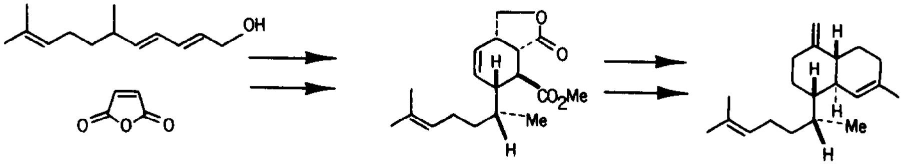
GRAPHICAL ABSTRACTS

Tetrahedron Lett.27,4813(1986)

SYNTHETIC STUDIES ON DITERPENES FROM A TERMITE SOLDIER: TOTAL SYNTHESIS OF (±)-BIFLORA-4,10(19),15-TRIENE

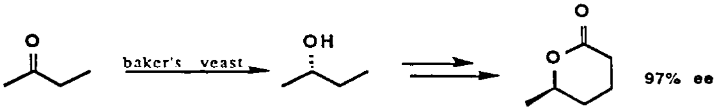
Paul A. Grieco* and Ravi P. Nargund
Department of Chemistry, Indiana University, Bloomington, IN 47405



Tetrahedron Lett.27,4817(1986)

CHEMISTRY OF BAKER'S YEAST REDUCTION PRODUCTS: USE OF OPTICALLY ACTIVE (S)-(+)-1-(p-TOLUENESULFONYL)PROPAN-2-OL AND (S)-(+)-1-(PHENYLSULFONYL)PROPAN-2-OL IN SYNTHESIS.

Alan P. Kozikowski*, B. B. Mugrage, C. S. Li, and (in part) L. Felder
Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

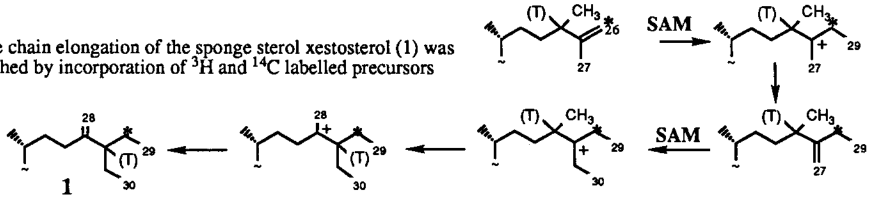


Tetrahedron Lett.27,4821(1986)

BIOSYNTHETIC STUDIES OF MARINE LIPIDS 10. DOUBLE SIDE CHAIN EXTENSION IN THE TRIPLY ALKYLATED SPONGE STEROL XESTOSTEROL

Ivan L. Stoilov, Janice E. Thompson and Carl Djerassi
Department of Chemistry, Stanford University, Stanford, CA 94305 USA

The side chain elongation of the sponge sterol xestosterol (1) was established by incorporation of ^{3}H and ^{14}C labelled precursors



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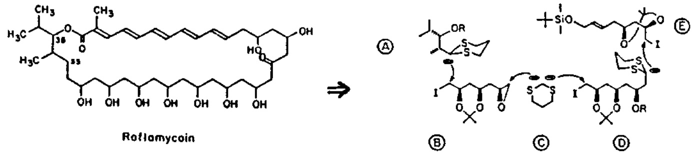
Tetrahedron Lett.27,4825(1986)

EN ROUTE TO POLYENE MACROLIDE TOTAL SYNTHESIS; THE KEY CHIRAL SEGMENTS OF ROFLAMYCOIN

Bruce H. Lipshutz*, Hiyoshizo Kotsuki, and (in part) Williard Lew
Department of Chemistry, University of California, Santa Barbara, CA 93106 USA

Four sections, A, B, D, E, of Roflamycoin corresponding to C-9 through C-35 of this polyene macrolide have been prepared.

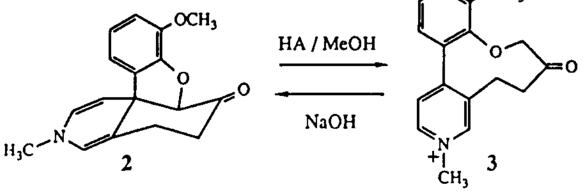


Tetrahedron Lett. 27, 4829 (1986)

SYNTHETIC STUDIES ON MORPHINE : RACEMIZATION OF BIARYL INTERMEDIATES

Dwight D. Weller* and Mark T. Runyan
Department of Chemistry, Oregon State University, Corvallis, OR 97331 USA

Benzofuroisoquinoline 2, projected intermediate for the synthesis of morphine, is racemized by ring opening to 3.

