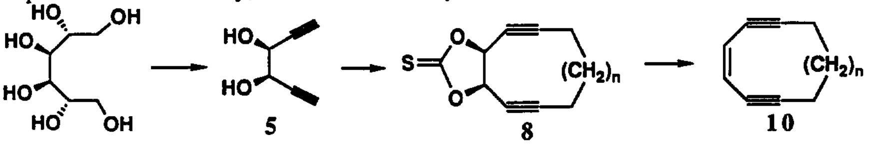
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1993**, *34*, 4121

CYCLIC CONJUGATED ENEDIYNES VIA ELIMINATION OF A THIONOCARBONATE IN A LATENT Z-HEX-3-ENE-1,5-DIYNE UNIT

M. F. Semmelhack and James Gallagher
Department of Chemistry, Princeton University, Princeton, NJ 08544

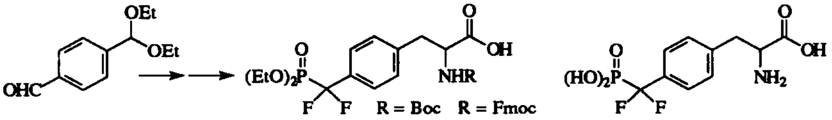


Tetrahedron Lett. **1993**, *34*, 4125

Synthesis of 4-Phosphono(difluoromethyl)-D,L-phenylalanine and N-Boc and N-Fmoc Derivatives Suitably Protected for Solid-Phase Synthesis of Nonhydrolyzable Phosphotyrosyl Peptide Analogues

Terrence R. Burke, Jr.*, Mark S. Smyth, Akira Otaka and Peter P. Roller

Laboratory of Medicinal Chemistry, Bldg. 37, Rm. 5C06, Developmental Therapeutics Program, Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, Bethesda, Maryland 20892

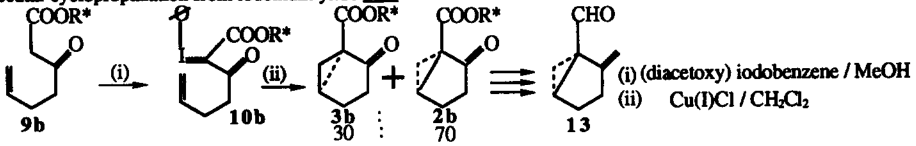


Tetrahedron Lett. **1993**, *34*, 4129

INTRAMOLECULAR CYCLOPROPANATION USING IODONIUM YLIDES. THE 3,5-CYCLOVITAMIN D RING A SYNTHON.

Robert M. Moriarty, Joonggon Kim, and Liang Guo,
Department of Chemistry, University of Illinois at Chicago 801 W. Taylor, St. Rm 4500 Chicago, IL 60607-7061

The key intermediate 2b for 3,5-cyclovitamin D ring A synthon 13 was prepared in 80% yield as a diastereomeric mixture (70:30) *via* intramolecular cyclopropanation from iodonium ylide 10b.

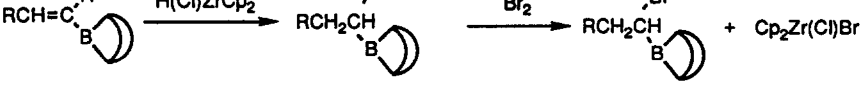


Tetrahedron Lett. **1993**, *34*, 4133

Preparation and Selective Cleavage Reactions of Boron-Zirconium 1,1-Bimetalloalkanes

Bin Zheng and Morris Srebnik*, Chemistry Department, University of Toledo, Toledo, OH 43606.

1,1-Bimetalloalkanes were prepared by hydrozirconation of alkenylboranes. Selective cleavage of the C-Zr bond provided α-bromoboranes.

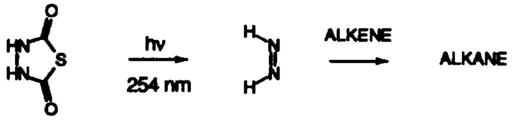


HYDROGENATION VIA PHOTOCHEMICALLY GENERATED DIIMIDE

Tetrahedron Lett. **1993**, *34*, 4137

Michael Squillacote,* James De Felippis and Yu Ling Lai
Department of Chemistry, Auburn University, Alabama 36948

Abstract: Diimide can be generated photochemically from 1-thia-3,4-diazolidine-2,5-dione (TDADH). The diimide thus produced can hydrogenate multiple bonds in high yields.

