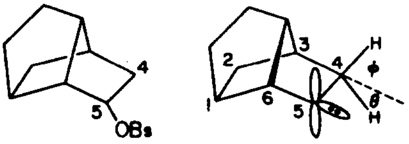
GRAPHICAL ABSTRACTS

Tet.Lett.,27,24,2675 (1986)

SOLVOLYSIS OF 5-BREXYL BROSYLATES: RELEVANCE TO CARBENE AND CARBOCATION CHEMISTRY

Alex Nickon and Raymond C. Weglein
Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218 USA

Exo- and endo-5-brexyl brosylate undergo acetolysis at nearly equal rates and produce acetates of largely inverted configuration. This atypical behavior helps us understand exo vs endo H shifts in the carbene 5-brexylidene.

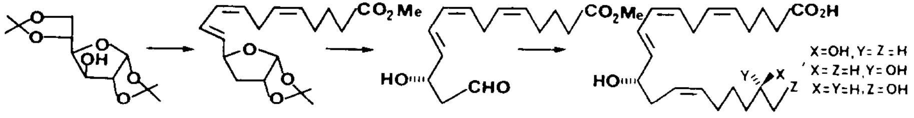


Tet.Lett.,27,24,2679 (1986)

SYNTHESIS OF 12(S),20-, 12(S),19(R)-, AND 12(S),19(S)-DIHYDROXY-EICOSA-CIS-5,8,14-TRANS-10-TETRAENOIC ACIDS, METABOLITES OF 12(S)-HETE

Sukumar Manna, Jacques Viala, Pendri Yadagiri, and J.R. Falck, Dept. Molecular Genetics, Univ. Texas Health Science Center, Dallas, Texas 75235 USA

The 20- and both 19-hydroxy metabolites of 12(S)-HETE were synthesized according to

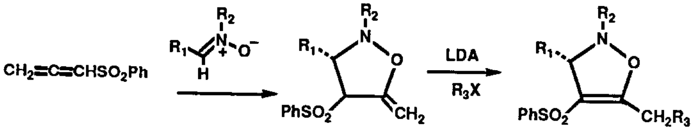


Tet.Lett.,27,24,2683 (1986)

DIPOLAR CYCLOADDITION REACTION OF (PHENYLSULFONYL) PROPADIENE WITH NITRONES AND ALKYLATION STUDIES OF THE CYCLOADDUCTS

Albert Padwa*, Stephen P. Carter, Ugo Chiacchio and Donald N. Kline
Department of Chemistry, Emory University, Atlanta, GA 30322 USA

Dipolar cycloaddition of nitrones with (phenylsulfonyl)propadiene gives 4-sulfonyl substituted isoxazolidines whose reactions with base and several electrophiles have been studied.

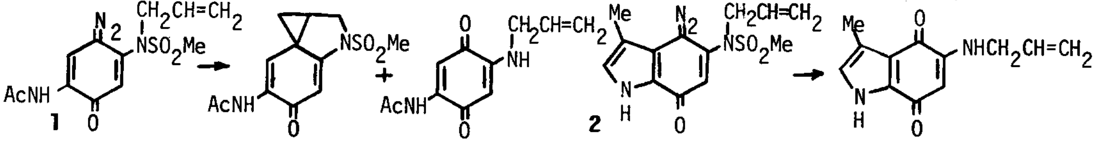


Tet.Lett.,27,24,2687 (1986)

PHOTOCHEMISTRY OF QUINONE DIAZIDES. INTRAMOLECULAR OXYGEN TRANSFER AND CARBENOID ADDITION DURING PHOTOLYSIS OF N-ALLYLSULFONAMIDO QUINONE DIAZIDES.

Richard J. Sundberg and Ellen W. Baxter, Department of Chemistry, University of Virginia, Charlottesville, VA 22901, USA

Model quinone diazide 1 gives a spiro-cyclopropane-cyclohexadienone but indole quinone diazide 2 gives only a product resulting from intramolecular transfer of a sulfonyl oxygen.

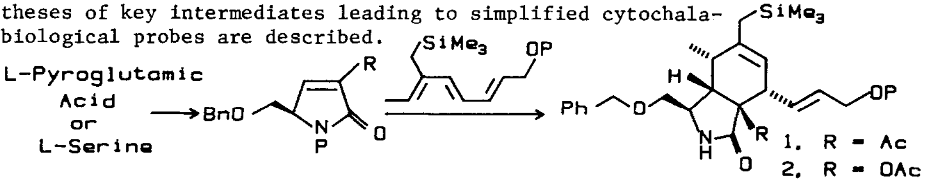


Tet.Lett.,27,24,2691 (1986)

SIMPLIFIED CYTOCHALASINS. 1. SYNTHESIS OF VERSATILE PERHYDROISOINDOLONE INTERMEDIATES.

