

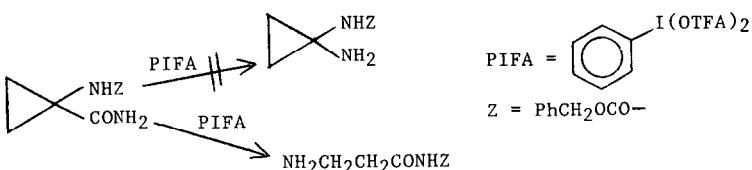
## GRAPHICAL ABSTRACTS

Tetrahedron Lett. 27, 5435 (1986)

THE REACTION OF [I,I-BIS(TRIFLUOROACETOXY)IODO]BENZENE WITH  
N-(BENZYLOXYCARBONYL)-1-AMINOCYCLOPROPANE 1-CARBOXAMIDE

Masahiro Tamura, John Jacyno and Charles H. Stammer\*

Department of Chemistry, School of Chemical Sciences, University of GA., Athens, GA. 30602



Tetrahedron Lett. 27, 5437 (1986)

BISLACTONIZATIONS OF OLEFINIC DIACIDS WITH  
[HYDROXY(TOSYLOXY)IODO]BENZENE

Mayur Shah, Michael J. Taschner\*, Gerald F. Koser\*, Nancy Rach, Thomas Jenkins, Patrick Cyr, and David Powers  
Department of Chemistry, The University of Akron, Akron, Ohio 44325

The reactions of [hydroxy(tosyloxy)iodo]benzene with a series of olefinic diacids to produce bislactones are reported. The products are the result of a stereospecific cis-addition of the two carboxylic acid functions to the double bond.

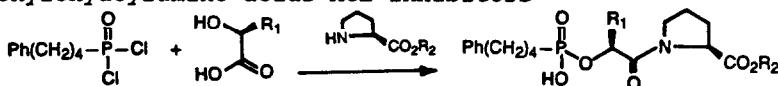


Tetrahedron Lett. 27, 5441 (1986)

A HIGHLY CONVERGENT\* PREPARATION OF PHOSPHONYLOXYACYLAMINO ACIDS

John K. Thottathil\* and Michael K. Y. Wong  
Squibb Chemical Division, P.O. Box 4000, Princeton, N. J. 08540

A one pot three component coupling for the preparation of phosphonyloxyacylamino acids ACE inhibitors



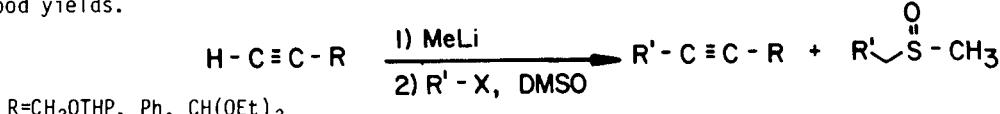
Tetrahedron Lett. 27, 5445 (1986)

ALKYLATION OF STABILIZED ACETYLIDES IN DMSO. PREPARATION  
OF  $\alpha,\beta$ -ACETYLENIC ALCOHOL AND ACETALS

J. Michael Chong\* and Susanna Wong

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo ON  
Canada N2L 3G1

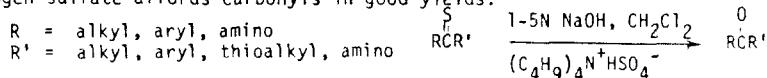
Terminal acetylenes with stabilizing groups may be deprotonated and alkylated in DMSO in good yields.



## AN EXCEPTIONALLY MILD, PHASE TRANSFER CATALYZED METHOD FOR THE CONVERSION OF THIOCARBONYL COMPOUNDS TO CARBONYLS

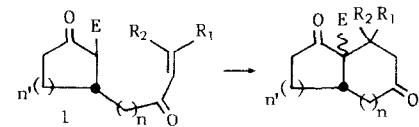
Howard Alper<sup>a</sup>, Caroline Kwiatkowska<sup>a</sup>, Jean-François Petrignanib, and Fazole Sibtain<sup>a</sup><sup>a</sup> Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4 Canada  
<sup>b</sup> I.P.S.O.I., Univ. d'Aix Marseille III, rue H. Poincaré, 13397 Marseille Cedex, France

Treatment of thiocarbonyl compounds with sodium hydroxide, methylene chloride, and tetrabutyl-ammonium hydrogen sulfate affords carbonyls in good yields.

