GRAPHICAL ABSTRACTS

ESSENTIALLY HOMOCHIRAL 1-SILYL ALCOHOLS FROM THE REDUCTION OF ALIPHATIC ACYLSILANES WITH CHLORODIISOPINOCAMPHEYLBORANE

Tetrahedron Lett. 1990, 31, 4677

John A. Soderquist,* Charles L. Anderson, Edgar I. Miranda, Isaac Rivera (Department of Chemistry, University of Puerto Rico, Rio Piedras, PR 00931) and George W. Kabalka (Department of Chemistry, University of Tennessee, Knoxville, TN 37996)

Tetrahedron Lett. 1990, 31, 4681

AN IMPROVED RADICAL CHAIN PROCEDURE FOR THE DEOXYGENATION OF SECONDARY AND PRIMARY ALCOHOLS USING DIPHENYLSILANE AS HYDROGEN ATOM DONOR AND TRIETHYLBORANE-AIR AS INITIATOR

Derek H. R. Barton*, Doo Ok Jang and Joseph Cs. Jaszberenyi Department of Chemistry, Texas A&M University, College Station, TX 77843

Et₂B/air Q = 0 or SR-O-CS-OR' RH + Ph2HSiQR PhoSiHo 80-96%

Secondary thionocarbonates, especially those derived from 4-fluorophenol, are easily deoxygenated at room temperature with this novel reagent system.

A NEW NMR TECHNIQUE FOR MEASURING THE GROUND STATE POPULATIONS OF FORMATE ESTERS: POLAR APROTIC SOLVENTS FAVOR THE s-CIS (E)-ISOMER OF t-BUTYL FORMATE

Tetrahedron Lett. 1990, 31, 4685

Tetrahedron Lett. 1990, 31, 4689

Michael E. Jung* and Jacquelyn Gervay, Department of Chemistry, University of California, Los Angeles, CA 90024 A new NMR technique for measuring the conformational population of t-butyl formate in a rapidly equilibrating mixture (3JCH averaging) has been developed and used to show that polar aprotic solvents favor the E-isomer (to a maximum of 33% in DMSO at 25°C).

REVERSAL OF REGIOSELECTIVITY WITH INCREASING RING SIZE OF ALKENE IN [2+2] PHOTOADDITIONS

Gordon L. Lange, Michael G. Organ and Moses Lee Guelph-Waterloo Centre for Graduate Work in

Chemistry, Department of Chemistry & Biochemistry, University of Guelph, Guelph, Ont., N1G 2W1, Canada

TRISUBSTITUTED OXETANES FROM 2,7-DIOXA-BICYCLO-

Tetrahedron Lett. 1990, 31, 4693

[3,2,0]-HEPT-3-ENES

Robert Hambalek and George Just*

Department of Chemistry, McGill University, Montréal, Québec, Canada H3A 2K6

Photoadducts of aldehydes with furan were transformed to trisubstituted monocyclic oxetanes, using a modification of the Fraser-Reid-Mootoo glycosidation procedure.

Tetrahedron Lett. 1990, 31, 4697

A CONVENIENT PREPARATION OF 1-PHENYLSULFONYL - 3 - IODOMETHYLINDOLE

Michito Sato and Michael Kahn*

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

A facile and efficient synthesis of the title compound is outlined.

Tetrahedron Lett. 1990, 31, 4699

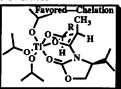
ASYMMETRIC ALDOL REACTIONS. MECHANISM OF SOLVENT EFFECT ON STEREOSELECTIVITY IS SPECIFIC, STOICHIOMETRIC BINDING OF TETRAHYDROFURAN TO

A CHIRAL TITANIUM ENOLATE
Shailaja Shirodkar, Maryellen Nerz-Stormes, and Edward R. Thornton*

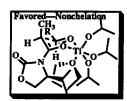
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323 USA

Diethyl ether gives nearly 5-fold higher diastereofacial selectivity than THF with an acyloxazolidinone-derived titanium enolate.

• We show that this strong solvent effect arises from stoichiometric binding of THF in the transition structure, indicating that THF interferes with chelation control.



bryostatins.



