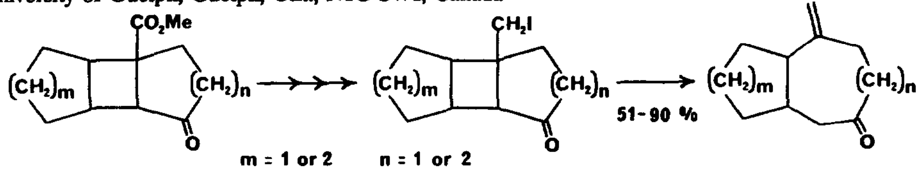


8 a (E)
8 b (Z)
2

Tetrahedron Lett. **1990**, *31*, 5985

FREE RADICAL FRAGMENTATION OF DERIVATIVES OF [2 + 2] PHOTOADDUCTS

Gordon L. Lange* and Christine Gottardo
Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry,
University of Guelph, Guelph, Ont., N1G 2W1, Canada



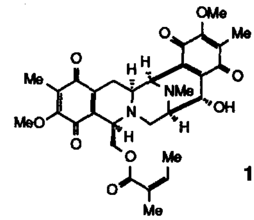
m = 1 or 2 n = 1 or 2

Tetrahedron Lett. **1990,** *31,* 5989

A STEREOCONTROLLED TOTAL SYNTHESIS OF (±)-RENIERAMYCIN A

Tohru Fukuyama,* Steven D. Linton, and Min Min Tun
Department of Chemistry, Rice University, Houston, Texas 77251

The first total synthesis of (±)-renieramycin A (**1a**) is described. The stereochemistry of the angelate side chain was unequivocally determined by X-ray crystallographic analysis of the penultimate intermediate.

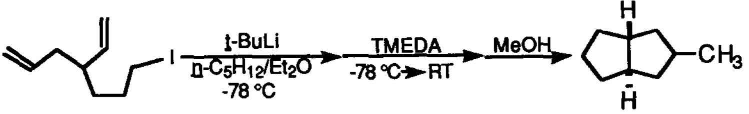


1a

Tetrahedron Lett. **1990,** *31,* 5993

FORMATION OF A <u>TRANS</u>-BICYCLO[3.3.0]OCTANE BY TANDEM ANIONIC CYCLIZATION: EVIDENCE FOR THE HIGHLY STEREOSELECTIVE IRREVERSIBLE NATURE OF 5-HEXEN-1-YLLITHIUM CYCLIZATIONS

William F. Bailey* and Atmaram D. Khanolkar
Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060

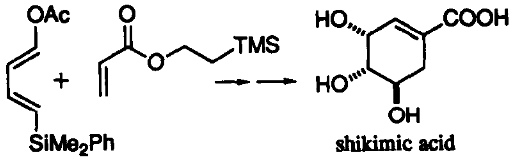


Tetrahedron Lett. **1990,** *31,* 5997

(1*E*,3*E*)-4-Acetoxy-1-phenyldimethylsilyl-1,3-butadiene as a Surrogate for (1*E*,3*E*)-1,4-Diacetoxy-1,3-butadiene: A Highly Efficient Synthesis of (±)-Shikimic Acid

Masato Koreeda,* Kelly Teng, and Toshiki Murata, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

The 5-step synthesis of (±)-shikimic acid has been achieved in 55.2% overall yield from (1*E*,3*E*)-4-acetoxy-1-phenyldimethylsilyl-1,3-butadiene, starting with its Diels-Alder reaction with 2-(trimethylsilyl)ethyl acrylate and featuring the use of Fleming's one-pot procedure for the conversion of the phenyldimethylsilyl group to the hydroxyl as the salient, pivotal step in the synthesis.