INTRAMOLECULAR MICHAEL ADDITION OF CYCLIC  $\beta$ -KETOESTER ON CONJUGATED OLEFINIC KETONE, A STEREOELECTRONICALLY CONTROLLED PROCESS

Gilles Berthiaume, Jean-François Lavallée, and Pierre Deslongchamps.

Département de chimie, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, QC, Canada J1K 2R1

The base-catalyzed ring-closure of 1 ( $E = \text{COOCH}_3$ ,  $n' = 1-2$ ,  $n = 0-3$ , and  $R_1 = R_2 = \text{H}$  and/or  $\text{CH}_3$ ) is reported and the results can be explained on the basis of steric and stereochemical effects at the transition state level.INTRAMOLECULAR MICHAEL ADDITION OF CYCLIC  $\beta$ -KETOESTER ON CONJUGATED ACETYLENIC KETONE

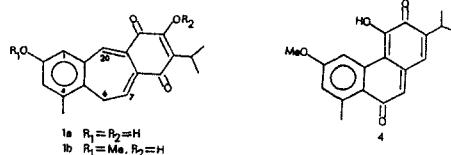
J.-F. Lavallée, G. Berthiaume, P. Deslongchamps, and F. Grein (University of New Brunswick).

Department of Chemistry, Université de Sherbrooke, Sherbrooke, QC, Canada J1K 2R1

The base-catalyzed ring-closure of  $\beta$ -ketoester-ynone 1 ( $E=\text{COOCH}_3$ ,  $n' = 1, 2$ ,  $n = 0-3$ ) is reported. Unexpectedly, the formation of five and six-membered enone takes place with ease and in good yield.NEW HIGHLY OXIDIZED DITERPENE QUINONES FROM SALVIA FRUTICULOSA ( LABIATAE ).

Rodríguez-Hahn L., Esquivel B., Sánchez C., Cárdenas J., Estebanez L., Soriano-García M., Toscano A. and T.P. Ramamoorthy.

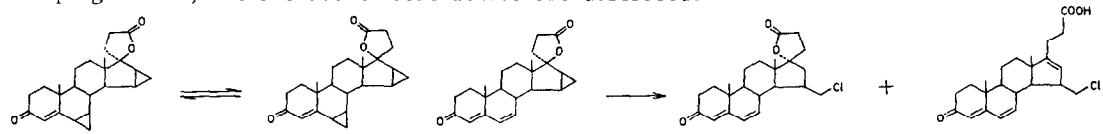
Instituto de Química. Univ. Nac. Autónoma de México. Coyoacan 04510, México D.F.

The diterpenoid constituents of Salvia fruticulosa ( Labiatae )

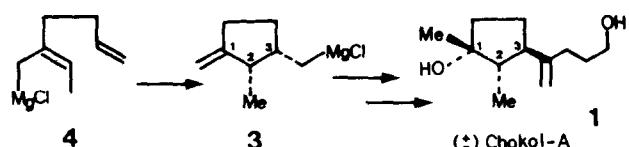
ACID CATALYZED REARRANGEMENTS OF 15 $\alpha$ ,16 $\beta$ -METHYLENE-17 $\alpha$ -PREGNENE-21,17-CARBOLACTONE DERIVATIVES

Klaus Nickisch\*, Dieter Bittler, Henry Laurent and Rudolf Wiechert  
Research Laboratories of Schering AG Berlin and Bergkamen, D-1000 Berlin 65

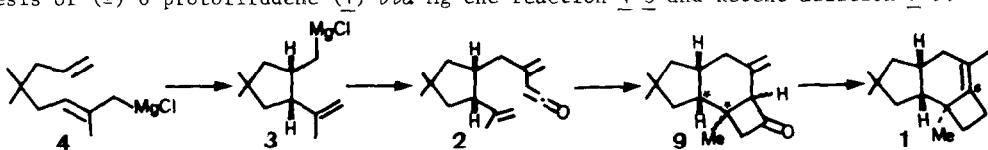
The different acid catalyzed rearrangements of 15,16-substituted 17 $\alpha$ -pregnene-21,17-carbolactone derivatives are described.