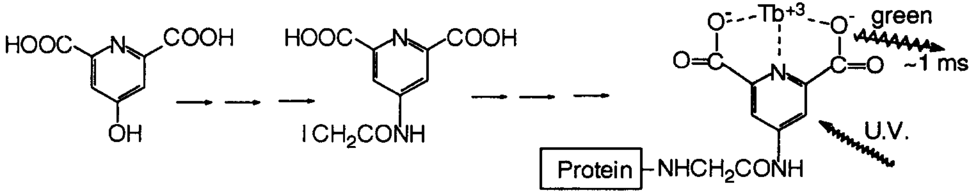


TDADH

A NOVEL REAGENT FOR LABELLING MACROMOLECULES WITH INTENSELY LUMINESCENT LANTHANIDE COMPLEXES

Tetrahedron Lett. **1993**, *34*, 4141

Jagannath B. Lamture and Theodore G. Wensel, Department of Biochemistry, Baylor College of Medicine, Houston, TX 77030.

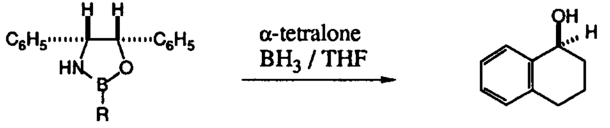


Diphenyloxazaborolidine
A New Catalyst For Enantioselective Reduction Of Ketones

Tetrahedron Lett. **1993**, *34*, 4145

George J. Quallich* and Teresa M. Woodall
Process Research and Development, Central Research Division, Pfizer Inc., Groton, CT 06340

A variety of ketones can be reduced in high enantioselectivity with the oxazaborolidines derived from commercially available erythro aminodiphenylethanol.



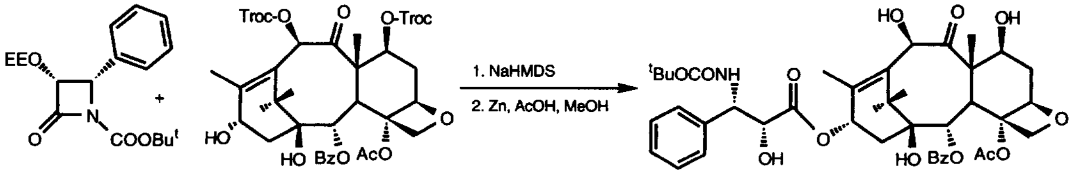
R = H 86% ee
R = Me 94% ee
R = Bu 90% ee
R = C_6H_5 88% ee

A HIGHLY EFFICIENT ROUTE TO TAXOTERE BY THE β-LACTAM SYNTHON METHOD.

Tetrahedron Lett. **1993**, *34*, 4149

I. Ojima*, C.M. Sun, M. Zucco, Y.H. Park, O. Duclos, S.D. Kuduk
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794

Efficient synthesis of Taxotère by means of *β-Lactam Synthon Method*

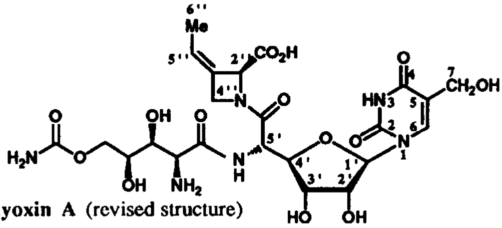


Tetrahedron Lett. **1993**, *34*, 4153

STRUCTURAL IDENTITY AND STEREOCHEMICAL REVISION OF POLYOXIMIC ACID

Stephen Hanessian*, Jian-Min Fu and Yongxue Tu
Department of Chemistry, Université de Montréal, P.O. Box 6128, Station A, Montréal, P.Q. CANADA, H3C 3J7; Kiyoshi Isono, Institute of Physical and Chemical Research, Yamato-machi, Saitama, Japan

The stereochemistry of the exocyclic double bond in polyoximic acid has been revised to *cis*-3-ethylidene-L-azetidine-2-carboxylic acid, based on the single crystal X-ray analysis of the racemic naturally-derived acid, on NMR studies of polyoxin A, and of synthetic samples of *cis*- and *trans*-polyoximic acids.



