

## GRAPHICAL ABSTRACTS

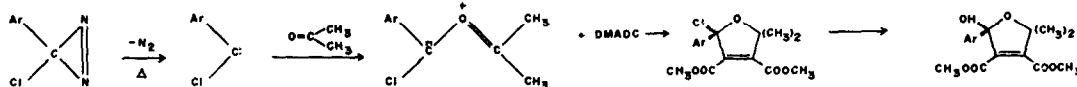
Tetrahedron Lett. 27, 4383 (1986)

Carbonyl Ylide from 3-Chloro-3-p-nitrophenylcarbene  
and Acetone

Toshikazu Iyata<sup>a</sup>, Michael T.H. Liu<sup>b\*</sup> and Jiro Toyoda<sup>a</sup>

a. Institute of Chemistry, College of General Education, Osaka  
University, Toyonaka, Osaka 560, Japan.

b. Department of Chemistry, University of Prince Edward Island,  
Charlottetown, P.E.I., CANADA, C1A 4P3

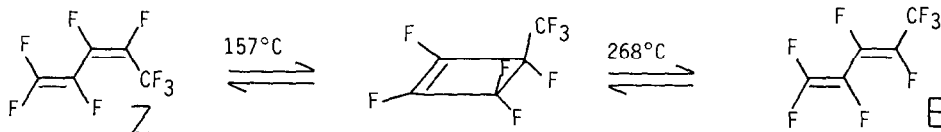


Tetrahedron Lett. 27, 4387 (1986)

THE ELECTROCYCLIC INTERCONVERSION OF PERFLUORO-3-METHYLCYCLO-  
BUTENE WITH Z- AND E- PERFLUORO-1,3-PENTADIENE; William R.

Dolbier, Jr.\* and Henryk Koroniak, Dept. of Chemistry, University of Florida, Gainesville, FL 32611;  
and Donald J. Burton\* and Pam Heinze, Dept. of Chemistry, University of Iowa, Iowa City, IA 52242

Thermal interconversion of Z- and E- perfluoro-1,3-pentadienes to perfluoro-3-methylcyclobutene.



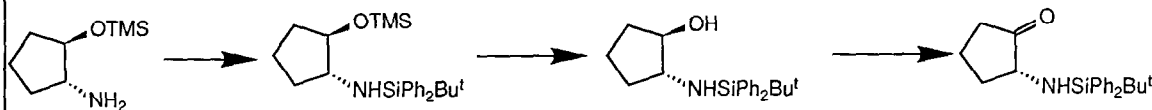
Tetrahedron Lett. 27, 4391 (1986)

tert-BUTYL DIPHENYLSILYLAMINES: USEFUL PROTECTING GROUPS FOR PRIMARY AMINES

Larry E. Overman,\* Mark E. Okazaki, and Pratibha Mishra

Department of Chemistry, University of California, Irvine, CA 92717

The stability and utility of tert-BDPSi as a primary amine protecting group is described.



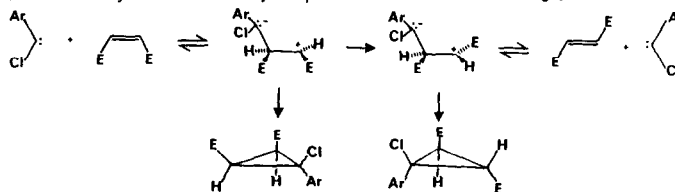
Tetrahedron Lett. 27, 4395 (1986)

FORMATION OF A DIPOLAR ADDUCT IN THE REACTION OF ARYL-  
CHLOROCARBENES WITH DIETHYL MALEATE

M.P. Doyle\*, K.-L. Loh, L.I. Nishioka, M.B. McVickar, Department of Chemistry, Trinity  
University, San Antonio, Texas 78284; M.T.H. Liu, Department of Chemistry, University  
of Prince Edward Island,

Charlottetown, Prince  
Edward Island, Canada  
C1A 4P3

Non-concerted addition of  
arylchlorocarbenes to  
diethyl maleate:



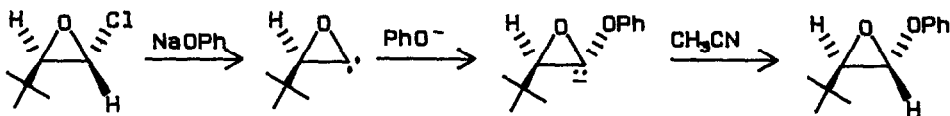
OXIRANYLIDENE INTERMEDIATE IN THE REACTION OF TRANS-2-CHLORO-3-(T-BUTYL)OXIRANE WITH SODIUM PHENOXIDE.

