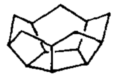
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 27, 5315 (1986)

AB-INITIO HEATS OF FORMATION OF MEDIUM-SIZED HYDROCARBONS. 6. PERISTYLANE

Jerome M. Schulman* and Raymond L. Disch
Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367

Peristylane (I) is shown by ab-initio and molecular mechanics calculations to be unstable with respect to methylene breathing motions about C_{5v} symmetry. Its heat of formation is estimated to be ca. 0.5 kcal/mol.



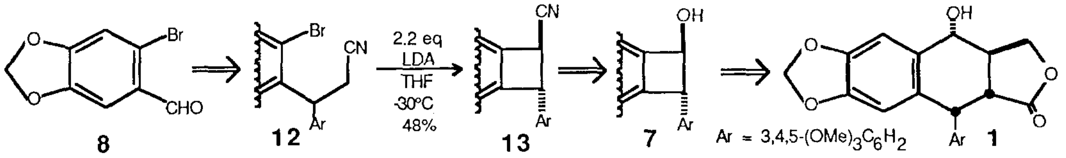
I

Tetrahedron Lett. 27, 5319 (1986)

A DIRECT SYNTHESIS OF TRANS 2-ARYLBENZOCYCLOBUTENOL, A POTENTIAL INTERMEDIATE FOR PODOPHYLLOTOXIN SYNTHESIS: USE OF LDA FOR BENZYNE FORMATION AND TRAPPING

Michael E. Jung and Gregory T. Lowen, Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90024

Treatment of m-alkoxyaryl bromides such as **12** with LDA in THF gives the corresponding aryne which can be trapped intramolecularly to produce the nitrile, **13**, the precursor of a trans arylbenzocyclobutenol **7**, potentially useful for the synthesis of podophyllotoxin **1**.

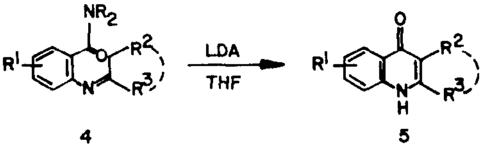


Tetrahedron Lett. 27, 5323 (1986)

SYNTHETIC CONNECTIONS TO THE AROMATIC DIRECTED METALATION REACTION. A MODIFIED von NIEMENTOWSKI QUINOLINE SYNTHESIS FROM ANTHRANILAMIDES

R.J. Chong, M.A. Siddiqui and V. Snieckus*
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Canada N2L 3G1

A general quinoline synthesis, 4 → 5 from directed ortho metalation-derived anthranilamides is described.

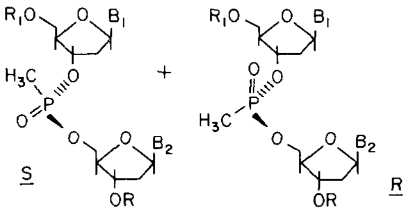


Tetrahedron Lett. 27, 5327 (1986)

SEPARATION OF DIASTEREOMERS OF METHYLPHOSPHONATE DINUCLEOTIDES

S.B. Katti and Kan Agarwal
Departments of Chemistry, and Biochemistry and Molecular Biology
The University of Chicago, Chicago, IL 60637

A chiral derivatizing agent, l-menthyl chloroformate, has been used as a 3'-OH blocking group to facilitate the resolution of diastereomers of methylphosphonate dinucleotides by silica gel column chromatography.

