GRAPHICAL ABSTRACTS

HYDROGEN REARRANGEMENTS IN CARBENES.

Tetrahedron Lett. 1993, 34, 1391

Tetrahedron Lett. 1993, 34, 1395

INHERENT H_{AX}/H_{BQ} MIGRATION RATIOS IN THERMAL AND PHOTIC BAMFORD-STEVENS REACTIONS

Alex Nickon, Alfred G. Stern, and Martin C. Ilao Department of Chemistry, The Johns Hopkins University, Baltimore MD, 21218–2685

The inherent migration ratio H_{ax}/H_{eq} is ~1.7 in thermolysis and ~1.2 in photolysis. These experimental ratios are free of chair—boat ambiguity.

A SYNTHESIS OF (-)-INDOLACTAM V

M. F. Semmelhack and Hakjune Rhee Department of Chemistry, Princeton University, Princeton NJ 08544

FORMAL SYNTHESIS OF TELEOCIDIN A

VIA INDOLE-Cr(CO)₃ COMPLEXES M. F. Semmelhack and Hakjune Rhee

Department of Chemistry, Princeton University, Princeton, NJ 08544

Tetrahedron Lett. 1993, 34, 1403

Tetrahedron Lett. 1993, 34, 1399

SYNTHESIS OF (-)-3-HOMOSHIKIMIC ACID AND (-)-3-HOMOSHIKIMATE-3-PHOSPHATE

Harold B. Wood, Jr. and Bruce Ganem*
Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853-1301 USA

$$\begin{array}{c} \text{CO}_2\text{H} \\ \text{2 R= H} \\ \text{3 R= PO}_3\text{H}_2 \\ \text{OH} \end{array}$$

BIS-HOMO AVERMECTIN B_{1a} - A SEMI-SYNTHETIC ANALOG WITH A TRIENIC18-MEMBERED MACROCYCLIC RING

Stephen Hanessian*, Philippe Chemla and Yongxue Tu Department of Chemistry, Université de Montréal, P.O. Box 6128, Station A, Montréal, P.Q. CANADA, H3C 3J7

An analog of avermectin B_{1a} in which the diene portion was homologated to a triene was synthesized from the natural product.

Tetrahedron Lett. 1993, 34, 1411

A NEW SYNTHESIS OF SUBSTITUTED BUTENOLIDES VIA CATION-INITIATED RING EXPANSION/ELIMINATION OF $\beta\text{-LACTONES}$

T. Howard Black* and Jianhua Huang, Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920

When treated with silver ion in refluxing acetic acid, γ -bromo- β -lactones, available via bromolactonization, undergo a ring elimination reaction to afford substituted butenolides.

Tetrahedron Lett. 1993, 34, 1413

Tetrahedron Lett. 1993, 34, 1415

One-Pot Conversion of Fluorenyimethyl Carbamates into tert-Butyl Carbamates

Wen-Ren Li, Jianjun Jiang, and Madeleine M. Joullié* Department of Chemistry, University of Pennsylvania Philadelphia, PA 19104-6323

N-Fluorenylmethoxycarbonyl groups may be efficiently converted to the corresponding N-tert-butoxycarbonyl compound by potassium fluoride/Et₃N in the presence of Boc₂O.

SYNTHESIS OF POLYAMINO AMIDO DERIVATIVES OF ETHIDIUM

Michael V. Keck and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of

Technology, Cambridge, MA 02139

The tetraphenyl borate salt of ethidium was modified to produce to polyamino amido derivatives.

$$H_2N$$
 NH_2
 H_2N
 NH_2
 H_2N
 H_2N
 H_3
 H_4
 H_4
 H_5
 H_5
 H_5
 H_6
 H_6
 H_7
 H_7
 H_8
 H_8

CONFORMATIONAL PREFERENCES OF C1-OXYGENATED ACYCLIC CHIRAL ALKENES: THE EFFECT OF VINYL AND ALLYL SUBSTITUENTS

Benjamin W. Gung*, Mark A. Wolf, Keith Ohm, and Andrew J. Peat Department of Chemistry, Miami University, Oxford, Ohio 45056

Ha Ha Hb
$$\Delta E$$
 Ha Ha OP H Ha Hb ΔE R Ha OP H Ha Hb H Ha OP H Ha

Tetrahedron Lett. 1993, 34, 1421

Triphenylsilanol as a Water Surrogate for Regioselective Pd Catalyzed Allylations