Grant A. Krafft,* Ester A. Garcia, Anil Guram, Brian O'Shaughnessy and Xialong Xu Department of Chemistry, Syracuse University, Syracuse, NY 13244-1200

Chiral syntheses of key intermediates leading to simplified cytochalasin based biological probes are described.



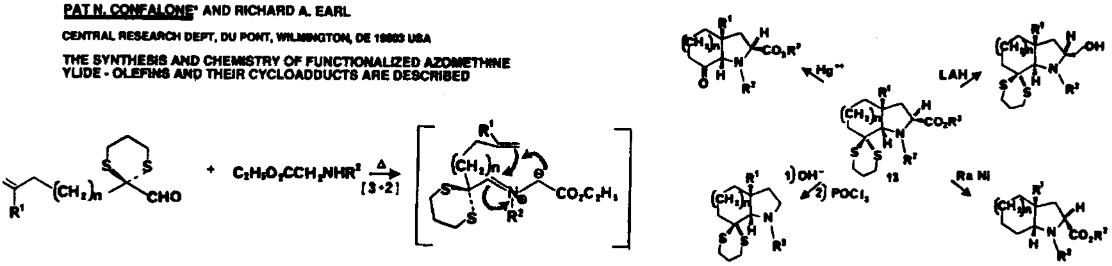
Tet.Lett.,27,24,2695 (1986)

INTRAMOLECULAR [3+2] CYCLOADDITIONS OF FUNCTIONALIZED AZOMETHINE YLIDES

PAT N. CONFALONE* AND RICHARD A. EARL

CENTRAL RESEARCH DEPT, DU PONT, WILMINGTON, DE 19898 USA

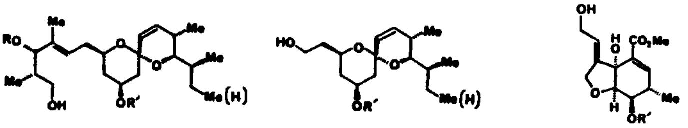
THE SYNTHESIS AND CHEMISTRY OF FUNCTIONALIZED AZOMETHINE YLIDE - OLEFINS AND THEIR CYCLOADDUCTS ARE DESCRIBED



Tet.Lett.,27,24,2699 (1986)

THE CONTROLLED DEGRADATION OF AVERMECTIN B_{1a}

Stephen Hanessian*, Antonio Ugolini, Paul J. Hodges and Daniel Dubé.
Department of Chemistry, Université de Montréal, Montréal, Québec, Canada, H3C 3V1.

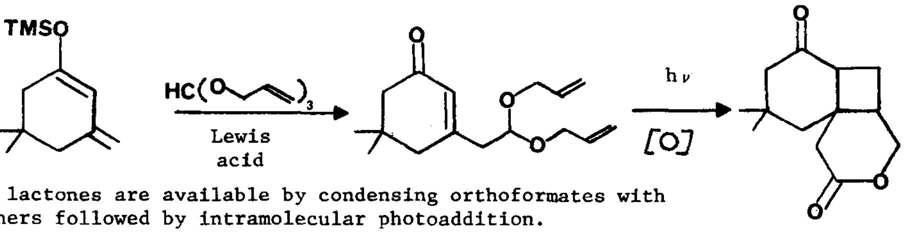


C_1-C_{10} and C_{11}-C_{28} segments via the controlled degradation of Avermectin B_{1a}.

Tet.Lett.,27,24,2703 (1986)

INTRAMOLECULAR [2+2] PHOTOCYCLOADDITION OF ENONE-ACETALS

Michael C. Pirrung and Stephen A. Thomson, Stanford University, Stanford, CA 94305



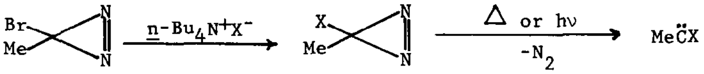
Tricyclic lactones are available by condensing orthoformates with dienyl ethers followed by intramolecular photoaddition.

Tet.Lett.,27,24,2707 (1986)

EXCHANGE REACTIONS OF DIAZIRINES: 3-X-3-METHYLDIAZIRINES AND DERIVED CARBENES

Robert A. Moss, Michał Fedorynski, Grażyna Kmiecik-Ławrynowicz, and Jacek Terpinski
Department of Chemistry, Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903 USA

3-Bromo-3-Methyldiazirine readily undergoes exchange reactions with MeO^-: F^-, CN^-, or N_3^-. New carbene precursors can thus be prepared.