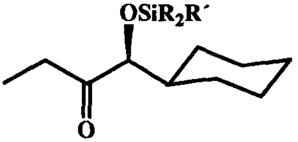


Tetrahedron Lett. **1990,** *31,* 6001

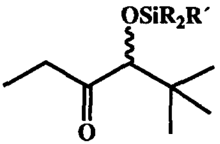
STERIC INFLUENCE OF SILYL GROUPS IN TITANIUM- AND LITHIUM-MEDIATED ALDOL CONDENSATIONS

Chitchanun Panyachotipun and Edward R. Thornton*
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 USA

- Solves a mechanistic puzzle by showing that the difference between $SiMe_3$ and $SiMe_2t$-Bu accounts for the differing aldol stereoselectivites of enolates of **1a**–**2b**.
- Ketone **1a**, readily prepared in monochiral form, gives a potential route to synthetically useful β-hydroxy-α-methylcarboxylic acids of *opposite configurations* (Ti-enolate, 99:1; Li-, 10:90) from *the same precursor* **1a**.



1a R = R′ = Me
1b R = Me; R′ = CMe3

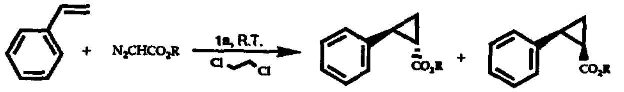


2a R = R′ = Me
2b R = Me; R′ = CMe3

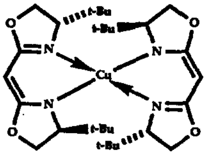
Tetrahedron Lett. **1990**, *31*, 6005

Asymmetric Catalytic Cyclopropanation of Olefins: Bis-Oxazoline Copper Complexes

Richard E. Lowenthal, Atsushi Abiko, and Satoru Masamune*
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139



Trans : Cis ratios up to 86:14
Enantioselectivity up to 98 %ee



1a

Tetrahedron Lett. **1990**, *31*, 6009

NEW CHEMISTRY OF DIAZOESTERS FROM THERMAL REARRANGEMENT OF N-ALKYL-N-NITROSOAMIDES

Nicholas Nikolaides, Alexander G. Godfrey and Bruce Ganem*
Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853 USA

$$RCH_2N(NO)COCH_2Cl \xrightarrow[DMSO]{N\text{-methylmorpholine-}N\text{-oxide}} RCHO$$

Tetrahedron Lett. **1990**, *31*, 6013

ALKYL ISOCYANIDES AS PRECURSORS FOR THE FORMATION OF CARBON-CARBON BONDS

C. Chatgilialoglu, B. Giese,* and B. Kopping, Institut für Organische Chemie der Universität Bas
St. Johanns-Ring 19, CH-4056 Basel, Switzerland

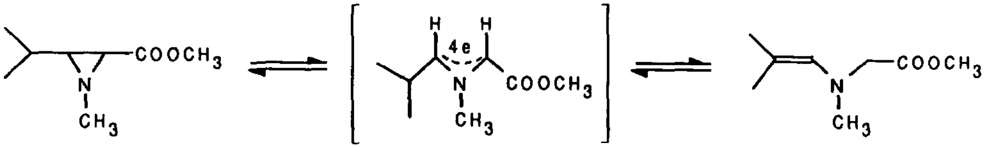
Isonitriles can be used as precursors for radical C,C-bond formation with tris(trimethylsilyl)silane as mediator.

$$R{-}N{=}C \;+\; H_2C{=}CHY \xrightarrow[AIBN/\Delta]{(Me_3Si)_3SiH} RCH_2{-}CH_2Y$$

Tetrahedron Lett. **1990**, *31*, 6017

FLASH VACUUM THERMOLYSIS OF 2-ISOPROPYL OXAZOLIDINES. MECHANISM OF THE TAUTOMERISM BETWEEN AZOMETHINE YLID, AZIRIDINE AND ENAMINE.

Ronan Bureau(1) and Marc Joucla*(2).
(1) Groupe de Physicochimie Structurale, associé au CNRS, Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France.
(2) Present address: Unité Mixte CNRS- Rhône Poulenc, CID, 24 rue Jean Jaurès, BP 166 Décines-Charpieu , France.