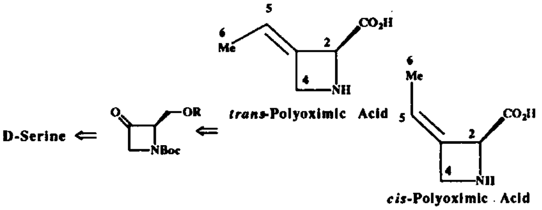
Polyoxin A (revised structure)

Tetrahedron Lett. **1993**, *34*, 4157

TOTAL SYNTHESIS OF (+)-POLYOXIMIC ACID – *CIS*-3-ETHYLIDENE-L-AZETIDINE-2-CARBOXYLIC ACID

Stephen Hanessian*, Jian-Min Fu, José-Luis Chiara and Romano Di Fabio
Department of Chemistry, Université de Montréal, P.O. Box 6128, Station A, Montréal, P.Q. CANADA, H3C 3J7

The stereocontrolled total synthesis of (natural) *cis*- and (unnatural) *trans*-polyoximic acids is described starting with D-serine as a chiral template.

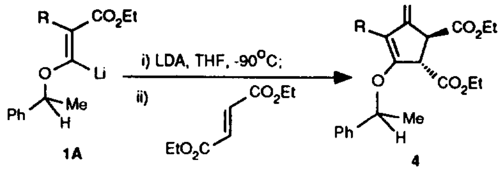


Tetrahedron Lett. **1993**, *34*, 4161

CHIRAL β-C-LITHIATED β-ALKOXY ACRYLATES: EFFICIENT SYNTHONS FOR HIGHLY FUNCTIONALIZED CYCLOPENTENONES

Apurba Datta and Richard R. Schmidt
Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz, Germany

A one step synthesis of highly functionalized cyclopentenones has been developed by the Michael addition of the readily available β-lithiated acrylate **1A** with suitable acceptors.

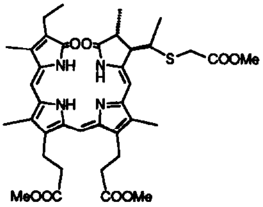


Tetrahedron Lett. **1993**, *34*, 4165

The Addition of Methyl-2-mercaptoacetate to Phycocyanobilin Dimethyl Ester: A Model Reaction for Biliprotein Biosynthesis?

Hugo Stumpe, Norbert Müller, and Karl Grubmayr*, Institut für Chemie, Johannes Kepler Universität Linz, Altenbergerstraße 69, A-4040 Linz, Austria

Addition of methyl-2-mercaptoacetate to the ethylidene double bond of phycocyanobilin dimethyl ester results in a quantitative formation of two diastereomeric adducts. Their structural and chemical properties correspond to those found for the protein bound chromophores of biliproteins.

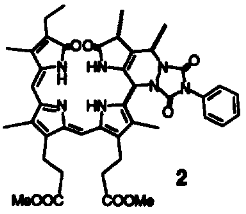


Tetrahedron Lett. 1993, 34, 4169

The Diels-Alder Adduct of Phycocyanobilin Dimethyl Ester and 4-Phenyl-1,2,4-triazolin-3,5-dione: A Model Intermediate for Chromatic Adaption of Biliprotein Chromophores?

Thomas Koini, Hugo Stumpe, Rainer Gagstädter, and Karl Grubmayr*, Institut für Chemie, Johannes Kepler Universität Linz, Altenbergerstraße 69, A-4040 Linz, Austria

Addition of 4-phenyl-1,2,4-triazolin-3,5-dione (PTAD) to the outer ring diene of phycocyanobilin dimethyl ester results in the formation of the [4+2] cycloadduct 2, which is the first isolated representative of 2,5-dihydrobilindiones. Thermal rearrangement of 2 yields blue colored 2,3-dihydrobilindiones, whereas acid catalyzed tautomerization results in the formation of red colored 4,5-dihydrobilindiones.



