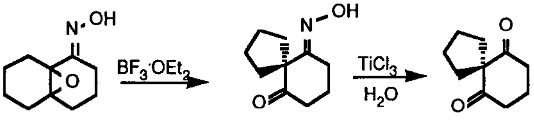
GRAPHICAL ABSTRACTS

Tet.Lett.,27,31,3565 (1986)

A LEWIS ACID CATALYZED REARRANGEMENT OF STRUCTURALLY RELATED α, β - UNSATURATED EPOXY KETONES AND OXIMES. A COMPLEMENTARY APPROACH TO THE SYNTHESIS OF ISOMERIC 1,4 -DIKETOSPIRO[n,m] ALKANES.

Robert D. Bach*, Mark W. Tubergen, and Russell C. Klix Department of Chemistry, Wayne State University, Detroit MI, 48202

Rearrangement of α, β - epoxy oximes proceeds by oxirane cleavage with an attendant pinacol type alkyl migration to a carbenium ion center affording a 1,3 - diketo - mono oxime.

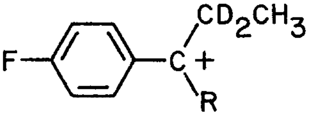


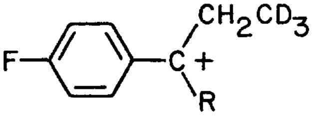
Tet.Lett.,27,31,3569 (1986)

CARBOCATION NMR ISOTOPE SHIFTS ANALOGOUS TO INVERSE γ-DEUTERIUM ISOTOPE EFFECTS

David A. Forsyth*, James S. Puckace and
Frances E. Shawcross, Northeastern University, Boston, MA 02115

Long-range NMR isotope shifts at fluorine due to γ-deuteration in carbocations are upfield, in contrast to downfield shifts for β-deuteration.



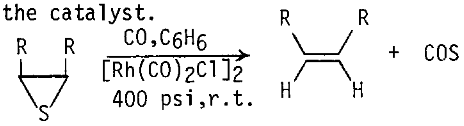


Tet.Lett.,27,31,3573 (1986)

STEREOSPECIFIC RHODIUM(I) CATALYZED DESULFURIZATION OF THIIRANES

Serge Calet and Howard Alper*
Ottawa-Carleton Chemistry Institute, Department of Chemistry
University of Ottawa, Ottawa, Ontario K1N 9B4 Canada

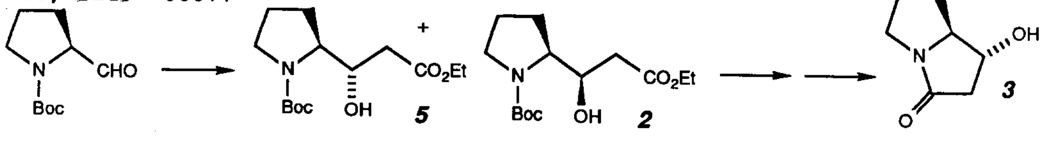
The desulfurization of thiiranes occurs with retention of stereochemistry using $[Rh(CO)_2Cl]_2$ as the catalyst.



Tet.Lett.,27,31,3577 (1986)

STEREOSELECTIVE ADDITION OF LITHIOETHYL ACETATE TO BOC-PROLINAL. A CONVENIENT CHIRAL SYNTHETIC BUILDING BLOCK FOR THE PYRROLIZIDINE ALKALOID RING SYSTEM

Gunnar J. Hanson, John S. Baran and Thomas Lindberg
Department of Medicinal Chemistry, G.D. Searle & Co., 4901 Searle Pkwy.,
Skokie, Ill. 60077