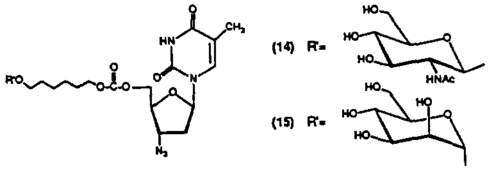


Tetrahedron Lett. **1990**, *31*, 6021

ALKYLGLYCOSIDE CARBONATES OF 3'-AZIDO-3'-DEOXYTHYMIDINE

by Sylvie Pochet[1], Vinod Kansal[1], Florence Destouesse[2] and Simon R. Sarfati[1]
Institut Pasteur, [1]Unité de Chimie Organique, [2]Unité d'Oncologie Virale, associées au CNRS,
28, rue du Docteur Roux, 75724 Paris Cedex 15, France.

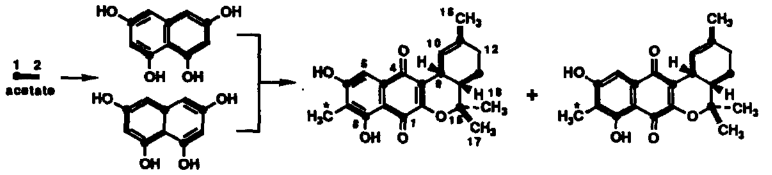
Two analogues of 3'-azido-3'-deoxythymidine (AZT) have been synthesized by coupling glycosides of D-mannose and N-acetyl-D-glucosamine with AZT through a carbonate bridge.



Tetrahedron Lett. **1990**, *31*, 6025

BIOSYNTHESIS STUDIES ON NAPHTERPIN, A TERPENOID METABOLITE OF *STREPTOMYCES*

K. Shin-ya, K. Furihata, Y. Hayakawa and H. Seto*
Institute of Applied Microbiology, The University Tokyo, Bunkyo-ku, Tokyo, Japan, 113



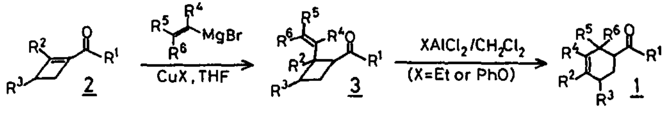
* : from methionine

Tetrahedron Lett. **1990**, *31*, 6027

RING ENLARGEMENT REACTION OF 2-(1-ALKENYL)-1-CYCLOBUTYL KETONES. A NEW METHOD FOR THE PREPARATION OF 4-ACYL-1-CYCLOHEXENES

Tooru FUJIWARA and Takeshi TAKEDA*
Department of Applied Chemistry, Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184, Japan

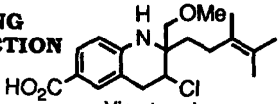
Verious 4-acyl-1-cyclohexenes (1) were obtained by the ethylaluminum dichloride promoted ring enlargement reaction of 2-(alkenyl)-1-cyclobutyl ketones (3) prepared by the conjugate addition of 1-alkenylmagnesium bromides with 1-cyclobutenyl ketones (2).

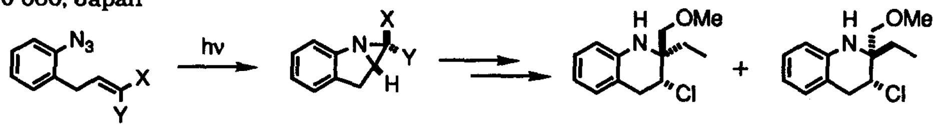


Tetrahedron Lett. **1990**, *31*, 6031

AN EFFICIENT APPROACH TOWARD VIRANTMYCIN: STEREOSPECIFIC CONSTRUCTION OF TETRAHYDROQUINOLINE RING SYSTEM EMPLOYING INTRAMOLECULAR NITRENE-ADDITION REACTION

Yoshiki Morimoto, Fuyuhiko Matsuda, and Haruhisa Shirahama*
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060, Japan

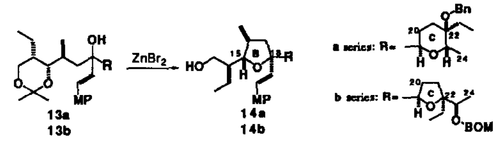

Virantmycin

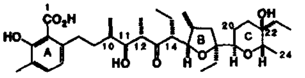


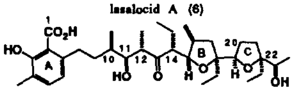
Tetrahedron Lett. **1990**, *31*, 6035

STEREOSELECTIVE SYNTHESIS OF POLYETHER ANTIBIOTICS, LASALOCID A AND ISOLASALOCID A, VIA A CHELATION-CONTROLLED FORMATION OF TETRAHYDROFURAN RINGS UNDER THERMODYNAMIC CONDITIONS