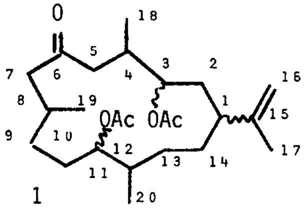


Tetrahedron Lett. 27, 4833 (1986)

APPLICATIONS OF COSY AND HOMONUCLEAR RELAY 2D-NMR IN THE DETERMINATION OF THE STRUCTURE OF A NEW CEMBRANE ISOLATED FROM THE MOLLUSC PLANAXIS SULCATUS

G.S. Linz, R. Sanduja, A.J. Weinheimer, M. Alam and G.E. Martin*, Department of Medicinal Chemistry, College of Pharmacy, University of Houston-University Park, Houston, Texas 77004

The structure of a new cembranoid diterpene, 3,11-diacetoxy-15,16-dehydrocembran-6-one (1), has been determined by combined usage of COSY and homonuclear RELAY 2D-NMR experiments.



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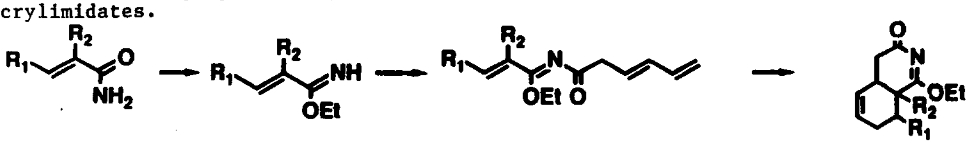
Tetrahedron Lett. 27, 4837 (1986)

THE INTRAMOLECULAR DIELS-ALDER CYCLOADDITION OF N-DIENOYL ACRYLIMIDATES. NEW METHODOLOGY FOR THE CONSTRUCTION OF NITROGEN HETEROCYCLES.

Kenneth J. Shea and J.J. Svoboda
Department of Chemistry, University of California, Irvine, California 92717 U.S.A.

Hexahydroisoquinolines are prepared in good yield by intramolecular Diels-Alder Cycloadditions of N-Dienoyl Acrylimidates.

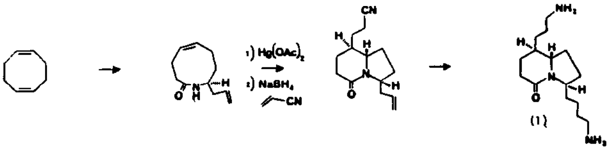


Tetrahedron Lett. 27, 4841 (1986)

THE DESIGN AND SYNTHESIS OF A NONPEPTIDE MIMIC OF AN IMMUNOSUPPRESSING PEPTIDE

Michael Kahn[1]* and Bruce Devens[2]
[1]Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607
[2]Department of Immunopharmacology, Hoffmann-La Roche, Nutley, NJ 07110

A synthesis of nonpeptide mimic (1) of the immunosuppressant tripeptide (Lys-Pro-Arg) is described.

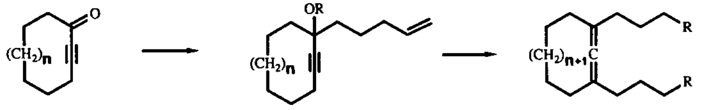


Tetrahedron Lett. 27, 4845 (1986)

SYNTHESIS OF OXABETWEENALLENES

James A. Marshall* and Scott D. Rothenberger
Department of Chemistry, University of South Carolina, Columbia, SC 29208 USA

The [11.9] and [12.11] oxabetweenallenes **7a** (n = 4) and **7b** (n = 7) have been synthesized from cyclododecynone (**1a**, n = 4) and cyclopentadecynone (**1b**, n = 7) by a sequence involving S_N2' addition to acetates **3a** and **3b** and macrocyclization of the hydroxy tosylates **6a** and **6b**.