Barry M. Trost, Nobuhiko Ito and Paul D. Greenspan

Department of Chemistry, Stanford University, Stanford, California 94305-5080

Triphenylsilanol participates in Pd catalyzed allylic alkylations of vinyl epoxides to give the product of distal attack with excellent regioselectivity in contrast to other oxygen nucleophiles. Ease of desilylation under the reaction conditions effects an equivalent of

4%dppb, 8%Ph₂P

nucleophilic attack of water, a species which does not serve as an effective nucleophile in these reactions

ASYMMETRIC INDUCTION IN CUPRATE AND PHOTO-ADDITIONS TO 2-1-BUTYL-2,6-DIMETHYL-1,3-DIOXIN-

4-ONE. ABSOLUTE BUT OPPOSITE FACE SELECTIVITIES.

G.L. Lange and M.G. Organ, Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada,

(n-Bu)₂CuLi

addition on bottom face only

Tetrahedron Lett. 1993, 34, 1429

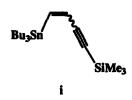
Tetrahedron Lett. 1993, 34, 1425

STEREOSELECTIVE SYNTHESES OF THREE DIFFERENT CLASSES OF NEOLIGNANS FROM THE SAME STARTING MATERIALS

Thomas A. Engler,* Dong (Donna) Wei and Michael A. Letavic Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

POLYENE CONSTRUCTIONS VIA PALLADIUM COUPLINGS OF ACTIVATED TRIFLATES WITH STANNYLATED ENYNES Bruce H. Lipshutz* and Mouad Alami Department of Chemistry, University of California Santa Barbara, CA 93106

Coupling reactions of E- and Z- forms of enyne i using a Pd(0) catalyst.



Tetrahedron Lett. 1993, 34, 1437

HIGHLY STEREOSELECTIVE AND GENERAL SYNTHESIS OF (Z)-3-METHYL-2-ALKEN-1-OLS VIA PALLADIUM-CATALYZED CROSS COUPLING OF (Z)-3-IODO-2-BUTEN-1-OL WITH ORGANOZINCS AND OTHER ORGANOMETALS

Ei-ichi Negishi*, Mehmet Ay, Yuri V. Gulevich, and Yumiki Noda Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

R= n-alkyl, i-alkyl, benzyl, homoallyl, homopropargyl, homobenzyl, alkenyl, aryl, and alkynyl The Pd-catalyzed reaction of O-protected derivatives of 2 with various organozines in DMF provides a highly stereoselective, general, and high-yielding procedure for preparing 1.

Tetrahedron Lett. 1993, 34, 1441

5'-dCCCCGGGG-3'

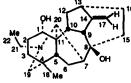
3'-dGGGGCCCC-5'

THE STRUCTURE OF AJABICINE, A NOVEL DITERPENOID ALKALOID FROM DEL-PHINIUM AJACIS

Balewant S. Joshi, ^{*a} Mohindar S. Puar, ^b Haridutt K. Desai, ^a Samir A. Ross, ^a Jing Lu, ^a and S. William Palletier ^a

Sinstitute for Natural Products Research and Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, U.S.A; ^bSchering-Plough Research Institute, 60 Crange Street, Bloomfield, NJ 07003, U.S.A.

The structure of ajabicine, a novel diterpenoid alkafold from *Delphinium ajacis*, has been established as 1. This is the first diterpenoid alkafold bearing a C-14 exceptible methylene group.



1 Ajabicine

Tetrahedron Lett. 1993, 34, 1445

DETECTION OF OLIGONUCLEOTIDE DUPLEX FORMS BY ION-SPRAY MASS SPECTROMETRY

Bruce Ganem,* Yu-Tsyr Li¶ and Jack D. Henion*¶
*Department of Chemistry, Baker Laboratory

¶Drug Testing and Toxicology, NYS College of Veterinary Medicine

Cornell University Ithaca, New York 14853 USA

Base-paired forms of double-stranded oligoucleotides have been detected by ion-spray mass spectrometry for the first time.

HIGHLY ENANTIOSELECTIVE SYNTHESIS OF PROPARGYL ALCOHOLS

R.C.Hartley, S.Lamothe, and T.H.Chan*

Department of Chemistry, McGill University, Montréal, P.Q., Canada, H3A 2K6.

Tetrahedron Lett. 1993, 34, 1453

AN EXTREMELY MILD 3-AZA-CLAISEN REACTION. 2. NEW

CONDITIONS AND THE REARRANGEMENT OF α-HETEROATOM SUBSTITUTED AMIDES.

M. A. Walters, * A. B. Hoem, H. R. Arcand, A. D. Hegeman, and C. S. McDonough

Dartmouth College, 6128 Burke Laboratory, Department of Chemistry, Hanover, NH 03755-3564

Several new and potentially useful reaction conditions for the 3-aza-Claisen rearrangement of N-allyl amides have been developed. These conditions have been applied to the cases where R1=Ph, OBn, and N-phthalimide.

Tetrahedron Lett. 1993, 34, 1457

Synthesis Of C₂-Symmetric HIV-Protease inhibitors With Sulfur-Containing Central Units.

Andrew Spaltenstein*a, Johann J. Lebana, and Eric S. Furfineb, Divisions of a) Organic Chemistry and b) Experimental Therapy

Burroughs Wellcome Co, 3030 Cornwallis Rd., Research Triangle Park, NC 27709 USA

Tetrahedron Lett. 1993, 34, 1461

REACTION OF LITHIUM ALKYNOLATES WITH ACID CHLORIDES:

A CONVENTIONAL APPROACH TO THE PREPARATION OF YNOL ESTERS

Viktor V. Zhdankin*, Peter J. Stang*, Chemistry Department, University of Utah, Salt Lake City, Utah 84112 USA

Order 1 (Me₃Si)₂NLi R-C-CHBr₂ (Me₃Si)₂NLi R-C=CBr₂ (T-BuLi R-C=C-OLi
$$\frac{\text{CIPO}(\text{OE}t)_2}{-20^{\circ}\text{C}, \text{ THF}}$$
 R-C=C-O-P(OEt)₂ 30-56%

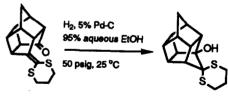
Synthesis of Substituted Hexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecanes. A Novel Method for Bridging Across the 8,11-Positions of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione and Related Diketones

Alan P. Marchand* and Dayananda Rajapaksa

Department of Chemistry, University of North Texas, Denton, Texas 76203-0068

A novel method for reductive cyclization of 1,4-dione mono(ketene dithioacetals) which possess spatially proximate reaction centers is described.

Tetrahedron Lett. 1993, 34, 1463



SYNTHESIS OF CYCLODODECA-2.8-DIVNE-1.7-DIONE

Tetrahedron Lett. 1993, 34, 1467

Bernhard Bodenmann and Reinhart Keese*

Institut für organische Chemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Tetrahedron Lett. 1993, 34, 1471

STEREOSELECTIVE HYDROGENATION OF METHACYCLINE TO DOXYCYCLINE CATALYSED BY RHODIUM-CARBORANE COMPLEXES B. Pirotte, A. Felekidis, M. Fontaine, A. Demonceau,* A.F. Noels and J. Delarge University of Liège, B-4000 Liège, Belgium

I.T. Chizhevsky, T.V. Zinevich, I.V. Pisareva and V.I. Bregadze Russian Academy of Sciences, 117813 Moscow, Russia

SmCl3-CATALYZED ELECTROCHEMICAL REDUCTIVE

Tetrahedron Lett. 1993, 34, 1475

ALLYLATION OF KETONES

H. Hebri, E. Duñach*, J. Périchon

Laboratoire d' Electrochimie, Catalyse et Synthèse Organique, C.N.R.S., 2, rue H. Dunant, 94320 Thiais, France

A Convenient Synthesis of Enamides and Dienamides by Horner-Wittig and Wadsworth-Emmons Reactions

Tetrahedron Lett. 1993, 34, 1479

Axel Couture, * Eric Deniau and Pierre Grandclaudon

Axel Couture, ^a Eric Deniau and Pietre Grandciaudon Laboratoire de Chimie Organique Physique associé au CNRS, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Asca, France

Various enamides and dienamides has been efficiently prepared by reacting suitable aldehydes and ketones with the lithium derivatives of phosphorylated carboxamides.