2

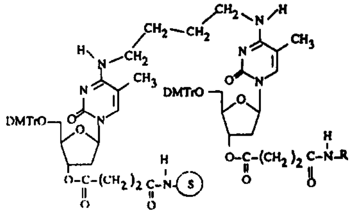
Tetrahedron Lett. 1993, 34, 4173

Oligonucleotides Tethered via Nucleic Bases. A Potential New Set of Compounds for Alternate Strand Triple-helix Formation.

Ulysse Asseline and Nguyen Thanh Thuong
Centre de Biophysique Moléculaire, 1 A Avenue de la Recherche Scientifique- 45071 Orléans Cedex 2.

$$d\text{-}\left[{}^{5'}T_4CT_4C_2\overset{*}{C}(CH_2)_2\text{-}\right]_2 \longleftarrow 2$$

3



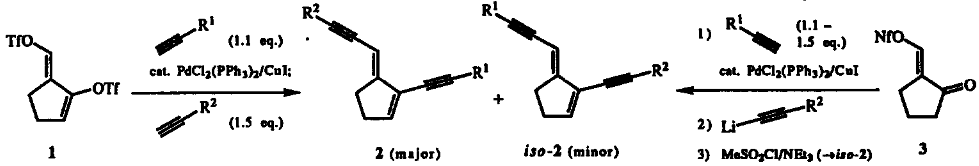
Tetrahedron Lett. 1993, 34, 4177

CONTRASTERIC REGIOSELECTIVITY OF PALLADIUM(0) CATALYZED COUPLINGS OF ALKYNES WITH A BIS(ENOLTRIFLATE). NOVEL SYNTHESES OF *E*-CONFIGURATED DIENEDIYNES

Jean Suffert§), Anke Eggers#), Stefan W. Scheuplein#), and Reinhard Brückner*#)*

#) Institut für Organische Chemie der Georg-August-Universität, Tammannstr. 2, D-3400 Göttingen, Germany; §) Laboratoire de Pharmacochimie Moléculaire, Centre de Neurochimie du CNRS, 5 rue Blaise Pascal, F-67084 Strasbourg Cedex, France

Consecutive $PdCl_2(PPh_3)_2$ catalyzed couplings of the *E*-bis(enoltriflate) 1 with two different alkynes provided 4:1 mixtures of dienediynes 2 and *iso*-2. Chemoselective syntheses of such dienediynes were realized starting from the *E*-configurated nonaflate 3.

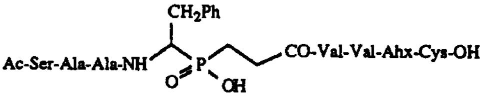


Tetrahedron Lett. 1993, 34, 4181

Solid Phase Synthesis of Phosphinic Peptides

Jean-Marc Campagne, Jacques Coste*, Laurent Guillou, Annie Heitz and Patrick Jouin.
UPR 9023 CNRS, CCIPE, Rue de la Cardonille,34094 Montpellier Cedex 05, France

The reagents BOP or PyBOP allow the synthesis of phosphinic peptides from phospho-analogues of dipeptides, unprotected on the phosphinic acid.



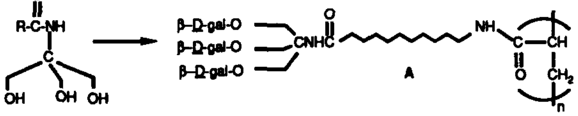
$$\text{Ac-Ser-Ala-Ala-NH-}\overset{CH_2Ph}{CH}\text{-}P(=O)(OH)\text{-}CH_2CH_2\text{-CO-Val-Val-Ahx-Cys-OH}$$

Tetrahedron Lett. **1993**, *34*, 4185

SYNTHESIS OF POLYMERIZABLE GLYCOLIPIDS DERIVED FROM TRIS-(HYDROXYMETHYL)AMINOMETHANE : PREPARATION OF POLYMERIZED MICELLES

B. Pucci[a)], A. Polidori[a)], N. Rakotomanomana[a)], M. Chorro[b)] et A.A. Pavia[a)*.a)]Laboratoire de Chimie Bioorganique, Faculté des Sciences , 33, rue Louis Pasteur, 84000 - Avignon - France. [b)]Laboratoire de Physico-chimie des Systèmes Polyphasés - associé au C.N.R.S - Université des Sciences et Techniques du Languedoc - 34095 - Montpellier Cedex 05 - France.