1

2 R=H
3 R=Ac

4 $R=CH=CH_2$
5 $R=CH_2CH_2OH$

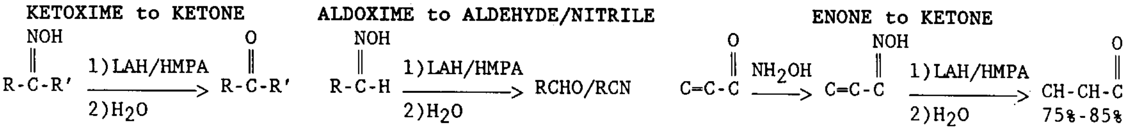
6 $R,R=CH_2CH_2OH, CH_2CH_2OTs$
7 $R,R=CH_2CH_2OCH_2CH_2$

Tetrahedron Lett. 27, 4849 (1986)

THE REACTION OF $LiAlH_4$/HMPA WITH OXIMES: MECHANISM AND SYNTHETIC APPLICATIONS

Natarajan Balachander, Shin Shin Wang, Chaim N. Sukenik*
Dept of Chemistry, Case Western Reserve University, Cleveland, OH 44106

The scope and mechanism of the reaction of $LiAlH_4$ in HMPA with ketoximes and aldoximes have been elucidated. The 1,4-reduction of enones via their oximes has also been achieved.



KETOXIME to KETONE

$R-\overset{\overset{NOH}{\|}}{C}-R' \xrightarrow[2)H_2O]{1)LAH/HMPA} R-\overset{\overset{O}{\|}}{C}-R'$

ALDOXIME to ALDEHYDE/NITRILE

$R-\overset{\overset{NOH}{\|}}{C}-H \xrightarrow[2)H_2O]{1)LAH/HMPA} RCHO/RCN$

ENONE to KETONE

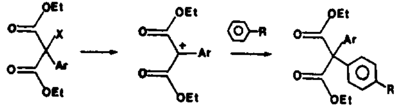
$C=C-\overset{\overset{O}{\|}}{C} \xrightarrow{NH_2OH} C=C-\overset{\overset{NOH}{\|}}{C} \xrightarrow[2)H_2O]{1)LAH/HMPA} CH-CH-\overset{\overset{O}{\|}}{C}$ 75%-85%

Tetrahedron Lett. 27, 4853 (1986)

DOUBLY-DESTABILIZED CARBOCATIONS. DETECTION AND TRAPPING OF ARYL-BISCARBOETHOXYCARBOCATIONS.

David Fletcher, Fred J. Ablenas, Alan C. Hopkinson and Edward Lee-Ruff*
Department of Chemistry, York University, Toronto, Ontario M3J 1P3 Canada.

Diethyl bromo(aryl)malonates undergo ionization in superacids at -78°C to give the corresponding cations. These doubly destabilized cations can be trapped with benzene or toluene to give the corresponding Friedel-Crafts adducts.

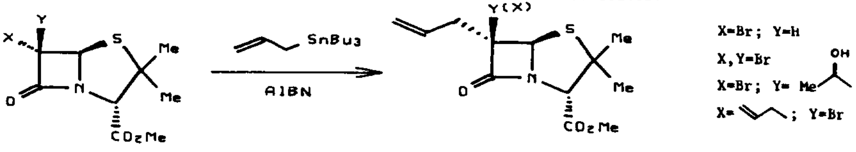


Tetrahedron Lett. 27, 4857 (1986)

HIGHLY CHEMOSELECTIVE AND STEREOCONTROLLED ACCESS TO 6-ALPHA-ALLYL PENICILLANATES

Stephen Hanessian* and Marco Alpegiani
Department of Chemistry, Université de Montréal
Montréal, Québec, Canada H3C 3J7

Treatment of 6-bromo penicillanates with allyltributyltin under free-radical conditions results in the formation of 6-alpha allyl derivatives.



Tetrahedron Lett. 27, 4861 (1986)

A FACILE SYNTHESIS OF AROMATIC TRIFLUOROMETHYL COMPOUNDS VIA ORTHOTHIO ESTERS

Donald P. Matthews, Jeffrey P. Whitten, James R. McCarthy*

A general synthetic route to aromatic trifluoromethyl compounds, which is carried out under normal laboratory reaction conditions, is described.

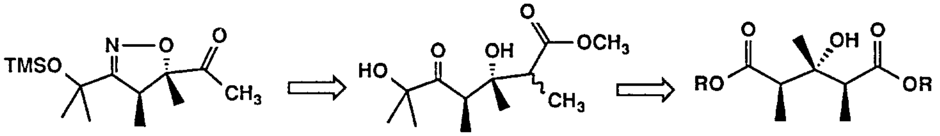
$$ArC(SR)_3 \longrightarrow ArCF_3$$

Tetrahedron Lett. 27, 4865 (1986)

REDUCTIVE CLEAVAGE OF HIGHLY SUBSTITUTED Δ2-ISOXAZOLINES. SYNTHESIS OF CRISPATIC ACID

Dennis P. Curran* and Christopher J. Fenk, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

The preparation of highly substituted β-hydroxy carbonyl compounds from isoxazolines is featured in a synthesis of crispatic acid. A β-hydroxy imine, the proposed intermediate in this transformation, is isolated for the first time and a stereoselective hydroboration of a 5-vinyl substituted isoxazoline is also reported.