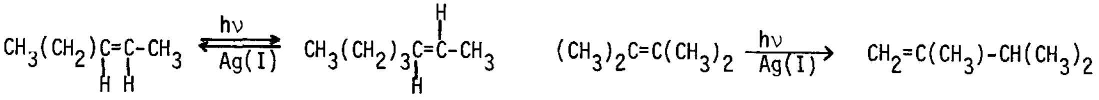


Tet.Lett.,27,24,2711 (1986)

SILVER ION PERTURBATION OF OLEFIN PHOTOCHEMISTRY

Harry Morrison* and Carol Koviak
Department of Chemistry, Purdue University, W. Lafayette, IN 47907 USA

Silver triflate catalysis of olefin phototransformations.

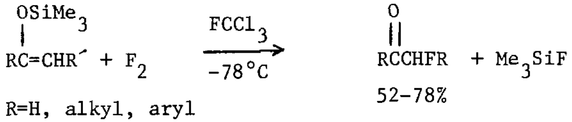


$$\mathrm{CH_3(CH_2)_2\underset{H}{C}{=}\underset{H}{C}\text{-}CH_3 \underset{Ag(I)}{\overset{h\nu}{\rightleftarrows}} CH_3(CH_2)_3\underset{H}{C}{=}\overset{H}{C}\text{-}CH_3 \qquad (CH_3)_2C{=}C(CH_3)_2 \xrightarrow[Ag(I)]{h\nu} CH_2{=}C(CH_3)\text{-}CH(CH_3)_2}$$

Tet.Lett.,27,24,2715 (1986)

PREPARATION OF α-FLUOROALDEHYDES AND α-FLUOROKETONES USING DILUTE FLUORINE

Suzanne T. Purrington,* Nicholas V. Lazaridis, Carl L. Bumgardner*
Department of Chemistry, North Carolina State University, Raleigh, N.C. 27695 USA



$$\mathrm{R\overset{OSiMe_3}{C}{=}CHR' + F_2 \xrightarrow[-78°C]{FCCl_3} R\overset{O}{\overset{\|}{C}}CHFR + Me_3SiF}$$

52-78%

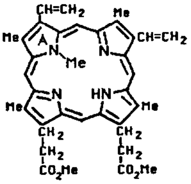
R=H, alkyl, aryl
R´=H, alkyl, aryl

Tet.Lett.,27,24,2717 (1986)

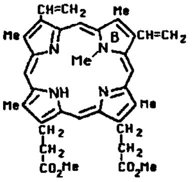
TOTAL SYNTHESES OF N-METHYLPROTOPORPHYRINS-IX

Kevin M. Smith* and Ravindra K. Pandey
Department of Chemistry, University of California, Davis, CA 95616

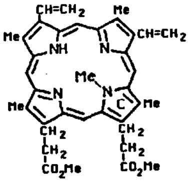
Total syntheses of the four N-methylated isomers (1)-(4) of protoporphyrin-IX dimethyl ester are accomplished from N-methylpyrroles <u>via</u> a,c-biladienes.



(1)



(2)



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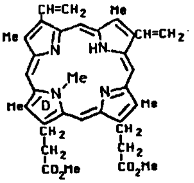


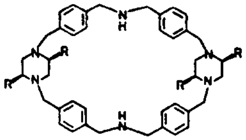
(4)

Tet.Lett.,27,24,2721 (1986)

CYCLOPIPERAZINES: A NEW APPROACH TO CHIRAL MACROCYCLIC RECEPTORS.

Helen L. Larkins and Andrew D. Hamilton*
Department of Chemistry, Princeton University, Princeton, N.J. 08544 USA

Synthesis and preliminary binding properties of macrocyclic receptors containing chiral 2,5-dialkyl piperazine units.

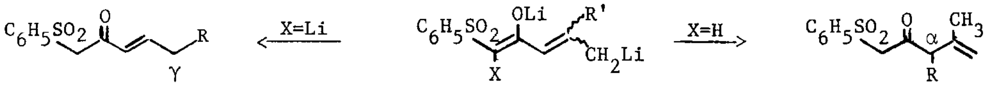


Tet.Lett.,27,24,2725 (1986)

γ-ALKYLATION OF α'-(PHENYLSULFONYL)-α,β-UNSATURATED KETONES: THE TRIANION IMPERATIVE

Peter T. Lansbury*, Ciro J. Spagnuolo and Erich L. Grimm
Department of Chemistry, SUNY at Buffalo, Buffalo, New York 14214 USA

γ-Alkylation of the title compounds with one equivalent of primary alkyl iodides is possible only when both α'-protons are first ionized.

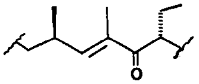


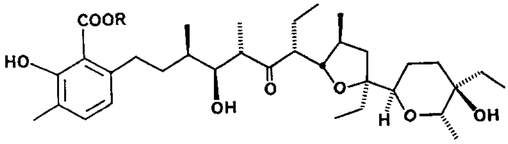
Tet.Lett.,27,24,2727 (1986)

STEREOCHEMICAL STUDIES OF LASALOCID ALDOL EPIMERS. ASSIGNMENTS AND INTERCONVERSIONS.

W. Clark Still, Dale Kempf and Peter Hauck.
Department of Chemistry, Columbia University, New York, NY 10027

Starting from the enone below, the stereochemistry of the aldol epimers was determined by chemical interconversion.



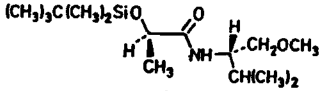


Tet.Lett.,27,24,2731 (1986)

ELECTROPHILIC ASYMMETRIC SYNTHESES OF α-HYDROXY ACIDS

Jerry W. Ludwig, Martin Newcomb and David E. Bergbreiter
Department of Chemistry, Texas A&M University, College Station, TX 77843 USA

Asymmetric syntheses of α-hydroxy carboxamides by alkylation of enolates formed from 2-8 are described (2; ^1R = $-CH_3$, X = -H: 3; ^1R = -H, X = $-OCH_3$: 4; R = $-CH_3$, X = $-OCH_3$: 5; ^2R = $-CH_3$, ^1R = $-C(CH_3)_3$: 6; ^1R = $-Si(CH_3)_2C(CH_3)_3$, ^2R = -H).



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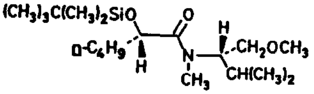

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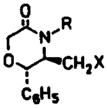
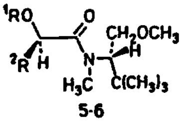


2-4



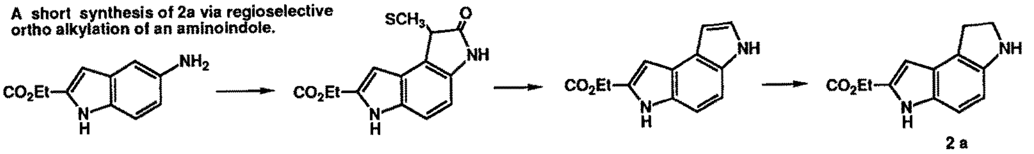
5-6

Tet.Lett.,27,24,2735 (1986)

REGIOSELECTIVE [2,3] SIGMATROPIC REARRANGEMENT TO THE PYRROLO [3,2-e] INDOLE RING SYSTEM OF CC-1065

Martha A. Warpehoski* and V. Susan Bradford
Cancer and Viral Diseases Research, The Upjohn Company, Kalamazoo, MI 49001

A short synthesis of 2a via regioselective ortho alkylation of an aminoindole.

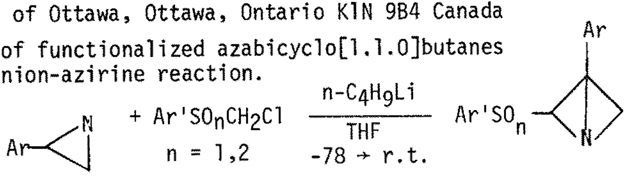


Tet.Lett.,27,24,2739 (1986)

A SIMPLE SYNTHESIS OF AZABICYCLO[1.1.0]BUTANE SULFONES AND SULFOXIDES

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

Synthesis of functionalized azabicyclo[1.1.0]butanes by a carbanion-azirine reaction.

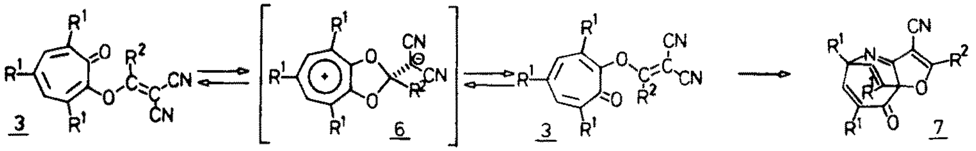


Tet.Lett.,27,24,2743 (1986)

TAUTOMERIC REARRANGEMENTS AND INTRAMOLECULAR DIELS-ALDER REACTIONS OF DICYANOVINYL AND (CYANOIMINO)ALKYL GROUPS IN THE TROPOLONE SERIES

Klaus Hartke*, Wolfgang Richter, Werner Massa and Gerhard Baum
Universität Marburg, Marbacher Weg 6, D-3550 Marburg/Lahn, Germany

Degenerate rearrangement of 3 via 6 and Diels-Alder reaction to 7

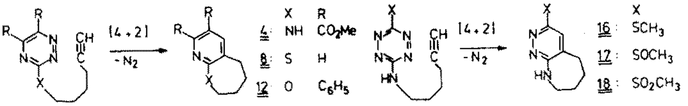


Tet.Lett.,27,24,2747 (1986)

INTRAMOLEKULARE DIELS-ALDER-REAKTIONEN MIT 1,2,4-TRIAZINEN UND 1,2,4,5-TETRAZINEN ZU NEUEN SIEBENRING-ANELLIERTEN PYRIDINEN UND PYRIDAZINEN.

Gunther Seitz*, Sabine Dietrich, Lucia Görge und Joachim Richter
Pharm.-Chem.Inst. der Universität D-3550 Marburg, W.-Germany

A synthesis of novel bicyclic pyridines 4,8,12 and pyridazines 16,17,18 via intramolecular Diels-Alder cycloaddition with inverse electron demand.

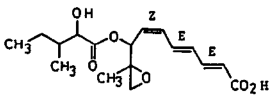


Tet.Lett.,27,24,2753 (1986)

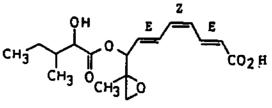
STRUCTURE OF AF-TOXIN II, ONE OF THE HOST-SPECIFIC TOXINS' PRODUCED BY ALTERNARIA ALTERNATA STRAWBERRY PATHOTYPE.

Shin-ichi Nakatsuka,* Kazuo Ueda, Toshio Goto, Mikihiro, Yamamoto, Shoyo Nishimura and Keisuke Kohmoto†; Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan. † Faculty of Agriculture, Tottori University, Tottori 680, Japan.

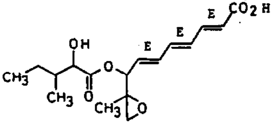
AF-toxin II was a mixture of three stereoisomers, whose structures were determined as 2a, 2b and 2c.



2a AF-toxin IIa



2b AF-toxin IIb



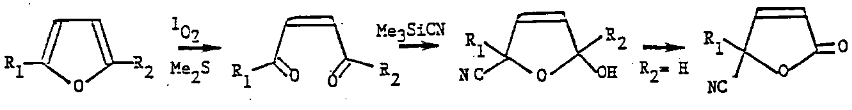
2c AF-toxin IIc

Tet.Lett.,27,24,2757 (1986)

PHOTOOXYGENATION OF FURANS IN THE PRESENCE OF TRIMETHYLSILYL CYANIDE. OXIDATIVE CYANATION OF FURANS

Isao Saito*, Yueh-Hsiung Kuo and Teruo Matsuura
Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan

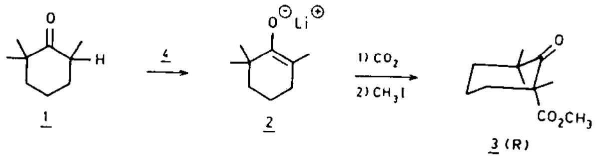
Furans were transformed into 2-cyano-5-hydroxy-2,5-dihydrofurans and 4-cyanobutenolides.



Tet.Lett.,27,24,2767 (1986)

ENANTIOSELECTIVE CARBOXYLATION OF A PROCHIRAL ENOLATE IN THE PRESENCE OF A CHIRAL LITHIUM AMIDE.

H. Hogeveen and W.M.P.B. Menge,
Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands



Low temperature carboxylation of lithium 2,2,6-trimethylcyclohexenolate (2), prepared from ketone 1 and 2 eq. of lithium (S,S)-α,α'-dimethyldibenzylamide (4), afforded after methylation the ester 3 (R) with an e.e. of 67%

Tet.Lett.,27,24,2775 (1986)

SYNTHESIS OF VINCA ALKALOIDS AND RELATED COMPOUNDS XXXII UNUSUAL POLONOVSKI REACTION OF SOME VINCA ALKALOIDS

István Moldvai[a/], András Vedres[a/], Gábor Tóth[b/], Csaba Szántay Jr.[b,c/] and Csaba Szántay[d/]*

a/ Chemical Works of Gedeon Richter Ltd. H-1475, POB 27
b/ NMR Laboratory of the Institute for General and Analytical Chemistry H-1521
c/ On leave from a/
d/ Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525, POB 17, Budapest, Hungary

In the course of the Polonovski reaction of some indole alkaloids a new type of dimerization has been found.