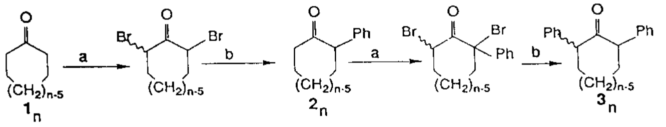
GRAPHICAL ABSTRACTS

Tetrahedron Lett.27,4671(1986)

SYNTHESIS AND STRUCTURE OF LARGE RING 2-PHENYLCYCLOALKANONES AND 2,n-DIPHENYLCYCLOALKANONES

Xuegong Lei, Charles Doubleday, Jr.*, and Nicholas J. Turro*
Department of Chemistry, Columbia University, New York, NY 10027 USA

Syntheses for 2,3 (n=10,11,12,15) and X-ray structures for 3_{15} are reported.

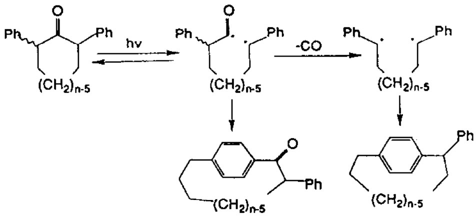


Tetrahedron Lett.27,4675(1986)

PHOTOCHEMISTRY OF LARGE RING 2-PHENYLCYCLOALKANONES AND 2,n-DIPHENYLCYCLOALKANONES, by Xuegong Lei, Charles Doubleday, Jr.*, and Nicholas J. Turro*

Department of Chemistry, Columbia University,
New York, NY 10027 USA

Photolysis of the title compounds yields cyclophanes as the major products.

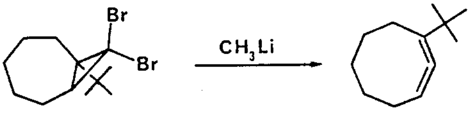


Tetrahedron Lett.27,4679(1986)

SMALL-RING CYCLIC CUMULENES: SYNTHESIS OF A KINETICALLY STABLE EIGHT MEMBERED RING ALLENE

John D. Price, Department of Chemistry, Iowa State University, Ames, Iowa 50011 and Richard P. Johnson, Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

1-tert-Butyl-1,2-cyclooctadiene is synthesized and is found to be stable to dimerization. The allene moiety is predicted to be bent 22°. Rearrangements occur with acid or base.



Tetrahedron Lett.27,4683(1986)

A COMPARISON OF GROUP ELECTRONEGATIVITY AND FIELD EFFECTS

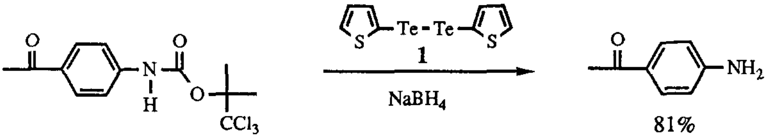
E. Sacher, Groupe des Couches Minces and Département de Génie Physique
Ecole Polytechnique de Montréal, CP 6079, Succ. "A",Mtl, PQ. H3C 3A7

A statistical analysis in used to demonstrate that the two group electronegativity scales, one thought to represent through-bond effects and the other, through-space effects, in fact differ only numerically.

Tetrahedron Lett. 27, 4687 (1986)

Tellurolate-Induced Deprotection of 2,2,2-Trichloro-*tert*-butyloxycarbonyl (TCBOC) Derivatives

M. V. Lakshmikantham, Yvette A. Jackson, Robert J. Jones,
Gerard J. O'Malley, K. Ravichandran, and Michael P. Cava*
Department of Chemistry, University of Alabama, University (Tuscaloosa), Alabama 35486



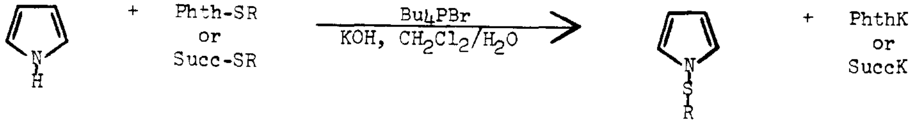
Sodium-2-thiophenetellurolate efficiently regenerates amines from their 2,2,2-trichloro-*tert*-butyloxycarbonyl (TCBOC) and 2,2,2-trichloroethoxycarbonyl derivatives.