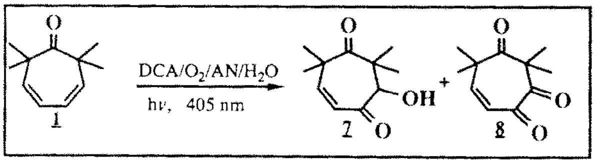


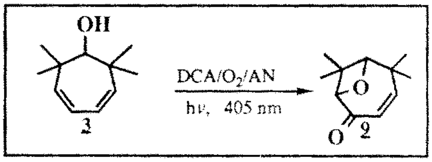
Tetrahedron Lett. 27, 5331 (1986)

ELECTRON TRANSFER PHOTOOXYGENATION OF 3,5-CYCLOHEPTADIENONES AND RELATED COMPOUNDS

W.A Wilczak and D.I. Schuster*, Department of Chemistry, New York University, N.Y., N.Y. 10003

Photooxygenation of 1 and the derived methyl ether under electron-transfer conditions in presence of water results in formation of hydroperoxide-derived products. Methanol also traps the radical cation of 1. In acetonitrile (AN), alcohol 3 gives a product suggestive of intramolecular capture of a diene radical cation.



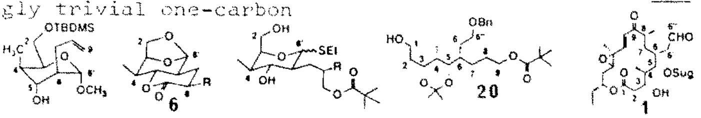


Tetrahedron Lett. 27, 5335 (1986)

SYNTHETIC STUDIES RELATING TO THE C1-C9 "EASTERN" HALF OF ROSARAMICIN, 1

Ustun Sunay and Bert Fraser-Reid*
Department of Chemistry, Duke University, Durham, NC 27706, USA

A "pyranosidic homologation" approach to the "eastern half" of rosaramicin, <u>via</u> 6 is described. The seemingly trivial one-carbon displacements for introducing C1 and C6'' of 20 could not be achieved. These have been obviated.

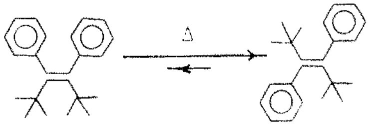


Tetrahedron Lett. 27, 5339 (1986)

PHOTOCHEMICAL SYNTHESIS AND THERMAL CHEMISTRY OF Z-2,2,5,5-TETRAMETHYL-3,4-DIPHENYLHEX-3-ENE, A STERICALLY CONGESTED STILBENE[1]

Dieter Lenoir*,#, James E. Gano*,+ and Jerome McTague+
#Department of Ecological Chemistry, University of Bayreuth, D-8580 Bayreuth, Germany: +Department of Chemistry, University of Toledo, Toledo, Ohio, USA, 43606

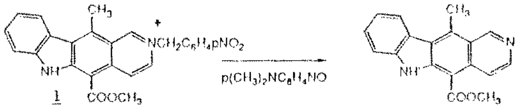
Z-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene isomerized to its Z-isomer with an unusually low rotational barrier, $\Delta H^{\ddagger} = 31.2 \pm 1.3$ and $\Delta S^{\ddagger} = -4.8 \pm 3.1$.



Tetrahedron Lett. 27, 5343 (1986)

SYNTHESIS OF 5-HYDROXYMETHYL-6-PYRIDO[4,3-b]-CARBAZOLE AND 5-FORMYL-11-METHYL-6H-PYRIDO[4,3-b]-CARBAZOLE (17-OXOELLIPTICINE

Bruce S. Ross and Sydney Archer*
Department of Chemistry, Cogswell Laboratory, Rensselaer Polytechnic Institute, Troy, NY 12180-3590



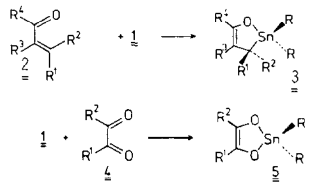
The title compounds were synthesized by an adaptation of the Weller ellipticine synthesis, the key step of which was the debenzylation of 1 at 25°C with the aid of p-nitrosodimethylaniline (Kröhnke aldehyde synthesis).