Ichio NODA, Kiyoshi HORITA, Yuji OIKAWA, and Osamu YONEMITSU
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan




lasalocid A (6)

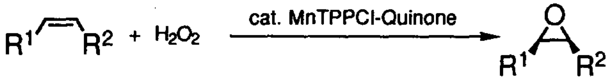

isolasalocid A (7)

Tetrahedron Lett. **1990**, *31*, 6039

MEDIATION OF ORTHOQUINONES IN THE MnTPPCl-CATALYZED EPOXIDATION WITH HYDROGEN PEROXIDE

Toshikazu Hirao, Mitsuru Ohno, and Yoshiki Ohshiro
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita 565, Japan

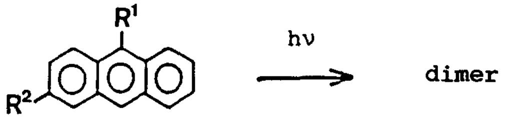
The MnTPPCl-catalyzed epoxidation of olefins with hydrogen peroxide is efficiently enhanced by mediation of orthoquinones (phenanthrenequinone and trimethyl ester of coenzyme PQQ).



Tetrahedron Lett. **1990**, *31*, 6043

SUBSTITUENT EFFECT IN THE PHOTODIMERIZATION OF AMPHIPHILIC ANTHRACENES: REACTIONS IN MONOLAYER ASSEMBLIES AND IN SOLUTIONS

Akihiko Ouchi,* Hiroyuki Niino, Yasujiro Kawabata, Motoo Tanaka, and Akira Yabe
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

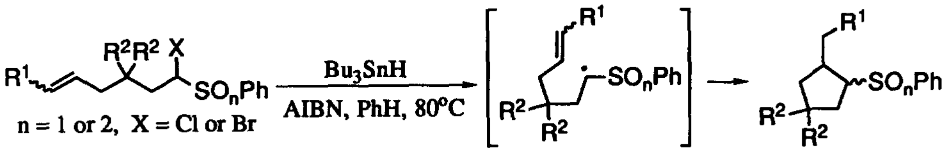


Reactions in monolayer assemblies and in solutions
R^1 = H, n-C_6H_{13}, n-$C_{11}H_{23}$
R^2 = H, $(CH_2)_5COOH$, $(CH_2)_{11}COOH$

Tetrahedron Lett. **1990**, *31*, 6047

THE STUDY OF INTRAMOLECULAR FREE RADICAL CYCLIZATIONS OF α-SULFONYL AND α-SULFINYL RADICALS

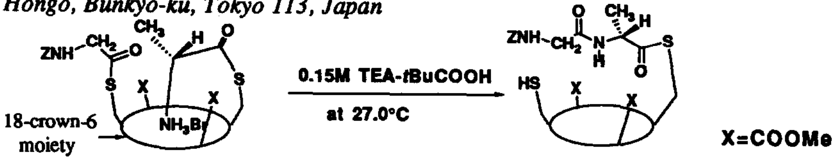
Yeun-Min Tsai,* Bor-Wen Ke, and Chao-Hsiung Lin
Department of Chemistry, National Taiwan University, Taipei 10764, Taiwan, Republic of China



Tetrahedron Lett. **1990**, *31*, 6051

AN ATTEMPT ON ACCELERATION OF PEPTIDE SYNTHESIS USING THE ENZYME MODEL HAVING PREORGANIZED CATALYTIC GROUPS

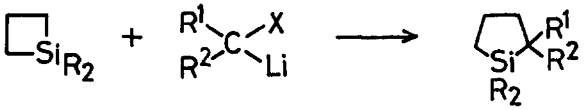
Shigeki Sasaki, Yasutaka Takase, and Kenji Koga*
Faculty of Pharmaceutical Sciences, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan



Tetrahedron Lett. **1990**, *31*, 6055

STEREOSELECTIVE FORMATION OF SILACYCLOPENTANES BY THE REACTION OF SILACYCLOBUTANE WITH LITHIUM CARBENOIDS

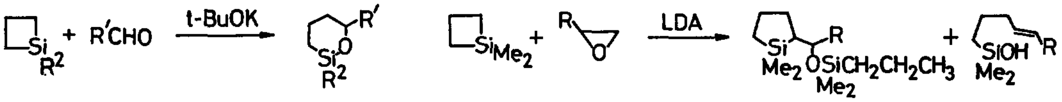
Kozo Matsumoto, Koichiro Oshima*, and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan



Tetrahedron Lett. **1990**, *31*, 6059

BASE INDUCED REACTION OF SILACYCLOBUTANE WITH ALDEHYDE OR EPOXIDE

Y. Takeyama, Koichiro Oshima,* and Kiitiro Utimoto*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto
University, Sakyo-ku, Kyoto 606 Japan

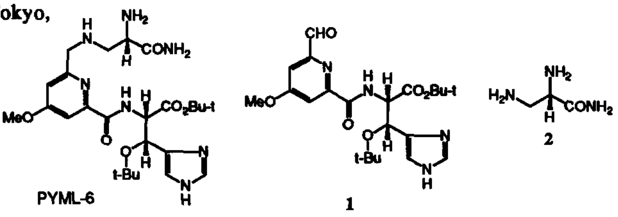


Tetrahedron Lett. **1990**, *31*, 6063

A MODEL STUDY ON THE MECHANISM OF THE AUTOXIDATION OF BLEOMYCIN

Takashi Owa, Toru Sugiyama, Masami Otsuka, Masaji Ohno,* Kenji Maeda#
Faculty of Pharmaceutical Sciences, University of Tokyo,
Japan and #Institute of Microbial Chemistry, Japan

A synthetic model of bleomycin, PYML-6, is treated with Fe(III)-H_2O_2 or Fe(II)-O_2, and the degradation products **1** and **2** are isolated and characterized.

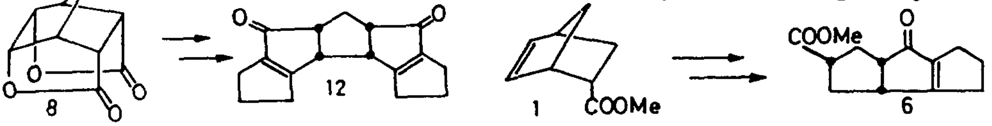


Tetrahedron Lett. **1990**, *31*, 6067

A NEW ROUTE TO LINEARLY FUSED POLYQUINANES

Narayana Murty Y.V.S. and C. Narayana Pillai* Department of Chemistry
Indian Institute of Technology, Madras -600 036, INDIA.

Syntheses of the triquinane [6] and the C_{17}-pentaquinane [12] are reported utilizing di-Grignard species as key reagents.

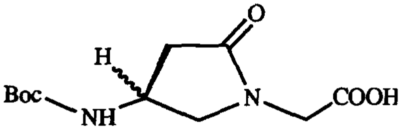


Tetrahedron Lett. **1990**, *31*, 6071

A NEW PROTECTED LACTAM-BRIDGED DIPEPTIDE

Nicholas J. Ede, Ian D. Rae*, and Milton T.W. Hearn.
Departments of Chemistry and Biochemistry,
Monash University. Clayton. 3168. Australia.

The synthesis of a new protected lactam-bridged dipeptide and its incorporation into an hGH(7-13) peptide analogue is described.