$$R^{1} \xrightarrow{N} H \xrightarrow{1) (CH_{2}O)_{n}} R^{1} \xrightarrow{N} R^{3} \xrightarrow{1) LDA, -78 \circ C} R^{1} \xrightarrow{N} R^{5}$$

$$R^{2} \xrightarrow{R^{2}} R^{2} \xrightarrow{R^{2}} R^{4} COR^{5}, \Delta \xrightarrow{R^{2}} R^{4}$$

Tetrahedron Lett. 1993, 34, 1483

THE YELLOW TOXINS PRODUCED BY CERCOSPORA BETICOLA, PART II : ISOLATION AND STRUCTURE OF BETICOLINS 3 AND 4.

M.-L. Milat¹, J.-P. Blein¹, Jacques Einhorn², J.-C. Tabet³, P.-H. Ducrot⁴ and J.-Y. Lallemand⁴.

1 Lab. de Phytopharmacic, INRA, BV1540, F-21034 Dijon Cedex; ²Lab. de Phytopharmacic, INRA, F-78026 Versailles Cedex; ³Lab. de Chimie structurale, Université P. et M. Curie, F-75005 Paris Codex; ⁴Lab. de Synthèse Organique de l'Ecole Polytechnique, P. Codes (1 on 1) Proposition (2 on 1) Proposition (3 on 1) Proposition (4 on 1) Propo

F-91128 Palaiseau Cedex, France.

The isolation and the structures of beticolins 3 and 4 are described; they are shown to be hydroxy derivatives of beticolins 1 and 2 respectively.

J.-Y. Lallemand⁴.

opharmacic,
M. Curie,
OH
OH
OH
Bedicolin 3

Stereoselective Bakkane Synthesis: (±)-Palmosalide C

Tetrahedron Lett. 1993, 34, 1487

Benoît Hartmann, Jean-Pierre Deprés, and Andrew E. Greene*

Université Joseph Fourier, LEDSS, BP 53X, 38041 Grenoble Cedex, France, and Marco E. Freire de Lima, Universidade Federal do Rio de Janeiro, Inst. de

Quimica, RJ, 21,944 Brazil

Palmosalide C, a spiro β,γ -epoxy- γ -butyrolactone sesquiterpene from the soft coral *Coelogorgia palmosa*, has been stereoselectively prepared in racemic form from 1, 6-dimethylcyclohexene.

CH₃ CH₃ CH₃ PALMOSALIDE C

Tetrahedron Lett. 1993, 34, 1491

First General Synthesis of Monosilyl Acetals.

Trimethylsilyl Trapping of the Intermediate in DIBALH Reduction of Carboxylic Acid Esters using Trimethylsilyl Trifluoromethanesulfonate Syun-ichi Kiyooka,* Masashi Shirouchi, and Yuichi Kaneko
Department of Chemistry, Kochi University, Akebono-cho, Kochi 780, Japan

The intermediate generated by the DIBALH reduction of carboxylic acid esters reacts with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in the presence of pyridine to afford the corresponding monosilyl acetals in good yields.

Formation and Reactions of a Kinetically Stabilized Diarylplumbylene

Kazusato Shibata, Norihiro Tokitoh, and Renji Okazaki*

Department of Chemistry, Faculty of Science,

The University of Tokyo,

TipLi
$$\xrightarrow{Pb[N(SiMe_3)_2]_2}$$
 \xrightarrow{Tip} \xrightarrow{TipLi} \xrightarrow{Tip} \xrightarrow{TipLi} \xrightarrow{Pb} $\xrightarrow{products}$ insertion products

Reaction of TipLi (Tip = 2.4.6-triisopropylphenyl) with Pb(II) electrophiles resulted in the formation of a plumbylene which was trapped by MeI, (PhS)2, (PhSe)2 to give insertion products.

Tetrahedron Lett. 1993, 34, 1499

X-ray Structural Analysis of Hexakis[2-(3,5-di-t-butylphenyl)-2-methylpropyl]diplumbane Kazusato Shibata, Norihiro Tokitoh, and Renji Okazaki*

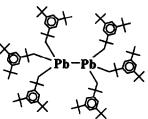
Department of Chemistry, Faculty of Science,

The University of Tokyo,

Hongo, Tokyo 113, Japan

$$Pb-Pb = 2.9448(6) \text{ Å}$$

X-ray structural analysis has shown that the titled sterically congested diplumbane has the longest Pb-Pb distance ever reported.