Tetrahedron Lett. 27,5347(1986)

ADDITIONS OF A STABLE STANNYLENE R_2Sn TO VINYL CARBONYL COMPOUNDS AND 1,2-DIKETONES

Knut Hillner and Wilhelm P. Neumann
Lehrstuhl für Organische Chemie I der Universität,
D-4600 Dortmund 50, FRG

1,4-Cycloadditions of the stable stannylene R_2Sn 1 ($R = (Me_3Si)_2CH$) with conjugated α,β-unsaturated vinyl carbonyl compounds 2 and 1,2-diketones 4 give the corresponding heterocyclopentenes 3 or, resp., 5.

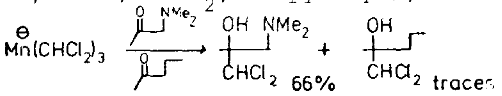


Tetrahedron Lett. 27,5351(1986)

E-DON-GRUPPIERUNGEN ORGANISCHER VERBINDUNGEN ALS BEVORZUGTE ANGRIFFSSTELLEN FÜR NUCLEOPHILE, ALKYLIERENDE ÜBERGANGSMETALLREAGENZIEN; EINE ERSTE ÜBERSICHT

T. Kauffmann*, K. Abel, W. Bonrath, M. Kolb, T. Möller, C. Pahde, S. Raedeker, M. Robert, M. Wensing und B. Wichmann; Organisch-Chemisches Institut der Universität, Orléans-Ring 23, D-4400 Münster, Bundesrepublik Deutschland

Groupings, consisting of an electrophilic group (keto group, oxirane group) and a neighbouring electron donor group (-OH, -OMe, $-NMe_2$, -2-pyridyl), proved to be especially attractive for various alkylating organotransition metal reagents (Ti, Hf, V, Cr, Cr, Mn, Cu).

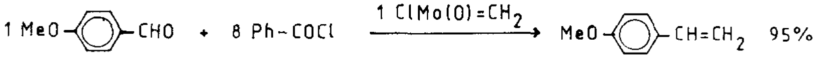


Tetrahedron Lett. 27,5355(1986)

ÜBERRASCHENDE RESISTENZ VON CARBONSÄURECHLORIDEN UND -ANHYDRIDEN GEGEN ÜBERGANGSMETALLHALTIGE ALKYLIERUNGS- UND CARBONYLOLEFINIERUNGSREAGENZIEN

T. Kauffmann*, T. Abel, C. Beirich, G. Kieper, C. Pahde, M. Schreer, E. Toliopoulos und R. Wieschollek; Organisch-Chemisches Institut der Universität, Orléans-Ring 23, D-4400 Münster, Bundesrepublik Deutschland

Carboxylic acid chlorides proved to be resistent towards alkyl transition metal complexes (Cr, Ti, Zr, Hf, Nb, Ta, Ce, Sm) and molybdenum carbene complexes, which are able to methylate or carbonylolefinate aldehydes.

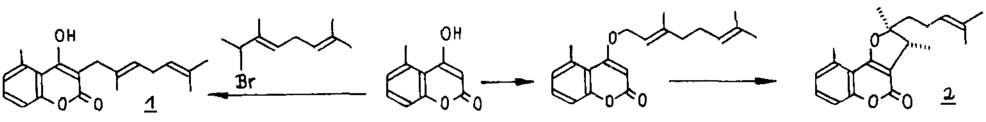


Tetrahedron Lett. 27,5359(1986)

SYNTHESIS OF BRACHYCOUMARIN AND CYCLOBRACHYCOUMARIN

F. Bohlmann and A. Steinmeyer
Institute of Organic Chemistry, TU Berlin , D-1000 Berlin 12, C 3

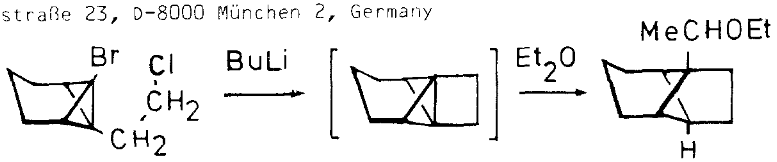
A synthesis of brachycoumarin (1) and cyclobrachycoumarin (2) via 5-methyl-4-hydroxy coumarin