Tetrahedron Lett. **1990**, *31*, 6075

SYNTHESIS OF UNSYMMETRICAL DISULFIDES WITH THIOLSULFONATES IMMOBILISED ON A POLYSTYRENE SUPPORT

Andrzej RAJCA[a,*] and Manfred WIESSLER[b]

a - Institute of Organic Chemistry and Technology, Silesian Technical University, Krzywoustego 4, 44-100 Gliwice, Poland
b - Institute of Toxicology and Chemotherapy, German Cancer Research Center, 6900 Heidelberg,
Im Neuenheimer Feld 280, West Germany

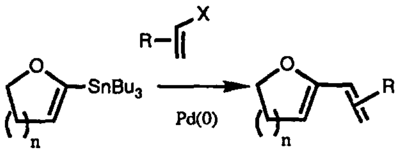
$$Ⓟ - SO_2Na + R^1SNO \longrightarrow Ⓟ - SO_2SR^1 + NaNO$$

$$Ⓟ - SO_2SR^1 + R^2SH \longrightarrow R^1SSR^2 + Ⓟ - SO_2H$$

Tetrahedron Lett. **1990**, *31*, 6077

The Palladium(0)-Catalysed Coupling Reactions of 2-(Tri-n-Butylstannyl)-3,4-Dihydrofuran and -5,6-Dihydropyran

Donald MacLeod, and Peter Quayle*. Department of Chemistry.
University of Manchester. Manchester M13 9PL. UK.
Michael R.J. Dorrity and John F. Malone. School of Chemistry
The Queens University of Belfast. Belfast BT9 5AG.
Gareth M. Davies
ICI Pharmaceuticals
Alderley Park. Macclesfield SK10 4TG. UK.

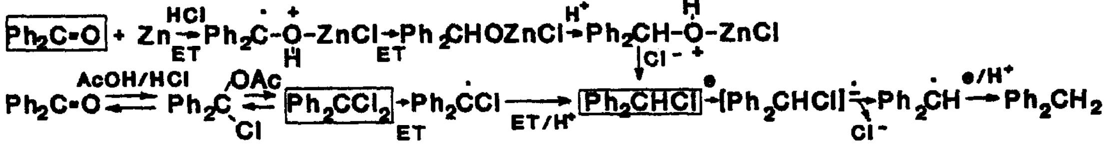


The palladium mediated synthesis of fuctionalised dienes and their subsequent chemistry is described.

Tetrahedron Lett. **1990**, *31*, 6081

SINGLE ELECTRON TRANSFERS IN ZINC-PROMOTED REACTIONS. THE MECHANISMS OF THE CLEMMENSEN REDUCTION AND RELATED REACTIONS.

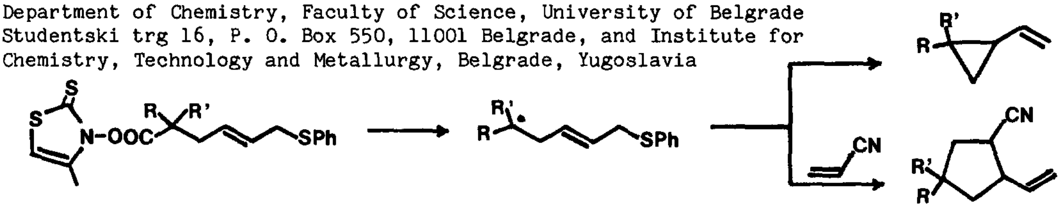
M.L.DI VONA, B.FLORIS, L.LUCHETTI, and V.ROSNATI*
Dipartimento di Scienze e Tecnologie Chimiche, II Università di Roma, 'Tor Vergata', ROMA (Italy).



Tetrahedron Lett. **1990**, *31*, 6085

RADICAL CYCLIZATION REACTIONS. CYCLOPROPANE RING FORMATION BY 3-exo-CYCLIZATION OF 5-PHENYLTHIO-3-PENTENYL RADICALS

Živorad Čeković* and Radomir Saičić
Department of Chemistry, Faculty of Science, University of Belgrade
Studentski trg 16, P. O. Box 550, 11001 Belgrade, and Institute for
Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

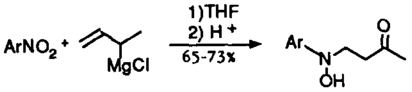


Tetrahedron Lett. **1990**, *31*, 6089

REARRANGEMENT OF NITRONES: ACID PROMOTED CONVERSION OF VINYLNITRONES INTO N-(γ-KETOALKYL)-N-PHENYLHYDROXYLAMINES

Giuseppe Bartoli*[a], Marino Petrini[a], Enrico Marcantoni[a], Marcella Bosco[b], Renato Dalpozzo[b]
a. Dipartimento di Scienze Chimiche, via S. Agostino 1, I-62032 Camerino (MC), Italy
b. *Dipartimento* di Chimica Organica "A. Mangini", viale Risorgimento 4, I-40136 Bologna, Italy

Title Compounds can be obtained from α-vinyl-α-methyl-N-phenylnitrones in the presence of anhydrous trifluoroacetic acid via sigmatropic rearrangement of a protonated oxaziridine intermediate.