Tetrahedron Lett. 1993, 34, 1501

TOTAL SYNTHESIS OF UPIAL

Hiroto Nagaoka, ** Kimiyuki Shibuya b and Yasuji Yamada **

^aTokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

^bTokyo Research Laboratories Kowa Co. Ltd., 2-17-43 Noguchi-cho, Higashimurayama, Tokyo 189, Japan

Highly stereocontrolled synthesis of marine sesquiterpene upial was achieved from D-mannitol via fragmentation reaction of tricyclic compound 10 and SmI2-induced cyclization of diformate 2.

SYNTHESIS AND ABSOLUTE CONFIGURATION OF TREHAZOLIN AMINOCYCLITOL MOIETY

Yoshiyuki Kobayashi, Hideki Miyazaki, Masao Shiozaki*

New Lead Research Laboratories, Sankyo Co., Ltd. Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140, Japan

Tetrahedron Lett. 1993, 34, 1505

Chiral Quarternary Ammonium Fluoride

A New Reagent for Catalytic Asymmetric Aidol Reaction

Akira Ando, Toshiro Miura, Toshiaki Tatematsu, and Takayuki Shioiri

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanae-dori, Mizuho-ku, Nagoya 467, JAPAN

Tetrahedron Lett. 1993, 34, 1511

Toxadocial A: A Novel Thrombin Inhibitor from the Marine Sponge Toxadocia cylindrica

Youichi Nakao, Shigeki Matsunaga, and Nobuhiro Fusetani*
Laboratory of Marine Biochemistry, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo, 113, Japan

Abstract. A unique thrombin inhibitor, named toxadocial A (1) has been isolated from the marine sponge *Toxadocia cylindrica*, and its structure was determined by spectroscopic and chemical methods to be a per-sulfated 7, 17, 31, 41-tetrahydroxyheptatetracontane-23-carbaldehyde.

Tetrahedron Lett. 1993, 34, 1515

Studies on Organophosphorus Compounds 68.

A New and Facile Synthetic Approach to

Alkylidenebisphosphonates. Chaozhong Li and Chengye Yuan*, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.

1. MsCl/toluene RCHO (EtO)₂PHO/Py RCH[P(O)(OEt)₂] 2. (EtO)₂PHO/Py RCH[P(O)(OEt)₂];

Tetrahedron Lett. 1993, 34, 1517

On the Formation of Biacetyl Trimers in Acidic Media

Kai Baldenius, P Daltman and John Hudec*, Department of Chemistry.

The University, Southampton, SO9 5NH

Biactyl trimerises in acidic media via biacetyl hydrates.

LACK OF MANIFESTATION OF THE EXO-ANOMERIC EFFECT IN S-C-P(:) SYSTEM

Piotr P. Graczyk and Marian Mikołajczyk

Centre of Molecular and Macromolecular Studies, P.A.S.

Lodz 90-363, Sienkiewicza 112, POLAND

$$\mathbb{R}^2$$
 \mathbb{R}^2
 \mathbb{R}^2
 \mathbb{R}^2
 \mathbb{R}^2
 \mathbb{R}^2
 \mathbb{R}^2
 \mathbb{R}^1
 \mathbb{R}^1
 \mathbb{R}^1
 \mathbb{R}^2 -Ph, Me

Tetrahedron Lett. 1993, 34, 1525

THE SYNTHESIS OF PSEUDO-SUGARS RELATED TO

ALLOSAMIZOLINE, David F. Corbett, David K. Dean,* and Stephen R.

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

Bicyclic pseudo-sugars 4 and 5 were synthesised from D-glucosamine utilizing a Ferrier rearrangement as a key step.

A MILD AND SELECTIVE C-3 REDUCTIVE ALKYLATION OF INDOLES

Tetrahedron Lett. 1993, 34, 1529

Julie E. Appleton, Kevin N. Dack, Andrew D. Green and John Steele*

Discovery Chemistry Department, Pfizer Central Research, Sandwich, Kent CT13 9NJ

The TFA-EtqSiH mediated reaction of indoles with aromatic aldehydes generates good yields of the C-3 reductive alkylation products.