Tetrahedron Lett. 27,5363(1986)

TETRACYCLO[5.2.0.0^{1,6}.0^{2,7}]NONANE, A [2.1.1]PROPELLANE DERIVATIVE AS A REACTION INTERMEDIATE

Jan Morf and Günter Szeimies, Institut für Organische Chemie der Universität München
Karlstraße 23, D-8000 München 2, Germany

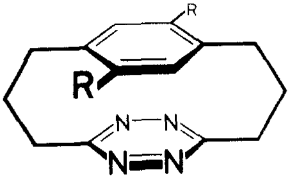


Tetrahedron Lett. 27,5367(1986)

5,6,8,9-TETRAAZA[3.3]PARACYCLOPHANE, TRANSANNULAR EFFECT ON THE n→π* TRANSITION

Franz A. Neugebauer* and H. Fischer
Abteilung Organische Chemie
Max-Planck-Institut für medizinische Forschung
Jahnstrasse 29, D-6900 Heidelberg, West Germany

The [3.3]paracyclophanes 3a and 3b were prepared; transannular interaction leads to a hypsochromic shift of the first n→π* band.



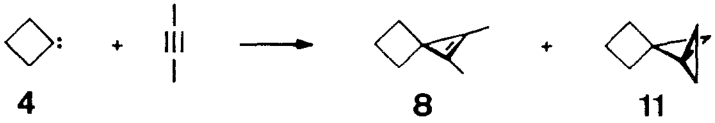
	R
3a	H
3b	OCH_3

Tetrahedron Lett. 27,5371(1986)

1,2-DIMETHYLSPIRO[2.3]HEX-1-ENE BY ADDITION OF CYCLOBUTYLIDENE TO 2-BUTYNE

Udo H. Brinker and Jürgen Weber*
Fakultät für Chemie der Ruhr-Universität, 4630 Bochum 1, Federal Republic of Germany

By C_4+C_2-coupling of cyclobutylidene (4) and 2-butyne the spiro[2.3]-system 8 is constructed. 4, also adds to methylenecyclopropane, its intramolecular reaction product, to give the novel dispiro[2.1.3.0]octane 11.

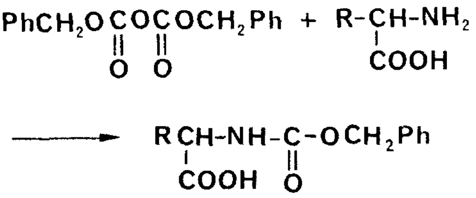


Tetrahedron Lett. 27,5375(1986)

SYNTHESIS AND USE OF DIBENZYLPYROCARBONATE : PREPARATION OF DIPEPTIDE FREE N-BENZYLOXYCARBONYL GLYCINE.

Gérard Sennyey, Gérard Barcelo
and Jean-Pierre Senet
SNPE, Centre de Recherche du Bouchet.
91710-Vert-le-Petit, France.

Dibenzylpyrocarbonate was prepared and reacted with amino acids. The quantity of dipeptides formed was evaluated.



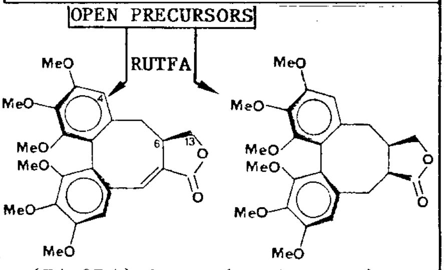
$$PhCH_2O\underset{\underset{O}{\|}}{C}O\underset{\underset{O}{\|}}{C}OCH_2Ph + R\text{-}\underset{\underset{COOH}{|}}{CH}\text{-}NH_2 \longrightarrow R\underset{\underset{COOH}{|}}{CH}\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}OCH_2Ph$$