Tetrahedron Lett. 27, 4689 (1986)

THE SYNTHESIS OF 1-ALKYLTHIOPYRROLES

Helmuth M. Gilow
Department of Chemistry, Rhodes College, Memphis, TN 38112

1-Alkylthiopyrroles can be easily synthesized under phase transfer conditions.



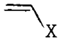
Tetrahedron Lett. 27, 4693 (1986)

AN EXPERIMENTAL & THEORETICAL INVESTIGATION OF THE INFLUENCE OF ALKENE HOMO ENERGY LEVEL UPON THE HYDROBORATION REACTION. ADDITIONAL EVIDENCE SUPPORTING AN EARLY TRANSITION STATE WHICH HAS RETENTION OF ALKENE CHARACTER

Donna J. Nelson* and Penny J. Cooper
Department of Chemistry, University of Oklahoma, Norman, OK 73019 USA

Effects of some substituents X upon hydroboration with 9-BBN of alkenes were examined. Ordering of the pi MO energy levels correlates with that of the alkene relative reactivities: a higher MO energy level corresponds to a higher relative reactivity. Regioselectivity of boron-carbon bond formation correlates with a.o. coefficient size in alkene HOMO. Substituents are listed in order of alkene reactivity and HOMO.

X=SiMe$_3$>*n*-propyl>SMe, OAc, OMe>I>CN>Br>Cl



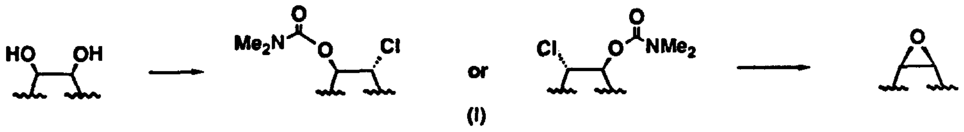
X=OBu>*n*-Bu>OAc, SiMe$_3$>SPh and BR$_2$>Br>Cl

Tetrahedron Lett. 27, 4697 (1986)

A READY ROUTE FROM VICINAL CIS-DIOLS TO EPOXIDES

Ustun Sunay, David Mootoo, Bruce Molino and Bert Fraser-Reid*
Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706

A two-step procedure for converting vicinal cis-diols into epoxides is described which involves the preparation of a chloro carbamate intermediate (I) by the use of (dichloromethylene)dimethylammonium chloride.

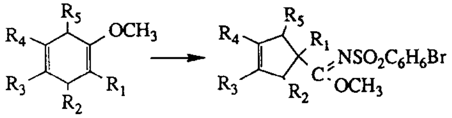


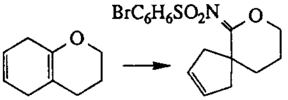
Tetrahedron Lett.27,4701(1986)

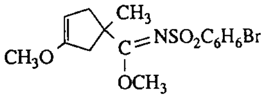
CYCLOADDITION- REARRANGEMENT OF CYCLOHEXADIENOL ETHERS. A VERSATILE AND SELECTIVE SYNTHESIS OF CYCLOPENTENOID SYSTEMS

David J. Goldsmith and José J. Soria
Department of Chemistry, Emory University, Atlanta, GA. 30322 USA

Cyclohexadienol methyl ethers (R_1 - R_5 = H or CH_3) yield cyclopentenecarboximidates. Chemo-, regio-, and stereoselectivity are displayed.