Synthetic polymerizable glycolipids derived from Tris-(hydroxymethyl) aminomethane (TRIS) are reported. Polymerized micellar structure (A) were obtained by UV irradiation of 11-*N*-acrylamido-N-Tris-(β-D-galactopyranosyloxymethyl)methyl undecanamide.

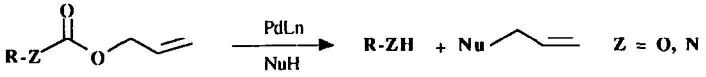


Tetrahedron Lett. **1993**, *34*, 4189

Palladium-Catalyzed Reactions in Aqueous Media. An Efficient Removal of Allyloxycarbonyl Protecting Group from Oxygen and Nitrogen

Jean Pierre Genêt*, Errol Blart, Monique Savignac, Stéphane Lemeune and Jean-Marc Paris.§ Laboratoire de Synthèse Organique associé au CNRS. Ecole Nationale Supérieure de Chimie de Paris 11, rue Pierre et Marie Curie - 75231 Paris - France. § Rhône Poulenc Rorer - Centre de recherche Vitry-Alfortville - 13 Quai Jules Guesde - 94403 Vitry sur Seine.

The Allyloxycarbonyl (Alloc) moiety can be removed smoothly and selectively in good yield (70-99%) from allylic esters, carbamates and carbonates by aqueous Pd (0) catalyzed allyl transfer to diethylamine as the accepting nucleophile.



Tetrahedron Lett. **1993**, *34*, 4193

REGIOSELECTIVE PALLADIUM(0) CATALYZED AZIDATION AND AMINATION OF 1-ALKENYLCYCLOPROPYL ESTERS: A NEW ROUTE TO 2,3-METHANOAMINO ACIDS

Pierre Aufranc, Jean Ollivier, Andreas Stolle, Claudia Bremer, Mazen Es-Sayed, Armin de Meijere* and Jacques Salaün*

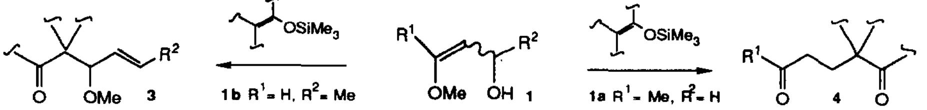
Laboratoire des Carbocycles, Associé au C.N.R.S., Institut de Chimie Moléculaire d'Orsay, Bât. 420; Université de Paris-Sud, 91405 Orsay, France; Institut für Organische Chemie der Georg-August Universität, D-3400 Göttingen, Germany.

Tetrahedron Lett. **1993**, *34*, 4197

Aldolisation-Type Reaction versus Michael-Type Addition. Hemiacetal Vinylogs: Versatile Synthons.

Pierre Duhamel*, Jérôme Guillemont and Jean-Marie Poirier Unité de Recherches Associée au CNRS n°464, Faculté des Sciences et des Techniques de Rouen et IRCOF BP 118 F-76134 Mont Saint Aignan Cedex - France
Pierre Chabardes Rhône Poulenc Recherches, Centre de Recherches des Carrières BP 62, F-69192 Saint Fons - France

Compound **1a** leads to a Michael-type addition contrarywise to compound **1b** which yields an aldolisation-type reaction.



A Convenient Method for Synthesis of Fmoc-Amino Acid p-Nitroanilides Based on Isobutyl Chloroformate as Condensation Agent.

Tetrahedron Lett. **1993**, *34*, 4201

Hinyu Nedev, Hanitra Naharisoa and Tomasz Haertlé*, Groupe Protéines, Institut National de la Recherche Agronomique BP 527, 44026 Nantes, FRANCE.