Tetrahedron Lett. 27,5377(1986)

RUTHENIUM(IV) TETRAKIS(TRIFLUOROACETATE), A NEW OXIDIZING AGENT. II. A NEW ACCESS TO SCHIZANDRINS SKELETON USING BIARYL COUPLING OF CIS-SUBSTITUTED BUTANOLIDES

Y. Landais, A. Lebrun, and J.P. Robin*
Université du Maine, Rte de Laval, 72017 Le Mans, France

The use of the title reagent **-RUTFA-** was applied to the first stereospecific synthesis of the bridged biaryl lactones **1** and **2**, from the corresponding *cis*-dibenzylbutanolide (*cis*-cordigerine) and olefinic lignans (savinin-type), respectively. Reduction of **2** afforded deoxyschizandrin and formation of gomisins K was established.



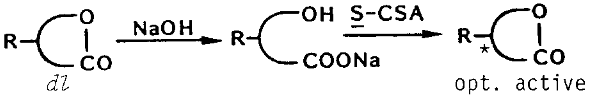
(P*,6R*)-**1** (P*,6R*,7S*)-**2**

Tetrahedron Lett. 27,5381(1986)

KINETIC RESOLUTION OF LACTONES BY ENANTIOSELECTIVE PROTONATION OF THE CORRESPONDING CARBOXYLATE WITH A CHIRAL ACID

Kaoru Fuji,* Manabu Node, and Makoto Murata
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
Shunji Terada and Keiji Hashimoto
Kyoto College of Pharmacy, Yamashina, Kyoto 607, Japan

Kinetic resolution of dl-lactones was performed through the hydrolysis followed by the partial neutralization with (1S)-(+)-10-camphorsulfonic acid in ethanol.



Tetrahedron Lett. 27,5383(1986)

NICKELOCENE/LITHIUM ALUMINIUM HYDRIDE--A "HOMOGENEOUS RANEY NICKEL" FOR CATALYTIC HYDROGENATION

Kin Man Ho, Man-Chor Chan and Tien-Yau Luh*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

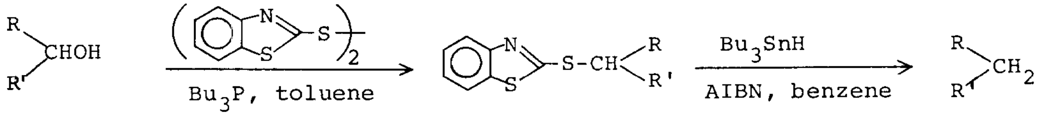
The title reagent is served as the homogeneous catalyst for the hydrogenation.

$$RCH{=}CHR' \xrightarrow[Cp_2Ni/LiAlH_4]{H_2} RCH_2CH_2R'$$

Tetrahedron Lett. 27,5385(1986)

A RADICAL DEOXYGENATION OF SECONDARY ALCOHOLS TO HYDROCARBONS BY USE OF TRIBUTYLTIN HYDRIDE

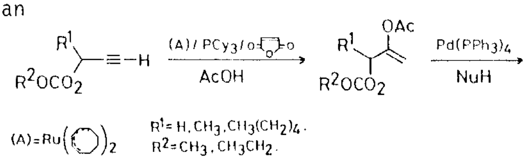
Yoshihiko Watanabe*, Takumi Araki, Yoshio Ueno, and Takeshi Endo
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan



Tetrahedron Lett. 27, 5389 (1986)

RUTHENIUM-CATALYZED SYNTHESIS OF 2-ACETOXYALLYL CARBONATES: A SYNTHON FOR PALLADIUM-CATALYZED 2-ACETOXYALLYLATION OF CARBONUCLEOPHILES

Yoji Hori, Take-aki Mitsudo,* and Yoshihisa Watanabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

