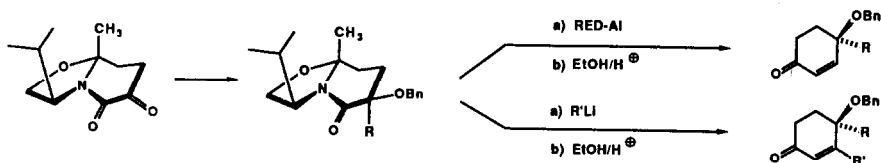ASYMMETRIC SYNTHESIS OF 4-ALKOXY-4-ALKYLCYCLOHEXEN-2-
ONES. APPLICATION TOWARD THE SYNTHESIS OF (+)-ABSCISIC
ACID.

A. I. Meyers* and Michael A. Sturgess
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 USA

SYNTHESIS OF DOLICHOLS VIA ASYMMETRIC HYDROGENATION OF PLANT
POLYPRENOLS

Barbara Imperiali* and Janet Warren Zimmerman
Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213

A one step conversion of plant polyprenols to (S)-dolichols via asymmetric hydrogenation of
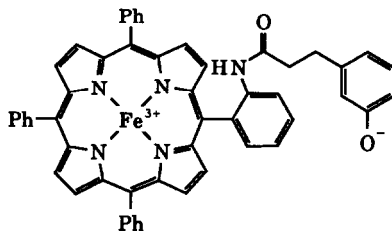of the α-terminal olefin is described.
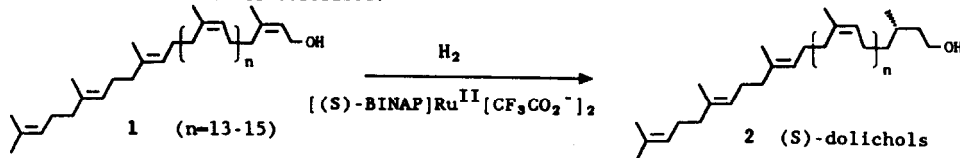
SYNTHESIS AND CHEMISTRY OF AN IRON(III) TETRAPHENYLPORPHYRIN WITH A COVALENTLY-ATTACHED PHENOLATE TAIL

Michael W. Nee*, Chongwoo A. Kim, Sandhya Garg,
Michael C. Griffith, Laura S. Mizoue, Paul E. Rauch,
and Wendy J. Dixon
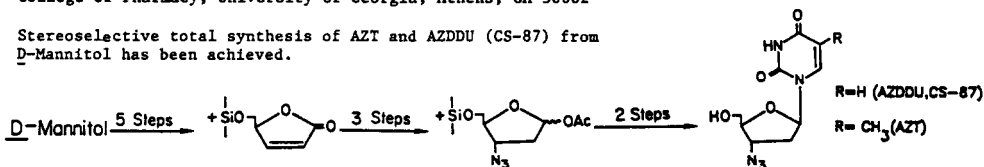Department of Chemistry, Oberlin College,
Oberlin, Ohio 44074

AN EFFICIENT TOTAL SYNTHESIS OF 3'-AZIDO-3'-DEOXYTHYMIDINE (AZT)
AND 3'-AZIDO-2',3'-DIDEOXYURIDINE (AZDDU, CS-87) FROM D-MANNITOL

Chung K. Chu*, J. Warren Beach, Giliyar V. Ullas and Yoshiyuki
Kosugi, Department of Medicinal Chemistry and Pharmacognosy,
College of Pharmacy, University of Georgia, Athens, GA 30602

Stereoselective total synthesis of AZT and AZDDU (CS-87) from
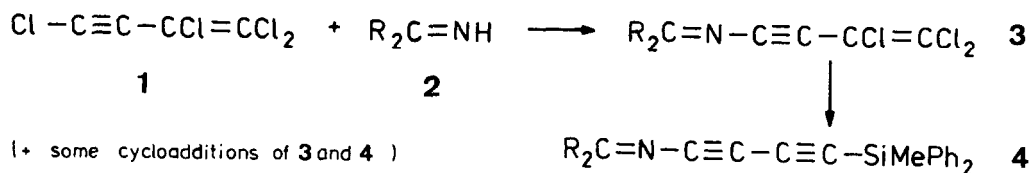D-Mannitol has been achieved.