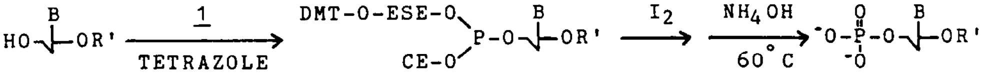


Tetrahedron Lett.27,4705(1986)

CHEMICAL 5'-PHOSPHORYLATION OF OLIGODEOXYNUCLEOTIDES THAT CAN BE MONITORED BY TRITYL CATION RELEASE

T. Horn and M.S. Urdea
CHIRON CORP., Emeryville, CA 94608, USA.

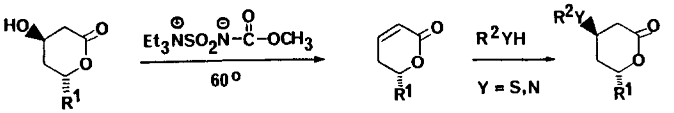
ESE = $-CH_2CH_2SO_2CH_2CH_2-$
CE = $-CH_2CH_2CN$
R = $-CH(CH_3)_2$

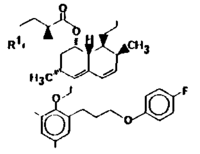


Tetrahedron Lett.27,4709(1986)

CONVENIENT TWO-STEP STEREOSPECIFIC HYDROXY-SUBSTITUTION WITH RETENTION IN β-HYDROXY-δ-LACTONES.

W. Bartmann, G. Beck, E. Granzer, H. Jendralla, B. v.Kerekjarto, G. Wess
Hoechst AG, Pharma Forschung, Postfach 80 03 20, D-6230 Frankfurt a.M. 80



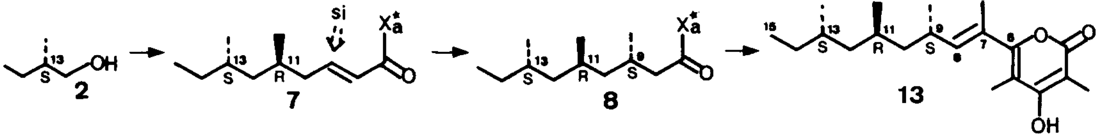


Tetrahedron Lett.27,4713(1986)

ENANTIOSELECTIVE SYNTHESIS OF THE ALLEGED STRUCTURE OF NORPECTINATONE

Wolfgang Oppolzer, Robert Moretti and Gérald Bernardelli
Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Switzerland

A synthesis of deoxypolypropionate 13 via face selective organocopper/enoate additions

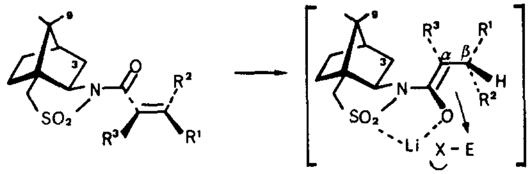


Tetrahedron Lett. 27, 4717 (1986)

ASYMMETRIC INDUCTION AT C(β) AND C(α) OF N-ENOYL SULTAMS BY 1,4-HYDRIDE ADDITION/ENOLATE TRAPPING[1]

Wolfgang Oppolzer* and Giovanni Poli
Département de Chimie Organique, Université de Genève, 1211 Genève 4, Switzerland

Starting from enoylsultams 1,4-reduction with L-Selectride followed by protonation or methylation gave α- and/or β-substituted imides with high asymmetric induction at both centers.

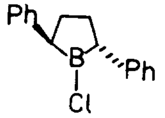


Tetrahedron Lett. 27, 4721 (1986)

CHIRAL LEWIS ACIDS FOR ENANTIOSELECTIVE C-C BOND FORMATION

M.T.Reetz*, F.Kunisch and P.Heitmann
Fachbereich Chemie der Universität, Hans-Meerwein-Str.,3550 Marburg, FRG

The optically active Lewis acid 6 has been prepared and used in enantioselective aldol additions and Me_3SiCN additions to RCHO.