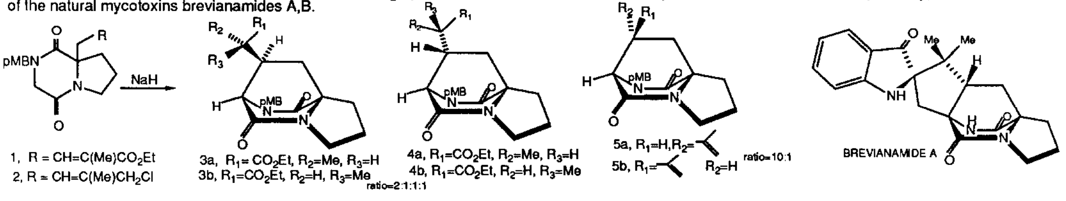


Tet.Lett.,27,31,3581 (1986)

PROMISING CYCLIZATION REACTIONS TO CONSTRUCT THE RING SYSTEMS OF BREVIANAMIDES A,B

Robert M. Williams * and Tomasz Glinka
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Intramolecular Michael cyclization and intramolecular S_N2' cyclization of 1 and 2 furnishes the tricyclic frameworks 3/4 and 5,respectively, of the natural mycotoxins brevianamides A,B.



1, R = $CH=C(Me)CO_2Et$
2, R = $CH=C(Me)CH_2Cl$

3a, R_1= CO_2Et, R_2=Me, R_3=H
3b, R_1=CO_2Et, R_2=H, R_3=Me

4a, R_1=CO_2Et, R_2=Me, R_3=H
4b, R_1=CO_2Et, R_2=H, R_3=Me

ratio=2:1:1:1

5a, R_1=H,R_2=
5b, R_1= R_2=H
ratio=10:1

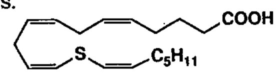
BREVIANAMIDE A

Tet.Lett.,27,31,3585 (1986)

A NEW IRREVERSIBLE INHIBITOR OF SOYBEAN LIPOXYGENASE; RELEVANCE TO MECHANISM

E. J. Corey, Marc d'Alarcao, and Seiichi P.T. Matsuda
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

13-Thiaarachidonic acid functions as an oxygen- and time-dependent inhibitor of soybean lipoxygenase, whereas the isomeric 7- and 10-thia acids are good substrates.

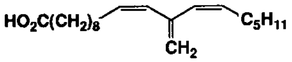


Tet.Lett.,27,31,3589 (1986)

12-METHYLIDENE-10(Z), 13(Z)-NONADECADIENOIC ACID, A NEW IRREVERSIBLE INHIBITOR OF SOYBEAN LIPOXYGENASE

E. J. Corey and Marc d'Alarcao
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

The trienoic acid **1** was synthesized and found to be an enzyme activated irreversible inhibitor of soybean lipoxygenase.


$HO_2C(CH_2)_8CH=CH-C(=CH_2)-CH=CH-C_5H_{11}$

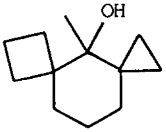
1

Tet.Lett.,27,31,3603 (1986)

SYNTHESIS AND REARRANGEMENT OF FUNCTIONALIZED DISPIRO-[2.1.3.3]UNDECANES - PREFERRED C_4-C_5 OVER C_3-C_4 RING ENLARGEMENTS

Lutz Fitjer[*a], Marita Majewski[a], Andreas Kanschik[a], Ernst Egert[*b] and George M. Sheldrick[b]
Institut für Organische Chemie der Universität Göttingen[a], Tammannstr.2, D-3400 Göttingen, Germany, and Institut für Anorganische Chemie der Universität Göttingen[b], Tammannstr.4, D-3400 Göttingen, Germany

Dispiro[2.1.3.3]undecanes 1 and 2 undergo cascade rearrangements via initial C_4-C_5 ring enlargements.