Tetrahedron Lett., 27, 4399 (1986)

Harlan L. Goering\* and Steven D. Paisley

University of Wisconsin Chemistry Department, Madison, WI 53706

The conversion of trans-2-chloro-3-(t-butyl)oxirane to trans-2-phenoxy-3-(t-butyl)oxirane by reaction with NaOPh in CH<sub>3</sub>CN involves α-elimination to give an oxiranylidene followed by stepwise conversion of this intermediate to product as follows.



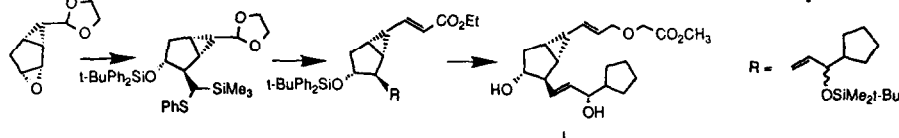
SYNTHESIS OF A NOVEL PROSTACYCLIN ANALOG CONTAINING THE BICYCLO(3.1.0)HEXANE RING SYSTEM. APPLICATION OF MOLECULAR MECHANICS CALCULATIONS TO ORGANIC SYNTHESIS

Tetrahedron Lett., 27, 4403 (1986)

S.W. Djuric\*, M. Miyano and J.P. Snyder

Dept. of Medicinal Chemistry, G.D. Searle & Co., Skokie, IL 60077, USA

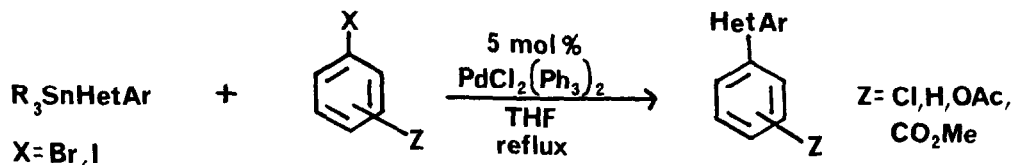
A synthesis of Prostacyclin Analog (I) via a completely regiocontrolled epoxide ring opening.



UNSYMMETRICAL HETEROBIARYL SYNTHESIS. A HIGHLY EFFICIENT PALLADIUM-CATALYZED CROSS-COUPLING REACTION OF HETEROARYL TRIALKYLSTANNANES WITH ARYL HALIDES.

Tetrahedron Lett., 27, 4407 (1986)

Thomas R. Bailey, Sterling-Winthrop Research Institute, Rensselaer, New York 12144



THE ETHYL, 1- AND 2-PROPYL, AND OTHER SIMPLE ALKYL "CARBANIONS" DO NOT EXIST.

Tetrahedron Lett., 27, 4411 (1986)

Paul von Ragué Schleyer\*, Günther W. Spitznagel, Jayaraman Chandrasekhar

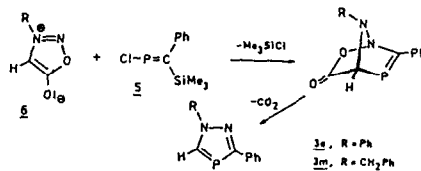
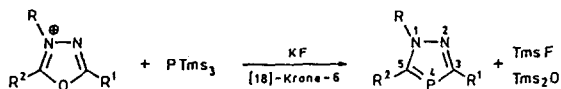
Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany, and Department of Chemistry, Indian Institute of Science, Bangalore, 560 012, India.

A combination of experimental data and theoretical calculations has been used to estimate the electron affinities of simple primary, secondary, and tertiary alkyl radicals and the proton affinities of the corresponding anions. With the exception of cyclopropyl, such "carbanions" are indicated to be unstable towards loss of an electron and are not expected to exist as long-lived species in the gas phase.

Tetrahedron Lett. 27, 4415 (1986)

1H-1,2,4- $\lambda^3$ -DIAZAPHOSPHOLE AUS 1,3,4-OXADIAZOLIUM-SALZEN BZW. SYDNONEN

Gottfried Märkl<sup>\*)</sup> und Siegfried Pflaum, Institut für Organische Chemie der Universität Regensburg, Universitätsstraße 31, D-8400 Regensburg

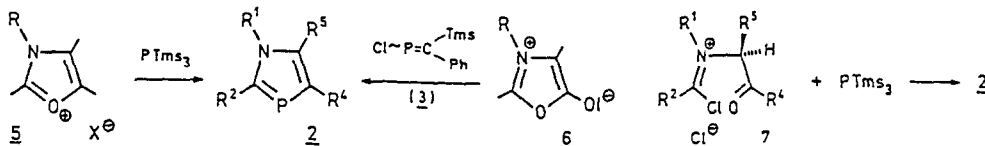


Tetrahedron Lett. 27, 4419 (1986)

1-R-1,3 $\lambda^3$ -AZAPHOSPHOLE

G. Märkl und G. Dorfmeister, Institut für Organische Chemie der Universität Regensburg, Universitätsstraße 31, D-8400 Regensburg

The title compounds are prepared by reaction of oxazoliumsalts and their equivalents with  $PTms_3$  and by reaction of "Münchnones" with phosphoralkanes.



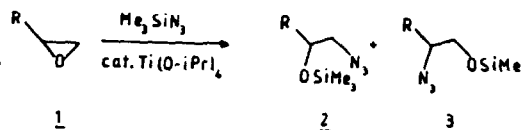
HIGHLY REGIOSELECTIVE RING OPENING OF EPOXYDES WITH  $Me_3SiN_3$  CATALYZED BY  $Ti(O-iPr)_4$

Tetrahedron Lett. 27, 4423 (1986)

Denis Sinou<sup>\*</sup> and Mohamed Emziane

Laboratoire de Synthèse Asymétrique, U.A. 463 CNRS, Université Lyon I 43 Bd du 11 Novembre 1918 - 69622 Villeurbanne Cedex, France.

$Ti(O-iPr)_4$  catalyzes the ring opening of fonctionnalized epoxides with  $Me_3SiN_3$  in a highly regioselective manner. [ratio 2 / 3 > 92/8].

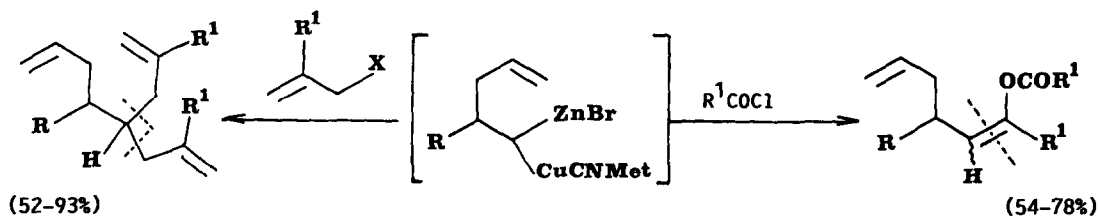


COPPER AND ZINC MIXED GEM-DIMETALLIC ORGANIC COMPOUNDS. SYNTHESIS AND REACTIVITY. PART 3<sup>1</sup>

Tetrahedron Lett. 27, 4427 (1986)

P. Knochel<sup>\*</sup> and J.F. Normant

Chimie des Organo-éléments, tour 44, Université P. & M. Curie, 4 place Jussieu 75252 PARIS 05



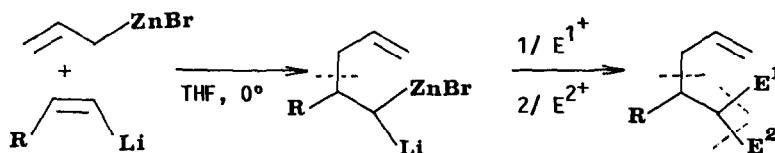
REACTIVITY OF THE 1-LITHIA-1-ZINCAALKENES. A FORMAL  
REGIOSPECIFIC ADDITION OF ALLYLZINC BROMIDE TO ALKENE.