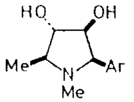


Tetrahedron Lett. 27, 5393 (1986)

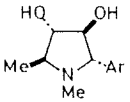
STEREOCHEMICAL REVISION AND ABSOLUTE CONFIGURATION OF CODONOPSININE

Hideo Iida, Naoki Yamazaki, and Chihiro Kibayashi*
Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan
Hiromasa Nagase
Hoshi University, Ebara, Shinagawa-ku,
Tokyo 142, Japan

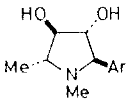
Stereochemical revision of codonopsinine from 1 to 2, establishing the absolute structure 3 for the natural (-)-enantiomer.



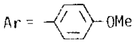
1



2



3

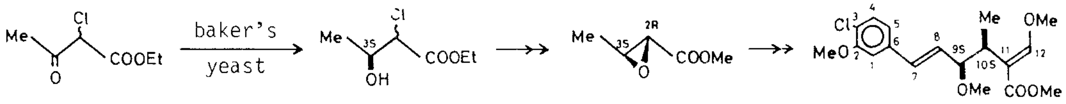


Tetrahedron Lett. 27, 5397 (1986)

DETERMINATIN OF ABSOLUTE STRUCTURE OF (-)-OUDEMANSIN B

Hiroyuki Akita,* Hiroko Matsukura and Takeshi Oishi*
RIKEN (The Institute of Physical and Chemical Research),
2-1, Hirosawa, Wako-shi, Saitama 351-01, Japan

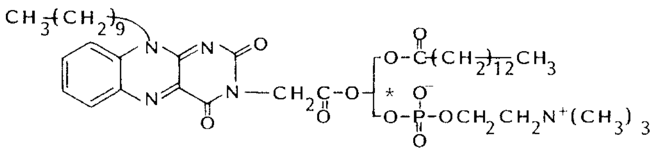
Absolute structure of oudemansin B was determined as 9S, 10S by the total synthesis from optically pure (2R,3S)-epoxy ester, which was derived from α-chloroacetoacetate *via* baker's yeast reduction.



Tetrahedron Lett. 27, 5401 (1986)

FIRST MEMBER OF ARTIFICIAL FLAVOLIPID FAMILY, ITS SYNTHESIS AND INCORPORATION INTO ARTIFICIAL LIPOSOMES.

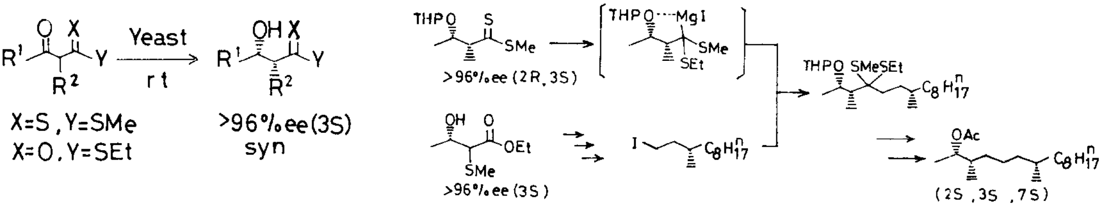
Iwao Tabushi* and Itaru Hamachi
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan



Tetrahedron Lett. 27, 5405 (1986)

STEREOCONTROL BY INTRODUCTION OF A SULFUR FUNCTIONAL GROUP IN THE ASYMMETRIC REDUCTION OF β-KETOESTERS WITH BAKER'S YEAST: PREPARATION OF OPTICALLY PURE 3S-HYDROXYDITHIOESTERS AS A NEW CHIRAL SYNTHON OF NATURAL PRODUCT SYNTHESIS

Toshiyuki Itoh, Yoshihiro Yonekawa, Toshio Sato, and Tamotsu Fujisawa*
Chemistry Department of Resources, Mie University, Tsu, Mie 514, Japan