Isobutyl chloroformate could be used as efficient activation agent for the synthesis of N$^{\alpha}$-FMOC-protected bi- and tri-functional amino acid p-nitroanilides by the mixed anhydrides method.

$$\text{Fmoc-AA-OH} + \text{i-BuOCOCl} \xrightarrow[-15^{\circ}\text{C}]{\text{NMM}} \text{Fmoc-AA-OCOi-Bu} \xrightarrow{\text{NH}_2\text{-C}_6\text{H}_4\text{-NO}_2\text{(p)}} \text{Fmoc-AA- NH-C}_6\text{H}_4\text{-NO}_2\text{(p)}$$

AA = Pro-, Ala-, Leu-, Ile-, Trp-, Asp(OtBu)-, Gln(Trt)-, Hyp-, Hyp(OtBu)-

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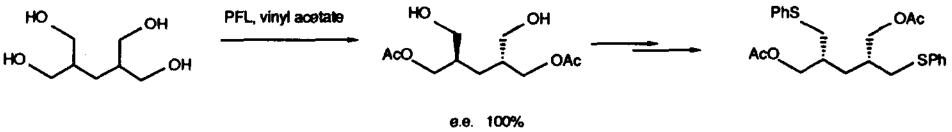
The Double-Meso Trick

Tetrahedron Lett. **1993**, *34*, 4205

P. Breuilles, T. Schmittberger, and D. Uguen*
Laboratoire de Synthèse Organique, Ecole Européenne des Hautes Etudes des Industries Chimiques, 1 rue B.Pascal, F-67008-Strasbourg, France.

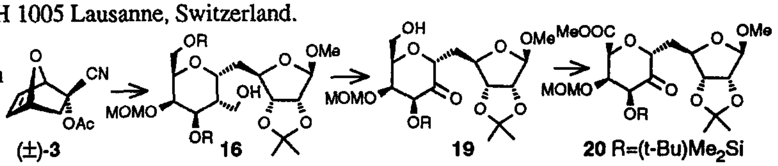


Total Synthesis of Undeculofuranosiduronic Acid Derivatives Related to Herbicidins.

Tetrahedron Lett. **1993**, *34*, 4209

Fabienne Emery, Pierre Vogel*, Section de Chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005 Lausanne, Switzerland.

The Diels-Alder adduct of furan with 1-cyanovinyl acetate has been converted to the branched dodecose derivative **16** and to the undecose derivatives **19** and **20**.

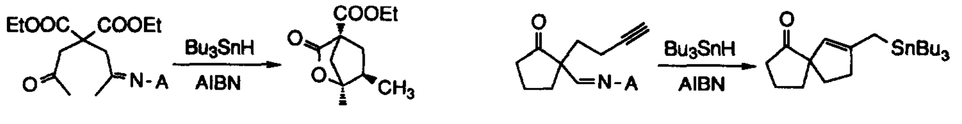


FURTHER STUDIES ON RADICAL CYCLIZATIONS OF N-AZIRIDINYL IMINES. CARBONYL AND ALKENYL GROUP vs. N-AZIRIDINYL IMINO GROUP COMPETITION

Tetrahedron Lett. **1993**, *34*, 4213

Sunggak Kim* and In Seo Kee, Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

Carbonyl and alkenyl groups vs. N-aziridinyl imino groups competitions as radical precursors as well as radical acceptors are described.

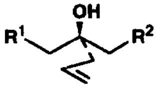


Tetrahedron Lett. **1993**, *34*, 4215

Preparation of a New Chiral Building Block for Synthesizing Broadly Varied Types of Tertiary Alcohols

Toshiyuki ITOH[a*], Hiroyuki OHARA[a], Yumiko TAKAGI[a*], Naoki KANDA[a] and Kenji UNEYAMA[b]
a. Department of Chemistry, Faculty of Education, Okayama University. b. Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama 700, JAPAN

1



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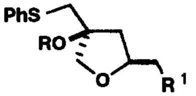


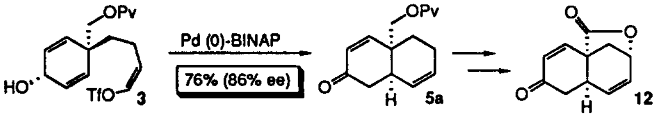
11a

Tetrahedron Lett. **1993**, *34*, 4219

Asymmetric Heck Reaction. A Catalytic Asymmetric Synthesis of the Key Intermediate for Vernolepin

Kazuhiro Kondo,† Mikiko Sodeoka,† Miwako Mori,‡ and Masakatsu Shibasaki†*
Faculty of Pharmaceutical Sciences, †University of Tokyo, Tokyo 113, Japan, and ‡Hokkaido University, Sapporo 060, Japan

Enone 5a, a functionalized decalin derivative, has been synthesized in up to 86% ee by an asymmetric Heck reaction starting with the allylic alcohol 3. Enone 5a was converted to a key intermediate 12 for vernolepin.