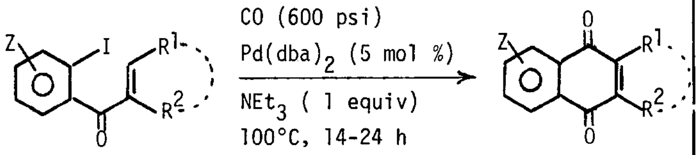


Tetrahedron Lett. 27, 4869 (1986)

COMPLETE REVERSAL OF REGIOCHEMISTRY IN CYCLIC ACYLPALLADATION. NOVEL SYNTHESIS OF QUINONES.

Ei-ichi Negishi,* and James M. Tour
Department of Chemistry, Purdue University, W. Lafayette, IN 47907

Cyclicacylpalladation reaction of *o*-iodoaryl alkenyl ketones in an "endo" mode provides bicyclic and polycyclic quinones in high yields.

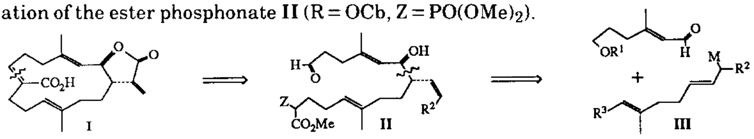


Tetrahedron Lett. 27, 4873 (1986)

STEREOSELECTIVE TOTAL SYNTHESIS OF THE CEMBRANOID DITERPENE ANISOMELIC ACID

James A. Marshall* and Bradley S. DeHoff
Department of Chemistry, University of South Carolina, Columbia, SC 29208 USA

The first total synthesis of (±)-anisomelic acid (**I**) has been achieved via anti coupling of the allyl titanate **IV** ($R^2 = CH = CHOCb$, $R^3 = CH = CH_2$, $M = Ti(O\text{-}i\text{-}Pr)_3$) with aldehyde **III** ($R^1 = TBS$) followed by (Z)-selective macrocyclization of the ester phosphonate **II** ($R = OCb$, $Z = PO(OMe)_2$).



I II III

Tetrahedron Lett. 27, 4877 (1986)

STEREOSELECTIVITIES OF THERMAL AND LEWIS ACID CATALYZED INTRAMOLECULAR DIELS-ALDER REACTIONS OF INTERNALLY ACTIVATED DIENOPHILES TO FORM 5-11 MEMBERED RINGS[1]

Douglas A. Smith, Kunio Sakan, and K.N. Houk
Departments of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

The thermal and Lewis acid catalyzed intramolecular Diels-Alder reactions of **1** (n = 5-11) have been studied

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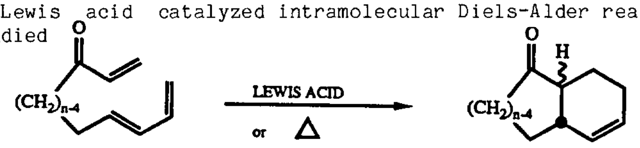
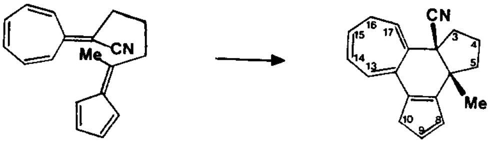


Tetrahedron Lett. 27, 4881 (1986)

AN INTRAMOLECULAR [8+6] CYCLOADDITION

Ching-Yang Liu, Douglas A. Smith, and K.N. Houk
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

An intramolecular [8+6] cycloaddition of a heptafulvene linked to a fulvene by a trimethylene chain has been observed.

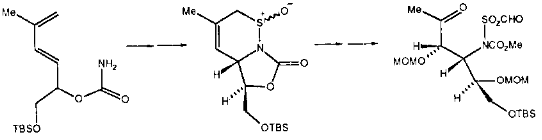


Tetrahedron Lett. 27, 4885 (1986)

AN APPROACH TO THE ARYL-C-GLYCOSIDE DEF-RING SYSTEM OF NOGALAMYCIN

Richard P. Joyce, M. Parvez, and Steven M. Weinreb*
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

Ketone **16**, a key intermediate in synthesis of the nogalamycin DEF-rings, has been efficiently and stereospecifically synthesized in nine steps using a strategy centered on an intramolecular N-sulfinyl dienophile Diels-Alder cycloaddition.