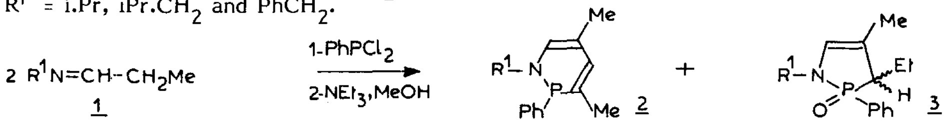
6

Tetrahedron Lett. 27, 4725 (1986)

FIRST SYNTHESIS OF 1,2-DIHYDRO 1,2-λ^3-AZAPHOSPHORINES.

Catherine Bourdieu and André Foucaud *
Groupe de Physicochimie Structurale associé au C.N.R.S.,Université de Rennes,35042Rennes, France.

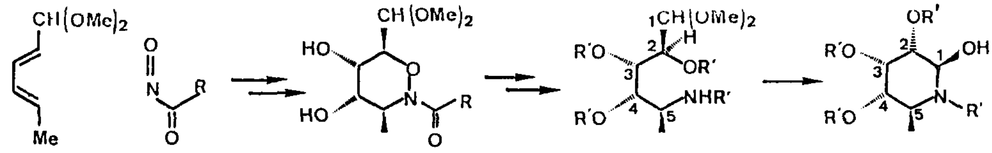
1,2-Dihydro 1,2-λ^3-azaphosphorines 2 were prepared from imines 1 (R^1 = t.Bu, t.octyl, i.Pr, $iPr.CH_2$, $PhCH_2$) by treatment with $PhPCl_2$; 2-oxo 1,2-azaphospholenes 3 were also obtained when R^1 = i.Pr, $iPr.CH_2$ and $PhCH_2$.



Tetrahedron Lett. 27, 4727 (1986)

TOTAL SYNTHESIS OF A (±) AMINOALLOSE DERIVATIVE

Albert DEFOIN, Hans FRITZ, Guillaume GEFFROY and Jacques STREITH
Ecole Nationale Supérieure de Chimie Université de Haute-Alsace F-68093 Mulhouse-Cédex
and Physikalische Abteilung CIBA-GEIGY CH-4002 Basel.

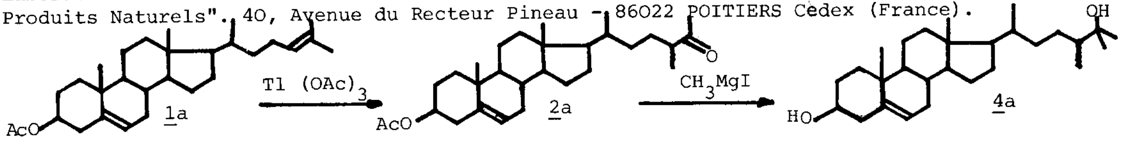


R=OCH₂Ph
R'=Ac

Tetrahedron Lett. 27, 4731(1986)

REARRANGEMENT OF A Δ^{24} STEROID : APPLICATION TO THE SYNTHESIS OF A 24-METHYLATED MARINE STEROL

P. Bisseck, G. Charles
Departement de Chimie Organique-Faculté des Sciences - B.P. 812 Yaoundé (Cameroun)
C. BERRIER
Laboratoire de CHIMIE XII - Faculté des Sciences - UA CNRS N° 489 "Synthèse et Réactivité de Produits Naturels". 40, Avenue du Recteur Pineau - 86022 POITIERS Cedex (France).

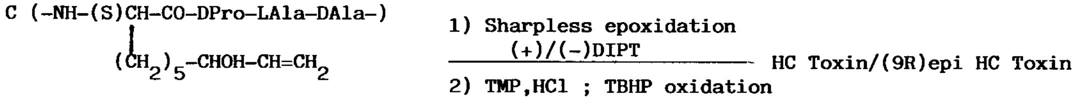


Tetrahedron Lett. 27, 4735(1986)

STEREOSELECTIVE SYNTHESIS OF HC TOXIN AND ITS (9R) EPOXIDE EPIMER

Robert Jacquier, René Lazaro*, Hanta Ranirisehemo and Ph. Viallefont
U.A. 468, U.S.T.L. Place E. Bataillon 34060-Montpellier Cedex France

HC Toxin and (9R)-epi HC Toxin have been synthesized via the Sharpless epoxidation of the following cyclopeptidic allylic alcohol.