Tetrahedron Lett. **1993**, *34*, 4223

Electron Affinities of Benzaldehydes. Substituent Effects on Stabilities of Aromatic Radical Anions

Masaaki MISHIMA,* Chul HUH, Hirotaka NAKAMURA, Mizue FUJIO,† and Yuho TSUNO†*
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan
†Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

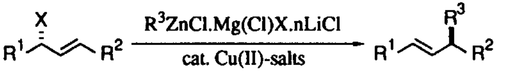
electron-transfer equilibrium

Tetrahedron Lett. **1993**, *34*, 4227

S_N2' SELECTIVE ALKYLATION OF ALLYLIC CHLORIDES AND MESYLATES WITH RZnX REAGENTS GENERATED FROM GRIGNARD REAGENTS, ZINC CHLORIDE, LITHIUM CHLORIDE, AND Cu(II)-SALTS

N. Fujii,* K. Nakai, H. Habashita, H. Yoshizawa, and T. Ibuka* Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto 606, Japan
F. Garrido and A. Mann* Centre de Neurochimie-CNRS, 5, rue Blaise Pascal, F-67084 Strasbrourg Cedex, France
Y. Chounan and Y. Yamamoto* Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Soluble organozinc reagents, derived from RMgX, $ZnCl_2$, LiCl, and a catalytic amount of Cu(II)-salt in THF-Et_2O, reacted with allylic chloride and mesylates to give S_N2' products in high yields.

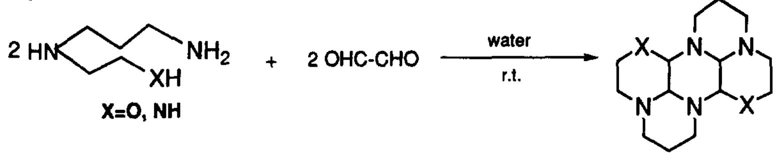


R^1 = H, alkyl; R^2 = H, alkyl, aryl, ester; R^3 = alkyl
X = Cl, OMs

Tetrahedron Lett. **1993**, *34*, 4231

7,15-DIOXA-4,8,12,16-TETRAAZA AND 4,7,8,12,15,16-HEXAAZA PERHYDROPERYLENES FROM GLYOXAL AND POLYFUNCTIONALIZED COMPOUNDS

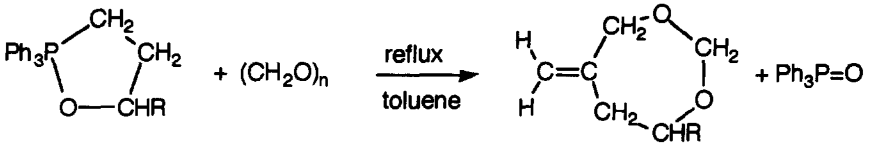
Tadashi Okawara,* Shuji Ehara, Masashi Eto, Kazunobu Harano, and Mitsuru Furukawa
Faculty of Pharmaceutical Sciences, Kumamoto University, Kumamoto 862, Japan



Tetrahedron Lett. **1993**, *34*, 4233

A Novel Reaction of Oxaphosphoranes Leading to 7-membered Cyclic Vinylidene Acetals

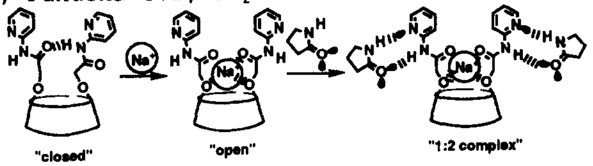
Kentaro Okuma,* Yuichiro Tanaka, and Hiroshi Ohta
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-01, Japan