TOTAL SYNTHESIS OF ( $\pm$ )-CHOKOL-A VIA AN INTRAMOLECULAR TYPE-I-MAGNESIUM ENE REACTION  
Wolfgang Oppolzer\* and Allan F. Cunningham

A synthesis of ( $\pm$ )-chokol-A (1) via the Mg-ene reaction 4  $\rightarrow$  3.

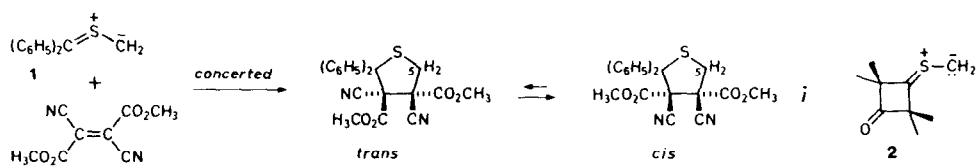
SYNTHESIS OF ( $\pm$ )-6-PROTOILLUDENE AND ( $\pm$ )-3-EPI-6-PROTOILLUDENE BY INTRAMOLECULAR MAGNESIUM-ENE- AND KETENE/ALKENE ADDITION REACTIONS  
Wolfgang Oppolzer\* and Akio Nakao

Département de Chimie Organique, Université de Genève, CH-1211 Genève, Switzerland  
Synthesis of ( $\pm$ )-6-protoilludene (1) via Mg-ene reaction 4  $\rightarrow$  3 and ketene-addition 2 + 9.

FURTHER CONTRIBUTIONS TO THE STEREOSELECTIVITY OF 1,3-DIPOLAR CYCLOADDITIONS OF THIOCARBONYL YLIDES  
Rolf Huisgen,\* Elke Langhals, and Heinrich Nöth\*

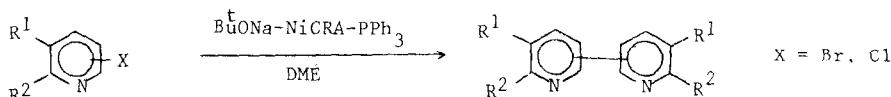
Institut für Organische und Anorganische Chemie der Universität München, FRG

In contrast to 2, 1 adds stereospecifically to dimethyl dicyanofumarate; X-ray analysis of cis-adduct. The additions of 2 to fumaro- and maleonitrile are stereospecific (>99.95%).



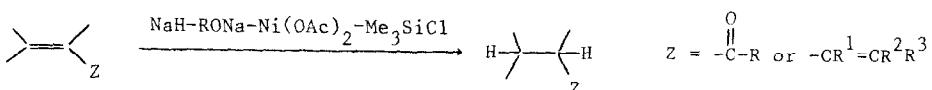
ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS 23.  
SYMMETRICAL COUPLING OF NITROGEN-CONTAINING HETEROCYCLIC HALIDES  
R. Vanderesse, M. Lourak, Y. Fort and P. Caubère\*  
Laboratoire de Chimie Organique I, Associé au CNRS, Université de Nancy I, BP 239  
54506 Vandoeuvre-les-Nancy (France)

NiCRA-bpy is shown to be one of the most efficient Ni containing reagents for the homo-coupling of heteroaromatic halides and in particular chlorides.



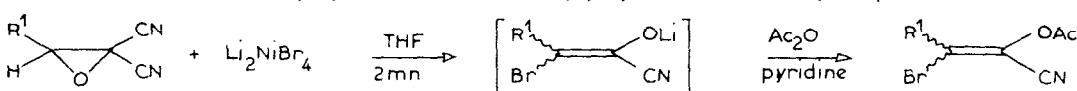
ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS 24.  
BENEFICIAL EFFECT OF Me₃SiCl ON THE REDUCING PROPERTIES OF NiCRA  
Y. Fort, R. Vanderesse, and P. Caubère\*  
Laboratoire de Chimie Organique I, Associé au CNRS, Université de Nancy I, BP 239  
54506 Vandoeuvre-les-Nancy (France)

Selective reduction of polyunsaturated hydrocarbons or unsaturated ketones are easily performed with NiCRASI (nickel containing CRA, activated by Me₃SiCl).