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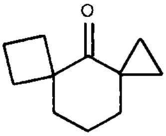


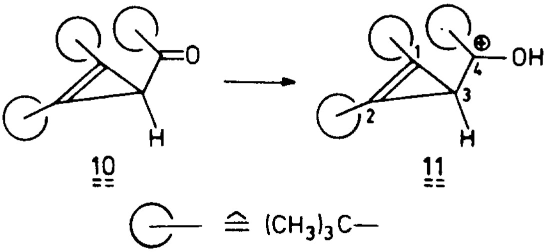
2

Tet.Lett.,27,31,3607 (1986)

ERSTER NACHWEIS EINES CYCLOPROPENYLCARBINYL-KATIONS

Günther Maier, Klaus Euler und Rolf Emrich*
Institut für Organische Chemie der Justus-Liebig-Universität
Heinrich-Buff-Ring 58, D-6300 Gießen

Treatment of ketone 10 with magic acid leads to the stable cyclopropenylcarbinyl cation 11.

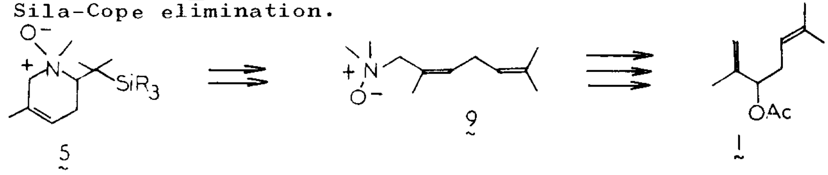


Tet.Lett.,27,31,3611 (1986)

SYNTHESIS OF THE PHEROMONE OF THE COMSTOCK MEALYBUG VIA A SILA-COPE ELIMINATION

Yagamare Fāll, Nguyen Van Bac and Yves Langlois
Institut de Chimie des Substances Naturelles, CNRS, F 91190 Gif-sur-Yvette

The pheromone 1 was synthetized from the tetrahydropyridine N-oxide 5 via a Sila-Cope elimination.



Tet.Lett.,27,31,3615 (1986)

METALLIC COPPER CATALYSIS OF N-ARYLATION OF AMINES BY TRIARYLBISMUTH DIACYLATES

Derek H.R. Barton, Jean-Pierre Finet and Jamal Khamsi
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

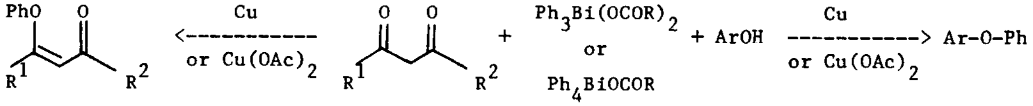
$$Ar_3Bi(OCOR^1)_2 + R^2\text{-}NH_2 \xrightarrow[Cu^\circ]{CH_2Cl_2} R^2\text{-}NH\text{-}Ar$$

R^2 : aliphatic and aromatic

Tet.Lett.,27,31,3619 (1986)

COPPER CATALYSED O-PHENYLATION OF PHENOLS AND ENOLS BY PENTAVALENT ORGANOBISMUTH COMPOUNDS

Derek H.R. B[illegible] ean-Pierre Finet, Jamal Khamsi and Clotilde Pichon
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

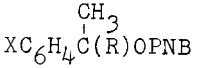


Tet.Lett.,27,31,3623 (1986)

β-DEUTERIUM KINETIC ISOTOPE EFFECTS IN THE SOLVOLYSIS OF 2-ARYL-1,1,1-TRIFLUORO-2-PROPYL TOSYLATES AND OF 2-ARYL-2-PROPYL p-NITROBENZOATES

Kwang-Ting Liu* and Yuh Wern Wu**
*Department of Chemistry, National Taiwan University, Taipei 10764, R. O. C.
**Department of Chemistry, Soochow University, Taipei 11102, R. O. C.

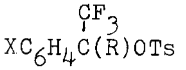
The rates of solvolysis for 1-4 in 80% ethanol were measured.