Tetrahedron Lett. 27, 4431 (1986)

Part 4<sup>1</sup>.

P. Knochel and J.F. Normant

Université P. et M. Curie, tour 44-45, 4 place Jussieu F-75252 PARIS Cédex 05



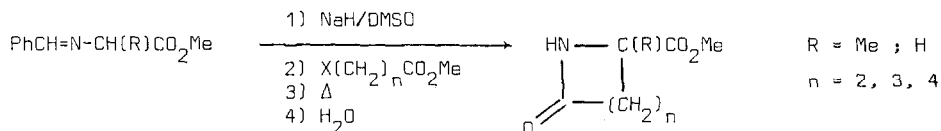
ALKYLATION OF SCHIFF BASE ANIONS WITH  $\omega$ -HALOGENO ESTERS :  
A LACTAM SYNTHESIS.

Tetrahedron Lett. 27, 4435 (1986)

A. MKHAIRI and J. HAMELIN

Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France.

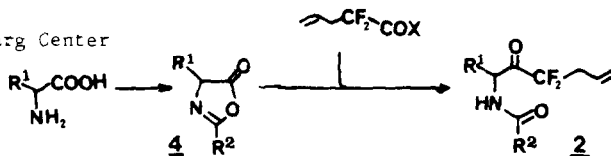
Alkylation of imines by halogenoesters followed by thermolysis leads to lactams.



SYNTHESIS OF FLUORINATED  $\alpha$ -AMINO KETONES.  
PART II:  $\alpha$ -ACYLAMINOALKYL  $\alpha'$ ,  $\alpha'$ -DIFLUOROALKYL KETONES

Tetrahedron Lett. 27, 4437 (1986)

Michael Kolb\* and Bernhard Neises  
Merrell Dow Research Institute, Strasbourg Center  
16 rue d'Ankara  
67084 Strasbourg Cedex, France



The synthesis of  $\alpha$ -acylaminoalkyl  
1,1-difluoro-3-butenyl ketones 2,

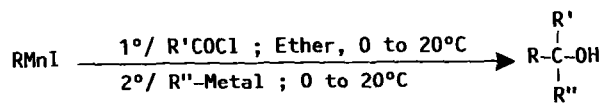
useful intermediates in the preparation of fluorinated  $\alpha$ -amino ketones as protease inhibitors,  
is described. Reaction of 5(4H)-oxazolones 4, obtained from  $\alpha$ -amino acids, with 2,2-difluoro-  
4-pentenoic acid chloride or anhydride affords the target structures.

ORGANOMANGANESE (II) REAGENTS XII. AN EFFICIENT ONE-POT  
PREPARATION OF UNSYMMETRICAL SECONDARY OR TERTIARY ALCOHOLS

Tetrahedron Lett. 27, 4441 (1986)

G. CAHIEZ\*, J. RIVAS-ENTERRIOS, H. GRANGER-VEYRON

Université P. et M. Curie, tour 44-45, 4 place Jussieu F-75252 PARIS Cédex 05



R''-Metal = R''Li, R''MgX, LiAlH<sub>4</sub> and NaBH<sub>4</sub>

Various unsymmetrical secondary or tertiary alcohols are rapidly prepared, in high yields,  
between 0 and 20°C according to the above procedure (18 examples are given).

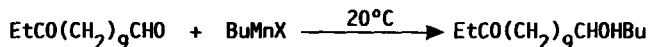
**ORGANOMANGANESE (II) REAGENTS XIII : HIGHLY SELECTIVE**

Tetrahedron Lett., 27, 4445 (1986)

**ADDITION OF ORGANOMANGANESE HALIDES TO ALDEHYDES IN THE PRESENCE OF KETONES**

G. CAHIEZ\*, B. FIGADERE

Université P. & M. Curie, tour 44-45, 4 place Jussieu F-75252 PARIS Cédex 05



BuMnBr, ether : 90%

BuMnCl, THF : 89%

13 examples of aldehyde-ketone competitions in ether (RMnBr) and THF (RMnCl) are given.

Different Selectivities in Bromofluorination Reactions using N-Bromosuccinimide/

Tetrahedron Lett., 27, 4449 (1986)

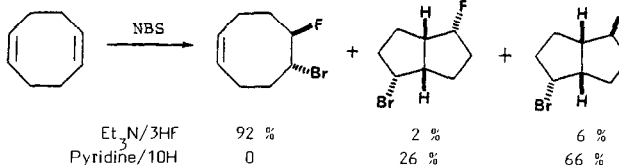
Triethylamine Tris Hydrofluoride or Olah's Reagent

Günter Haufe, Gérard Alverne\* and André Laurent\*

Karl-Marx-Universität, Sektion Chemie, Liebigstrasse 18, DDR-7010 Leipzig (G.D.R.)

\*Université Claude Bernard, Lab. Chimie Organique III, associé au CNRS 69622 Villeurbanne Cedex (France)

A new reagent is used for bromofluorination and its selectivity is compared to that of a known one.



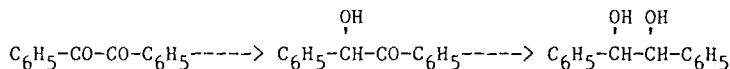
**YEAST-CATALYZED ASYMMETRIC REDUCTION OF BENZIL AND BENZOIN TO HYDROBENZOIN**

Tetrahedron Lett., 27, 4453 (1986)

Didier BUISSON, Sana EL BABA and Robert AZERAD

Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UA 400 du CNRS, Université René Descartes, 75270- PARIS Cedex 06 - FRANCE

The double reduction of benzil by various selected yeast strains is used to prepare optically pure (R,R) or (S,S)-hydrobenzoin.



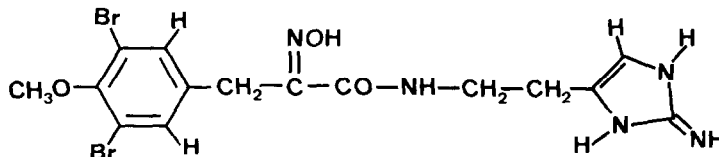
**IANTHELLINE** : A NEW DERIVATIVE OF DIBROMOTYROSINE FROM THE SPONGE *IANTHELLA ARDIS*.

Tetrahedron Lett., 27, 4455 (1986)

Marc Litaudon et Michèle Guyot

Laboratoire de Chimie, UA 401 CNRS, Muséum National d'Histoire Naturelle, 63 rue Buffon, 75231 - Paris Cedex 05 (France).

Structure was established by spectral data

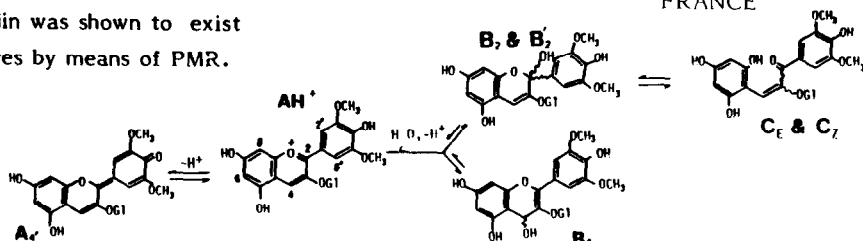


**PMR INVESTIGATION OF 3-O-( $\beta$ -D-GLUCOSYL)MALVIDIN  
STRUCTURAL TRANSFORMATIONS IN AQUEOUS SOLUTIONS.**

Tetrahedron Lett. 27, 4457 (1986)

A. CHEMINAT and R. BROUILLARD - Institut de Chimie - Université Louis Pasteur - STRASBOURG FRANCE

3-O-( $\beta$ -D-glucosyl)malvidin was shown to exist in seven different structures by means of PMR.