SYNTHESE DES ACETOXY-2 BROMO-3 PROPENE-2 NITRILES SUBSTITUÉS À PARTIR DES GEM DICYANO EPOXYDES  
Layachi Khamliche et Albert Robert \*  
Groupe de Chimie Structurale, Unité associée au C.N.R.S. n° 704, Université de Rennes I, Campus de Beaulieu, 35042 RENNES CEDEX. FRANCE.

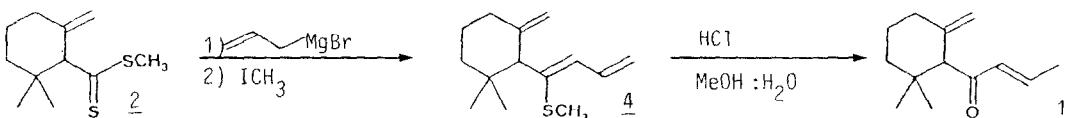
New 2-acetoxy 3-bromo 2-propene nitriles are easily prepared from  $\alpha,\alpha$ -dicyanooxides.



NOUVELLE APPLICATION DE LA REACTION DES ORGANOMAGNESIENS SUR LES DITHIOESTERS : SYNTHESE DE LA GAMMA-DAMASCONE

P. GOSELIN, Laboratoire de Synthèse Organique, UA CNRS 482, Faculté des Sciences, BP 535, F-72017 Le Mans Cedex

A new synthetic route to  $\gamma$ -damascone 1 starting from methyl- $\gamma$ -dithiocyclogeranate 2 is described. Addition of HMPT is found necessary to perform the reaction of allylmagnesium bromide with dithioester 2. A new, very mild hydrolysis method is developed in order to transform the resulting vinylsulfide 4 into 1.

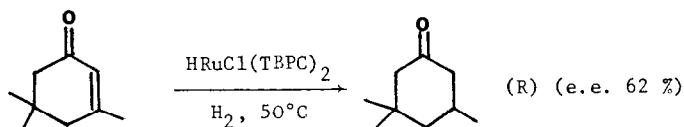


CATALYTIC ASYMMETRIC HYDROGENATION OF  $\alpha,\beta$ -UNSATURATED KETONES USING CHIRAL RUTHENIUM HYDRIDE COMPLEXES.

Tetrahedron Lett. 27, 5497 (1986)

V. Masonneau, P. Le Maux and G. Simonneaux\*

Laboratoire de Chimie des Organométalliques associé au CNRS,  
Université de Rennes I, Campus de Beaulieu, 35042 Rennes, France.



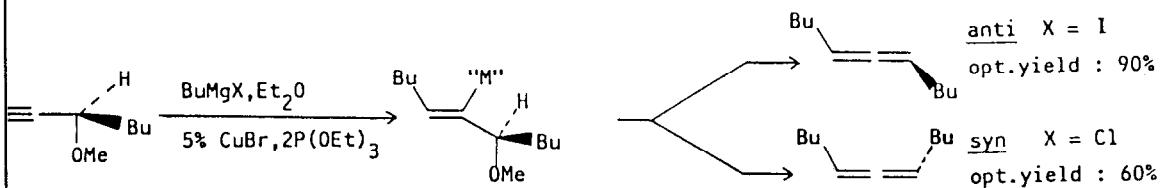
TPBC : trans-1,2 bis(diphenylphosphinomethyl)cyclobutane.

ARE ALLENES FORMED FROM PROPARGYLIC ETHERS THROUGH A SYN OR ANTI DISPLACEMENT ?

Tetrahedron Lett. 27, 5499 (1986)

I. Marek, P. Mangeney, A. Alexakis\*, J.F. Normant

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



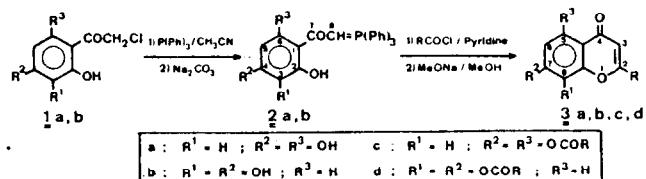
SYNTHESIS OF TRIHYDROXYPHENACYLIDENETRIPHENYLPHOSPHORANES  
NEW PRECURSORS OF FLAVONOIDS : 5,7- AND 7,8-DIHYDROXY FLAVONES

Tetrahedron Lett. 27, 5503 (1986)

Y. Le Floc'h\* and M. Lefevre

E.N.S.C.R.