Tetrahedron Lett. **1993**, *34*, 4237

"Metal-Switched" Molecular Receptor Site Designed on a Calix[4]arene Platform

Hiroto Murakami and Seiji Shinkai*
Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan



Tetrahedron Lett. **1993**, *34*, 4241

A NOVEL TRIFLUOROMETHYLATION METHOD OF SATURATED ORGANIC HALIDES

Qing-Yun Chen* and Jian-Xing Duan
Shanghai Institute of Organic Chemistry, Academia Sinica 345 Lingling Lu, Shanghai 200032, China

$$XCF_2CO_2Me + RY + KF \xrightarrow{CuI,CdI_2} RCF_3 + CO_2 + MeX(Y)$$

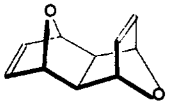
$X=Cl$ (**1a**), Br (**1b**)

Tetrahedron Lett. **1993**, *34*, 4245

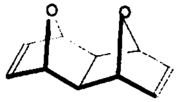
ELECTRONIC STRUCTURE OF FUSED 7-OXANORBORNENES. PHOTOELECTRONSPECTROSCOPIC STUDY

M. Eckert-Maksić[*,a)], Lj. Maksimović[a)] and M. Hodošček[b], Department of Organic Chemistry and Biochemistry, Ruder Bošković Institute, Zagreb, Republic of Croatia[a] and Institute of Chemistry, Ljubljana, Republic of Slovenia[b]

He(I) photoelectron spectra of bis-epoxides 1 and 2 are discussed.



(1)



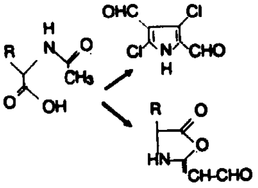
(2)

Tetrahedron Lett. **1993**, *34*, 4249

SYNTHETIC STUDIES ON N-ACETYL, DERIVATIVES OF AMINO ACIDS AND THIOLACTONE BY VILSMEIER-HAACK REAGENT

B. Balasundaram, M. Venugopal and
Paramasivan T. Perumal
Organic Chemistry Division, Central Leather
Research Institute, Adyar, Madras - 600 020, India.

A new Method for the Preparation of substituted Pyrroles, Oxazolidinones and 5-Chloro-3-formyl thieno (2,3-b) pyridine is reported

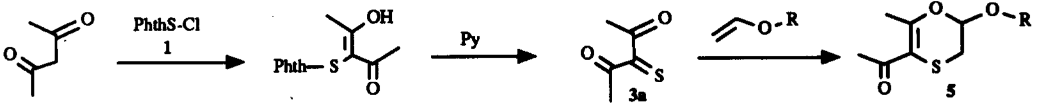


Tetrahedron Lett. **1993**, *34*, 4253

PHTHALIMIDESULFENYL CHLORIDE PART 6[1]. THE FIRST EXAMPLE OF AN α-OXOTHIONE ACTING AS HETERODIENE: SYNTHESIS OF 2,3-DIHYDRO-1,4-OXATHIINES.

Giuseppe Capozzi[#a], Stefano Menichetti[a], Cristina Nativi[a], Alessandro Rosi[a] and Richard W. Franck[b].
[a]*Centro C.N.R. "Chimica Composti Eterociclici". Dipartimento di Chimica Organica Universita' di Firenze, Via G. Capponi 9 I-50121, Firenze Italy*
[b]*Hunter College. The City University of New York, Departement of Chemistry, 695 Park Avenue, New York, N.Y. 10021-5024 USA.*

α-Oxathione **3a** acts as heterodiene toward enol ethers affording 2,3-dihydro-1,4-oxathiines **5** in good yields.



Tetrahedron Lett. **1993**, *34*, 4257

MODEL STUDIES OF THE COBALAMIN DEPENDENT METHIONINE SYNTHASE REACTION

E. Hilhorst, A.S. Iskander, T.B.R.A. Chen and U.K. Pandit
University of Amsterdam, The Netherlands.

Cobalamin is methylated by a N(5)-methyl-pteriniumsalt in a nonenzymatic reaction