$XC_6H_4C(CH_3)(R)OPNB$

1 R = CH_3 , 3 R = CD_3

KIE (60°C)
1.02 (X = 4'-CH_3)
1.18 (X = H)
1.40 (X = 3'-Cl)



$XC_6H_4C(CF_3)(R)OTs$

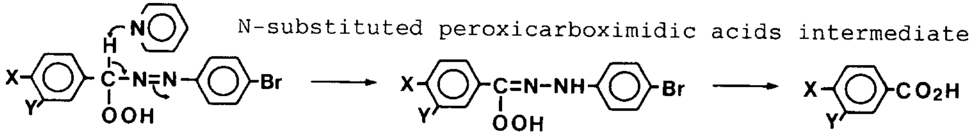
2 R = CH_3, 4 R = CD_3

KIE (60°C)
1.04 (X = 4'-CH_3)
1.38 (X = H)
2.13 (X = 3'-Cl)

Tet.Lett.,27,31,3627 (1986)

FORMATION AND REACTION OF N-SUBSTITUTED PEROXYCARBOXIMIDIC ACIDS FROM α-AZOBENZYL HYDROPEROXIDE BY PYRIDINE-CATALYZED REACTION

T. Tezuka,* T. Otsuka, P. C. Wang, and M. Murata
Department of Chemistry, University of Tsukuba,
Sakura-mura, Ibaraki 305, Japan



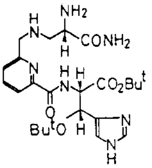
N-substituted peroxicarboximidic acids intermediates

Tet.Lett.,27,31,3631 (1986)

TRANSITION-METAL BINDING SITE OF BLEOMYCIN. A REMARKABLY EFFICIENT DIOXYGEN-ACTIVATING MOLECULE BASED ON BLEOMYCIN-Fe(II) COMPLEX.

A. Kittaka, Y. Sugano, M. Otsuka, M. Ohno*, Y. Sugiura, H. Umezawa*
Faculty of Pharmaceutical Sciences, University of Tokyo, Japan,
Faculty of Pharmaceutical Sciences, Kyoto University, Japan, and
Inatitute of Microbial Chemistry, Japan

A synthetic model of bleomycin, PYML-4, showed improved dioxygen activation up to 71% of that of bleomycin.



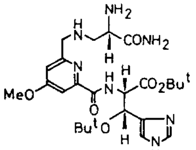
PYML-4

Tet.Lett.,27,31,3635 (1986)

TRANSITION-METAL BINDING SITE OF BLEOMYCIN. A SYNTHETIC ANALOGUE EQUIVALENT TO BLEOMYCIN IN ACTIVATING MOLECULAR OXYGEN.

Y. Sugano, A. Kittaka, M. Otsuka, M. Ohno*, Y. Sugiura, H. Umezawa*
Faculty of Pharmaceutical Sciences, University of Tokyo, Japan,
Faculty of Pharmaceutical Sciences, Kyoto University, and
Institute of Microbial Chemistry, Japan

A synthetic model of bleomycin, PYML-6, showed efficient dioxygen-activation comparable to bleomycin.



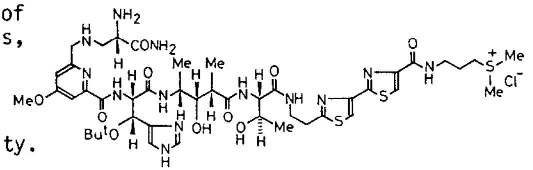
PYML-6

Tet.Lett.,27,31,3639 (1986)

SYNTHETIC STUDY TOWARDS MAN-DESIGNED BLEOMYCINS. SYNTHESIS OF A DNA CLEAVING MOLECULE BASED ON BLEOMYCIN.

M. Otsuka, A. Kittaka, M. Ohno*, T. Suzuki, J. Kuwahara, Y. Sugiura, H. Umezawa*
Faculty of Pharmaceutical Sciences, University of Tokyo, Japan, Faculty of Pharmaceutical Sciences, Kyoto University, and Institute of Microbial Chemistry, Japan

A synthetic analogue of bleomycin, PYML(6)-Bleomycin, showed efficient DNA cleaving activity.



