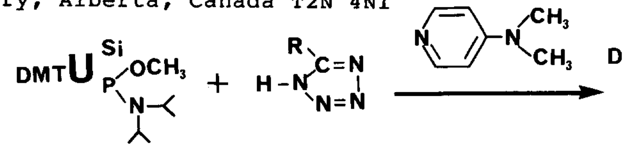
Tetrahedron Lett. 28, 3643 (1987)

ENHANCED COUPLING EFFICIENCY USING 4-DIMETHYLAMINOPYRIDINE (DMAP) AND EITHER TETRAZOLE, 5-(o-NITROPHENYL)TETRAZOLE, OR 5-(p-NITROPHENYL)TETRAZOLE IN THE SOLID PHASE SYNTHESIS OF OLIGORIBONUCLEOTIDES BY THE PHOSPHORAMIDITE PROCEDURE.

Richard T. Pon Dept. of Medical Biochemistry, University of Calgary
Calgary, Alberta, Canada T2N 4N1

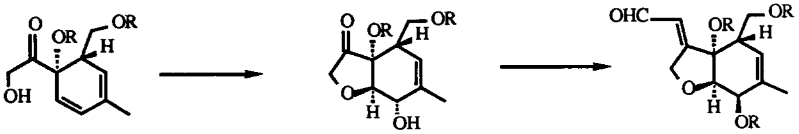


Tetrahedron Lett. 28, 3647 (1987)

SELENIUM INITIATED CYCLIZATION-2,3-SIGMATROPIC REARRANGEMENT: SYNTHESIS OF THE C1 TO C10 FRAGMENT OF THE MILBEMYCINS AND THE AVERMECTINS

Michael T. Crimmins*, W. Gary Hollis, Jr. and John G. Lever
Department of Chemistry, University of North Carolina, Chapel Hil, North Carolina 27514

A synthesis of the hexahydrobenzofuran subunit of the milbemycins and the avermectins is described. The crucial step involves a selenium mediated electrophilic cyclization in tandem with a 2,3 sigmatropic reaarangement of an allylic selenoxide.

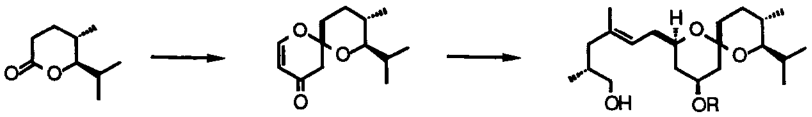


Tetrahedron Lett. 28, 3651 (1987)

STUDIES DIRECTED TOWARD THE TOTAL SYNTHESIS OF THE MILBEMYCINS: SYNTHESIS OF THE C11 TO C31 FRAGMENT OF MILBEMYCIN D

Michael T. Crimmins*, W. Gary Hollis, Jr. and Danute' M. Bankaitis-Davis
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

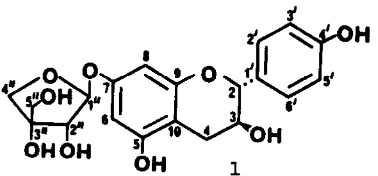
A unique hydrolysis-cyclization and a stereocontrolled conjugate addition to a spiroketal template serve as the key steps in the construction of the spiroketal and bridging chain of milbemycin D.



Tetrahedron Lett. 28, 3655 (1987)

USE OF THE SELECTIVE INEPT NMR TECHNIQUE IN THE STRUCTURE ELUCIDATION OF (+)-AFZELECHIN-7-*O*-β-D-APIOSIDE, A BITTER PRINCIPLE OF *POLYPODIUM GLYCYRRHIZA*

Jinwoong Kim and A. Douglas Kinghorn*, Program for Collaborative Research in the Pharmaceutical Sciences and Dept. of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, University of Illinois at Chicago, Chicago, IL 60612



1

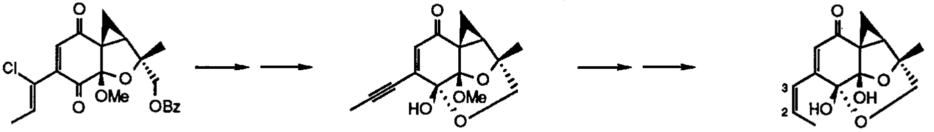
Selective INEPT NMR studies were used to directly determine the position of sugar attachment of a novel bitter glycoside, (+)-afzelechin-7-*O*-β-D-apioside (**1**), a constituent of the rhizomes of *Polypodium glycyrrhiza*.