CONTRASTING THERMAL REACTIONS OF ALLYLIC SULFILIMINES
AND PHOSPHINIMINES [*]

Raymond D. Baechler[*], Margaret Blohm, and Karen Rocco
Department of Chemistry and Physics, Russell Sage College, Troy NY 12180

Whereas allylic sulfilimines undergo (2,3)-sigmatropic rearrangement to form isomeric sulfenamides, structurally analogous allylic phosphinimines are converted to isomeric vinylic structures as a result of spontaneous double bond shift.
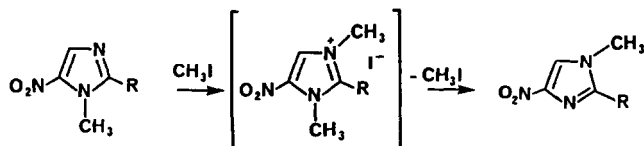
$$\underset{Ar-N}{\overset{Ar_2P-CH=CH-CH_3}{}} \xleftarrow{30^\circ} \underset{Ar-N}{\overset{Ar_2P-CH_2-CH=CH_2}{}} \qquad \underset{Ar-N}{\overset{Ar-S-CH_2-CH=CH_2}{}} \xrightarrow{0^\circ} \underset{Ar-N-CH_2-CH=CH_2}{\overset{Ar-S}{}}$$

INIMINES and DIINIMINES

Gerhard Himbert[*] and Dieter Faul
Fachbereich Chemie der Universität, Postfach 3049, D-6750 Kaiserslautern

$$Cl-C\equiv C-CCl=CCl_2 \quad + \quad R_2C=NH \quad \longrightarrow \quad R_2C=N-C\equiv C-CCl=CCl_2 \quad \textbf{3}$$
$$\textbf{1} \qquad\qquad\qquad \textbf{2}$$

(+ some cycloadditions of **3** and **4**)

$$R_2C=N-C\equiv C-C\equiv C-SiMePh_2 \quad \textbf{4}$$

AMPHIPHILIC LIQUID CRYSTALS I. SYNTHESIS OF
trans-4-n-ALKYL-trans-2-HYDROXYMETHYLCYCLOHEXANOLS

C. Tschierske and H. Zaschke

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg
Weinbergweg 16, DDR-4050 Halle (Saale), GDR

$$R-\bigcirc=O \to \to \to R-\bigcirc-O^- \, Zn^{2+}/_2 \to \to R-\underset{CH_2OH}{\bigcirc}=O \longrightarrow R-\underset{CH_2OH}{\bigcirc}\cdots OH$$
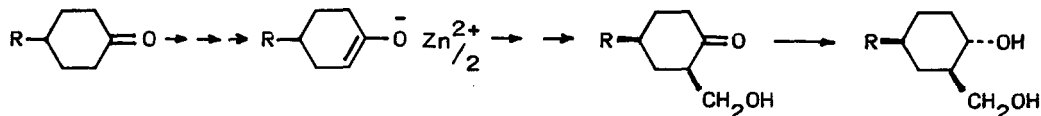
STUDY OF CATALYSED ISOMERIZATION OF 5-NITRO TO
4-NITROIMIDAZOLES

P. Vanelle*[ab], O. Jentzer[b], M. BAHNOUS[b] et M.P. CROZET[b]
[a]Laboratoire de Chimie Organique, Faculté de Pharmacie - 13398 Marseille Cédex 4 - France
[b]Laboratoire de Chimie Organique B, CNRS UA 109 - Fac. St Jérôme - 13397 Marseille Cédex 13

$$O_2N-\underset{CH_3}{\overset{N}{\bigg\langle}}-R \xrightarrow{CH_3I} \left[O_2N-\underset{CH_3}{\overset{\overset{+}{N}-CH_3}{\bigg\langle}}-R \; I^- \right] \xrightarrow{-CH_3I} O_2N-\underset{}{\overset{N-CH_3}{\bigg\langle}}-R$$

REGIOSELECTIVE SYNTHESIS OF ISOPROPENYL ESTERS BY RUTHENIUM CATALYSED ADDITION OF N-PROTECTED AMINOACIDS TO PROPYNE.

Christophe Ruppin, Pierre H. Dixneuf and Serge Lecolier
Campus de Beaulieu, Université de Rennes, 35042 Rennes (France)
SNPE, Centre de Recherches du Bouchet, 91710 Vert le Petit (France)
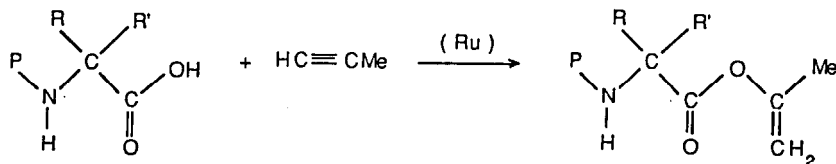
ULTRASOUND IN ORGANIC SYNTHESIS 16.
OPTIMISATION OF THE CONJUGATE ADDITIONS TO α-β UNSATURATED CARBONYL COMPOUNDS IN AQUEOUS MEDIA.

LUCHE J.L. and ALLAVENA C.
LEDSS, Université J. FOURIER, 38041 Grenoble Cedex FRANCE

$R = n-C_5H_{11}$, $i-C_3H_7$
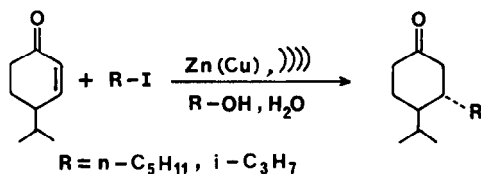
Optimal yields result from adjustment of several parameters, especially the solvent composition. Media with high sound absorption properties, appear to be preferable.

ULTRASOUND IN ORGANIC SYNTHESIS 17.
MECHANISTIC ASPECTS OF THE CONJUGATE ADDITIONS TO α-ENONES IN AQUEOUS MEDIA.

LUCHE J.L. ALLAVENA C. PETRIER C. and DUPUY C
LEDSS, Université J. FOURIER, BP 53X - 38041 Grenoble Cedex FRANCE

A mechanism is proposed for the addition of R group to the conjugate position of α-enones.
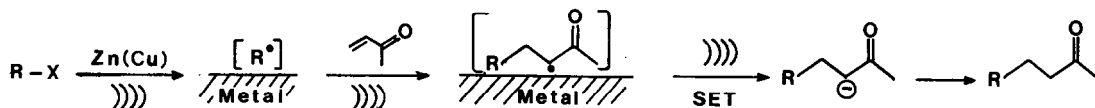
INTRAMOLECULAR [2 + 2] PHOTOCYCLOADDITION. 2.
MECHANISM OF INTRAMOLECULAR PHOTOCYCLIZATION OF α,ω-BIS(p-VINYLPHENYL)ALKANES

J. Nishimura,* A. Ohbayashi, Y. Wada, and A. Oku
Dept. of Chem., Kyoto Inst. of Tech., Kyoto 606, Japan
S. Ito, A. Tsuchida, M. Yamamoto, and Y. Nishijima
Dept. of Polym. Chem., Kyoto Univ., Kyoto 606, Japan

In relation to styrene photocyclo-dimerization, the mechanism of the title reaction toward cyclophanes 2 was investigated by photophysical measurements and MM2 calculation.
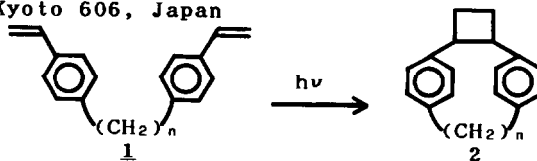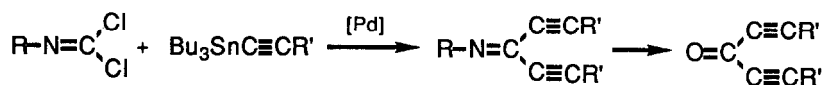
PALLADIUM-CATALYZED COUPLING OF N-SUBSTITUTED ISOCYANIDE DICHLORIDES WITH ALKYNYLTIN COMPOUNDS : NEW SYNTHESIS OF DIALKYNYLKETONES

Yoshihiko Ito,* Masahiko Inouye and Masahiro Murakami
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

N-Substituted isocyanide dichlorides were coupled with alkynyltin compounds in the presence of palladium catalyst to produce N-substituted dialkynylimines, of which hydrolysis gave dialkynylketones.

$$R-N=C\overset{Cl}{\underset{Cl}{}} + Bu_3SnC\equiv CR' \xrightarrow{[Pd]} R-N=C\overset{C\equiv CR'}{\underset{C\equiv CR'}{}} \longrightarrow O=C\overset{C\equiv CR'}{\underset{C\equiv CR'}{}}$$

SYNTHESIS OF OLIGORIBONUCLEOTIDES BY THE PHOSPHORAMIDITE APPROACH USING 5'-LEVULINYL AND 2'-TETRAHYDROFURANYL PROTECTION
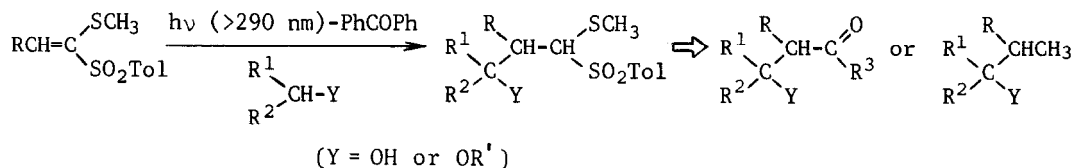
Shigenori Iwai and Eiko Ohtsuka
Faculty of Pharmaceutical Sciences,
Hokkaido University, Sapporo 060, Japan

Oligoribonucleotides were synthesized with an automatic synthesizer using 5'-O-levulinyl-2'-O-tetrahydrofuranyl-nucleoside 3'-phosphoramidite.

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}O-$$

$$NCCH_2CH_2O-\overset{}{P}-N(iPr)_2$$
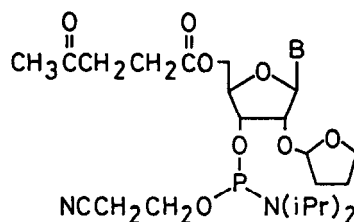
AN EFFICIENT ACCEPTOR OF 1-HYDROXY(OR ALKOXY)ALKYL RADICALS — KETENE DITHIOACETAL S,S-DIOXIDE —

Katsuyuki OGURA,* Atsushi YANAGISAWA, Takeo FUJINO, and Kazumasa TAKAHASHI
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University,
1-33 Yayoicho, Chiba 260, Japan

$$RCH=C\overset{SCH_3}{\underset{SO_2Tol}{}} \xrightarrow[\underset{R^2}{R^1}CH-Y]{h\nu\ (>290\ nm)-PhCOPh} R^1\overset{R}{\underset{R^2}{C}}\overset{CH-CH}{\underset{Y}{}}\overset{SCH_3}{\underset{SO_2Tol}{}} \Rightarrow R^1\overset{R}{\underset{R^2}{C}}\overset{CH-C}{\underset{Y}{}}\overset{O}{\underset{R^3}{}} \text{ or } R^1\overset{R}{\underset{R^2}{C}}\overset{CHCH_3}{\underset{Y}{}}$$

(Y = OH or OR')

A NEW AMIDOALKYNYLATION USING ALKYNYL-ZINC REAGENT

Sachio Mori*, Hikozo Iwakura and Shozo Takechi
Shionogi Research Laboratories, Shionogi & Co.,
Ltd., Fukushima-ku, Osaka 553, Japan

A new amidoalkynylation using a combination of alkynylzinc and α-thio-lactam is described.
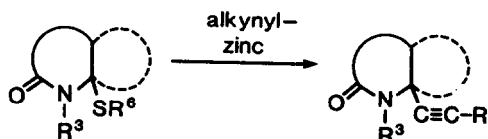
A NEW CLASS OF INDOLE ALKALOID ELEGANSAMINE CONSTRUCTED FROM A MONOTERPENOID INDOLE ALKALOID AND AN IRIDOID

Dhavadee Ponglux,[a] Sumphan Wongseripipatana,[a] Hiromitsu Takayama,[b] Koreharu Ogata,[c] Norio Aimi,[b] and Shin-ichiro Sakai[b*]
Faculty of Pharmaceutical Sciences, Chulalongkorn University,[a] Bangkok, 10500, Thailand. Faculty of Pharmaceutical Sciences,[b] and Chemical Analysis Center,[c] Chiba University, 1-33 Yayoi, Chiba 260, Japan.

The structure of a new type of oxindole alkaloid, elegansamine, isolated from *Gelsemium elegans* was established by the spectroscopic analysis and by the X-ray diffraction method.

Elegansamine
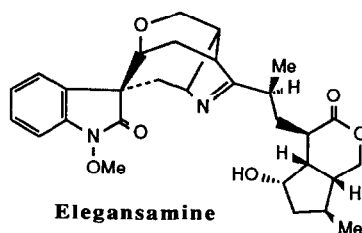
HIGH-PRESSURE MEDIATED DIELS-ALDER REACTION
OF DI-ℓ-MENTHYL ACETOXYMETHYLENEMALONATE
WITH FURAN: ENANTIOSELECTIVE SYNTHESIS OF β-D-RIBOFURANOSYLMALONATE,
A PROSPECTIVE SYNTHON FOR C-NUCLEOSIDE: Nobuya Katagiri*, Hidenori Akatsuka,
Chikara Kaneko*, Pharmaceutical Institute, Tohoku University, Sendai 980,
Japan: Sera Akira, Department of Chemistry, Kobe University, Kobe 657, Japan

$E=CO_2-\ell-menthyl$

11kbar
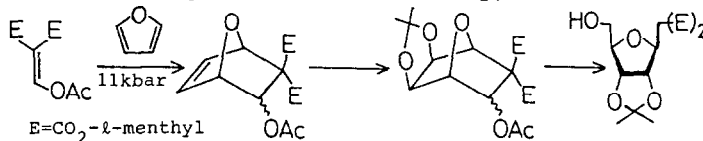
TRANSANNULAR BOND FORMATION BETWEEN THE ANTIMONY
AND THE NITROGEN ATOMS IN DIBENZ[c,f][1,5]AZA-
STIBOCINE SYSTEM. FORMATION OF X-Sb-X and X-Sb-N[+]
HYPERVALENT BOND
Katsuo Ohkata, Masako Ohnishi, and Kin-ya Akiba[*]
Department of Chemistry, Faculty of Science, Hiroshima University
Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

Halogenation of dibenzazastibocine (1)
afforded dihalide (4a-c and 5d) and
the reaction of 4b and 4c with SbCl$_5$
or AgBF$_4$ resulted in the formation of
X-Sb-N[+4]bond (5b,c).

a: X=F, b: X=Cl, c: X=Br, d: X=I.
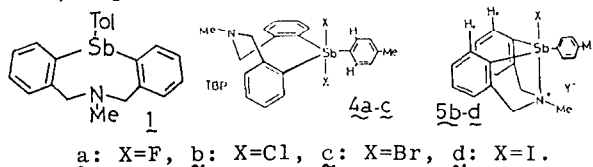
REGIOSELECTIVE SYNTHESIS OF <u>N</u>-SUBSTITUTED DIHYDROPYRIMIDIN-2(1<u>H</u>) OR (3<u>H</u>)-ONES
Hidetsura Cho, Yumi Takeuchi, Masaru Ueda, and Akira Mizuno
<u>Suntory Institute for Biomedical Research, Mishimagun, Osaka, 618, Japan</u>.

Compounds 2 and 3 were regioselectively
synthesized under the different reaction
conditions.

NaH
ClCOOR²

Cl₂COCCl
R²OH, Et₃N
or Et₃N-NaH
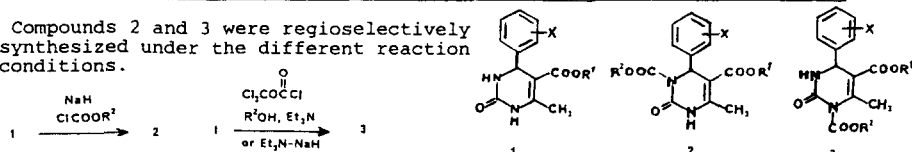
SILOXY-[2,3]WITTIG REARRANGEMENT: A NEW METHOD FOR DIASTEREOSELECTIVE PREPARATION OF 1,2-DIOL SYSTEMS

Ei-ichi Nakai and Takeshi Nakai*, Department of Chemical Technology, Tokyo Institute of Technology, Megro-ku, Tokyo 152, Japan

$G = CH=CH_2$; $C(CH_3)=CH_2$; C_6H_5; $C\equiv C-SiMe_3$

n-BuLi

82~98% anti
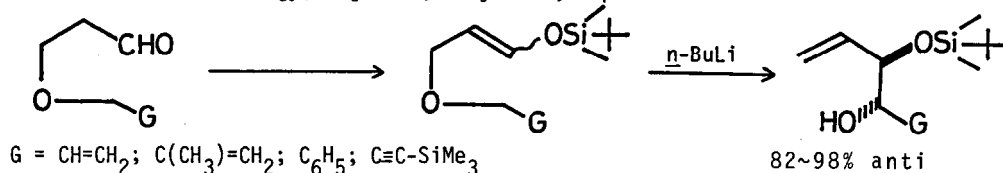
## NEW METHODS FOR β-CONJUGATE ADDITION AND β-HYDROXYALKYLATION OF ENONES

Sunggak Kim* and Phil Ho Lee
Department of Chemistry, Korea Advanced Institute of Science & Technology, Seoul 130-012, Korea

1) RCHO + TMSOTf
2) n-Bu₄NF

OTBDMS

+PPh₃

1) $CH_2=CH-EWG$ + TMSOTf
2) n-Bu₄NF
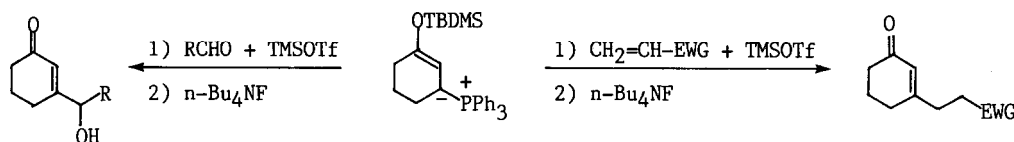
EFFECTIVE DEPROTECTION OF 2-(TRIMETHYLSILYLETHOXY)METHYLATED ALCOHOLS (SEM ETHERS). SYNTHESIS OF THYRSIFERYL-23 ACETATE.

Toshiyuki Kan, Masaru Hashimoto, Mitsutoshi Yanagiya and Haruhisa Shirahama* Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

MOMO OSEM

TBAF, MS 4A
HMPA, 100°C
(98%)

MOMO OH

Br

thyrsiferyl-23 acetate OAc
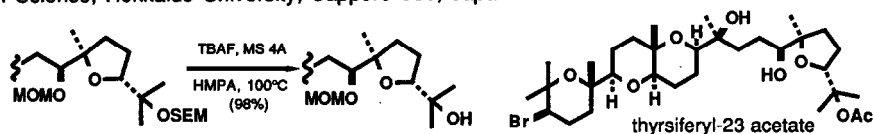
STEREOSELECTIVE REDUCTION OF β-ALKOXY KETONES: A SYNTHESIS OF SYN-1,3-DIOLS
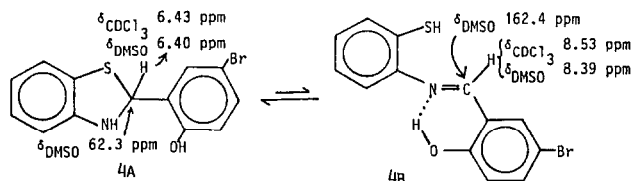
Yuji Mori, Miki Kuhara, Akio Takeuchi, and Makoto Suzuki
Faculty of Pharmacy, Meijo University, Tempaku, Nagaya 468, Japan

A highly syn-stereoselective reduction of β-alkoxy ketones was achieved using LiAlH₄ in the presence of LiI.

O O R OTBDPS

R=OH, H

LiAlH₄
LiI

O OH R OTBDPS

syn:anti = 95:5
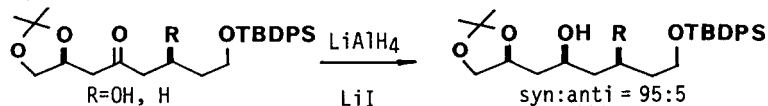
A CONVERGENT GENERAL SYNTHETIC PROTOCOL FOR
SYN-1,3-POLYOLS

Yuji Mori, Akio Takeuchi, Hitomi Kageyama, and Makoto Suzuki
Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

A method for the stereoselective synthesis of syn-1,3-polyols using chiral
building block 1 is described.
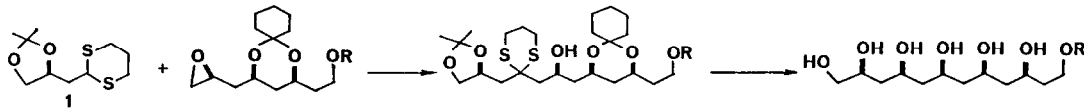
DIRECT   NMR   SPECTROSCOPIC PROOF FOR THE   RING-CHAIN TAUTOMERISM
IN THE THIAZOLIDINE SYSTEM

Ferenc Fülöp, Jorma Mattinen, and Kalevi Pihlaja
Department of Chemistry, University of Turku, SF-20500 Turku, Finland

Summary: 2-(2'-Hydr-
oxy-5'-bromophenyl)-
benzothiazoline
exists as a ring-
chain tautomeric
mixture in $CDCl_3$ and
DMSO-d_6 as proved by
NMR spectroscopy.

δ_{CDCl_3} 6.43 ppm
δ_{DMSO} 6.40 ppm

δ_{DMSO} 162.4 ppm

δ_{CDCl_3} 8.53 ppm
δ_{DMSO} 8.39 ppm

δ_{DMSO} 62.3 ppm

4A   4B

INTRAMOLECULAR HYDROGEN ABSTRACTION. THE USE OF
ORGANOSELENIUM   REAGENTS   FOR   THE   GENERATION   OF
ALKOXY RADICALS

R.L. Dorta, C.G. Francisco, R. Freire, and E. Suárez[*]
Instituto de Productos Naturales Orgánicos del C.S.I.C.; C. La Esperanza 2. La Laguna, Tenerife, Spain.

The photolysis of hydroxy compounds, *i.e.* (1), leads, through intramolecular hydrogen abstraction of the intermediate alkoxy
radicals, to cyclic ethers such as (2), in good yields.

EtO_2C — (1) EtO_2C — (2)

CHEMISTRY OF INSECT ANTIFEEDANTS FROM AZADIRACHTA
INDICA (Part 3): REACTIONS ON THE C-22,23 ENOL ETHER
DOUBLE BOND OF AZADIRACHTIN AND CONVERSION TO
22,23-DIHYDRO-23-B-METHOXYAZADIRACHTIN.

Steven V. Ley*, James C. Anderson, Wally M. Blaney, Zev Lidert,
E. David Morgan, Nicholas G. Robinson and Monique S.J. Simmonds.
Department of Chemistry, Imperial College of Science and Technology,
South Kensington, London SW7 2AY, U.K.

Selective transformations of the azadirachtin C-22,23 double bond may be
achieved in high yields and conversion of azadirachtin to the natural product
22,23-dihydro-23-β-methoxyazadirachtin.
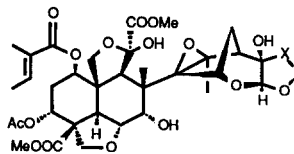
X,Y = CH=CH azadirachtin
X,Y = CH₂-CHOMe 22,23-dihydro-23-b-methoxyazadirachtin (2)
X,Y = CH₂-CHOAc 23-a,b-acetoxy-22,23-dihydroazadirachtin (3)

STUDIES ON GUEST SELECTIVE MOLECULAR RECOGNITION ON AN
OCTADECYL SILYLATED SILICON SURFACE USING ELLIPSOMETRY

Lars I. Andersson, Carl F. Mandenius and Klaus Mosbach
Pure and Applied Biochemistry, University of Lund, Box 124, S-221 00 Lund, Sweden

Application of the optical surface method ellipsometry to guest selective recognition is for the first time described. Detection of affinity binding by guest recognition to an octadecyl-silane derivatized silicon surface with vitamin K1 is examplified with the technique.

SYNTHESIS FROM D-GLUCOSE OF ALEXINE [(1R,2R,3R,7S,8S)-3-HYDROXYMETHYL-
1,2,7-TRIHYDROXYPYRROLIZIDINE], 3-EPIALEXINE AND 7-EPIALEXINE

George W.J. Fleet,[a] Martin Haraldsson,[a] Robert J. Nash[b] and Linda E. Fellows,[b]
[a]Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford OX1 3QY
[b]Jodrell Laboratory, Royal Botanic Gardens, Kew, Richmond, Surrey TW9 3DS

A protected 2-azido-2-deoxymannose
is a key intermediate in the
synthesis of alexine, 3-epialexine
and 7-epialexine.
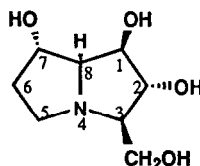
CHEMICAL MODELLING OF THE THYMIDYLATE SYNTHASE REACTION:
EVIDENCE FOR THE FORMATION OF AN EXOCYCLIC METHYLENE
INTERMEDIATE FROM ANALOGUES OF THE COVALENT TERNARY
COMPLEX FORMED BY INTRAMOLECULAR THIOL ADDITION TO C(6) OF
5-AMINOMETHYLURACIL DERIVATIVES

Paul F.C. van der Meij and Upendra K. Pandit*, Organic Chemistry Laboratory,
University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam,
The Netherlands.

The intramolecular thiol addition to C(6) of 1-(3-mercaptopropyl)- 5-aminomethyl -
uracil derivatives leads to bicyclic dihydrouracil derivatives, which fragment in protic
media to give an exocyclic methylene intermediate and the corresponding amines.