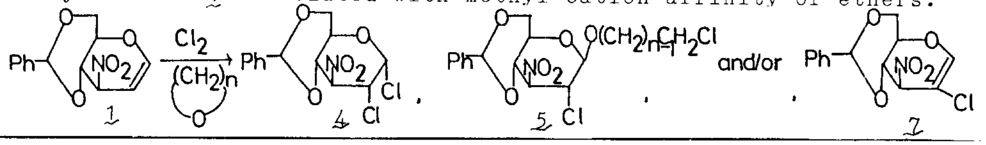


Tetrahedron Lett. 27, 5409 (1986)

CHLORINATION OF 1,5-ANHYDRO-3-NITRO-1-ENITOL DERIVATIVE IN VARIOUS ETHERS AND ITS MNDO STUDY

Tohru Sakakibara, Kohji Yoshino, Hiroyuki Iizuka, and Yoshiharu Ishido
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookaya, Meguro-ku, Tokyo 152, Japan

Chlorination of 1 in various ethers gave 4, 5, and/or 7 depending on the ethers used. The yields of 4 correlated with methyl cation affinity of ethers.

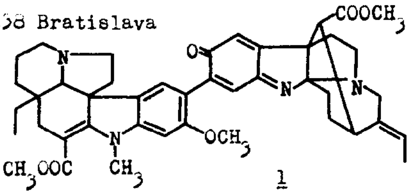


Tetrahedron Lett. 27, 5413 (1986)

VINCARUBINE, A NOVEL BISINDOLE ALKALOID

B.Proksa, D.Uhrín, E.Grossmann and Z.Votický
Institute of Chemistry, Slovak Academy of Sciences, 84238 Bratislava
Czechoslovakia

The structure of Vincarubine /1/, the first bisindole alkaloid from Vinca minor L. was adduced from the spectral data



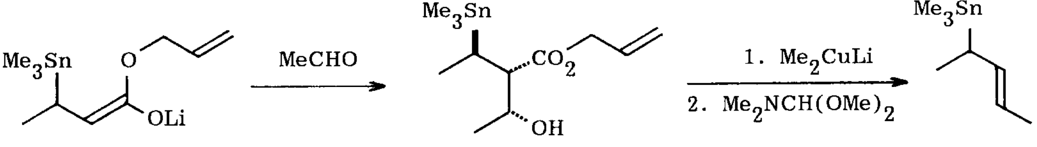
1

Tetrahedron Lett. 27, 5417 (1986)

A REGIOCONTROLLED SYNTHESIS OF ALLYLSTANNANES

Ian Fleming* and Michael Rowley
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Lithium β-stannylenolates react stereoselectively with aldehydes, and the products can be converted into regiostable allylstannanes.



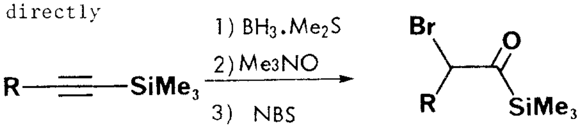
Tetrahedron Lett.27,5421(1986)

A Convenient One-Pot Synthesis of α-Haloacylsilanes

Philip C. Bulman Page and Stephen Rosenthal

Department of Organic Chemistry, Robert Robinson Laboratories, P.O.Box 147,
Liverpool, L69 3BX.

α-Bromoacyl silanes may be prepared directly from trimethylsilyl acetylenes by hydroboration - oxidation and work-up with NBS.



Tetrahedron Lett.27,5423(1986)

IMPROVED SYNTHESIS OF α-METHYLENE-γ-LACTONES VIA ORGANOTIN REAGENTS.

*Jack E. Baldwin, Robert M. Adlington and Joseph B. Sweeney.
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY.

Allylstannane (1) is an efficient precursor to α-methylene-γ-lactones via reaction with aldehydes, as shown: