

GRAPHICAL ABSTRACTS

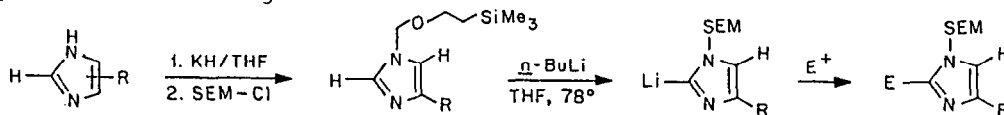
Tetrahedron Lett. 27, 4095 (1986)

PROTECTION OF IMIDAZOLES AS THEIR  $\beta$ -TRIMETHYLSILYLETHOXYMETHYL (SEM) DERIVATIVES

Bruce H. Lipshutz\*, Wayne Vaccaro and Bret Huff

Department of Chemistry, University of California, Santa Barbara, CA 93106 USA

An imidazole N-H is protected as its SEM derivative, metalated and alkylated at C-2, then deprotected with  $F^-$  or  $H_3O^+$ .

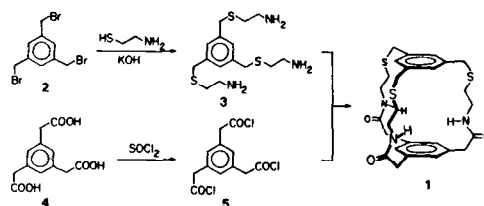


Tetrahedron Lett. 27, 4099 (1986)

SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF A (1,3,5)CYCLOPHANE WITH THREE AMIDE N-H GROUPS SURROUNDING A CENTRAL CAVITY. A NEUTRAL HOST FOR ANION COMPLEXATION.

R. A. Pascal, Jr.,\* J. Spergel, and D. Van Engen  
Department of Chemistry, Princeton University,  
Princeton, New Jersey 08544

The synthesis of compound 1 and its X-ray crystal structure are described.



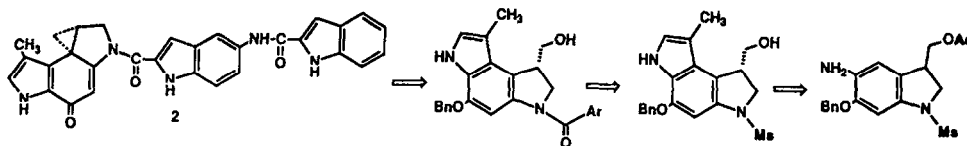
Tetrahedron Lett. 27, 4103 (1986)

TOTAL SYNTHESIS OF U-71,184, A POTENT NEW ANTITUMOR AGENT MODELED ON CC-1065

Martha A. Warpehoski

Cancer and Viral Diseases Research, The Upjohn Company, Kalamazoo, MI 49001

Total synthesis of potent antitumor agent 2.

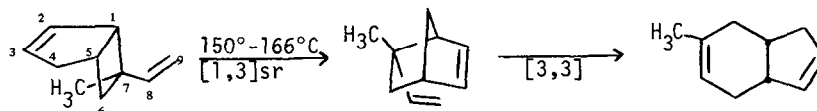


Tetrahedron Lett. 27, 4107 (1986)

THE THERMAL REARRANGEMENT OF ENDO-7-METHYL-EXO-7-VINYLBICYCLO[3.2.0]HEPT-2-ENE

Mark A. Forman and Phyllis A. Leber\*

Franklin & Marshall College, P.O. Box 3003, Lancaster, PA 17604 (USA)



sr = suprafacial migration of C-7 to C-3 with retention of configuration at the migrating carbon

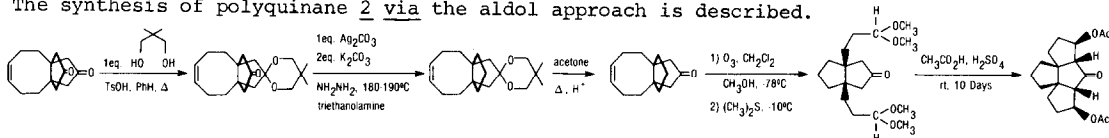
A GENERAL APPROACH TO THE SYNTHESIS OF POLYQUINANES.

SYNTHESIS OF TRANS, TRANS-4,8-DIACETOXY-TETRACYCLO-  
[9.3.0.0<sup>1,5</sup>.0<sup>7,11</sup>]TETRADECA-6-ONE VIA THE ALDOL APPROACH

M. Venkatachalam, G. Kubiak, S. Wehrli, U. Weiss and J. M. Cook\*

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI 53201 USA

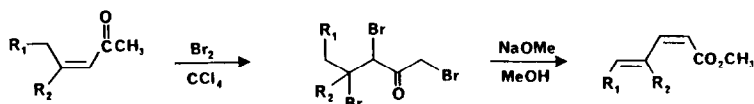
The synthesis of polyquinane **2** via the aldol approach is described.



A FACILE, STEREOSELECTIVE PREPARATION OF (Z)-  
2,4-PENTADIENOATES BY FAVORSKII REARRANGEMENT

Thomas A. Engler and Wolfgang Falter

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

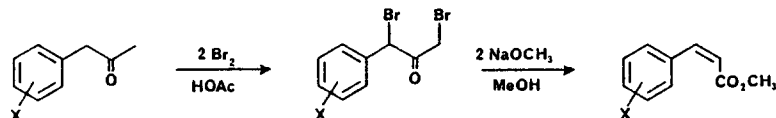


$R_1R_2 = -(CH_2)_n-$  or  $R_1 = H, R_2 = CH_3$  or Ph

STEREOSELECTIVE PREPARATION OF METHYL (Z)-CINNAMATES BY  
FAVORSKII REARRANGEMENT

Thomas A. Engler and Wolfgang Falter

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045



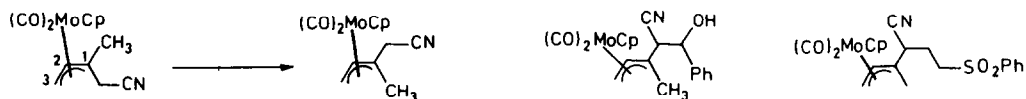
X = H, 4-CH<sub>3</sub>, 3-CF<sub>3</sub>, 4-Cl, 2,4-Cl<sub>2</sub>, 3,4-Cl<sub>2</sub>

GENERATION AND REACTIONS OF CARBANIONS IN THE  
PRESENCE OF A NEIGHBORING  $\eta^3$ -ALLYL-Mo(CO)<sub>2</sub>Cp MOIETY;

A NOVEL REARRANGEMENT SUGGESTING PARTICIPATION OF Mo IN CARBANION STABILIZATION

Anthony J. Pearson\*, Michael S. Holden and Robert D. Simpson, Department of Chemistry,  
Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

The following conversions are described:



## ARE PHENYLHALOCARBENES AMBIPHILIC?

R. A. Moss\*, W. Ławrynowicz, L. M. Hadel, N. P. Hacker,  
N. J. Turro\*, I. R. Gould, and Y. ChaDepartments of Chemistry, Rutgers, The State University of New Jersey, New Brunswick,  
New Jersey 08903 and Columbia University, New York, New York 10017 USA

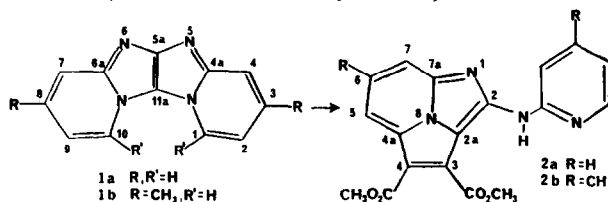
In additions to simple alkenes ( $\text{Me}_2\text{C}=\text{CMe}_2$ ,  $\text{Me}_2\text{C}=\text{CHMe}$ ,  $\text{Me}_2\text{C}=\text{CH}_2$ , trans- $\text{MeCH}=\text{CHMe}$ ,  
 $\text{CH}_2=\text{CHCOOMe}$ ,  $\text{CH}_2=\text{CHCN}$ ) and  $p\text{-XC}_6\text{H}_4\text{CH}=\text{CH}_2$  ( $\text{X} = \text{MeO}$ ,  $\text{Me}$ ,  $\text{H}$ ,  $\text{Cl}$ ,  $\text{CF}_3$ ), the selectivities  
of  $\text{PhCF}$  and  $\text{PhCCl}$  are best described as electrophilic.

A MASKED  $[\pi 8 + \pi 2]$  CYCLOADDITION REACTION INVOLVING THE  
1,3,4,6-TETRAAZAPENTALENE RING SYSTEM

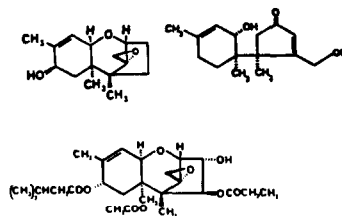
David E. Pereira and Nelson J. Leonard\*

Roger Adams Laboratory, School of Chem. Sciences, Univ. of Illinois, Urbana, IL 61801

Dipyrido[1,2-a:2',1'-f]-1,3,4,6-tetra-  
azapentalene (**1a**) and its 3,8-dimethyl  
homolog **1b** undergo  $[\pi 8 + \pi 2]$  cyclo-  
addition reactions with dimethyl  
acetylenedicarboxylate to give, upon  
C-N bond cleavage, substituted 1-aza-  
cyl[3.2.2]azines **2a**, **b**.

NEW TRICHOHECENE MYCOTOXINS OF Fusarium sporotrichioides  
(MC-72083)David G. Corley<sup>+</sup>, George E. Rottinghaus,<sup>++</sup> John K. Tracy<sup>++</sup>  
and Michael S. Tempesta<sup>++</sup>, Department of Chemistry<sup>+</sup> and  
Veterinary Medical Diagnostic Laboratory,<sup>++</sup> University  
of Missouri, Columbia, Missouri 65211

Isolation and characterization of three new trichothecene  
mycotoxins from Fusarium sporotrichioides MC-782083 are  
reported.

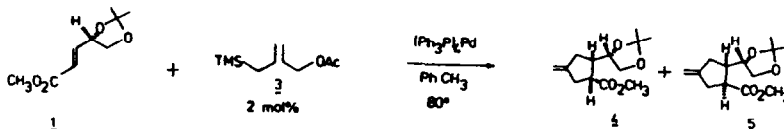


## A STEREOSPECIFIC PALLADIUM MEDIATED [3+2] CYCLOADDITION

Barry M. Trost\* and Serge M. Mignani

University of Wisconsin, Department of Chemistry, 1101 University Ave., Madison, WI 53706

The [3+2] palladium mediated cycloaddition to methyl (E)- and (Z)- (R)-4,5-di-*O*-  
-isopropylidene-pent-2-enoates parallels the Diels-Alder reactions of these same acceptors.

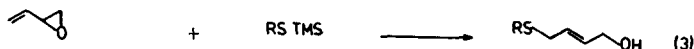


**SYNTHESIS OF ALLYL SULFIDES VIA A PALLADIUM MEDIATED ALLYLATION**

Barry M. Trost\* and Thomas S. Scanlan

Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, WI 53706

A mild chemo-, regio-, and diastereoselective substitution of allyl carbonates and vinyl epoxides by sulfur nucleophiles catalyzed by palladium can overcome difficulties in and complement conventional displacement without poisoning of the catalyst.

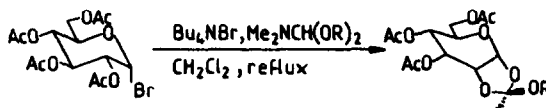


**An efficient and stereoselective synthesis of 3,4,6-tri-O-acetyl- $\alpha$ -D-glucopyranose 1,2-(exo-alkyl orthoacetates)**

J. Banoub, P. Boullanger, M. Potier and G. Descotes

Laboratoire de Chimie Organique 2, Université Lyon I, 69622 Villeurbanne, France.

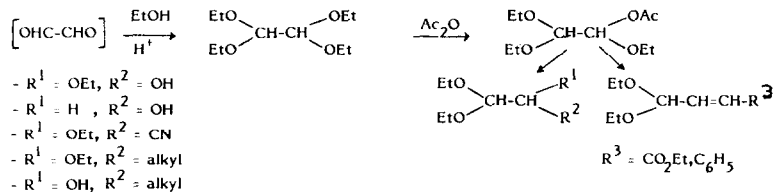
Stereoselective synthesis of 1,2-exo-orthoacetates from the corresponding fully acetylated glycosyl bromide.



Dissymmetrization of Glyoxal I. Synthesis and reactivity of 1-acetoxy-1,2,2-triethoxyethane.

A. STAMBOULI, F. CHASTRETTE, R. AMOUROUX, M. CHASTRETTE - Laboratoire de Chimie Organique Physique, LYON I, 69622 Villeurbanne Cédex France.

G. MATTIODA, A. BLANC - Société Française HOECHST - STAINS France.



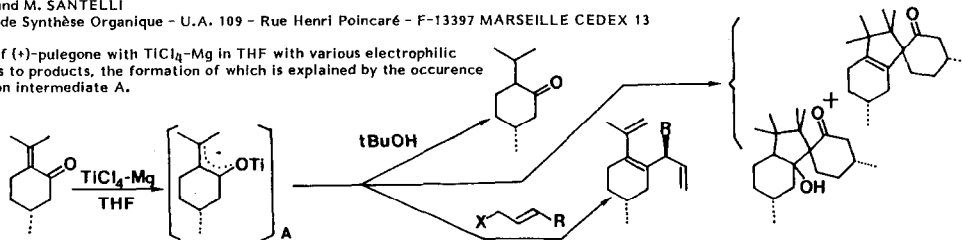
**REDUCTIVE COUPLING OF  $\alpha$ - $\beta$  UNSATURATED KETONES II.**

(+)-PULEGONE: AN EXAMPLE OF UMPOLUNG.

J.M. PONS and M. SANTELLI

Laboratoire de Synthèse Organique - U.A. 109 - Rue Henri Poincaré - F-13397 MARSEILLE CEDEX 13

Treatment of (+)-pulegone with  $\text{TiCl}_4$ -Mg in THF with various electrophilic species leads to products, the formation of which is explained by the occurrence of the dianion intermediate A.

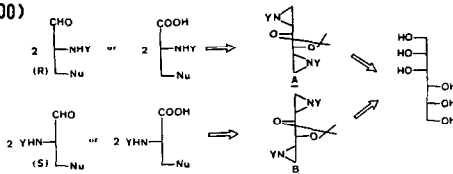


**DIASTEREOSPECIFIC SYNTHESIS OF DIAZIRIDINES  
FROM D-MANNITOL.ACCESS TO CHIRAL  $\alpha$ -AMINOACIDS.**

A. Duréault, C. Gréck and J.-C. Depezay\*

 Université René Descartes- Laboratoire de Chimie et Biochimie  
 Pharmacologiques et Toxicologiques (Unité Associée au CNRS n° 400)  
 45 rue des Sts Pères-75270 Paris Cedex 06 FRANCE

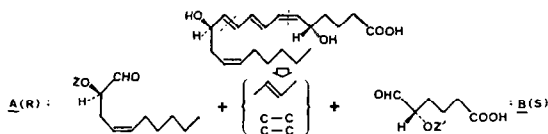
Nucleophilic opening of chiral diastereoisomeric diaziridines obtained from D-mannitol leads to precursors of D or L  $\alpha$ -aminoacids (or aldehydes) and also provides a means of synthesizing polyhydroxylated piperidines.


**TOTAL SYNTHESIS OF LEUKOTRIENE (+)-LTB<sub>4</sub>  
FROM D-MANNITOL**

Y. Le Merrer, C. Gravier, D. Languin-Micas and J.-C. Depezay\*

 Université René Descartes-Laboratoire de Chimie et Biochimie  
 Pharmacologiques et Toxicologiques (Unité Associée au CNRS n° 400)  
 45 rue des Sts Pères-75270 Paris Cedex 06 FRANCE

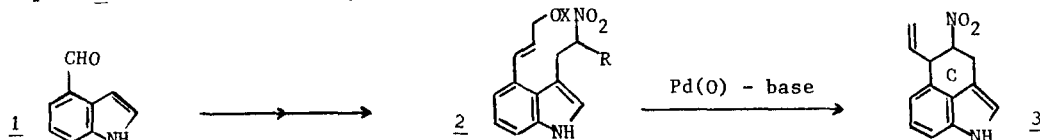
A total convergent synthesis of leukotriene LTB<sub>4</sub> has been carried out via two enantiomerically pure  $\alpha$ -hydroxyaldehydes, chiral key intermediates both obtained from D-mannitol and connected at a four carbon atoms interval by Wittig reactions.


**ERGOLINE PRECURSORS 3. AN EFFICIENT SYNTHESIS OF C  
RING BY PALLADIUM (0) CATALYZED REACTIONS**

J.P. GENET, S. GRISONI

Laboratoire de Chimie Organique et Organométallique - 8, rue Cuvier - 75005 - Paris

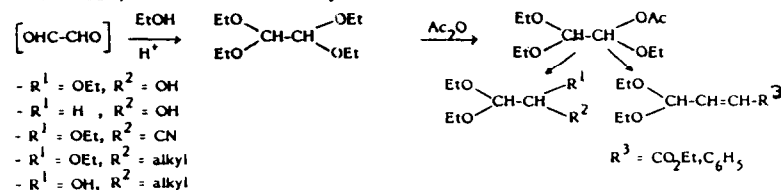
A six step synthesis of the tricyclic ergoline 3 synthon is described from indole-4 carboxaldehyde 1 in 38-43 % overall yield, via Pd(0)-catalyzed cyclisation of nitroderivatives 2.



Dissymmetrization of Glyoxal I. Synthesis and reactivity of 1-acetoxy-1,2,2-triethoxyethane.

 A. STAMBOULLI, F. CHASTRETTE, R. AMOUROUX, M. CHASTRETTE - Laboratoire de Chimie Organique Physique,  
 LYON I, 69622 Villeurbanne Cédex France.

G. MATTIODA, A. BLANC - Société Française HOECHST - STAINS France.

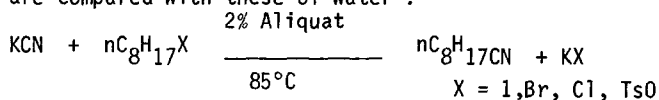


Tetrahedron Lett. 27, 4171 (1986)

Effect of water and other additives on alkylation of KCN  
by liquid-solid phase transfer catalysis without solvent

Bram G., Loupy A., Pedoussaut M., UA CNRS 478, Bâtiment 410, Université de Paris Sud  
F 91405 ORSAY, France .

The alkylation of KCN by solid-liquid phase transfer catalysis without added solvent is  
optimal when a definite amount of water is added. The efficiencies of ten other additives  
are compared with these of water .



Electrosynthesis of ketones from organic halides and  
anhydrides.

Tetrahedron Lett. 27, 4175 (1986)

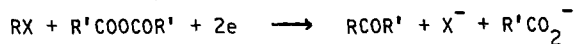
Esther d'INCAN, Soline SIBILLE, Jacques PERICHON.

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, C.N.R.S., 94320 THIAIS, France.

Marie-Odile MOINGEON, Jacques CHAUSSARD

S.N.P.E. Le Bouchet, 91710 VERT-LE-PETIT, France.

An Electrochemical synthesis of ketones from organic halides and anhydrides :



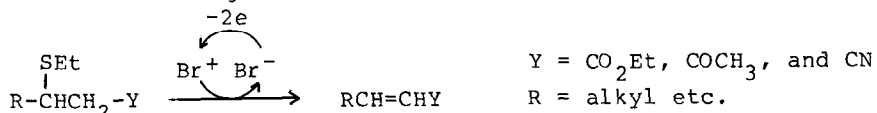
using sacrificial anodes of magnesium or aluminium in an undivided cell.

ELECTROOXIDATIVE DESULFENYLATION OF MICHAEL-TYPE  
THIOL ADDUCTS OF  $\alpha,\beta$ -UNSATURATED ESTERS, KETONS,  
AND NITRILES

Tetrahedron Lett. 27, 4177 (1986)

Makoto Kimura, Shinichi Matsubara, Yasuhiko Sawaki\* and Hiizu Iwamura\*  
Department of Applied Chemistry, Faculty of Engineering, Nagoya  
University, Chikusa-ku, Nagoya 464, Japan

A useful deprotection of protected electron-deficient olefins by an indirect  
electrooxidation involving bromide-bromonium ions



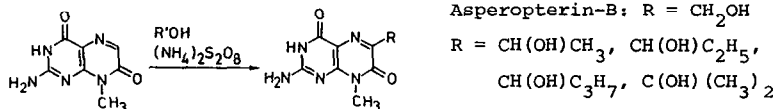
SYNTHESIS OF ASPEROPTERIN-B AND SOME ANALOGUES

Takashi Sugimoto,\* Shizuaki Murata, Sadao Matsuura, and Wolfgang Pfleiderer†

Department of Chemistry, College of General Education, Nagoya University, Nagoya 464, Japan

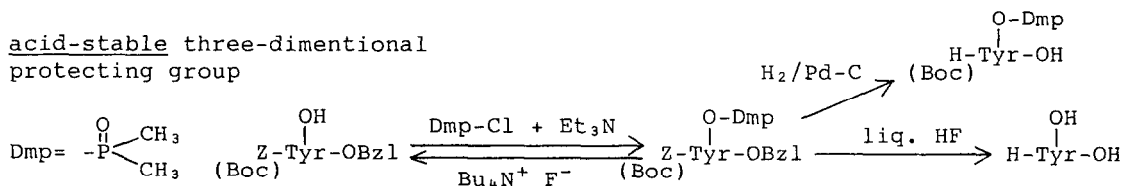
†Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz, West Germany

A homolytic hydroxyalkylation of 8-methylisoxanthopterin,

Tetrahedron Lett. 27, 4179 (1986)

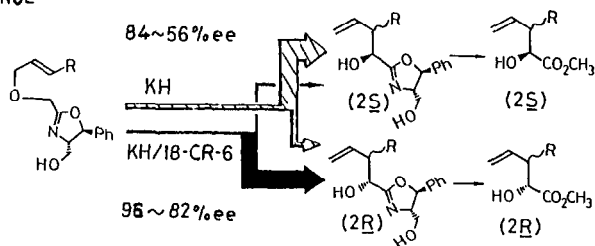
Dimethylphosphinyl(Dmp): A New Protecting Group of Tyrosine Suitable for Peptide Synthesis by Use of Boc-amino Acids, M. Ueki, Y. Sano, I. Sori, K. Shinozaki, H. Oyamada, S. Ikeda

acid-stable three-dimensional protecting group



ASYMMETRIC [2,3]WITTIG REARRANGEMENT INVOLVING POTASSIUM AZAENOLATES. THE DRAMATIC INFLUENCE OF THE POTASSIUM COUNTERION AND ITS COMPLEXATION WITH 18-CROWN-6

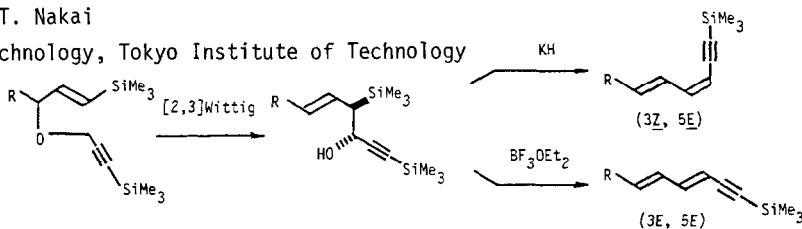
K. Mikami, T. Kasuga, K. Fujimoto, T. Nakai  
Department of Chemical Technology,  
Tokyo Institute of Technology,  
Meguro, Tokyo 152, Japan



[2,3]WITTIG REARRANGEMENT-PETERSON OLEFINATION SEQUENCE: A STEREOCONTROLLED APPROACH TO CONJUGATED DIENYNES

K. Mikami, T. Maeda, and T. Nakai

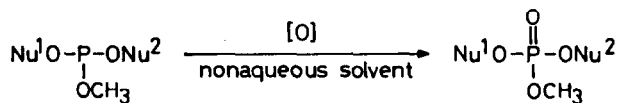
Department of Chemical Technology, Tokyo Institute of Technology  
Meguro, Tokyo 152, Japan.



NONAQUEOUS OXIDATION OF NUCLEOSIDE PHOSPHITES TO THE PHOSPHATES

Y. Hayakawa,\* M. Uchiyama,<sup>†</sup> and R. Noyori<sup>†\*</sup>

Chemical Instrument Center and <sup>†</sup>Department of Chemistry, Nagoya University,  
Chikusa, Nagoya 464, Japan



NuOH = protected nucleoside

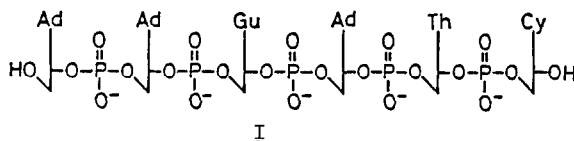
Tetrahedron Lett. 27, 4195 (1986)

SOLID-PHASE SYNTHESIS OF OLIGODEOXYRIBO-  
NUCLEOTIDES USING THE BIS(TRIMETHYLSILYL)  
PEROXIDE OXIDATION OF PHOSPHITES

Y. Hayakawa,\* M. Uchiyama,<sup>†</sup> and R. Noyori<sup>†\*</sup>

Chemical Instrument Center and <sup>†</sup>Department of Chemistry, Nagoya University,  
Chikusa, Nagoya 464, Japan

Synthesis of an oligonucleotide **I**,  
a part of the probe for chum salmon  
prolactin, using TMSOOTMS oxidation  
of phosphites.

Tetrahedron Lett. 27, 4197 (1986)

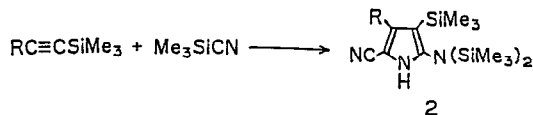
SYNTHESIS OF 5-AMINO-2-CYANO-4-SILYLPYRROLES  
FROM SILYLACETYLENES AND TRIMETHYLSILYL CYANIDE

Tetsuo Kusumoto, Tamejiro Hiyama,\* and Koreharu Ogata<sup>#</sup>

Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Kanagawa 229, Japan

<sup>#</sup>Analytical Center, Chiba University, Yayoi-cho, Chiba 260, Japan

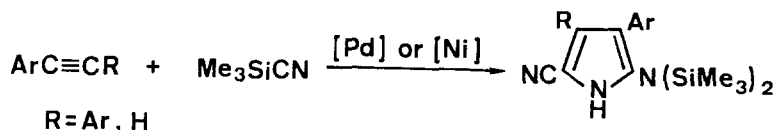
The title reaction of **1** with Pd catalysts gives **2** selectively.

Tetrahedron Lett. 27, 4201 (1986)

PALLADIUM- OR NICKEL-CATALYZED REACTION OF ALKYNES  
WITH TRIMETHYLSILYL CYANIDE. A NEW SYNTHESIS OF  
5-AMINOPYRROLE-2-CARBONITRILES

Naoto Chatani\* and Terukiyo Hanafusa

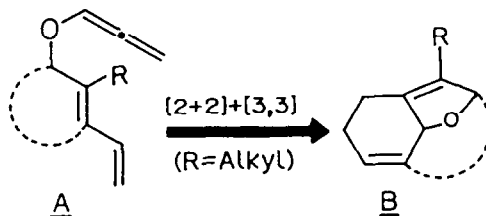
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, 567, Japan

Tetrahedron Lett. 27, 4205 (1986)

A Highly Efficient Synthesis of Bicyclo-  
[n.3.1] Ring Systems By Allene Intra-  
molecular Cycloaddition: Tandem Intra-  
molecular [2+2] Cycloaddition-[3.3]-  
Sigmatropic Rearrangement

K. Hayakawa, S. Ohsuki, K. Kanematsu\*  
Faculty of Pharmaceutical Sciences,  
Kyushu University, Fukuoka 812, Japan

A Novel construction of tricyclic[5.3.1]  
undecane skeleton via tandem [2+2], [3,3]  
reactions of allenyl ethers is described.



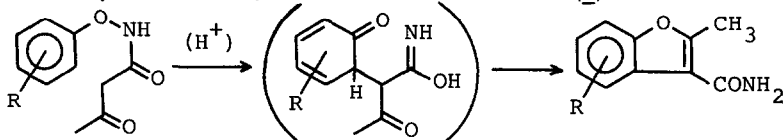


**CHEMISTRY OF O-ARYLHYDROXYLAMINES. A NOVEL ACID-CATALYZED REARRANGEMENT OF O-ARYL-N-ACETOACETYLHYDROXYLAMINES TO BENZOFURANS.**

Tetrahedron Lett. 27, 4209 (1986)

Yasuyuki Endo, Kohshi Namikawa and Koichi Shudo\*

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, JAPAN  
Treatment of O-aryl-N-acetoacetylhydroxylamines (1) with an acid causes rearrangement to the 2-methylbenzofuran-3-carboxamide derivatives (2).



1

2

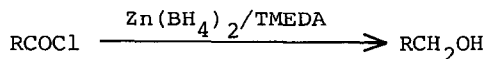
R = alkyl, aryl, alkoxy

**EFFICIENT REDUCTION OF ACYL CHLORIDES WITH ZINC BOROHYDRIDE/N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE**

Tetrahedron Lett. 27, 4213 (1986)

Hiyoshizo Kotsuki,\* Yasuyuki Ushio, Naka Yoshimura, and Masamitsu Ochi  
Department of Chemistry, Faculty of Science, Kochi University,  
Akebono-cho, Kochi 780, Japan

Various types of aliphatic and aromatic acyl chlorides are reduced in good yields.



**PALLADIUM CATALYZED ALLYLATION OF REFORMATSKY REAGENTS. SYNTHESIS OF  $\gamma,\delta$ -UNSATURATED ESTERS.**

Tetrahedron Lett. 27, 4223 (1986)

G.P. Boldrini, M. Mengoli, E. Tagliavini, C. Trombini and A. Umani-Ronchi

Istituto Chimico "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, ITALY