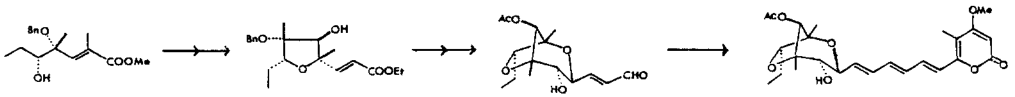
PYML(6)-Bleomycin

Tet.Lett.,27,31,3643 (1986)

TOTAL SYNTHESIS AND THE ABSOLUTE CONFIGURATION OF AUROVERTIN B

Shigeru Nishiyama, Hiroaki Toshima, Hiroki Kanai, and Shosuke Yamamura*
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama, Japan

A total synthesis of aurovertin B starting from D-glucose.

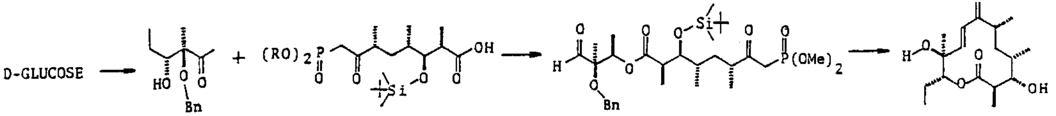


Tet.Lett.,27,31,3647 (1986)

HIGHLY STEREOSELECTIVE SYNTHESIS OF METHYNOLIDE, THE AGLYCONE OF THE 12-MEMBERED RING MACROLIDE METHYMYCIN, FROM D-GLUCOSE

Yuji Oikawa, Tatsuyoshi Tanaka, and Osamu Yonemitsu*
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Methynolide was efficiently synthesized from D-glucose with 89% overall stereoselectivity using some stereoselective reactions and benzyl-type protecting groups.

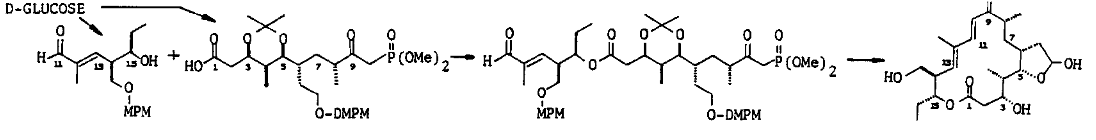


Tet.Lett.,27,31,3651 (1986)

TOTAL SYNTHESIS OF TYLONOLIDE, THE AGLYCONE OF THE 16-MEMBERED RING MACROLIDE TYLOSIN, FROM D-GLUCOSE. SELECTIVE APPLICATION OF MPM AND DMPM PROTECTING GROUPS FOR HYDROXY FUNCTIONS

Tatsuyoshi Tanaka, Yuji Oikawa, Tatsuo Hamada, and Osamu Yonemitsu*
Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Tylonolide was synthesized from D-glucose by employing some stereoselective reactions and deprotection of benzyl-type protecting groups at crucial synthetic steps.

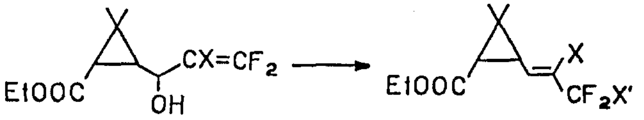


Tet.Lett.,27,31,3655 (1986)

HIGHLY REGIO- AND STEREOCONTROLLED HALOGENATION OF 1,1-DIFLUORO-2-HALO-1-ALKEN-3-OLS AS APPLIED TO POLYFLUORINATED PYRETHROID SYNTHESIS

Makoto Fujita and Tamejiro Hiyama*
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

Highly regio- and stereoselective halogenation of 1,1-difluoro-2-halo-1-alken-3-ols.



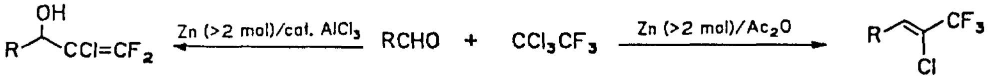
X, X' = F or Cl

Tet.Lett.,27,31,3659 (1986)

PRACTICAL WAYS FROM ALDEHYDES TO 2-CHLORO-1,1,1-TRIFLUORO-2-ALKENES AND 2-CHLORO-1,1-DIFLUORO-1-ALKEN-3-OLS

Makoto Fujita and Tamejiro Hiyama*
Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

Highly selective transformation of RCHO to 1 and 2.