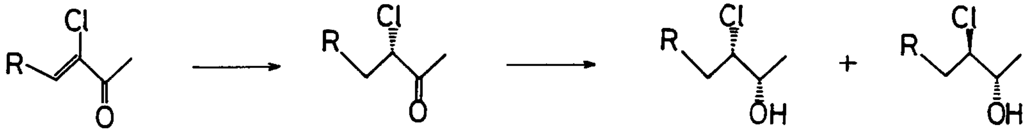


$$\underset{\displaystyle (CH_2)_5\text{-CHOH-CH=CH}_2}{\text{C (-NH-(S)CH-CO-DPro-LAla-DAla-)}} \xrightarrow[\text{2) TMP,HCl ; TBHP oxidation}]{\text{1) Sharpless epoxidation (+)/(-)DIPT}} \text{HC Toxin/(9R)epi HC Toxin}$$

Tetrahedron Lett. 27, 4737(1986)

ASYMMETRIC REDUCTION OF Z-3-CHLORO-3-ALKEN-2-ONES WITH FERMENTING BAKER'S YEAST

Masanori Utaka, Satoshi Konishi, and Akira Takeda*
Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700, Japan



R = C_2H_5, n-C_5H_{11}, n-C_8H_{17}

(S)
44~84% ee

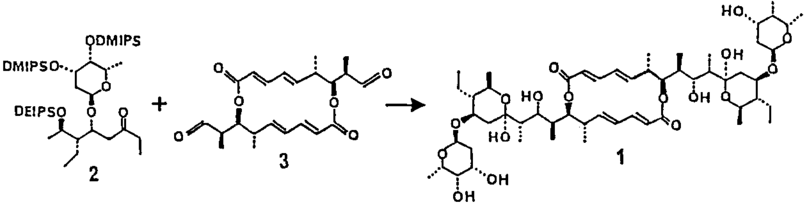
syn(2S,3S):anti(2S,3R)
= 2.8~18.3:1, >98% ee

Tetrahedron Lett. 27, 4741(1986)

TOTAL SYNTHESIS OF ELAIOPHYLIN (AZALOMYCIN B)

Kazunobu Toshima, Kuniaki Tatsuta, and Mitsuhiro Kinoshita*
Department of Applied Chemistry, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, JAPAN

The first synthesis of elaiophylin(1) was achieved via the coupling of the appropriately protected ethyl ketone(2) and the dialdehyde(3).

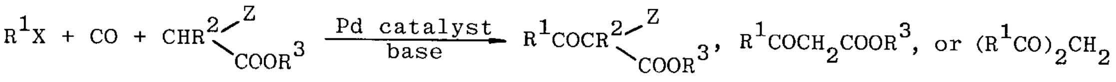


Tetrahedron Lett. 27, 4745 (1986)

ACYLATION OF ACTIVE METHYLENE COMPOUNDS VIA PALLADIUM COMPLEX-CATALYZED CARBONYLATIVE CROSS-COUPLING OF ORGANIC HALIDES

Toshi-aki Kobayashi and Masato Tanaka*
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305, Japan

New methods for acylation of active methylene compounds *via* palladium complex-catalyzed carbonylation with organic halides



$$R^1X + CO + CHR^2(Z)COOR^3 \xrightarrow[\text{base}]{\text{Pd catalyst}} R^1COCR^2(Z)COOR^3,\ R^1COCH_2COOR^3,\ \text{or}\ (R^1CO)_2CH_2$$

Tetrahedron Lett. 27, 4749 (1986)

FACILE SYNTHESIS OF AZIDES: CONVERSION OF HYDRAZINES USING DINITROGEN TETROXIDE

Yong Hae Kim, Kweon Kim, and Sung Bo Shim, Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box. 150, Chong-Yang, Seoul, Korea