Control of Remote Enoate Geometry in the Bryostatins with a Tethered Horner-Wadsworth-Emmons Reagent

David A. Evans* and Erick M. Carreira

Department of Chemistry, Harvard University, Cambridge, Mass. 02138

The stereochemistry of the exocyclic unsaturated ester at C₁₃ of the bryostatins may be established with a tethered phosphonate reagent anchored to a proximal hydroxyl function at C₁₆ of an advanced intermediate en route to the total synthesis of the

Tetrahedron Lett. **1990**, 31, 4703

ASYMMETRIC ALLYLBORATIONS OF DIENE
ALDEHYDE Fe(CO)₃ DERIVATIVES: EFFICIENT
KINETIC RESOLUTION OF RACEMIC COMPLEXES AND THE HIGHLY ENANTIOTOPIC
GROUP AND FACE SELECTIVE ALLYLBORATION OF A MESO SUBSTRATE

William R. Roush* and Jae Chan Park
Department of Chemistry, Indiana University, Bloomington, IN 47405

Efficient kinetic resolutions of complexes 4 and 5 and the highly enantiotopic group and face selective allylboration of meso complex 8 are described.

SELECTIVE SEMISYNTHETIC MODIFICATION OF L-156,602, A NOVEL CYCLIC HEXADEPSIPEPTIDE ANTIBIOTIC Ihor E. Kopka

Department of Medicinal Chemical Research, Merck Sharp & Dohme Research Laboratories P.O. Box 2000 Rahway, New Jersey 07065 USA

The cyclic hexadepsipeptide antibiotic undergoes a wide variety of selective oxidation, reduction, acylation and alkylation reactions under acid or neutral conditions.

Tetrahedron Lett. 1990, 31, 4711

Tetrahedron Lett. 1990, 31, 4715

THE STEREOCHEMICAL COURSE OF FRAGMENTATION OF BENZYLOXYCHLOROCARBENE

R.A. Moss and H-R. Kim, Department of Chemistry, Rutgers University, New Brunswick, NJ 08903

The fragmentation of α -deuteriobenzyloxychlorocarbene to α -deuteriobenzyl chloride in acetonitrile occurs via an ion pair with $\geq 60\%$ net retention of stereochemistry.

Tetrahedron Lett. 1990, 31, 4719

SELECTIVE HETEROGENEOUS PALLADIUM-CATALYZED
HYDROGENATIONS OF WATER-SOLUBLE ALKENES AND ALKYNES

James M. Tour* and Shekhar L. Pendalwar
Department of Chemistry, University of South Carolina, Columbia, SC, 29208

$$(EtO)_3SiH \frac{Pd(OAc)_2}{NaOH, H_2O} \left[(SiO_3)_n Pd(0) + H_2 \right] \frac{R - (CH_2)_5CO_2H}{R} R (CH_2)_5CO_2H$$

ELECTROPHILIC FORMAMIDINES. ORGANOMETALLIC ADDITION TO 2-METHOXY PYRROLIDINE OR PIPERIDINE N-1-BUTYL FORMAMIDINES. FORMATION OF 2-SUBSTITUTED PYRROLIDINES AND PIPERIDINES.

Levi Gottlieb and A. I. Meyers*

Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

Tetrahedron Lett. 1990, 31, 4727

Formal 1,6-insertion of an Alkylidenecarbene into a Carbon-Hydrogen Bond. Unveiling of a Stepwise Reaction Mechanism.

John C. Gilbert* and Brent K. Blackburn Department of Chemistry, The University of Texas at Austin Austin, TX 78712

Formation of 6 does not result from a concerted insertion of the carbene 7 into an aromatic C-H bond.

STEREOSELECTIVE SYNTHESIS OF 1,2,3-TRISUBSTITUTED CYCLOPROPANES AS NOVEL DIPEPTIDE ISOSTERES

Stephen F. Marlin,* Richard E. Austin, and Christopher J. Oalmann Department of Chemistry, The University of Texas, Austin, Texas 78712

The design and stereoselective synthesis of the peptide surrogates 4 and 5 from a common intermediate 3 is described.

Tetrahedron Lett. 1990, 31, 4735

Tetrahedron Lett. 1990, 31, 4731

ELECTRON-TRANSFER ACTIVATION - PHOTOCYANATION OF TERTIARY AMINES

J. SANTAMARIA, M.T. KADDACHI and J. RIGAUDY Laboratoire de Recherches Organiques de l'ESPCI, 75005 Paris.

$$\begin{array}{c|c} R_1 \\ \hline R_2 \\ \hline N-CH_2-R_3 \end{array} \xrightarrow{hv/O_2/DAP^{2+}} \left[\begin{array}{c} R_1 \\ \hline R_2 \\ \hline \end{array} \right] \xrightarrow{N-CH-R_3} \left] \xrightarrow{Me_3SiCN} \begin{array}{c} R_1 \\ \hline R_2 \\ \hline \end{array} \right] \xrightarrow{N-CH-R_3}$$

DAP2+=N,N'-dimethyl-2,7-diazapyrenium

75-95 %

SYNTHESIS AND PRELIMINARY DNA-INTERACTION STUDIES OF A NEW CATIONIC PORPHYRIN

N. Robic, ¹ C. Bied-Charreton, ¹ M. Perrée-Fauvet, ¹ C. Verchère-Béaur, ¹ L. Salmon, ¹ A. Gaudemer, ¹ and R.F. Pasternack ² 1. Université Paris-Sud, ICMO, Laboratoire de Chimie Bioorganique et Bioinorganique associé au CNRS, Bât. 420, 91405 Orsay, France. ² Department of Chemistry, Swarthmore College, ⁵ Swarthmore, PA 19081, USA.

A new water-soluble porphyrin containing benzyl-trimethylammonium groups was synthesized in a two-step sequence and preliminary studies show that it binds strongly to DNA in an outside manner.

Synthesis of new thiophene compounds with large second order optical non-linearities.

Tetrahedron Lett. 1990, 31, 4743

G.MIGNANI, F. LEISING, R. MEYRUEIX and H. SAMSON

Rhône-Poulenc, Centre de Recherches des Carrières 85, avenue des Frères Perret B.P. 62 69192 Saint-Fons Cedex - France.

A synthesis of new thiophenes with large second order optical non-linearities is described. These products display a very good stability under irradiation.

Tetrahedron Lett. 1990, 31, 4747

PALLADIUM CATALYZED STEREOSPECIFIC CYCLIZATION OF HYDROXY EPOXIDES. STEREOCONTROLLED SYNTHESIS OF CIS- AND TRANS-2-ALKENYL-3-HYDROXYTETRAHYDROPYRANS

Toshio Suzuki, Ohki Sato, and Masahiro Hirama*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

CHIRAL ALCOHOL-INDUCED DIASTEREO-SELECTIVE CONJUGATE ADDITION AND CYCLIZATION

Chenglin Fang, Hiroshi Suomune, and Kiyoshi Sakai* Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan

Tetrahedron Lett. 1990, 31, 4751

A NOVEL APPROACH TO (+)-YOHIMBINE

Yoshiro Hirai, Takashi Terada, Yukiko Okaji, Takao Yamazaki, and Takefumi Momose*

Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University 2630 Sugitani, Toyama 930-01, Japan

The piperidine derivative (B), obtained from the acyclic compound (A) by an asymmetric intramolecular Michael reaction, has been stereoselectively converted to 2,3-seco-yohimbine (C).

Tetrahedron Lett. 1990, 31, 4757

A SHORT STEREOSELECTIVE SYNTHESIS OF (-)-SERRICORNIN

Isao SHIMIZU,* Kaoruko HAYASHI, and Masato OSHIMA Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ookubo 3-4-1, Shinjuku-ku, Tokyo 169, Japan

Tetrahedron Lett. 1990, 31, 4759

Tetrahedron Lett. 1990, 31, 4761

TOTAL SYNTHESIS OF (+)-PTILOCAULIN

Morio ASAOKA, Masahito SAKURAI, and Hisashi TAKEI

Department of Life Chemistry, Tokyo Institute of Technology,

Nagatsuta, Midoriku, Yokohama 227, Japan

SYNTHESIS AND UTILIZATION OF OPTICALLY ACTIVE

2-SUBSTITUTED 4-(TRIMETHYLSILYL)CYCLOPENTANONES:

SYNTHESIS OF (-)-MASSOLALACTONE AND (+)-\$-CUPARENONE

Morio ASAOKA, Satoshi HAYASHIBE, Svuzo SONODA, and Hisashi TAKEI

Department of Life Chemistry, Tokyo Institute of Technology, Midoriku,

Yokohama 227, Japan

(-)-massoialactone

(+)-B-cuparenone

INTRAMOLECULAR REDUCTIVE CYCLIZATION OF ALDEHYDES AND KETONES WITH ALKYNES PROMOTED BY SAMARIUM(II) IODIDE

Sang Chul Shim* and Jin-Taik Hwang, Department of Chemistry, KAIST, Seoul 130-012, KOREA Han-Young Kang* and Moon Ho Chang, Chemistry Division, KIST, Seoul 130-650, KOREA

$$X = \frac{\text{SmI}_2}{\text{(CH}_2)_n \text{ O}} \text{ a } X = \text{CH}_2; \text{ b } X = \text{O}; \text{ c } X = \text{BOC-N}$$

$$(CH_2)_n = \frac{\text{R}_2}{\text{OH}} \text{ OH}$$

$$(CH_2)_n = \frac{\text{R}_2}{\text{OH}} \text{ OH}$$

$$(CH_2)_n = \frac{\text{R}_2}{\text{OH}} \text{ OH}$$

Tetrahedron Lett. 1990, 31, 4769

AN EXTREMELY MILD AND GENERAL METHOD FOR THE STEREOCONTROLLED CONSTRUCTION OF 1,2-CIS-GLYCOSIDIC LINKAGES VIA S-GLYCOPYRANOSYL PHOSPHORODIA MIDIMIDOTHIOATES

Shun-ichi Hashimoto, Takeshi Honda, and Shiro Ikegami*
Faculty of Pharmaceutical Sciences, Teikyo University, Sagamiko, Kanagawa 199-01, Japan

Tetrahedron Lett. 1990, 31, 4773

A NEW SELENIUM CATALYZED SYNTHESIS OF S-ALKYL CARBONOTHIOATES FROM ALCOHOLS, CARBON MONOXIDE, SULFUR, AND ALKYL HALIDES

Takumi Mizuno, Ikuzo Nishiguchi, Tsuneaki Hirashima, Akiya Ogawa, Nobuaki Kambe, and Noboru Sonoda Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536, Japan Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

S-Alkyl carbonothioates were synthesized in good yields from alcohols, carbon monoxide, sulfur, and alkyl halides using selenium-catalyst.

ROH + CO + S cat. Se, base [base·H]⁺[ROCS]⁻
$$R'X$$
 ROCSR

Tetrahedron Lett. 1990, 31, 4777

EVALUATION OF TWO POSSIBLE TRANSITION STATES IN INTRAMOLECULAR OXETANE / OXOLANE RING FORMATION $_{R}$ BASED ON AM1 CALCULATIONS

S. Nishiyama, S. Yamamura, K. Kato, M. Nagai, T. Takita, and Y. Terada

Dept of Chem., Faculty of Science and Technology, Keio Univ., Hiyoshi, Yokohama 223, Japan.

Research Lab., Pharmaceuticals Group, Nippon Kayaku Co., Ltd., Shimo Kita-ku. Tokyo 115, Japan.

Faculty of Pharmacy, Meijo Univ., Tempaku-Ku, Nagoya 468, Japan. R = H. OBn R

OH OH R R OH R OH

CO₂Me

A SYNTHESIS OF (±)-7-METHOXYCARBONYL-2-(3-METHOXYPHENYLMETHYLIDENE)-8-METHYL-3,8-DIAZABICYCLO[3.2.1]OCTAN-4-ONE USING DIPOLAR CYCLOADDITION TO A 3-OXIDOPYRAZINIUM

Philip A. Allway, James K. Sutherland, and John A. Joule, Chemistry Department, Manchester University, Manchester, M13 9PL, U.K.

3,8-Diazabicyclo[3.2.1]octane 1b, was prepared in eight steps from 3-methoxybenzaldehyde, utilising as the key step, a dipolar cycloaddition to 3-oxidopyrazinium, 5.