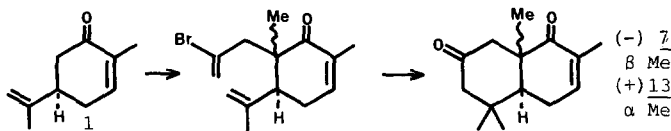
**A NEW ANNULATION OF CARVONE TO CHIRAL TRANS AND CIS FUSED BICYCLIC KETONES**

Tetrahedron Lett. 27, 4461 (1986)

J.P GESSON, J.C. JACQUESY and B. RENOUX

Laboratoire de CHIMIE XII - Faculté des Sciences - UA CNRS N° 489 "Synthèse et Réactivité de Produits Naturels" - 40, Avenue du Recteur Pineau - 86022 POITIERS Cedex (France).

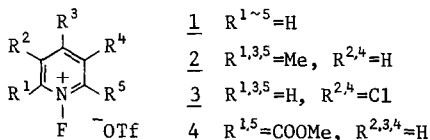
A three step synthesis of trans fused ketone 7 and cis fused ketone 13 from (-) carvone 1



**N-FLUOROPYRIDINIUM TRIFLATE AND ITS DERIVATIVES:  
USEFUL FLUORINATING AGENTS**

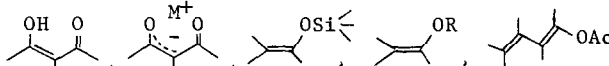
Tetrahedron Lett. 27, 4465 (1986)

Teruo Umemoto\*, Kosuke Kawada, and Kyoichi Tomita  
Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan



The title triflates serve as selective, broadly applicable reagents because of variable fluorinating power in addition to easy handling.

Substrates; ArH, RMgCl, ArMgCl,

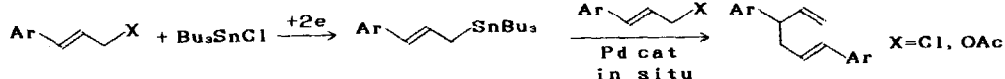


**PALLADIUM-CATALYZED COUPLING OF ELECTROGENERATED ALLYL TIN REAGENTS**

Tetrahedron Lett. 27, 4469 (1986)

Jun-ichi Yoshida, Hirokatsu Funahashi, Hiroya Iwasaki, Nariyoshi Kawabata  
Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606, JAPAN

Electrochemical synthesis of allyl tin reagents and their palladium-catalyzed coupling with allyl halides and acetates in situ.



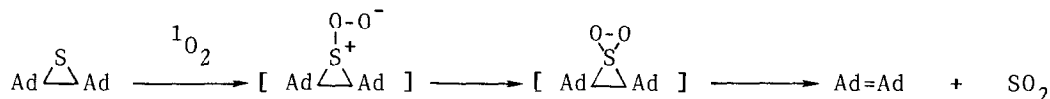
Tetrahedron Lett., 27, 4473 (1986)

REACTION OF SINGLET OXYGEN WITH THIIRANE:  
IMPLICATION FOR A SPIRODIOXATHIIRANE INTERMEDIATE

Wataru ANDO\*, Hideki SONOBE, and Takeshi AKASAKA

Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

Photosensitized oxygenation of biadamantylidene thiirane proceeded via a spirodioxathiirane intermediate.



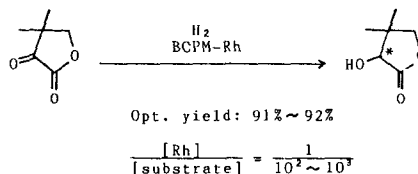
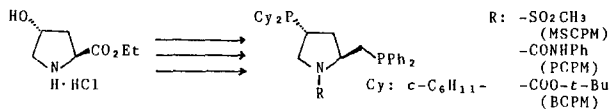
Tetrahedron Lett., 27, 4477 (1986)

PREPARATION OF CHIRAL PYRROLIDINEBISPHOSPHINES AS HIGHLY EFFECTIVE  
LIGANDS FOR CATALYTIC ASYMMETRIC SYNTHESIS OF R-(-)-PANTOLACTONE

Hisashi Takahashi, Masaaki Hattori, Mitsuo Chiba  
Toshiaki Norimoto, and Kazuo Achiwa\*

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

Asymmetric hydrogenation catalyzed by BCPM-Rh gave  
R-(-)-pantolactone in 92% optical yield.



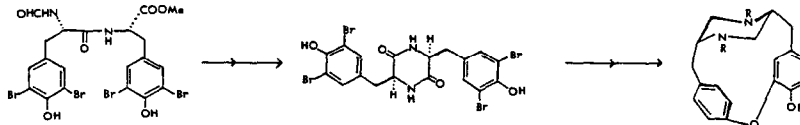
Tetrahedron Lett., 27, 4481 (1986)

SYNTHESIS OF PIPERAZINOMYCIN,  
A NOVEL ANTIFUNGAL ANTIBIOTIC

Shigeru Nishiyama, Kazuhiko Nakamura, Yoshikazu Suzuki, and Shosuke Yamamura\*

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi,  
Yokohama, Japan

A total synthesis of piperazinomycin starting from L-tyrosine.



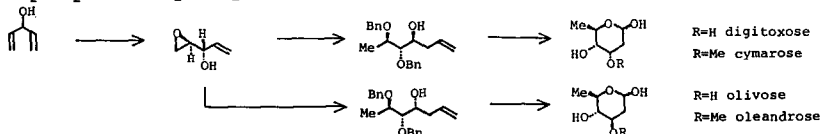
Tetrahedron Lett., 27, 4485 (1986)

ENANTIO- AND STEREO-SELECTIVE SYNTHESIS OF 2,6-  
DIDEOXYHEXOSES FROM DIVINYLCARBINOL

S. Hatakeyama, K. Sakurai, and S. Takano\*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Four 2,6-dideoxyhexoses have been synthesized from (2R,3S)-1,2-epoxypent-4-  
en-3-ol prepared by asymmetric epoxidation of divinylcarbinol.



Tetrahedron Lett. 27, 4489 (1986)

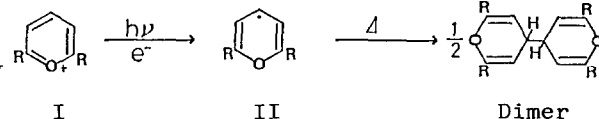
## PHOTODIMERIZATION OF 2,6-DIPHENYLPYRYLIUM SALT\*

Hiroki Kawata, Yoshizo Suzuki<sup>†</sup> and Shigeya Niizuma

College of Humanities and Social Sciences, Iwate Univ., Ueda, Morioka, 020 JAPAN

<sup>†</sup>Faculty of Education, Iwate Univ., Ueda, Morioka, 020 JAPAN

Photodimerization of 2,6-diphenylpyrylium tetrafluoroborate (I) via the pyranyl (II) in THF. Absorption spectrum of II observed by flash technique. Second order rate constant of the radical (II) decay estimated as  $(1.2 \pm 0.5) \times 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

Tetrahedron Lett. 27, 4493 (1986)

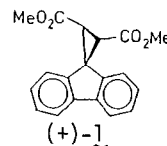
## ABSOLUTE STEREOCHEMISTRIES OF TRANS-2,3-DISUBSTITUTED SPIROCYCLOPROPANE-1,9'-FLUORENE DERIVATIVES: A STYRYL MODIFICATION CD-METHOD FOR CARBOXYL SUBSTITUTED CHIRAL CENTERS

Keiji Okada, Fumio Samizo, Masaji Oda\*, Nobuyuki Harada\*<sup>†</sup>, and Hisashi Uda<sup>†</sup>

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

<sup>†</sup>Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Sendai 980, Japan

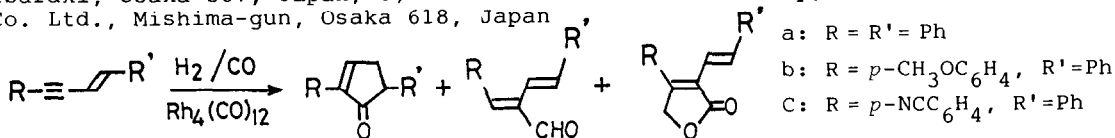
The absolute stereochemistries of (+)-**1** and related compounds were determined to be (2*S*,3*S*) by CD-study using a novel styryl modification method and by chemical degradation to a known compound.

