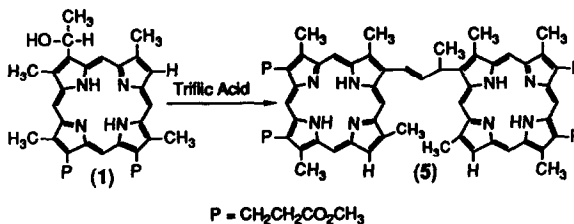


## GRAPHICAL ABSTRACTS

**EFFICIENT SYNTHESIS OF PORPHYRIN DIMERS WITH CARBON-CARBON LINKAGES.** Ravindra K. Pandey,\*  
Fuu-Yau Shiau, Craig J. Medforth, Thomas J. Dougherty,  
and Kevin M. Smith.\*

Oncologic Foundation of Buffalo, 225 Oak Street,  
Buffalo, NY 14203, Department of Chemistry,  
University of California, Davis, CA 95616, and  
Department of Radiation Biology, Roswell Park  
Memorial Institute, 666 Elm Street, Buffalo, NY 14263.



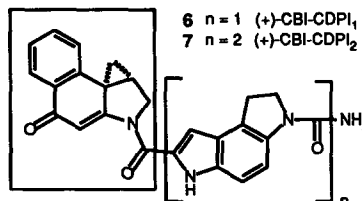
Treatment of [(1-hydroxy)ethyl]porphyrins e.g. (1) with triflic acid affords high yields of the carbon-carbon linked dimer e.g. (5).

**RESOLUTION OF A CBI PRECURSOR AND INCORPORATION INTO THE SYNTHESIS OF (+)-CBI, (+)-CBI-CDPI<sub>1</sub>, (+)-CBI-CDPI<sub>2</sub>; ENHANCED FUNCTIONAL ANALOGS OF (+)-CC-1065. A CRITICAL APPRAISAL OF A PROPOSED RELATIONSHIP BETWEEN ELECTROPHILE REACTIVITY, DNA BINDING PROPERTIES, AND CYTOTOXIC POTENCY.**

Dale L. Boger\* and Takayoshi Ishizaki, Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907, USA

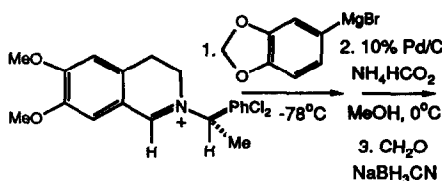
*Summary: Details of the resolution of an immediate CBI precursor and its subsequent incorporation into (+)- and (-)-CBI-CDPI<sub>n</sub>, optically-active enhanced functional analogs of (+)-CC-1065, are described. In marked contrast to a previously detailed direct relationship between electrophile reactivity and cytotoxic potency, an inverse relationship between the properties is detailed.*

*Tetrahedron Lett.* **1990**, *31*, 793



### DIASTEREOSELECTIVE ADDITION OF ORGANOMETALLIC

**REAGENTS TO CHIRAL IMINIUM IONS: SYNTHESIS OF (S)-(+)-CRYPTOSTYLINE I.**



*Tetrahedron Lett.* **1990**, *31*, 797  
Richard P. Polniaszek and Lawrence W. Dillard  
Department of Chemistry  
Duke University, Durham, NC 27706

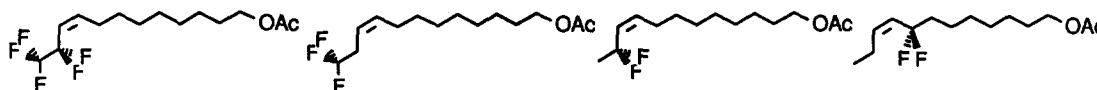
Stereospecific addition of 3,4-dimethoxyphenyl magnesium bromide to iminium ion 2c followed by hydrogenolysis and Borch reduction afforded (S)-(+)-cryptostyline I.

**PARTIALLY FLUORINATED ANALOGS OF (Z)-9-DODECENYL ACETATE: PROBES FOR PHEROMONE HYDROPHOBICITY REQUIREMENTS.**

Wei-Chuan Sun and Glenn D. Prestwich\*

Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400.

Allylic difluoromethylene, terminal trifluoromethyl, and pentafluoroethyl analogs of (Z)-9-dodecanyl acetate were synthesized to probe the requirements for hydrophobicity of the alkyl terminus in pheromone activity.



*Tetrahedron Lett.* **1990**, *31*, 801

## DIRECT RADICAL SUBSTITUTION ON THE CUBANE SKELETON

*Tetrahedron Lett.* 1990, 31, 805

D. Sivakumar Reddy,<sup>a</sup> Michele Maggini,<sup>b</sup> John Tsanaktsidis,<sup>b</sup> Philip E. Eaton<sup>a,b</sup>

<sup>a</sup>U.S. Army Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, NJ 07806-5000

<sup>b</sup>Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, IL 60637

**Summary:** Radical iodination of cubane and derivatives occurs on irradiation with *tert*-butyl hypiodite.

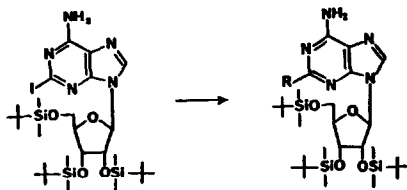


## COPPER MEDIATED REACTIONS IN NUCLEOSIDE SYNTHESIS

Vasu Nair\* and Todd B. Seils

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

*Tetrahedron Lett.* 1990, 31, 807



Regiospecific functionalization of nucleosides via copper mediated reactions is described.

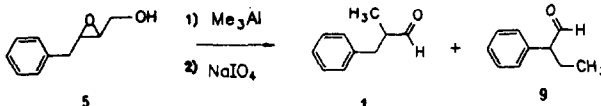
R = CN, SCN, NH<sub>2</sub>, N<sub>3</sub>, NHOH,  
C≡CC<sub>4</sub>H<sub>9</sub>, CH(CO<sub>2</sub>E)<sub>2</sub>

## SYNTHESIS OF CHIRAL ADENOSINE RECEPTOR RECOGNITION UNITS VIA A SHARPLESS ASYMMETRIC EPOXIDATION PROCEDURE

Nelsen L. Lentz and Norton P. Peet\*

Merrell Dow Research Institute, 2110 E. Galbraith Road, Cincinnati, OH 45215

Butyraldehydes **1** and **9** were prepared from epoxy alcohol **5** by treatment with trimethylaluminum followed by oxidation with sodium periodate. Opening of **5** with trimethylaluminum is a phenonium ion-mediated process.



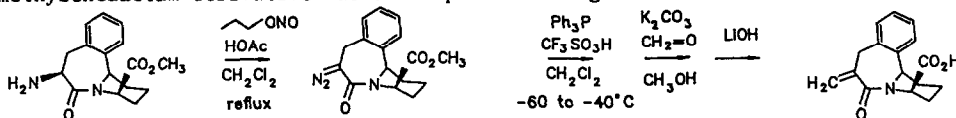
*Tetrahedron Lett.* 1990, 31, 811

## THE CONVERSION OF A DIAZOLACTAM TO AN $\alpha$ -METHYLENELACTAM: AN ENTRANCE TO NEW CONFORMATIONALLY RESTRICTED INHIBITORS OF ANGIOTENSIN-CONVERTING ENZYME

Gary A. Flynn\*, Douglas W. Beight, Edward W. Huber and Philippe Bey

Merrell Dow Research Institute, 2110 E. Galbraith Rd., Cincinnati, Ohio 45215, USA

Methodology for the conversion of an  $\alpha$ -aminolactam dipeptide mimic to an  $\alpha$ -methylenelactam derivative was developed utilizing an intermediate  $\alpha$ -diazolactam.



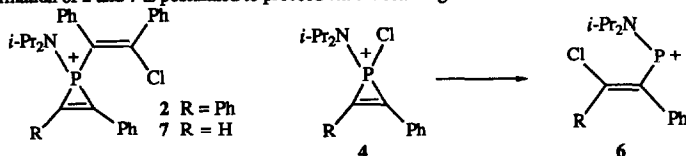
*Tetrahedron Lett.* 1990, 31, 815

## Evidence For The Rearrangement of P-Chloro-Phosphirenium Ions to P-Vinyl-Phosphonium Ions

Steven A. Weissman\* and S. G. Baxter

Fred Stark Pearson Memorial Laboratories, Department of Chemistry, Tufts University, Medford, MA 02155

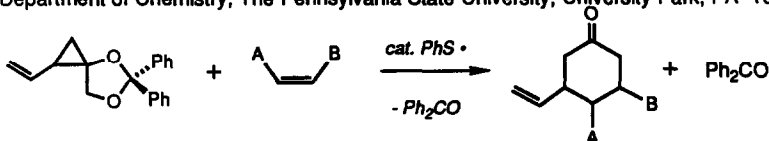
The formation of 2 and 7 is postulated to proceed via the rearrangement of 4 to 6.



## PHENYLTHIO RADICAL MEDIATED SYNTHESIS OF SUBSTITUTED 3-VINYLCYCLOHEXANONES. INTERRUPTION OF THE RING-OPENING POLYMERIZATION OF 1,3-DIOXOLAN-4-YL RADICALS.

Ken S. Feldman\* and Antonio Kuok Keong Vong

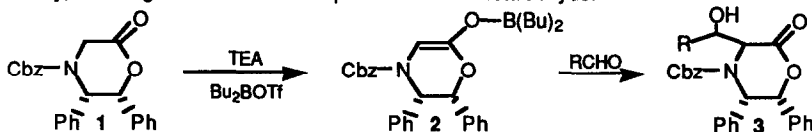
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802



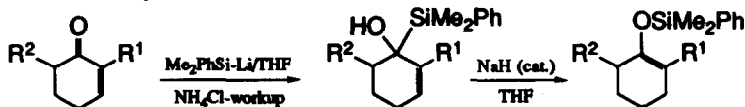
## ASYMMETRIC ALDOL REACTIONS USING BORON ENOLATES OF CHIRAL OXAZINONES, SYNTHESIS OF L-ALLO-THREONINE

Daniel S. Reno, Bruce T. Lotz, and Marvin J. Miller\*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556

The boron enolate of oxazinone 1 was allowed to react with several aldehydes. The reaction proceeded with *anti* selectivity, affording an L-*allo*-threonine precursor from acetaldehyde.1,2-ADDITION OF DIMETHYL(PHENYL)SILYLLITHIUM TO CYCLIC  $\alpha,\beta$ -UNSATURATED KETONES AND REGIO-SPECIFIC GENERATION OF CYCLIC SILYL ENOL ETHERS THROUGH BROOK REARRANGEMENT OF THE 1,2-ADDITION PRODUCTS

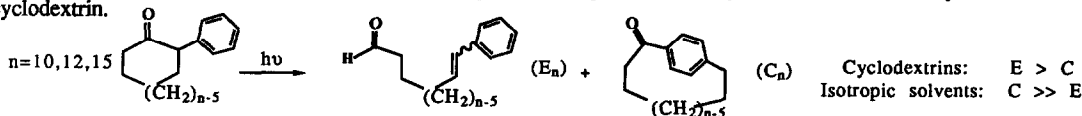
Masato Koreeda\* and Sangho Koo, Department of Chemistry, The University of Michigan, Michigan, Ann Arbor, Michigan 48109

A highly convenient two-step sequence for the regiospecific synthesis of cyclic silyl enol ethers has been developed involving the 1,2-addition of Me<sub>2</sub>PhSiLi to cyclic  $\alpha,\beta$ -unsaturated ketones in THF followed by the treatment of the resulting silyl carbinols with a catalytic amount of NaH at 25 °C.

**A FINE-TUNING OF PHOTOREACTIVITY OF LARGE RING  
2-PHENYLCYCLOALKANONES ADSORBED IN CYCLODEXTRINS**

V. Pushkara Rao, Nianhe Han and Nicholas J. Turro\*  
Chemistry Department, Columbia University, New York, NY 10027.

The Photochemistry of 2-phenylcycloalkanones adsorbed in cyclodextrin cavities results in significant yields of enals at the expense of para-cyclophane, depending on the ring size of the cyclanone and the cavity size of the cyclodextrin.



**ASYMMETRIC SYNTHESIS: MODIFICATION OF  
CHIRAL FERROCENYLAMINE LIGANDS FOR THE GOLD(I)-CATALYZED ALDOL REACTION**

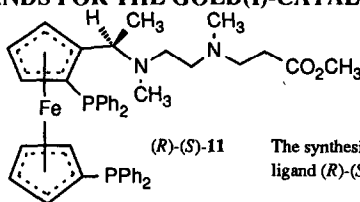
Stephen D. Pastor\* and Antonio Togni

Central Research Laboratories

CIBA-GEIGY Ltd., R-1060

P. O. Box

CH-4002 Basel, Switzerland

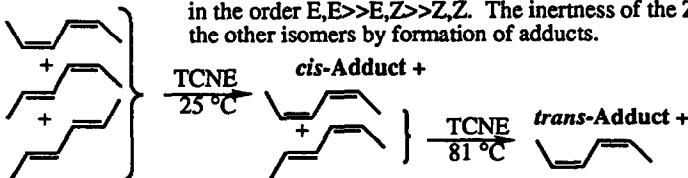


The synthesis of the ester functional chiral ligand (R)-(S)-11 is described

**Reactions of TCNE with Isomeric 2,4-Hexadienes**

Kevin E. O'Shea and Christopher S. Foote\* Department of Chemistry  
and Biochemistry, University of California, Los Angeles, CA 90024, USA

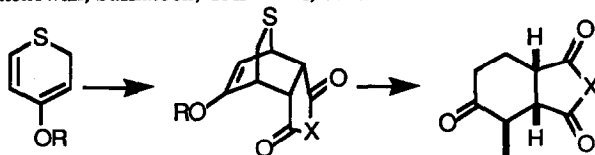
Reactivities of isomeric 2,4-hexadienes with tetracyanoethylene (TCNE) differ enormously, in the order E,E>>E,Z>>Z,Z. The inertness of the Z,Z isomer allows complete removal of the other isomers by formation of adducts.



**DIELS-ALDER REACTIONS OF 2H-THIOPYRANS.**

Dale E. Ward\*, Wajdi M. Zoghaib, Chung K. Rhee, and Yuanzhu Gai  
Department of Chemistry, University of Saskatchewan, Saskatoon, CANADA, S7N 0W0.

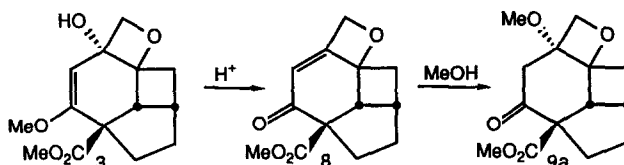
Activated 2H-thiopyrans react with typical dienophiles to give predominantly endo adducts in modest to good yield. Desulfurization provides compounds equivalent to an endo adduct of a cis-diene.



ACID-CATALYZED REARRANGEMENT OF METHYL (2 $\alpha$ ,4 $\alpha\beta$ ,6 $\alpha\beta$ ,7 $\beta$ )-2,2 $\alpha$ ,5,6,6 $\alpha$ ,7 $\beta$ -HEXAHYDRO-2 $\alpha$ -HYDROXY-4-METHOXY-CYCLOBUT[3,4]-INDENO[4,5-b]OXETE-4 $\alpha$ (7H)-CARBOXYLATE.

Arthur G. Schultz\* and Arthur G. Taveras, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180; Rudolph K. Kullnig, Sterling Research Group, Rensselaer, New York 12144

Acid-catalyzed rearrangement of **3** gives **9a** (presumably via bridgehead enone **8**) rather than a product of a pinacol-like rearrangement.

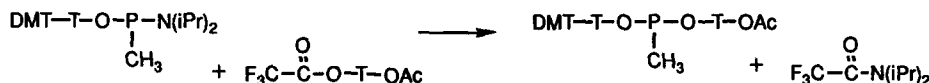


**A New DMAP-Catalyzed Phosphonamidite Coupling Reaction for Synthesis of Oligonucleotide Methylphosphonate Derivatives.**

Alexander V. Lebedev\*, George R. Wenzinger, and Eric Wickstrom†.

Department of Chemistry, University of South Florida, Tampa, Florida, 33620, USA

\*Institute of Bioorganic Chemistry, Siberian Division of the Academy of Sciences of the USSR, Novosibirsk 630090, USSR.

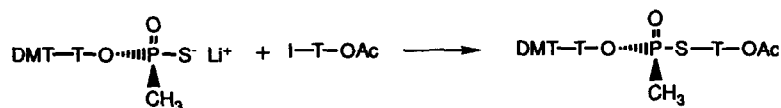


**Stereospecific Coupling Reaction for Internucleotide Methyl Phosphonothioate Linkage**

Alexander V. Lebedev\*, Jason P. Rife, Howard W. Seligsohn, George R. Wenzinger, and Eric Wickstrom†.

Department of Chemistry, University of South Florida, Tampa, Florida, 33620, USA

\*Institute of Bioorganic Chemistry, Siberian Division of the Academy of Sciences of the USSR, Novosibirsk 630090, USSR.



**ALKYLATION OF KETONES BY USE OF SOLID KOH IN DIMETHYL SULFOXIDE**

Elke Langhals<sup>a)</sup> and Heinz Langhals<sup>b)</sup>

a) present address: Consortium für Elektrochemische Industrie Zielstattstraße 20, D-8000 München 70, Germany

b) Institut für Organische Chemie der Universität München Karlstraße 23, D-8000 München 2, Germany



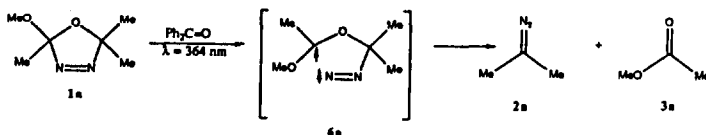
A mixture of solid KOH in dimethyl sulfoxide has a strong basicity, but only a low nucleophilicity and is used for  $\alpha$  methylation of ketones. With this simple and inexpensive reagent complete methylation with yields up to 90% can be achieved.

UV-LASER PHOTOCHEMISTRY: RETRO-CLEAVAGE IN THE BENZOPHENONE-SENSITIZED PHOTOLYSIS OF  $\Delta^3$ -1,3,4-OXADIAZOLINES INTO DIAZOALKANES

Waldemar Adam\*, Ralf Finzel

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, F.R.G.

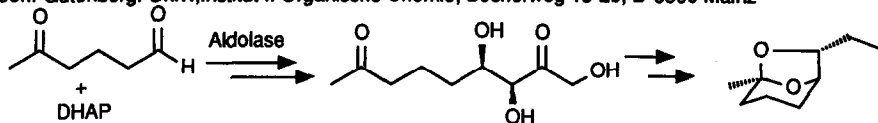
Triplet-sensitized photolysis of **1a** led to **2a** and **3a**, for which the triplet diazenyl diradical **6a** is postulated as precursor.



STEREOSPECIFIC C-C-BOND FORMATION WITH RABBIT MUSCLE ALDOLASE - A CHEMOENZYMIC SYNTHESIS OF (+)-EXO-BREVICOMIN

M. Schultz, H. Waldmann\*, W. Vogt and H. Kunz

Joh.-Gutenberg.-Univ., Institut f. Organische Chemie, Becherweg 18-20, D-6500 Mainz

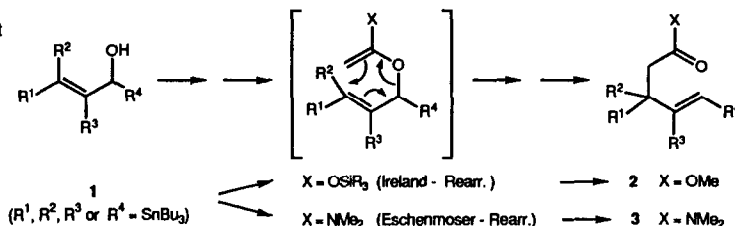


CLAISEN REARRANGEMENT OF ORGANOTIN COMPOUNDS

Kurt Ritter

Organisch-chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, F.R.G.

The Ireland and Eschenmoser variations of the Claisen rearrangement of various organotin compounds **1** afforded tributylstannyl-substituted,  $\gamma,\delta$ -unsaturated esters **2** or amides **3**.

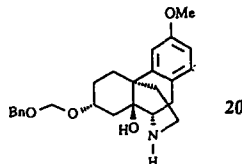


Enantioselective approach to morphinans

H. Sdassi, G. Revial, M. Pfau, J. d'Angelo

Unité de Chimie Organique, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

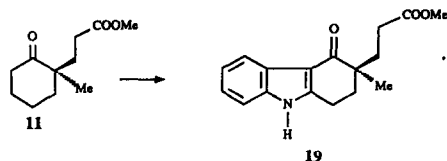
2,7-Dimethoxynaphthalene has been converted in 12 steps into morphinan derivative **20** (11 % overall yield)



A new strategy for the enantioselective synthesis of Aspidosperma alkaloids : I Construction of the [ABC]-type tricyclic intermediates.

Jean d'Angelo and Didier Desmaele  
Unité de Chimie Organique, ESPCI,  
10 rue Vauquelin, 75231 Paris Cedex 05, France.

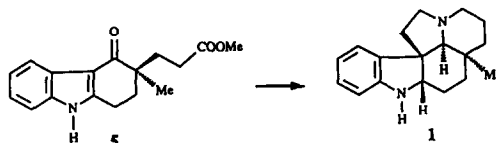
Carbazole **19** has been prepared in 8 steps from cyclohexanone **11** (36 % overall yield).



A new strategy for the enantioselective synthesis of Aspidosperma alkaloids : II Achievement of the pentacyclic system.

Didier Desmaele and Jean d'Angelo  
Unité de Chimie Organique, ESPCI,  
10 rue Vauquelin, 75231 Paris Cedex 05, France.

Carbazole **5** has been converted in 11 steps into alkaloid **1** (13 % overall yield)

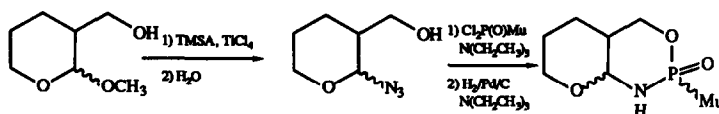


**SYNTHESIS AND CONFIGURATIONAL ASSIGNMENT OF BICYCLIC "PREACTIVATED" ANALOGUES OF CYCLOPHOSPHAMIDE**

B. Lilo, M. Moreau and D. Bouchu\*

*E.S.C.I.L., Université Claude Bernard, Laboratoire de Synthèse Organique Appliquée  
43, bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.*

The synthesis of a new class of bicyclic "preactivated" analogues of Cyclophosphamide, 3-[bis(2-chloroethyl)amino]-2-aza-3-phospha-4,10-dioxabicyclo(4.4.0)decane 3-oxide is described.

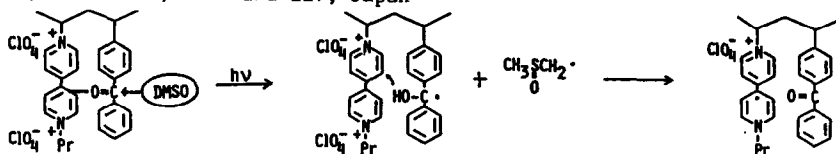


The configurational assignment of the stereoisomers was made by <sup>31</sup>P and <sup>1</sup>H NMR.

**UNUSUAL PHOTOREDUCTION OF VIOLOGEN BY DIMETHYL SULFOXIDE ON A NEW POLYMER HAVING DIRECT PENDANTS OF VIOLOGEN AND BENZOPHENONE STRUCTURES**

Yoko Nambu, Yokeai Gan, Chiho Tanaka, and Takeshi Endo\*

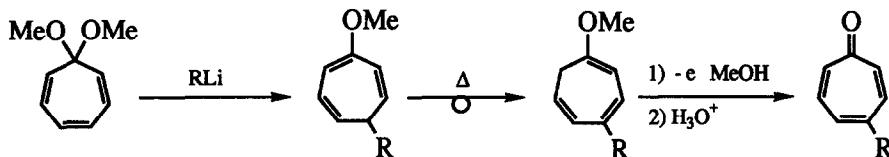
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,  
Nagatsuta, Midori-ku, Yokohama 227, Japan



A NOVEL REGIOSELECTIVE SYNTHESIS OF 4-SUBSTITUTED TROPONES

*Tetrahedron Lett.* 1990, 31, 895

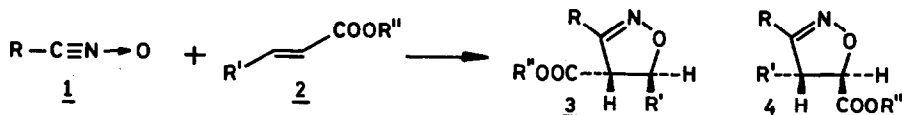
Tatsuya Shono,\* Hirofumi Maekawa, Tetsuo Nozoe, and Shigenori Kashimura  
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University,  
Yoshida, Sakyo, Kyoto 606, Japan



A REGIOSELECTIVE ENZYME CATALYZED CYCLOADDITION

*Tetrahedron Lett.* 1990, 31, 899

K.Rama Rao\*, N.Bhanumathi, T.N.Srinivasan and P.B.Sattur  
Organic Chemistry-I, Indian Institute of Chemical Technology, Hyderabad-500 007, India  
Reversal of regioselectivity is also observed in Baker's Yeast catalyzed cycloaddition  
by using  $\beta$ -cyclodextrin as an artificial enzyme.

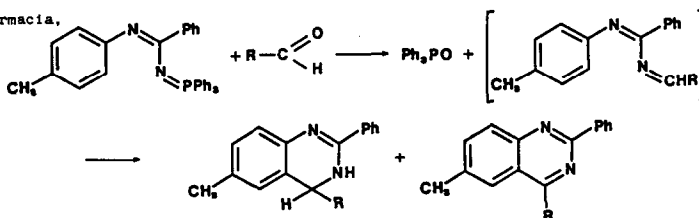


QUINAZOLINE BY ELECTROCYCLIC RING CLOSURE OF 1,3-DIAZA-1,3-DIENES

*Tetrahedron Lett.* 1990, 31, 903

E. Rossi\*, G. Celentano, R. Stradi and A. Strada.  
Istituto di Chimica Organica, Facoltà di Farmacia,  
Viale Abruzzi, 42 20131 Milano - Italy.

3,4-Dihydroquinazolines and quinazolines  
have been obtained by reacting N-imidoyl-  
iminotriphenylphosphorane with aldehydes.  
The reaction proceeds via an 1,3-diaza  
-1,3-diene intermediate.



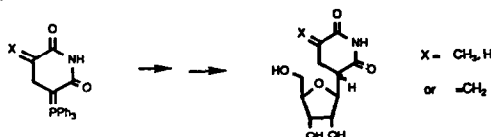
GLUTARIMIDE NUCLEOSIDES

*Tetrahedron Lett.* 1990, 31, 907

SYNTHESIS AND PROPERTIES OF ANALOGS OF 1-DEAZA-THYMIDINE

M.J.Wanner and G.J. Koomen\*, Organic Chemistry Laboratory, University of Amsterdam,  
Nieuwe Achtergracht 129, 1018 WS, Amsterdam, The Netherlands

Wittig reactions with functionalized glutarimide  
phosphorus ylids produced the corresponding  
glutarimide C-nucleosides. Conversion into  
1-deaza-thymidine was unsuccessful.

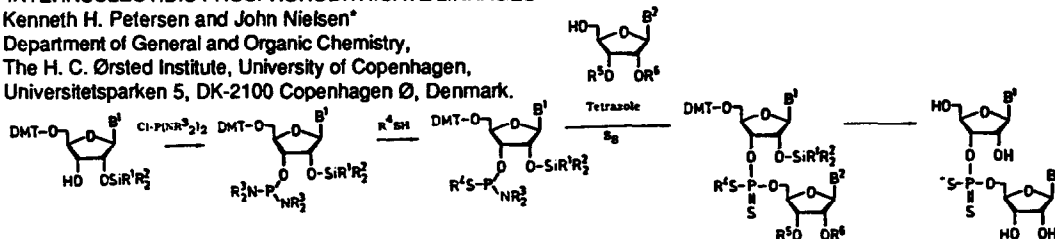




CHEMICAL SYNTHESIS OF DIMER RIBONUCLEOTIDES CONTAINING  
INTERNUCLEOTIDIC PHOSPHORODITHIOATE LINKAGES

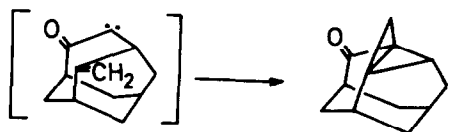
Kenneth H. Petersen and John Nielsen\*

Department of General and Organic Chemistry,  
The H. C. Ørsted Institute, University of Copenhagen,  
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark.



2,3-METHANO-2,4-DIDEHYDRO-11-HOMOADAMANTANONE:  
A [4.1.1]PROPELLANONE

Z. Majerski, V. Kostov, M. Hibšer and K. Mlinarić-Majerski\*  
Ruder Bošković Institute, 41001 Zagreb, Yugoslavia



2,3-Methano-2,4-didehydro-11-homoadamantanone has  
been prepared quantitatively by an intramolecular  
cycloaddition of 2-methylene-5-oxo-4-homoadamantylidene.

REDUCED AND RETRO-REDUCED PEPTIDE ANALOGUES-  
CONFORMATIONS AND ENERGIES

P. Dauber-Osguthorpe, D.J. Jones, M.M. Campbell, and D.J. Osguthorpe.  
Molecular Graphics Unit and Department of Chemistry, University of Bath, Claverton Down,  
Bath, BA2 7AY.

The natural peptide amide linkages in A can be replaced by the reduced and retro-reduced  
variants B and C. Effects on conformational accessibility are described.