Tetrahedron Lett. 28, 3659 (1987)

TOTAL SYNTHESIS OF DECHLOROMIKROLIN: A STRUCTURAL REASSIGNMENT WITH BIOSYNTHETIC IMPLICATIONS

Amos B. Smith III*, Yasushi Yokoyama, and Norma K. Dunlap
Department of Chemistry, The Laboratory for Research on the Structure of Matter and The Monell Chemical Senses Center, The University of Pennsylvania, Philadelphia, Pennsylvania 19104 USA

The first total synthesis of dechloromikrolin (2Z), a minor fungal metabolite derived from **Gilmaniella humicola** Barron, has been achieved. The synthesis resulted in a reassignment of the stereochemistry of the C(2,3)-disubstituted olefinic bond from **E** to **Z**.



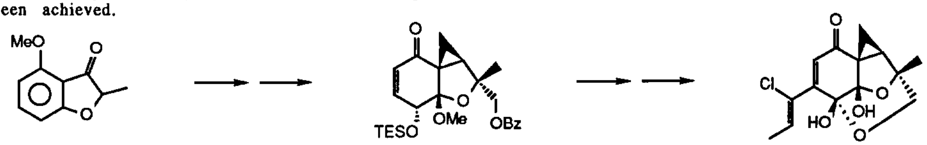
2Z

Tetrahedron Lett. 28, 3663 (1987)

TOTAL SYNTHESIS OF (+)-MIKROLIN

Amos B. Smith III*, Yasushi Yokoyama, Donna M. Huryn, and Norma K. Dunlap
Department of Chemistry, The Laboratory for Research on the Structure of Matter and The Monell Chemical Senses Center, The University of Pennsylvania, Philadelphia, Pennsylvania 19104 USA

The first total synthesis of (+)-mikrolin (**1a**), a novel fungal metabolite derived from **Gilmaniella humicola** Barron, has been achieved.



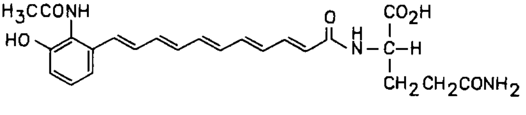
1a

Tetrahedron Lett. 28, 3667 (1987)

PHYSAROCHROME A, A PLASMODIAL PIGMENT FROM THE SLIME MOULD PHYSARUM POLYCEPHALUM (MYXOMYCETES)[1]

Bert Steffan, Monika Praemassing and Wolfgang Steglich
Institut für Organische Chemie und Biochemie der Universität Bonn

A new typ of pigment has been isolated from the slime mould Physarum polycephalum

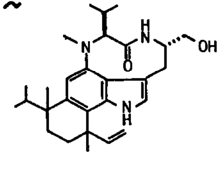


Tetrahedron Lett. 28, 3671 (1987)

TOTAL SYNTHESIS OF (±)-TELEOCIDIN B-3 and B-4

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

Teleocidin B (1) is one of the most potent tumor promoter. First total synthesis of teleocidin B-3 (1c) and B-4 (1d) was achieved starting from indole.



Teleocidin B (1)
[mixture of B-1(1a), B-2(1b), B-3(1c), and B-4(1d)]

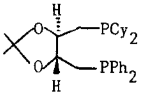
SYNTHESIS AND APPLICATION OF A NOVEL BISPHOSPHINE LIGAND, (-)-DIOCP, AS AN UNSYMMETRIZED DIOP TO PROVE THE GENERAL UTILITY OF NEW DESIGNING CONCEPT

Tetrahedron Lett. 28, 3675 (1987)

Mitsuo Chiba, Hitoe Takahashi, Hisashi Takahashi,
Toshiaki Morimoto, and Kazuo Achiwa*

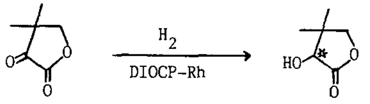
Shizuoka College of Pharmacy, 2-2-1 Oshika, Shizuoka 422, Japan

DIOCP-Rh complex prepared on the basis of new designing concept was found to show higher catalytic activity and enantioselectivity than DIOP-Rh.