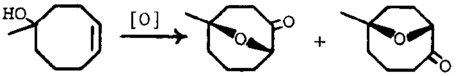
8 **10** **16**

Tetrahedron Lett. 27, 4889 (1986)

SUBSTITUENT-DIRECTED OXIDATION: TRANSANNULAR OXIDATIVE CYCLIZATION OF CYCLOALKENOLS TO β-KETO CYCLIC ETHERS.

Matthew F. Schlecht* and Ho-jin Kim
Department of Chemistry, Polytechnic University, 333 Jay St., Brooklyn, NY 11201

Transannular oxidative cyclization of 2 to bicyclic ethers such as 5 and 6 proceeds with different selectivity depending on the reagent [chromium(VI) vs lead(IV)].



2 5 6

[O] = PCC -or- CrO_3 / HOAc / Ac_2O -or-

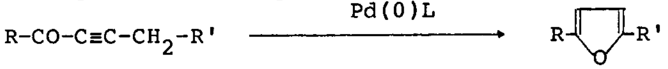
1) $Pb(OAc)_4$/HOAc
2) K_2CO_3/MeOH
3) PCC

Tetrahedron Lett.27,4893(1986)

A NOVEL PALLADIUM-CATALYZED REARRANGEMENT OF ACETYLENIC KETONES TO FURANS

Huaiyu Sheng,Shouyuan Lin,and Yaozeng Huang(Y.Z.,Huang)*
Shanghai Institute of Organic Chemistry,Academia Sinica,
345 Lingling Lu,Shanghai,China.

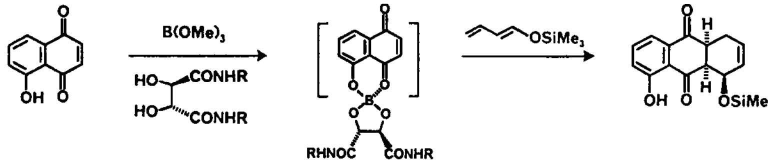
Synthesis of 2,5-disubstituted furans via the reaction of butynones with palladium catalyst,and it is suggested that,by means of the catalyst,the butynones were at first rearranged into allenyl ketones and then cyclized to corresponding furans.


$R\text{-}CO\text{-}C{\equiv}C\text{-}CH_2\text{-}R' \xrightarrow{Pd(0)L}$

Tetrahedron Lett.27,4895(1986)

ASYMMETRIC DIELS-ALDER REACTION DIRECTED TOWARD CHIRAL ANTHRACYCLINE INTERMEDIATES

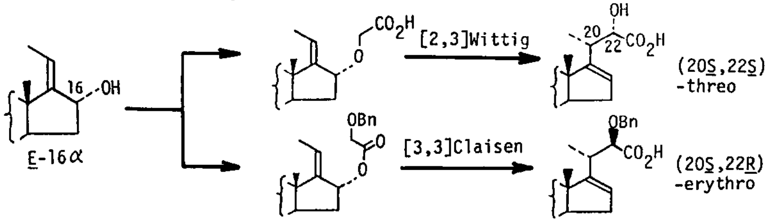
Keiji Maruoka, Minoru Sakurai, Junya Fujiwara, Hisashi Yamamoto*
Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan



Tetrahedron Lett.27,4899(1986)

APPLICATION OF [2,3]WITTIG AND [3,3]CLAISEN REARRANGEMENTS IN STEROID SIDE CHAIN SYNTHESIS. A HIGHLY STEREOCONTROLLED ENTRY TO EITHER (22S)- OR (22R)-HYDROXY-23-CARBOXYLIC ACID

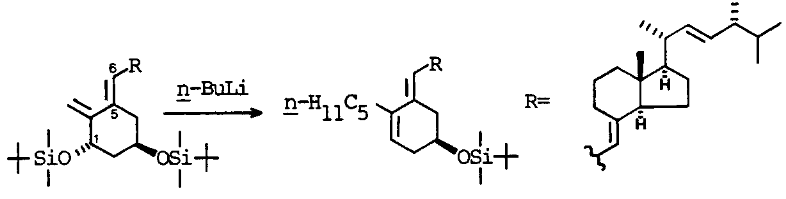
K. Mikami, K. Kawamoto, T. Nakai, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan



Tetrahedron Lett.27,4903(1986)

AN ALLYLIC NUCLEOPHILIC SUBSTITUTION REACTION OF 1α-HYDROXYVITAMIN D DERIVATIVES

M.J. Calverley
Leo Pharmaceutical Products, DK-2750 Ballerup, Denmark



The first transformation of the 5,6-*trans*-vitamin D triene system into that of isovitamin D under nucleophilic conditions is reported.