1

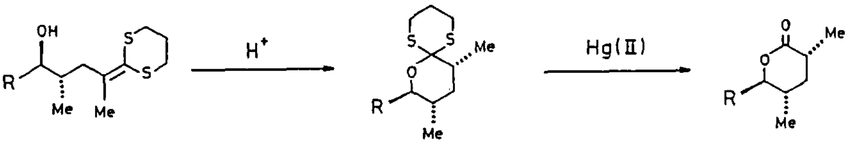
2

Tet.Lett.,27,31,3661 (1986)

C(2)-STEREOCONTROL OF δ-LACTONES VIA ACID-CATALYZED CYCLIZATION OF KETENE DITHIOACETALS HAVING AN INTERNAL HYDROXYL GROUP

K. Suzuki,* T. Masuda, Y. Fukazawa,† and G. Tsuchihashi*
Dept. Chem., Keio Univ., Yokohama 223, Japan. †Dept. Chem., Hiroshima Univ., Hiroshima 730.

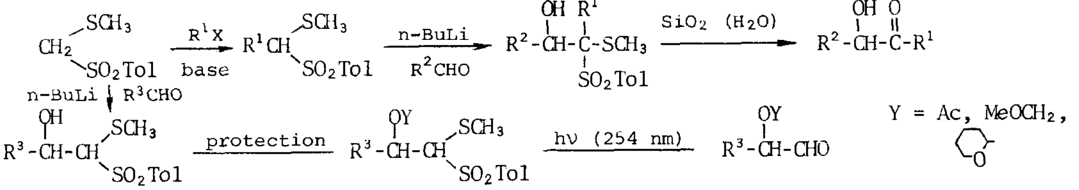
Stereocontrol of C(2)position of δ-lactones related to Prelog-Djerassi lactone.



Tet.Lett.,27,31,3665 (1986)

A VERSATILE REAGENT FOR SYNTHESIS OF α-HYDROXY ALDEHYDES AND KETONES —METHYLTHIOMETHYL p-TOLYL SULFONE—

Katsuyuki Ogura,* Toshihiko Tsuruda, Kazumasa Takahashi, and Hirotada Iida
Depratment of Synthetic Chemistry, Faculty of Engineering, Chiba University, Chiba 260, Japan

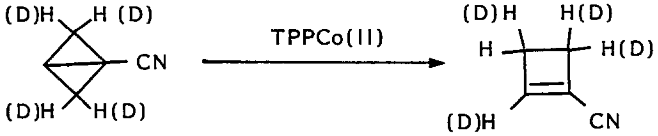


Tet.Lett.,27,31,3669 (1986)

Co(II)PORPHYRIN CATALYZED ISOMERIZATION OF BICYCLOBUTANECARBONITRILE

Sadao Miki, Sei-ichiro Matsumura, Toshinobu Ohno and Zen-ichi Yoshida*
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606 Japan.

TPPCo(II) causes a new type of reaction of bicyclobutane-1-carbonitrilr to give cyclobutene-1-carbonitrile.



Tet.Lett.,27,31,3673 (1986)

TANDEM [2,3]SIGMATROPIC REARRANGEMENT OF A SULPHONIUM YLIDE AND CYCLOPROPANATION OF THE RESULTING ELECTRON-RICH OLEFIN ON 4-METHOXY-2-PYRONE DERIVATIVE

P. de March[a], M. Moreno-Mañas[a*], I. Ripoll[a], F. Florencio[b], S. García-Blanco[b] and S. Martínez-Carrera[b]. [a]Departamento de Química. Universidad Autónoma de Barcelona. Bellaterra. Spain. [b] Instituto Rocasolano. C/Serrano 119. 28006 Madrid. Spain.

Functionalization at C-5 of triacetic acid lactone derivatives can be achieved by [2,3]sigmatropic rearrangement.