(-)-DIOCP

Cy: $c\text{-}C_6H_{11}\text{-}$



$[Rh]/[subst.]=1/10^3$, opt. yield 72%

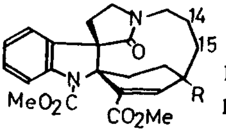
Tetrahedron Lett. 28, 3679 (1987)

ALKALOIDS OF KOPSIA JASMINIFLORA FROM THAILAND

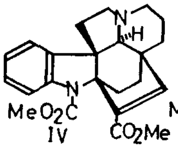
N. Ruangrungsi,[a] K. Likhitwitayawuid,[a,b] V. Jongbunprasert,[a] D. Ponglux,[a] N. Aimi,[b] K. Ogata,[c] M. Yasuoka,[b] J. Haginiwa,[b] and S. Sakai*[,b,c]

a) Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand. b) Faculty of Pharmaceutical Sciences, Chiba University, Chiba, Japan. c) Chemical Analysis Center, Chiba University, Chiba, Japan.

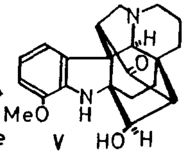
Structures of five new alkaloids, three (I - III) being of a new structural class, have been elucidated.



I R=OH
II R=H
III R=OH Δ^{14}



IV



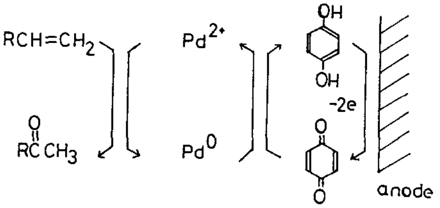
V

Tetrahedron Lett. 28, 3683 (1987)

OXIDATION OF OLEFINS TO KETONES IN COMBINATION WITH ELECTROOXIDATION

Jiro Tsuji* and Makoto Minato

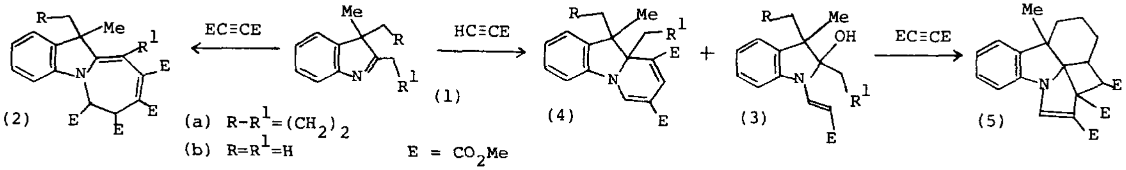
Department of Chemical Technology, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan



Tetrahedron Lett. 28, 3687 (1987)

3H-INDOLES AND ACETYLENECARBOXYLIC ESTERS

Roy M. Letcher* and Della W.M. Sin
Department of Chemistry, University of Hong Kong, Hong Kong.

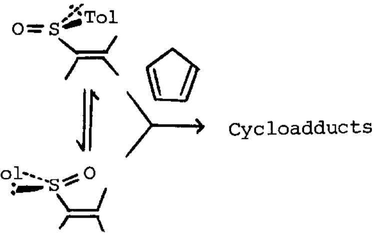


All structures have been elucidated by spectroscopy.