Tetrahedron Lett. 27,4905(1986)

HOMOLYTIC DISPLACEMENT AT CARBON: FIRST EXAMPLE OF α-ATTACK IN THE ALLENYL AND PROPARGYL COBALOXIMES

B.D. Gupta and Sujit Roy, Deptt. of Chemistry, I.I.T., Kanpur, India.

Allenyl and propargyl sulphones are formed by regiospecific attack of $R\dot{S}O_2$ on the α carbon bound to cobalt in 1 and 6.

$$CH_2{=}C{=}CH{-}Co^{III}(dmgH)_2Py\ (\underline{1}) + RSO_2Cl \xrightarrow{h\nu} CH_2{=}C{=}CH{-}SO_2R + ClCo^{III}(dmgH)_2Py$$

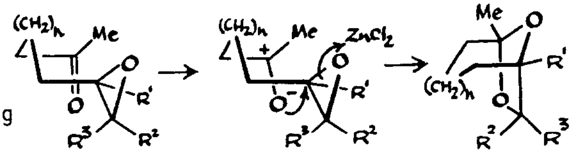
$$CH{\equiv}C{-}CH_2{-}Co^{III}(dmgH)_2Py\ (\underline{6}) + RSO_2Cl \xrightarrow{h\nu} CH{\equiv}C{-}CH_2{-}SO_2R + ClCo^{III}(dmgH)_2Py$$

Tetrahedron Lett. 27,4909(1986)

APPLICATION OF THE CARBONYL EPOXIDE REARRANGEMENT TO THE FORMATION OF DIOXABICYCLOALKANES AND ALKENES. SYNTHESIS OF THE MUS MUSCULUS PHEROMONE.

Harry H. Wasserman, Steven Wolff and Teruo Oku
Department of Chemistry, Yale University, New Haven, CT 06511 USA

Acid-catalyzed intramolecular opening of epoxides by carbonyl groups provides a general stereocontrolled method for forming dioxabicyclo systems, including the (+)-Mus musculus pheromone and products corresponding to certain insect pheromones.

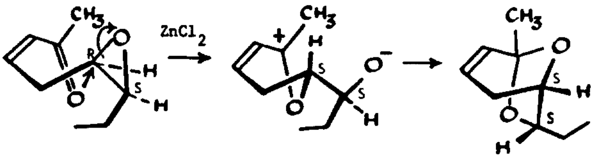


Tetrahedron Lett. 27,4913(1986)

THE CARBONYL EPOXIDE REARRANGEMENT. A CHIRAL SYNTHESIS OF THE MUS MUSCULUS PHEROMONE.

Harry H. Wasserman* and Teruo Oku
Department of Chemistry, Yale University, New Haven, CT 06511 USA

The carbonyl-epoxide rearrangement has been applied to an efficient synthesis of both enantiomers corresponding to the Mus musculus pheromone.



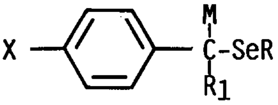
Tetrahedron Lett. 27,4917(1986)

ON THE STRUCTURE OF -METALLO BENZYLSELENIDES

M. Clarembeau and A. Krief*
Laboratoire de Chimie Organique
Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles B-5000 NAMUR (Belgium)

Decreasing electron attracting ability of the para substituent X leads to an upfield shift of the ^{77}Se signal of para substituted benzylselenides. Reverse results are however observed when the measurements are performed on the corresponding para substituted metallo benzylselenides.

M = H ; M = Li or K ; X = CN, Cl, H, Me, OMe



Tetrahedron Lett.27,4921(1986)

1-HYDRAZONYLTETRAZOLES: FRAGMENTATIVE CYCLISATION - A NEW ROUTE TO SUBSTITUTED 1,2,4-TRIAZOLES.

Richard N.Butler*,Kevin J.Fitzgerald and Mary T.Fleming,
Chemistry Department, University College, Galway, Ireland.