Conversion of Hydrazines into Azides under mild conditions at low temperature (-20~-40°C) in acetonitrile

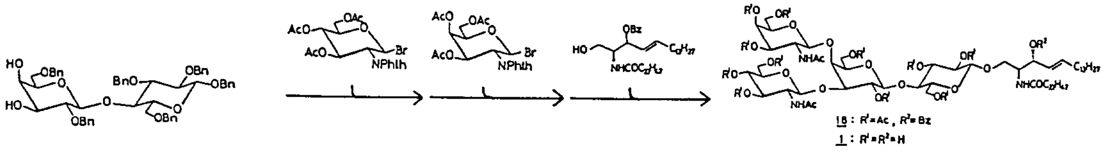
$$R\text{-}NH\text{-}NH_2 \xrightarrow[CH_3CN]{N_2O_4} R\text{-}N_3 \qquad R=\text{ aryl-, carbonyl-, sulfonyl-}$$

Tetrahedron Lett. 27, 4753 (1986)

TOTAL SYNTHESIS OF A LACTO-GANGLIO SERIES GLYCOSPHINGOLIPID, M1⁻XGL-1

Yukishige Ito, Mamoru Sugimoto, Susumu Sato, and Tomoya Ogawa
RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01, Japan

A novel glycolipid 1 was synthesized regio- and stereoselectively.



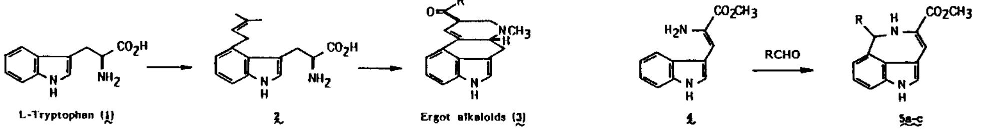
Tetrahedron Lett. 27, 4757 (1986)

INTRODUCTION OF SUBSTITUENT ONTO 4-POSITION OF INDOLE NUCLEUS BY INTERMOLECULAR CYCLIZATION OF α,β-DEHYDROTRYPTOPHAN METHYL ESTER WITH ALDEHYDE

Shin-ichi Nakatsuka,* Kozi Yamada, and Toshio Goto
Laboratory of Organic Chemistry, Faculty of Agriculture, Nagoya University, Nagoya 464, Japan

Intermolecular cyclization of 4 with aldehydes afforded 5a-c similarly to the biosynthesis of ergot alkaloids (3).

Scheme I. Biosynthesis of ergot alkaloids (3).

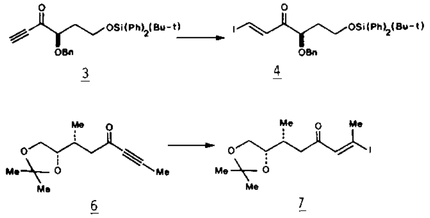


A PRACTICAL SYNTHESIS OF TRANS-IODOOLEFINS

Tetrahedron Lett. 27, 4759 (1986)

Seung Hoon Cheon, William J. Christ, Lynn D. Hawkins,
Haolun Jin, Yoshito Kishi*, and Mikio Taniguchi
Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA

Trimethylsilyl iodide was found to react smoothly with the acetylenic ketones 3 and 6 to yield the trans-β-iodovinyl ketones 4 and 7, respectively.

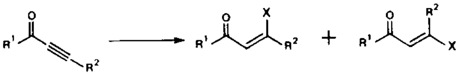


β-HALOVINYL KETONES: SYNTHESIS FROM ACETYLENIC KETONES

Tetrahedron Lett. 27, 4763 (1986)

Mikio Taniguchi*, Shozo Kobayashi, Masako Nakagawa,
and Tohru Hino
Faculty of Pharmaceutical Sciences, Chiba University, 1-33 Yayoi-cho, Chiba 260, Japan
Yoshito Kishi
Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA

Practical syntheses of β-iodo- and β-bromovinyl ketones from the corresponding acetylenic ketones are described. The reaction of terminal acetylenic ketones with NaI or LiBr gave almost exclusively E-β-iodo- or E-β-bromovinyl ketones in TFA, while Z-β-iodo- or Z-β-bromovinyl ketones were the major products in AcOH.

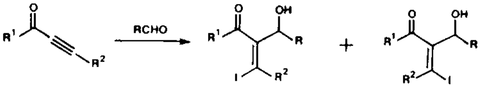


ALDOL REACTION OF ALLENOLATES GENERATED VIA 1,4-ADDITION OF IODIDE ANION OR ITS EQUIVALENT TO α,β-ACETYLENIC KETONES

Tetrahedron Lett. 27, 4767 (1986)

Mikio Taniguchi* and Tohru Hino
Faculty of Pharmaceutical Sciences, Chiba University, 1-33 Yayoi-cho, Chiba 260, Japan
Yoshito Kishi
Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA

Aldol reactions of allenolates, generated via 1,4-addition of an iodide anion equivalent to α,β-unsaturated ketones, are described. A high Z-stereoselectivity was achieved by use of (n-Bu)$_4$NI/TiCl$_4$ at -78°C, while a high E-stereoselectivity occurred at 0°C.

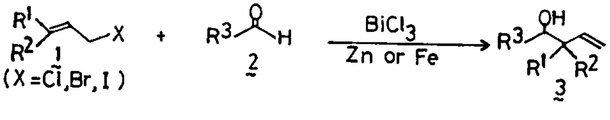


Tetrahedron Lett. 27, 4771 (1986)

CARBON-CARBON BOND FORMATION WITH BISMUTH SALT. A CHEMOSELECTIVE GRIGNARD-TYPE ADDITION OF ALLYL UNIT TO ALDEHYDES

Makoto Wada, Hidenori Ohki, and Kin-ya Akiba*
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

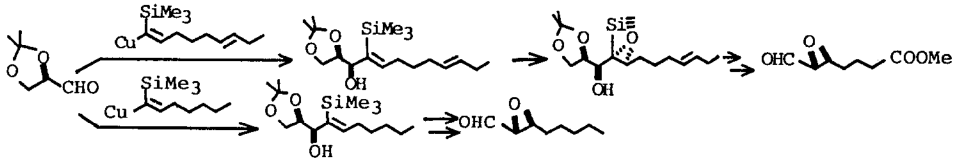
A Chemoselective Grignard-type allylation of aldehydes using allylic halides and BiCl$_3$-Zn, or BiCl$_3$-Fe is described.



Tetrahedron Lett.27,4775(1986)

A PRACTICAL METHOD FOR MULTIGRAM SCALE SYNTHESIS OF (+)-METHYL 5(S),6(R)-EPOXY-6-FORMYLHEXANOATE AND 2(R),3(S)-EPOXYOCTANAL, KEY INTERMEDIATES FOR SYNTHESIS OF LEUKOTRIENES A_4

Yuichi Kobayashi, Yasunori Kitano, Takashi Matsumoto, and Fumie Sato*
Department of Chemical Engineering, Tokyo Institute of Technology, Meguro Tokyo 152, Japan

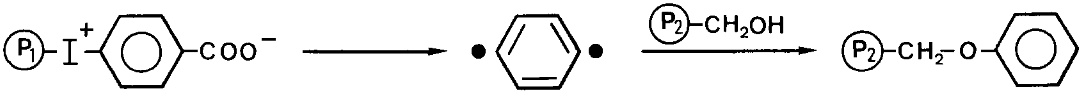


Tetrahedron Lett.27,4779(1986)

EVIDENCE FOR THE FORMATION OF 1,3- AND 1,4-DEHYDROBENZENES IN THE THERMAL DECOMPOSITION OF DIARYLIODONIUM- CARBOXYLATES

F. Gaviña*, S.V. Luis, V.S. Safont, P.Ferrer and A.M. Costero
Departamento de Química Orgánica, Colegio Universitario de Castellón,
Universidad de Valencia, Castellón de la Plana, Spain

Existence of m- and p-benzyne as free species in solution is demonstrated

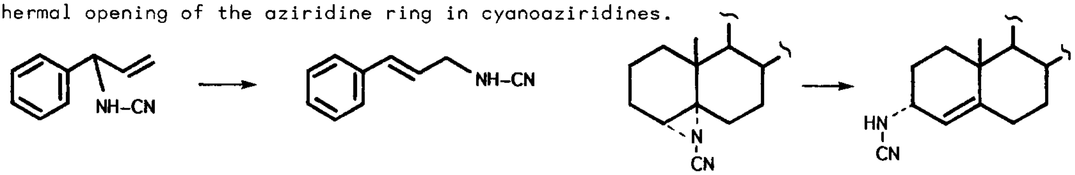


Tetrahedron Lett.27,4783(1986)

THERMAL REARRANGEMENT OF ALLYLIC CYANAMIDES

C. Betancor, R. Carrau, C.G. Francisco and E. Suarez*
Instituto de Productos Naturales Orgánicos, C.S.I.C.; C. la Esperanza 2, Tenerife, Spain

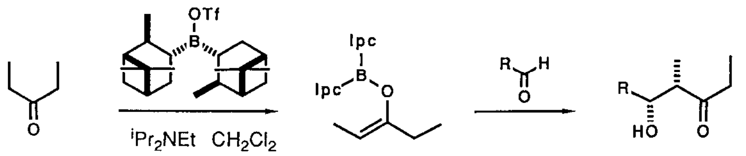
The allylic rearrangement of cyanamides has been achieved by pyrolysis in solution at temperatures between 125 and 190 °C. This rearrangement was also observed during the thermal opening of the aziridine ring in cyanoaziridines.



Tetrahedron Lett.27,4787(1986)

ENANTIOSELECTIVE ALDOL CONDENSATIONS:
THE USE OF KETONE BORON ENOLATES WITH CHIRAL LIGANDS ATTACHED TO BORON.

Ian Paterson*, M. Anne Lister, and Cynthia K. McClure
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.



syn:anti 10-30:1
66-90% ee

Tetrahedron Lett.27,4791(1986)

FAST ATOM BOMBARDMENT MASS SPECTROMETRY OF SERYL- AND O-PHOSPHOSERYL-CONTAINING PEPTIDES

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CSIRO, Division of Energy Chemistry, Sutherland 2232, N.S.W., Australia.
∞ Research School of Chemistry, Australian National University, ACT 2601, Australia.

FAB-MS was found to be a mild technique for distinguishing between O-phosphoserine 2 and serine 5, amino acid sequencing of the O-phosphoseryl-containing peptides 3,4 and for distinguishing these O-phosphopeptides from their non-phosphorylated conjeners 6,7.

PSer-Leu 3	Ser-Leu 7
Glu-PSer-Leu 4	Glu-Ser-Leu 6

Tetrahedron Lett.27,4795(1986)

SPIN TRAPPING REACTIONS WITH NITRIC OXIDES. V. REACTIONS WITH UNSATURATED MACROMOLECULAR CHAINS - A NEW SPIN LABELING METHOD

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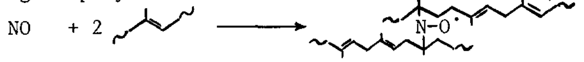
†also: Eötvös Loránd University, Department of Chemical Technology, H-1088 Budapest, Múzeum krt. 6-8, Hungary

Spin labeling of polydiene chains has been carried out by using nitric oxides.



Tetrahedron Lett.27,4799(1986)

TOTAL SYNTHESIS OF (±)-ANATOXIN-a VIA N-ACYLIMINIUM INTERMEDIATES

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Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.

(±)-Anatoxin-a (1) was synthesized from succinimide, 4-bromo-2-butene and dimethyl (2-oxo-propyl)phosphonate in 8 steps, the most crucial of which was the conversion of 2 to 3.