Tetrahedron Lett. 27, 4497 (1986)

## HYDROFOMYLATION AND HYDROCARBONYLATION OF ENYNES BY RHODIUM CARBONYL CLUSTER: A NEW ROUTE TO CYCLIC ENONES

Kazuo Doyama<sup>a</sup>, Takashi Joh<sup>a</sup>, Shigetoshi Takahashi\*<sup>a</sup>, Tomoo Shiohara<sup>b</sup>

a) The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan; b) Central Research Laboratory, Sekisui Chemical Co. Ltd., Mishima-gun, Osaka 618, Japan

Tetrahedron Lett. 27, 4501 (1986)

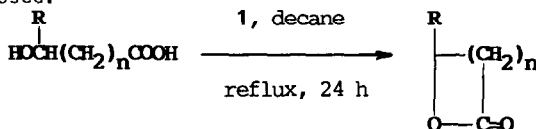
## A novel Template effect of distannoxane in

macrolactonization of ω-hydroxy carboxylic acids

J. Otera, T. Yano, Y. Himeno, and H. Nozaki

Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan

A novel template effect of distannoxanes in macrolactonization of ω-hydroxy carboxylic acids has been disclosed.



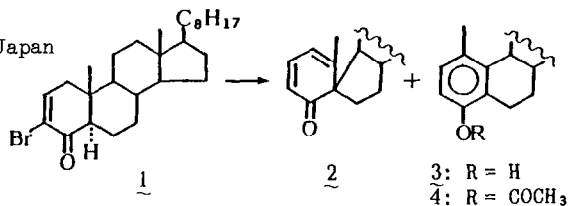


Tetrahedron Lett. 27, 4505 (1986)

THE ISOLATION OF A SPIRAN IN THE REARRANGEMENT OF AN  
 $\alpha$ -BROMO- $\alpha$ , $\beta$ -UNSATURATED STEROIDAL KETONE

Toshitaka Koga\* and Yasuyoshi Nogami  
 Daiichi College of Pharmaceutical Sciences  
 22-1, Tamagawa-cho, Minami-ku, Fukuoka 815, Japan

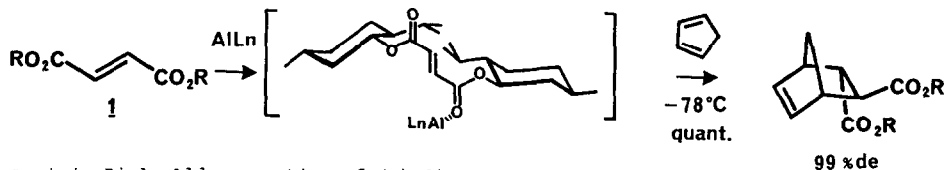
A new acid-catalyzed aromatization of  
 3-bromocholest-2-en-4-one(1) has been  
 found and a spiranic product(2) is  
 really captured in this rearrangement.



Tetrahedron Lett. 27, 4507 (1986)

ASYMMETRIC DIELS-ALDER REACTION.  
 COOPERATIVE BLOCKING EFFECT IN ORGANIC SYNTHESIS

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Asymmetric Diels-Alder reaction of (-)-dimenthyl fumarate

NOVEL SILYL TRIFLATE-MEDIATED "[2,3]WITTIG" SIGMATROPIC  
 REARRANGEMENT. THE POSSIBLE INTERVENTION OF AN OXYGEN YLIDE

Tetrahedron Lett. 27, 4511 (1986)

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