Tetrahedron Lett. 1990, 31, 4783

Regioselective Functionalization of Chiral Nickelacycles Derived from N-Protected Aspartic and Glutamic Anhydrides

Ana M. Castaño and Antonio M. Echavarren* Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Reaction of Ni(0) complexes with Asp and Glu anhydrides gave nickelacycles 1 and 2. Electrophilic cleavage furnished the corresponding Ala or Abu derivatives.

$$\frac{\text{Ni(COD)L}_2}{-\text{CO}} = \frac{\text{Ni(COD)L}_2}{\text{R}_2\text{N}} = \frac{\text{E}^+}{\text{R}_2\text{N}} = \frac{\text{COOH}}{\text{COOH}}$$

RING CONTRACTION OF 2-O-TRIFLUOROMETHANE-SULPHONATES OF α-HYDROXY-γ-LACTONES TO

OXETANE CARBOXYLIC ESTERS

D.R.Witty, G.W.J.Fleet, K.Vogt, F.X.Wilson, Y Wang, R.Storer, P.L.Myers, C.J.Wallis Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford OXI 3QY; Glaxo Group Research Limited, Greenford Road, Greenford, Middlesex UB6 0HE; Glaxo Group Research Limited, Park Road, Ware, Hertfordshire SG12 0DP.

Tetrahedron Lett. 1990, 31, 4791

Tetrahedron Lett. 1990, 31, 4787

MICELLIZATION TRIGGERS PSEUDO-INTRAMOLECULAR TRANSACYLATION IN Cu^{2+} COMPLEXES OF HYDROLYTIC METALLOMICELLES.

G. De Santi, P. Scrimin, and U. Tonellato Dipartimento di Chimica Organica and Centro CNR Meccanismi di Reazioni Organiche, Universita' di Padova, Padova, Italy

Acceleration of the cleavage of the p-nitrophenyl ester of picolinic acid by ligand 1 (R=n-C₁₆H₃₃;R'=H) in the presence of Cu²⁺ ions in aqueous buffer (pH=6-7) is attributed to a stereochemical modification of the geometry of the complex in micellar aggregates.

A NEW SYNTHESIS OF PIPERIDONES FROM RHODIUM CATALYSED REACTIONS OF UNSATURATED AMINES WITH

HYDROGEN AND CARBON MONOXIDE

Despina Anastasiou and W. Roy Jackson, Department of Chemistry, Monash University, Clayton. Victoria 3168, Australia.

Rhodium catalysed reactions of hydrogen and carbon monoxide with 5-aminopent-1-enes give piperidones in high yields under mild reaction conditions.

Tetrahedron Lett. 1990, 31, 4799

INTRODUCTION OF THE HALONITROMETHYL FRAMEWORK

INTO AROMATIC RINGS VIA A XeF2 MEDIATED RADICAL PROCESS

Valery K. Brel. Anatoly S. Koz'min, Ivan V. Martynov, Viktor V. Uvarov, Nikolai S. Zefirov*, Viktor V. Zhdankin Institute of Physiologically Active Compounds of Acad. Sci. USSR, Chernogolovka, Noginsk District. Moscow Region 142432 USSR.

and Peter J. Stang, Chemistry Department, University of Utah, Salt Lake City, Utah 84112 USA

Reactions of acids 1 with aromatic substrates in the presence of XeF2 results in alkylation of the aromatic ring:

O₂NFXCCOOH

XeF₂

O₂NFXCC₆H₄R X = F. CI

Tetrahedron Lett. 1990, 31, 4801

A PORPHYRIN-BASED CROWN ETHER CO-RECEPTOR FOR THE COMPLEXATION OF PARAQUAT.

Maxwell J. Gunter*, Martin R. Johnston

Department of Chemistry, University of New England Armidale, N.S.W. 2351, Australia.

> Compound (1) synthesised and it's binding ability with paraquat examined.

Tetrahedron Lett. 1990, 31, 4805

Eugenya N.Olsufyeva: Inst. New Antibiotics AMS USSR, B. Pirogovskaya 11, Moscow Leon V. Bakinowsky: N. D. Zelinsky Inst. Org. Chem. AS USSR, Leninsky Pr. 47, Moscow