Tetrahedron Lett. 28, 3689 (1987)

A DISPROOF OF KAHN-HEHRE'S PROPOSAL ON THE GROUND STATE CONFORMATIONS AND THE STERIC COURSE OF THE DIELS-ALDER REACTION OF VINYL SULFOXIDES

Toru Koizumi*, Yoshitsugu Arai, and Hiromitsu Takayama
Toyama Med. & Pharm. Univ., Sugitani, Toyama, Japan
Kaoru Kuriyama* and Motoo Shiro
Shionogi Research Laboratory, Sagisu, Osaka, Japan



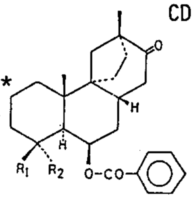
X ray and CD spectral analyses of vinyl sulfoxides indicated that their ground state conformations are affected by the substituents at α or β position and the most stable conformations dictates the observed diastereoselectivity.

Tetrahedron Lett. 28, 3693 (1987)

SCOPADULCIC ACID A AND B, NEW DITERPENOIDS WITH A NOVEL SKELETON, FROM A PARAGUAYAN CRUDE DRUG "TYPYCHÁ KURATŨ" (<u>SCOPARIA</u> <u>DULCIS</u> L.)

T. Hayashi,* M. Kishi, M. Kawasaki, M. Arisawa, M. Shimizu, S. Suzuzki, M. Yoshizaki, N. Morita, Y. Tezuka, T. Kikuchi,* L.H. Berganza, E. Ferro and I. Basualdo, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan and Universidad Nacional de Asunción, Casilla de Correo 1055, Asunción, Paraguay

The structures were elucidated based on 2-D NMR and CD spectral data



Scopadulcic acid A: R_1= COOH, R_2= CH_2OH
Scopadulcic acid B: R_1=CH_3, R_2= COOH

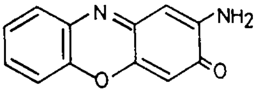
Tetrahedron Lett. 28, 3697 (1987)

STRUCTURES OF PHYTOTOXINS, AV-TOXINS C, D AND E, PRODUCED BY ZONATE LEAF SPOT FUNGUS OF MULBERRY

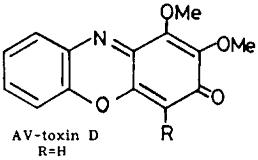
J.Kinjo, K.Yokomizo, Y.Awata, M.Shibata and T.Nohara*
Faculty of Pharmaceutical Sciences, Kumamoto University, Kumamoto 862, Japan

T.Teramine
Kochi Sericultural Experiment Station, Tosayamada, Kochi 782, Japan

T.Takahashi
National Sericultural Experiment Station, Tsukuba, Ibaraki 305, Japan



AV-toxin C



AV-toxin D
R=H

AV-toxin E
R=OMe

Tetrahedron Lett. 28, 3699 (1987)

N-PERHALOFLUOROALKYLATION OF SECONDARY AMINES BY THE REACTIONS OF THE AMINES AND AMIDES WITH PERHALOFLUOROALKANES. HALOPHILIC ATTACK OF NITROGEN NUCLEOPHILE ON C-Br BOND.

Xing-ya LI*, He-qi PAN, and Xi-kui JIANG
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, China

The title reactions proceed via an anionic chain process initiated by the bromophilic attack of nitrogen nucleophiles on C-Br bond

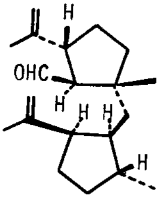
$$R^1R^2NM + BrCF_2CFBrX \longrightarrow R^1R^2NCF_2CFBrX + R^1R^2NCF_2CFXH + R^1R^2NCF{=}CFX$$
M = H, Li, Na

Tetrahedron Lett. 28, 3703 (1987)

DICTYMAL, A NEW SECO-FUSICOCCIN TYPE DITERPENE FROM THE BROWN ALGA DICTYOTA DICHOTOMA

Makoto Segawa, Nobuyasu Enoki, Mitsuhiko Ikura†, Kunio Hikichi†, Ryoichi Ishida††, Haruhisa Shirahama* and Takeshi Matsumoto†††
Department of Chemistry and †High-Resolution NMR Laboratory, Faculty of Science, Hokkaido University, Sapporo 060, Japan, ††Muroran Institute of Technology, Muroran 050, Japan, †††Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12, Japan

The structure determination on the basis of the 2D NMR studies.

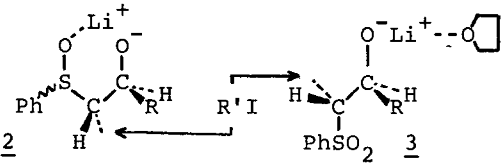


Tetrahedron Lett. 28, 3705 (1987)

STEREOCHEMISTRY IN ALKYLATIONS OF DIANIONS OF β-HYDROXYSULFOXIDES AND β-HYDROXYSULFONES

Rikuhei Tanikaga,* Ken Hosoya, Kazumasa Hamamura, and Aritsune Kaji
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Alkylations of dianions of 1-3 are affected by chelation of Li⁺ with a sulfinyl group or by coordination with tetrahydrofuran rather than a sulfonyl group.

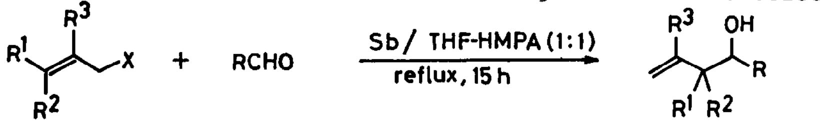


Tetrahedron Lett. 28, 3707 (1987)

BARBIER-GRIGNARD-TYPE ALLYLATION OF ALDEHYDES WITH METALLIC ANTIMONY

Yasuo BUTSUGAN,* Hirokazu ITO, and Shuki ARAKI
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Antimony-induced allylation of aldehydes with allylic halides and phosphates gave high yields of homoallylic alcohols regio- and chemo-selectively.

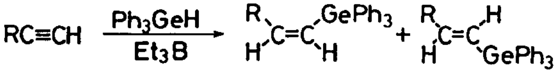


Tetrahedron Lett. 28, 3709 (1987)

Et$_3$B INDUCED STEREOSELECTIVE RADICAL ADDITION OF Ph$_3$GeH TO ACETYLENES AND ITS APPLICATION TO ISOMERIZATION OF OLEFINS

Y. Ichinose, K. Nozaki, K. Wakamatsu, K. Oshima, and K. Utimoto
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

The transformation was achieved under excellent control of regio- and stereoselectivities.



Tetrahedron Lett.28,3713(1987)

CATALYTIC ROLE OF DIORGANOTIN DICHLORIDE IN ESTERIFICATION OF CARBOXYLIC ACIDS

**Amal K. Kumar and Tapas K. Chattopadhyay*, Department of Chemistry,
North Bengal University, Darjeeling - 734430, INDIA.**

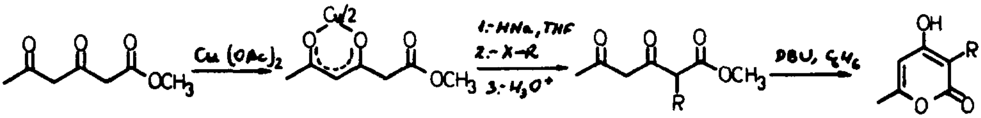
$$R_1COOH + R_2OH \xrightarrow[\text{2 hrs. reflux}]{Ph_2SnCl_2 \text{ or } Me_2SnCl_2} R_1COOR_2 \quad (40-97\%)$$

Tetrahedron Lett.28,3715(1987)

COPPER COMPLEX PROTECTION IN THE REGIOSELECTIVE ALKYLATION OF METHYL 3,5-DIOXOHEXANOATE. PREPARATION OF 3-ALKYL DERIVATIVES OF 4-HYDROXY-6-METHYL-2-PYRONE.

Jordi Cervelló, Jorge Marquet, Marcial Moreno-Mañas. Departamento de Química. Universidad Autónoma de Barcelona. Bellaterra. Barcelona 08193. Spain

The regioselective alkylation of a simple polyketide model.

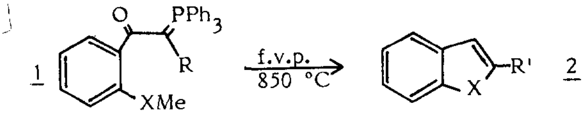


Tetrahedron Lett.28,3717(1987)

A NEW SYNTHESIS OF 2-SUBSTITUTED BENZOFURANS AND BENZOTHIOPHENS: NOVEL FRAGMENTATION REACTIONS OF SIMPLE ALKYL GROUPS

R. Alan Aitken* and Graham Burns
Department of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9ST, U.K.

Flash vacuum pyrolysis of 1 (X = O, S) gives 2-substituted benzofurans and benzothiophens 2. For aliphatic R the cyclisation is accompanied by novel transformations of the R group.

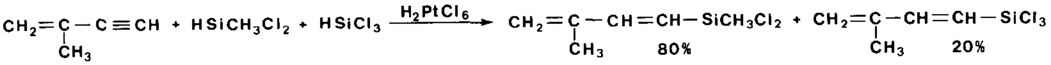


Tetrahedron Lett.28,3719(1987)

CATALYZED HYDROSILYLATION OF 2-METHYL-1-BUTEN-3-YNE WITH METHYLDICHLOROSILANE; PROMOTIONAL EFFECT IMPARTED BY THE PRESENCE OF A DIFFERENT CHLOROSILANE

Maurizio Licchelli and Alberto Greco
ENICHEM SINTESI S.p.A. - R&D Laboratories
Via Maritano 26, 20097 San Donato Milanese, Milan, Italy

Unexpected results from hydrosilylation of 2-Methyl-1-buten-3-yne



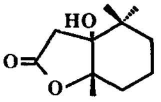
$$CH_2=\underset{CH_3}{\underset{|}{C}}-C\equiv CH + HSiCH_3Cl_2 + HSiCl_3 \xrightarrow{H_2PtCl_6} \underset{80\%}{CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH-SiCH_3Cl_2} + \underset{20\%}{CH_2=\underset{CH_3}{\underset{|}{C}}-CH=CH-SiCl_3}$$

Tetrahedron Lett. 28,3723(1987)

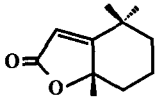
CONCISE ASYMMETRIC SYNTHESIS OF (5S, 6S)-AEGINETOLIDE AND (5S)- DIHYDROACTINIDIOLIDE

C. M. Cain and N. S. Simpkins
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Abstract: An asymmetric deprotonation reaction allows for short syntheses of the lactones (5S, 6S)- Aeginetolide (1) and (5S)-Dihydroactinidiolide (2).



(1)



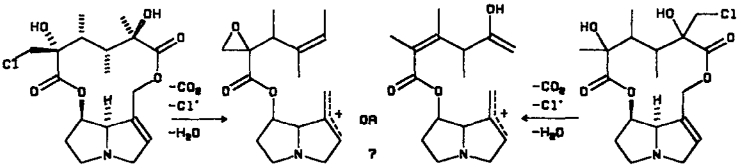
(2)

Tetrahedron Lett. 28,3725(1987)

DEVIATIONS FROM THE GENERALITY OF THE 'MASS SPECTROMETRIC - METHOD' FOR DETERMINING THE MODE OF ESTER ATTACHMENT IN PYRROLIZIDINE ALKALOIDS

Martin W Bredenkamp* and Adriaan Wiechers
Department of Chemistry, University of Pretoria, PRETORIA 0002, Republic of South Africa

The use of MS for determining the mode of ester attachment in macrocyclic pyrrolizidine alkaloids is suspect when applied to alkaloids containing an α-hydroxy necic acid moiety

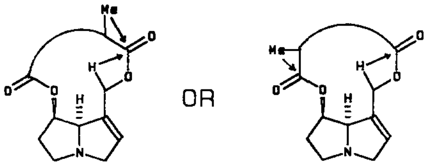


Tetrahedron Lett. 28,3729(1987)

NMR-SPI: A RELIABLE METHOD FOR DETERMINING THE MODE OF ESTER ATTACHMENT IN PYRROLIZIDINE ALKALOIDS

Martin W Bredenkamp* and Adriaan Wiechers
Department of Chemistry, University of Pretoria, PRETORIA 0002, Republic of South Africa

NMR-SPI is used to show connectivity between selected protons and carbonyl carbon nuclei of pyrrolizidine alkaloids with the purpose of determining the mode of ester attachment. General applicability is demonstrated

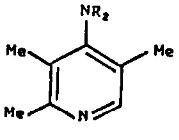


Tetrahedron Lett. 28,3733(1987)

SYNTHESIS OF STERICALLY HINDERED 4-DIALKYLAMINO-PYRIDINES

Karen A. Joiner and Frank D. King*
Beecham Pharmaceuticals, The Pinnacles, Harlow, Essex CM19 5AD

A different reaction sequence in the synthesis of sterically hindered 4-dialkylaminopyridines (1) by nucleophilic aromatic substitution under acidic and basic conditions is described.



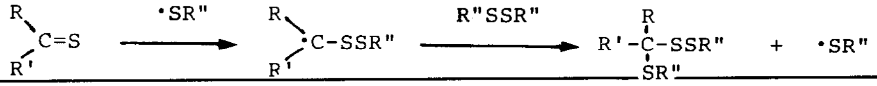
(1)

Tetrahedron Lett.28,3737(1987)

THIOKETONES AS SPIN TRAPS FOR GROUP VI RADICALS.

A. ALBERTI, B.F. BONINI, and G.F. PEDULLI - *I.Co.C.E.A. CNR, 40064-OZZANO EMILIA, Department of Organic Chemistry of the University, 40127-BOLOGNA, Italy*

Thiobenzophenone and other thiones react photolytically with disulphides to give 1,thioalkyl,1,dithioalkyl-compounds. The intermediate radicals have been detected by ESR. The C=S double bond is also susceptible of attack by sulphonyl and butoxyl radicals.



Tetrahedron Lett.28,3741(1987)

INTRAMOLECULAR RING CLOSURE OF α,β- UNSATURATED 3-ACYLINDOLES

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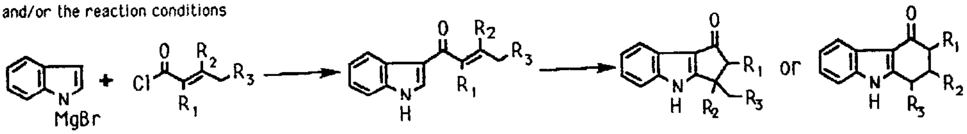
A number of unsaturated 3-acylindoles were prepared and annulated (with HCl or AlCl$_3$) to 3,4-dihydrocyclopent[b]indol-1(2H)-ones or 1,2,3,9-tetrahydro-4H-carbazol-4-ones depending on the structure of the substrate and/or the reaction conditions



Tetrahedron Lett.28,3747(1987)

A SYHTHESIS OF *pseudo*-GLOEOSPORONE

M. Mortimore, G.S. Cockerill, P. Kocieński, and R. Treadgold
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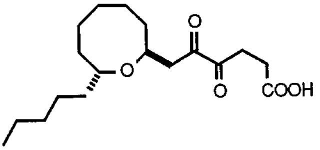
Key steps in a synthesis of *pseudo*-gloeosporone were an intramolecular directed aldol reaction used to construct the oxocane ring and the photo-oxidation of a silylfuran to construct the γ-keto acid moiety. The synthetic material does not correspond to the natural product.

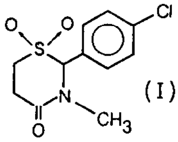


Tetrahedron Lett.28,3751(1987)

PREPARATIVE OPTICAL RESOLUTION OF CHLORMEZANONE ON MICROCRYSTALLINE TRIACETYLCELLULOSE

Stig Allenmark* and Richard A. Thompson
Laboratory of Microbiological Chemistry, University of Gothenburg,
Guldhedsgatan 10 A, S-413 46 Gothenburg, Sweden

The enantiomers of I, separated by chiral chromatography, have been isolated and characterized.



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