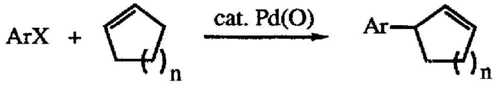
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 30,2603(1989)

IMPROVED PROCEDURES FOR THE PALLADIUM-CATALYZED INTERMOLECULAR ARYLATION OF CYCLIC ALKENES

Richard C. Larock,* William H. Gong and Bruce E. Baker
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Improved procedures for the palladium-catalyzed, intermolecular, allylic cross-coupling of aryl halides and cyclic alkenes inhibit double-bond isomerization and accommodate many important functional groups.

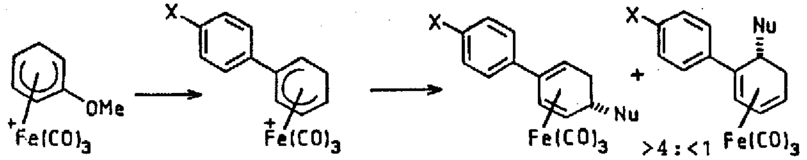


Tetrahedron Lett. 30,2607(1989)

TRANSITION METAL MEDIATED ORGANIC SYNTHESIS, Part 11: 2-ARYL SUBSTITUENTS: NEW DIRECTING GROUPS IN CYCLOHEXADIENYL Π-COMPLEXES

David A. Owen and G. Richard Stephenson, Harry Finch, and Stephen Swanson

Regioselective formation and alkylation of tricarbonyl(η^5-2-arylcyclohexadienyl)iron(1+) salts provides a new route to intermediates to 5-substituted 2-arylcyclohexadienes by preferential nucleophile addition to C-5 of the dienyl system.

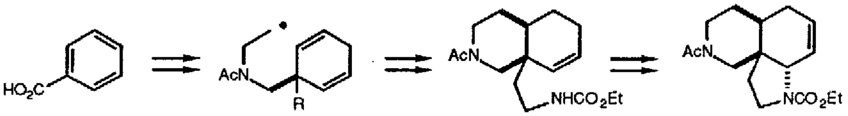


Tetrahedron Lett. 30,2611(1989)

SYNTHESIS OF THE PYRROLO[2,3-i]ISOQUINOLINE SUBSTRUCTURE OF THE MANZAMINE FAMILY OF ALKALOIDS

David J. Hart* and Jeffrey A. McKinney
Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

The title ring system was prepared from benzoic acid using a reductive alkylation / free radical cyclization / electrophile initiated cyclization reaction sequence.

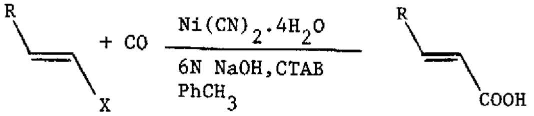


Tetrahedron Lett. 30,2615(1989)

STEREOSPECIFIC NICKEL AND PHASE TRANSFER CATALYZED CARBONYLATION OF VINYL BROMIDES AND CHLORIDES

H. Alper* and I. Amer, Dept. of Chemistry, University of Ottawa, Ottawa, Canda K1N 6N5
G. Vasapollo, Dept. of Chemistry, University of Bari, 70126, Bari, Italy

Vinyl bromides and chlorides are carbonylated to acids using $Ni(CN)_2$ as the catalyst.

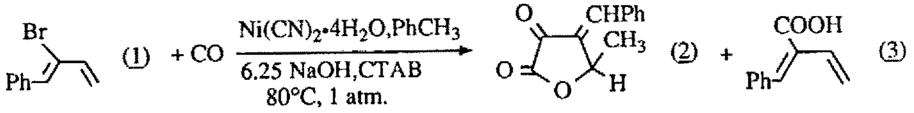


Tetrahedron Lett. 30, 2617 (1989

NOVEL NICKEL CATALYZED CONVERSION OF 2-BROMO-1-PHENYL-1,3-BUTADIENE TO AN α KETO LACTONE. AN EXAMPLE OF DOUBLE CARBONYLATION OF A HALODIENE

Alper*, Dept. of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5
Vasapollo, Dept. of Chemistry, University of Bari, 70126 Bari, Italy

Carbonylation of the bromodiene 1, affords the α-keto lactone (2) in 60% yield and a dienoic acid (3) in 15% yield.

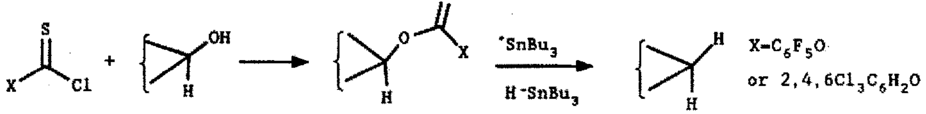


Tetrahedron Lett. 30, 2619 (1989)

IMPROVED METHODS FOR THE RADICAL DEOXYGENATION OF SECONDARY ALCOHOLS

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

Two new reagents, 2,4,6-trichlorophenoxythiocarbonyl chloride and pentafluorophenoxythiocarbonyl chloride, have been synthesized and used in the fast, efficient deoxygenation of secondary alcohols.

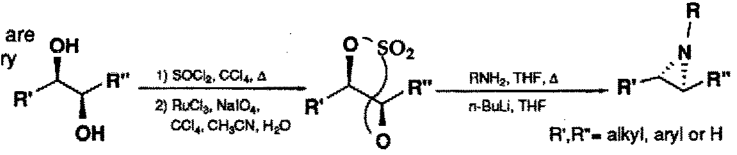


Tetrahedron Lett. 30, 2623 (1989)

ONE POT SYNTHESIS OF HOMOCHIRAL AZIRIDINES AND AMINOALCOHOLS FROM HOMOCHIRAL 1,2-CYCLIC SULFATES

B. Bhushan Lohray and K. Barry Sharpless*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

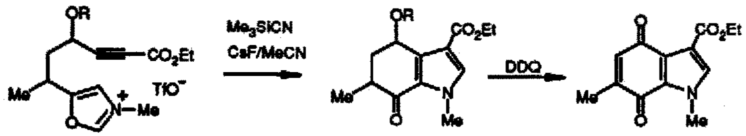
N-Substituted aziridines and aminoalcohols are efficiently prepared by the reaction of primary amines with homochiral 1,2-cyclic sulfates.



Tetrahedron Lett. 30, 2627 (1989)

INDOLOQUINONES FROM AZOMETHINE YLIDES VIA THE 4-OXAZOLINE ROUTE

Edwin Vedejs and Scott L. Dax, Chemistry Department, University of Wisconsin, Madison, Wis. 53706.

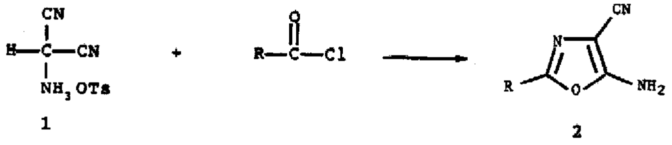


Tetrahedron Lett. 30, 2631 (1989)

PREPARATION OF 2-ALKYL- AND 2-ARYL-5-AMINO-4-CYANO-1,3-OXAZOLES

Fillmore Freeman* and Darrick S.H.L. Kim
Department of Chemistry, University of California, Irvine, Irvine, California 92717

Aminopropanedinitrile p-toluenesulfonate reacts with acid chlorides to give 2-alkyl- and 2-aryl-5-amino-4-cyano-1,3-oxazoles in good to excellent yields.

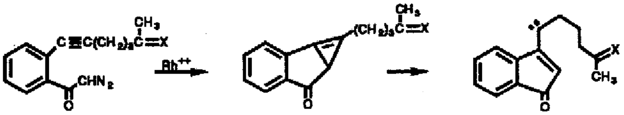


Tetrahedron Lett. 30, 2633 (1989)

CYCLOALKENONE FORMATION BY THE INTRAMOLECULAR ADDITION OF A α-DIAZOKETONE TO AN ACETYLENIC PI-BOND

Albert Padwa, Keith E. Krumpe and Lin Zhi*
Department of Chemistry, Emory University, Atlanta, GA 30322 USA

Treatment of several ortho alkynyl substituted α-diazoacetophenone derivatives with rhodium (II) acetate results in intramolecular addition to the acetylenic pi-bond to give a transient cyclopropene which spontaneously rearranges to a vinyl carbene intermediate.

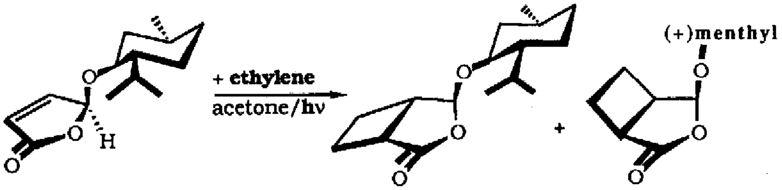


Tetrahedron Lett. 30, 2637 (1989)

CHIRAL INDUCTION IN PHOTOCHEMICAL REACTIONS XII
SYNTHESIS OF CHIRAL CYCLOBUTANE DERIVATIVES FROM (+)-5-MENTHYLOXY-2-[5H]-FURANONE AND ETHYLENE

Norbert Hoffmann, Hans-Dieter Scharf*, Jan Runsink, Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Str. 1, 5100 Aachen, F.R.G.

The temperature dependence of the diastereoselectivity in the presented reaction as well as the isolation of both diastereomers are described.

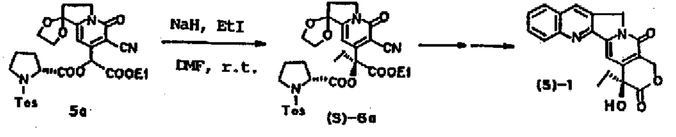


Tetrahedron Lett. 30, 2639 (1989)

ASYMMETRIC SYNTHESIS OF (S)-CAMPTOTHECIN

Akio Ejima, Hirofumi Terasawa, Masamichi Sugimori, and Hiroaki Tagawa*
Research Institute, Daiichi Seiyaku Co., Ltd., Kitakasai, Edogawa-ku, Tokyo 134, Japan

The title compound was synthesized via a novel diastereoselective ethylation process from indolizine derivative 5a bearing N-tosyl-(R)-proline.



Tetrahedron Lett. 30,2641(1989)

USE OF AN ALLYLIC ANCHOR GROUP AND OF ITS PALLADIUM CATALYZED HYDROSTANNOLYTIC CLEAVAGE IN THE SOLID PHASE SYNTHESIS OF PROTECTED PEPTIDE FRAGMENTS

F.GUIBE, O.DANGLES and G.BALAVOINE, Institut de Chimie Moléculaire d'Orsay, Laboratoire de Chimie Organique des Eléments de Transition, associé au CNRS, Bât 420 91405 ORSAY Cedex (France).
A.LOFFET, Propeptide, BP 12, 91710 VERT LE PETIT (France).

Protected peptide fragments have been synthetized on aminomethyl resin using the allylic handle O-CH_2CH=CH-CH_2-O-CH_2-CO- and Boc α-amino protection. The catalytic hydrostannolytic cleavage of the peptide chain from the resin occurs under especially mild conditions.

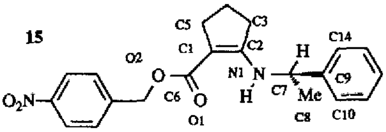
Tetrahedron Lett. 30,2645(1989)

THE ASYMMETRIC MICHAEL PROCESS INVOLVING CHIRAL IMINES : THE DIASTEREOFACIAL DIFFERENTIATION ASPECT.

d'Angelo J., Revial G., Guingant A., ESPCI, Paris
Riche C., Chiaroni A., CNRS, Gif-sur-Yvette (France)

A mechanism for the diastereofacial differentiation in the title reaction is proposed on the basis of the variation of the chiral auxiliary amines and of the examination of the crystal structure of enamino-ester **15**.

15



Tetrahedron Lett. 30,2649(1989)

N-ACETOXY-N-ALKOXYAMIDES - A NEW CLASS OF NITRENIUM ION PRECURSORS WHICH ARE MUTAGENIC.

Robert G. Gerdes, Stephen A.Glover*, José F. ten Have and Colleen A.Rowbottom
Department of Chemistry, University of New England, Armidale,N.S.W.2351, Australia

N-chloro-O-alkylbenzohydroxamates (11) react with silver acetate in ether giving N-acetoxy-N-alkoxybenzamides (14) which, have been shown to be mutagenic in the Ames test.

$$\underset{(11)}{\mathrm{PhCON(Cl)OR}} \xrightarrow{\mathrm{AgOAc/Et_2O}} \underset{(14)}{\mathrm{PhCON(OAc)OR}}$$

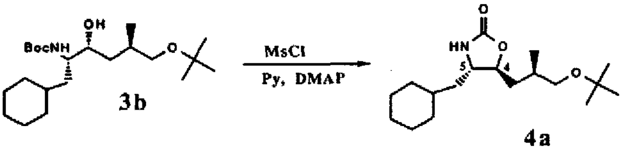
(a) R=Et [98%]
(b) R=n-Bu [82%]
(c) R=n-Oct [69%]
(d) R=Bz [89%]

Tetrahedron Lett. 30,2653(1989)

SYNTHESIS OF A NEW SULFUR-CONTAINING DIPEPTIDE ANALOGUE

J. Olle Karlsson*, Anita Lundblad, Bengt Malm, Ingemar Nilsson, Toivo Nitenberg, Ingemar Starke, Henrik Sörensen, and Christer Westerlund
Department of Organic Chemistry, AB Hässle, S-431 83 Mölndal, Sweden

A sulfur-containing Cha-Ala isostere for renin inhibitors has been synthesized.
The stereochemistry of the carbinol carbon of 3b was inverted by treatment with methanesulfonyl chloride in pyridine leading to 4a.

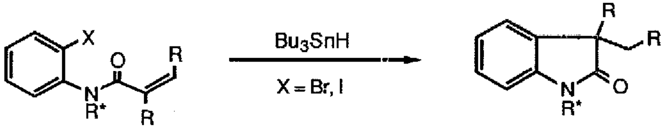


Tetrahedron Lett. 30, 2657 (1989)

CHIRAL INDUCTION IN ARYL RADICAL CYCLISATIONS

Keith Jones* and Clive McCarthy, Department of Chemistry, King's College London, Strand, London WC2R 2LS. U.K.

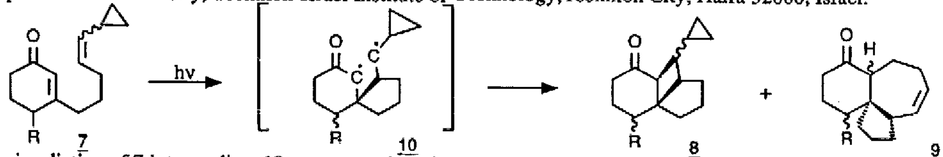
The diastereolectivity of the cyclisation of aryl radicals generated from the o-haloacryloylanilides (1) carrying a chiral group (R) on the nitrogen has been investigated:*



Tetrahedron Lett. 30, 2661 (1989)

TRAPPING OF 1,4-DIRADICAL INTERMEDIATE IN INTRAMOLECULAR [2+2] PHOTOCYCLOADDITION

D. Becker*, N. Haddad and Y. Sahali.
Department of Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa 32000, Israel.

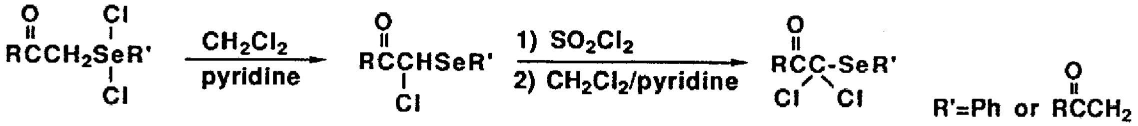


On irradiation of 7 intermediate 10 was trapped to give 9 in 43%yield. For the first time a 1,4-diradical was trapped in intramolecular [2+2] photocycloaddition of olefin to cyclohexenone.

Tetrahedron Lett. 30, 2665 (1989)

PUMMERER-LIKE REACTION OF SELENIUM(IV)-DICHLORIDES. SYNTHESIS OF α-CHLORO-α-PHENYLSELENENYLKETONES AND α,α-DICHLORO-α-PHENYLSELENENYLKETONES

Lars Engman,* Joachim Persson and Ulf Tilstam
Department of Organic Chemistry, Royal Institute of Technology
S-100 44 Stockholm, Sweden



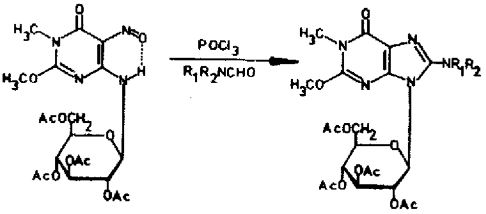
$$\mathrm{R\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Se}}R'} \xrightarrow[\mathrm{pyridine}]{\mathrm{CH_2Cl_2}} \mathrm{R\overset{\overset{O}{\|}}{C}\underset{\underset{Cl}{|}}{C}HSeR'} \xrightarrow[\mathrm{2)\ CH_2Cl_2/pyridine}]{\mathrm{1)\ SO_2Cl_2}} \mathrm{R\overset{\overset{O}{\|}}{C}\underset{Cl\ \ Cl}{C}\text{-}SeR'} \qquad \mathrm{R'=Ph\ or\ R\overset{\overset{O}{\|}}{C}CH_2}$$

Tetrahedron Lett. 30, 2669 (1989)

ON THE REACTION OF 6-GLYCOSYLAMINO-5-NITROSOPYRIMIDINES WITH VILSMEIER-TYPE REAGENTS. SYNTHESIS OF 8-AMINO-9-GLYCOSYLPURINES

M.Melguizo, M.Nogueras, A.Sánchez and Mª.L.Quijano
Dpt. Organic Chemistry. University College of Jaén
University of Granada. 23071-Jaén. Spain

Starting from 6-glycosylamino-5-nitrosopyrimidines, 8-amino(and methylamino)-9-glycosylpurines are obtained by reaction with $POCl_3$/Formamides

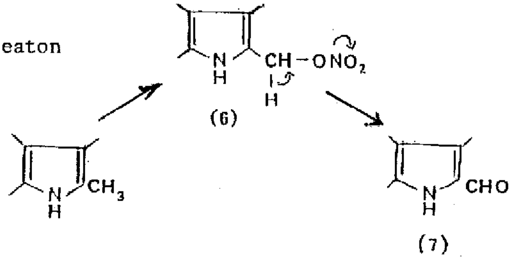


Tetrahedron Lett. 30,2673(1989)

REACTIONS ON SOLID SUPPORTS PART V[1] : THE MECHANISM OF OXIDATION OF α-METHYL PYRROLES TO α-FORMYL PYRROLES BY THALLIUM NITRATE ON CLAY

Anthony H. Jackson,* K.R. Nagaraja Rao and E. Smeaton
School of Chemistry & Applied Chemistry,
University of Wales College of Cardiff,
P.O. Box 912, Cardiff CF1 3TB, Wales, UK

Evidence is presented for the involvement of an intermediate nitrate ester in the thallium nitrate oxidation of α-methyl pyrroles to α-formyl pyrroles.

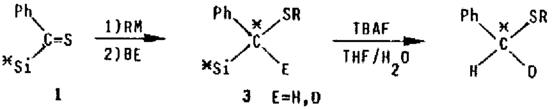


Tetrahedron Lett. 30,2677(1989)

CHIRAL SILICON IN ASYMMETRIC SYNTHESIS. ADDITION OF ORGANOMETALLIC REAGENTS TO A SILYL THIONE CHIRAL AT SILICON.

Bianca F. Bonini, Gaetano Maccagnani, Stefano Masiero, Germana Mazzanti and Paolo Zani.
Dipartimento di Chimica Organica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

α-Silylsulphides 3 are obtained, with medium to good levels of stereoselection, in the reaction of 1 with organometallic reagents RM (lithium and Grignard derivatives). The asymmetry induced at the α-carbon is retained in the subsequent desilylation of the deuteriosulphide 3 (E=D).



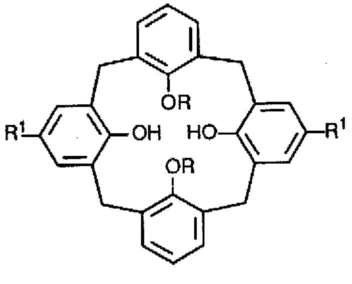
*Si=(α-Napht., Ph, MeSi-)

Tetrahedron Lett. 30,2681(1989)

SELECTIVE FUNCTIONALIZATION OF CALIX[4]ARENES AT THE UPPER RIM

J.-D. van Loon[a], A. Arduini[b], W. Verboom[a], R. Ungaro[b], G.J. van Hummel[a], S. Harkema[a], D.N. Reinhoudt[*a]

Laboratories of Organic Chemistry and Chemical Physics[a], University of Twente, The Netherlands and the Institute of Organic Chemistry[b], University of Parma, Italy



e.g. R = Alkyl, Allyl, Benzyl

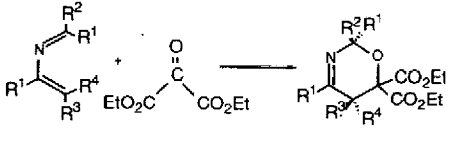
R^1 = Br, NO_2, CH=O, CH_2Cl, $CH_2N(CH_3)_2$

Tetrahedron Lett. 30,2685(1989)

DIELS-ALDER REACTION OF UNACTIVATED 2-AZA-1,3-DIENES WITH DIETHYL KETO MALONATE: A CARBON DIOXIDE EQUIVALENT

José Barluenga,* Francisco J. González, and Santos Fustero.
Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, 33071-Oviedo, Spain.

A synthesis of 6,6-bis(ethoxycarbonil)-5,6-dihydro-2*H*-1,3-oxazines by Diels-Alder reaction of unactivated 2-aza-1,3-dienes with diethylketomalonate is described.

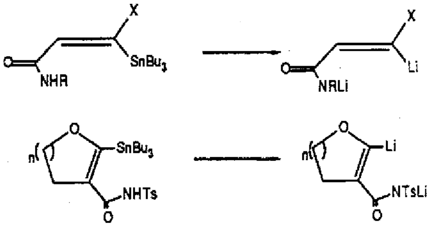


Tetrahedron Lett. 30, 2693 (1989)

THE USE OF ß-(TRI-N-BUTYLSTANNYL)ACRYLAMIDES AS ß-LITHIOACRYLAMIDE SYNTHONS.

H. Imanieh,[a] D. MacLeod,[a] P. Quayle,[a]* and G. M. Davies.[b]
[a] Department of Chemistry. Victoria University of Manchester. Manchester M13 9PL.
[b] ICI Pharmaceuticals. Alderley Park. Macclesfield. SK10 4TG.

Reaction of ß-(tri-n-butylstannyl)acrylamides with n-BuLi at low temperatures affords stable ß-acylvinyl anions which undergo alkylation reactions with a variety of electrophiles.

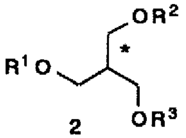


Tetrahedron Lett. 30, 2697 (1989)

ENZYMES AS SELECTIVE REAGENTS IN ORGANIC SYNTHESIS: ENANTIOSELECTIVE PREPARATION OF "ASYMMETRIZED *tris* (HYDROXYMETHYL)METHANE"

Giuseppe Guanti,* Luca Banfi, and Enrica Narisano, Istituto di Chimica Organica e C.N.R., Centro di Studio sui Diariloidi, corso Europa 26, 16132 Genova (Italy).

A new chiral building block, that is 2, where $R^1 \neq R^2 \neq R^3$, was prepared in high enantiomeric excess. The key step is a PPL catalysed dissymmetrization of a prochiral diacetate.



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Tetrahedron Lett. 30, 2699 (1989)

PALLADIUM-CATALYZED REACTIONS OF TRIALKYLSTANNYL PHENYL SULFIDES WITH ALKENYL BROMIDES. A NEW DIASTEREOSELECTIVE SYNTHESIS OF (E)-1-ALKENYL PHENYL SULFIDES.

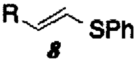
Adriano Carpita, Renzo Rossi(*), and Barbara Scamuzzi.
Dipartimento di Chimica e Chimica Industriale - Università di PISA - Via Risorgimento 35 - 56100 PISA - ITALY.

(E)-1-Alkenyl phenyl sulfides, (E)-8, have been diastereoselectively synthesized by Pd-catalyzed reactions of (E)/(Z)-7 with 1.

$R^1_3Sn-SPh$

1

7

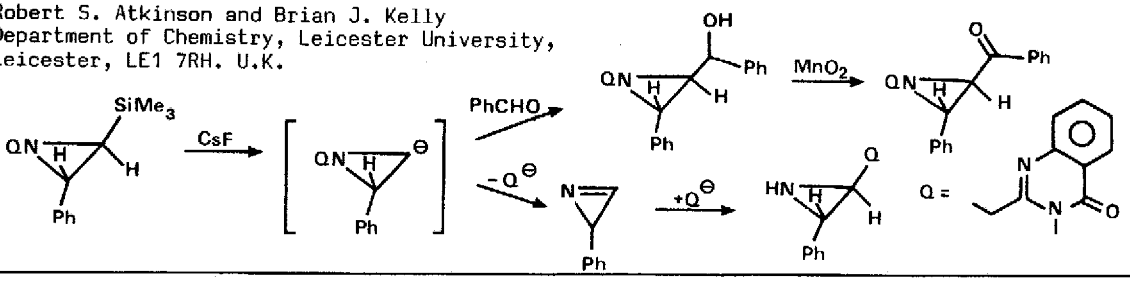


8

AZIRIDINE-AZIRINE TRANSFORMATION BY 1,2-ELIMINATION <u>via</u> AN AZIRIDINYL CARBANION INTERMEDIATE

Tetrahedron Lett. 30, 2703 (1989)

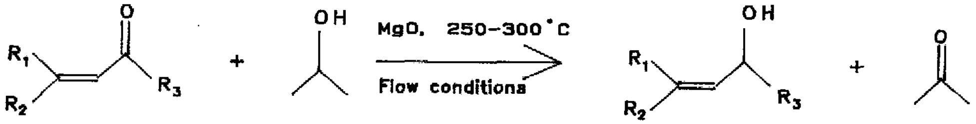
Robert S. Atkinson and Brian J. Kelly
Department of Chemistry, Leicester University,
Leicester, LE1 7RH. U.K.



Tetrahedron Lett. 30, 2705 (1989)

A MEERWEIN–PONNDORF–VERLEY TYPE REDUCTION OF α,β UNSATURATED KETONES TO ALLYLIC ALCOHOLS CATALYZED BY MgO.

J.Kaspar, M.Graziani, Dipartimento di Scienze Chimiche, Piazzale Europa 1, 34127 Trieste, Italy
A.Trovarelli, Istituto di Chimica, Facoltà di Ingegneria, Viale Ungheria 43, 33100 Udine, Italy
M.Lenarda, Dipartimento di Chimica, Calle Larga S.Marta 2137, 30123 Venezia, Italy

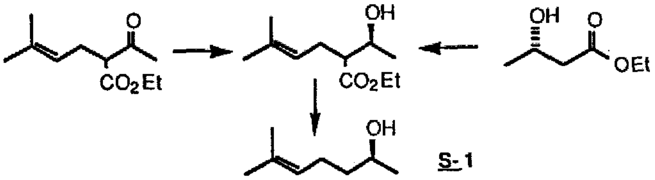


Tetrahedron Lett. 30, 2707 (1989)

A USEFUL METHOD FOR PREPARING OPTICALLY ACTIVE SECONDARY ALCOHOLS: A SHORT ENANTIOSPECIFIC SYNTHESIS OF (R)- AND (S)- SULCATOL.

Carlos M. Afonso, M. Teresa Barros, Licio Godinho and Christopher D. Maycock.
Faculdade de Ciências, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal.

The antipodes of sulcatol **1** have been prepared from readily available starting materials. A key step in the strategy is the use of the Barton method of decarboxylation.



Tetrahedron Lett. 30, 2709 (1989)

SUBSTITUENT INDUCED FINE-TUNING OF NOVEL CATIONIC REARRANGEMENTS IN [3.3.3] PROPELLANIC SYSTEMS

G. Mehta and D. Subrahmanyam, School of Chemistry, University of Hyderabad, Hyderabad - 500 134, India.

Summary: Profound effect of alkyl substituents at C(4) & C(8) positions on the course of cationic rearrangements of [3.3.3] propellan-3-ones has been observed.