Tetrahedron Lett. **1990**, *31*, 6093

STEREOCHEMISTRY OF ICHTHYOTOXIC DIACYGLYCEROLS FROM OPISTHOBRANCH MOLLUSCS

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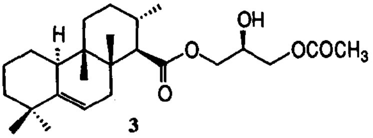
Istituto per la Chimica M.I.B., C.N.R., Via Toiano 6 - Arco Felice (NA) - Italy



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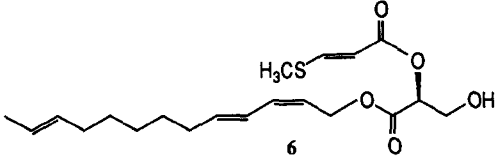

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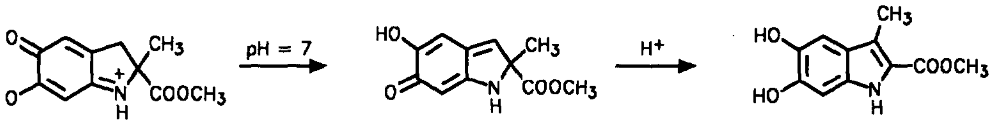
Tetrahedron Lett. **1990**, *31*, 6095

EVIDENCE FOR THE INTERMEDIACY OF QUINONE-METHIDES IN THE REARRANGEMENT OF AMINOCHROMES TO 5,6-DIHYDROXYINDOLES

O. Crescenzi, C. Costantini, G. Prota*,
Dipartimento di Chimica Organica e Biologica, Università di Napoli,Via Mezzocannone 16, I–80134 Napoli, Italy.



Tetrahedron Lett. **1990**, *31*, 6097

OXIDATIONS BY METHYL(TRIFLUOROMETHYL)DIOXIRANE. 4. OXYFUNCTIONALIZATION OF AROMATIC HYDROCARBONS.

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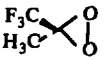
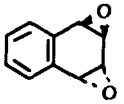
The title dioxirane (1a) has been employed in the direct oxyfunctionalization of the lower homologues of the polycyclic aromatic hydrocarbon series under mild conditions, e.g. naphthalene (2) to *anti*-naphthalene-1,2;3,4-dioxide (2') in 98% yield.


(1a)

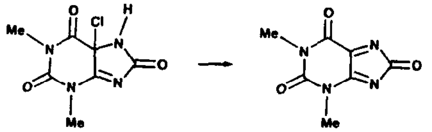

(2')

Tetrahedron Lett. **1990**, *31*, 6101

SYNTHESIS OF DEHYDRO-1,3-DIMETHYLURIC ACID

A. Palković and M. Poje*
Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, P. O. Box 153, 41001 Zagreb, Croatia, Yugoslavia

Pyrolytic dehydrochlorination of 1 allowed the first synthesis of a quinonoid dehydrouric acid 2b.



1 2b

Tetrahedron Lett. **1990**, *31*, 6103

SYNTHESIS OF A PYRIMIDINE BY ELIMINATION OF NITROGEN FROM A TRIAZOLO[4,5-*D*]PYRIMIDINE

Michael J. Dooley, Ronald J. Quinn*, Wyona C. Patalinghug and Allan H. White*, School of Science, Griffith University, Brisbane, 4111, Australia and Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, 6009, Australia

Treatment of 3-phenyl-1,2,3-triazolo[4,5-*d*]pyrimidine-5,7-dithione with butyl lithium and an alkylating agent resulted in loss of nitrogen, affording a bis-alkylated pyrimidine, incorporating one butyl side chain.