Av. Gal Leclerc - 35700 RENNES France  
Some dihydroxychromones 3 are prepared from 2 new ylids 2, by acylation of 2, intramolecular olefination and saponification of the two remaining ester groups.

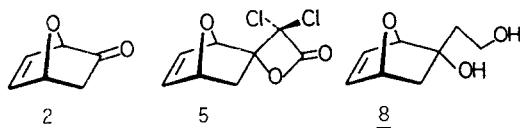


CHEMO- AND STEREOSELECTIVE FUNCTIONALIZATION OF 7-OXABICYCLO[2.2.1]HEPT-5-EN-2-ONE WITH DICHLOROKETENE.

Tetrahedron Lett. 27, 5505 (1986)

O. Arjona, R. Fernández de la Pradilla, S. Pérez, J. Plumet, P.-A. Carrupt and P. Vogel,  
Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain, and Institut de chimie organique de l'Université, CH-1005 Lausanne, Switzerland.

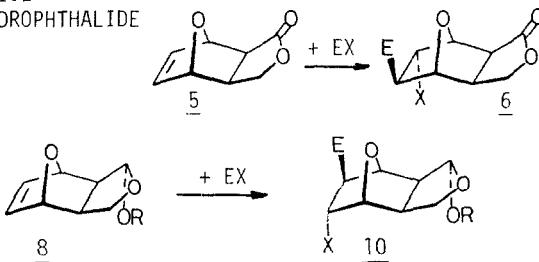
Dichloroketene does not add onto the C(5)-C(6) double bond of enone 2, but exclusively onto the exo face of the carbonyl group giving lactone 5 which was transformed into diol 8.



LONG-RANGE SUBSTITUENT EFFECTS. THE REGIOSELECTIVE ELECTROPHILIC ADDITIONS OF EXO-3,6-EPOXYTETRAHYDROPHthalide AND ITS DERIVATIVES.

Tarcisio Ferrari and Pierre Vogel\*  
Institut de chimie organique de l'Université  
CH 1005 Lausanne, Switzerland.

Electrophilic additions of 7-oxanorbornene derivative 5 gave 6 as major adducts, whereas acetal 8 gave 10 (major).

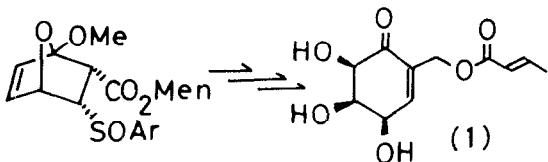


ENANTIOSELECTIVE TOTAL SYNTHESIS OF GLYOXALASE I INHIBITOR USING ASYMMETRIC DIELS-ALDER REACTION OF A NEW CHIRAL DIENOPHILE, (S)<sub>S</sub>-3-(3-TRIFLUOROMETHYL PYRID-2-YLSULFINYL) ACRYLATE.

H. Takayama, K. Hayashi, and T. Koizumi\*

Faculty of Pharmaceutical Sciences,  
Toyama Med. & Pharm. Univ., Sugitani,  
Toyama 930-01, Japan

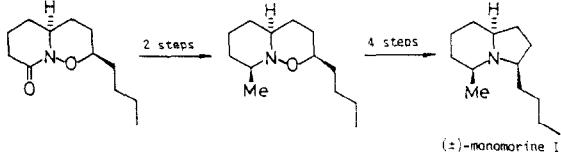
First enantioselective total synthesis of glyoxalase I inhibitor (1) was achieved by the asymmetric Diels-Alder reaction.



A STEREOSELECTIVE SYNTHESIS OF THE ANT TRAIL PHEROMONE ( $\pm$ )-MONOMORINE I

Hideo Iida, Yohya Watanabe, and Chihiro Kibayashi\*  
Tokyo College of Pharmacy, Horinouchi,  
Hachioji, Tokyo 192-03, Japan

A stereoselective synthesis of the ant trail pheromone monomorine I in racemic form utilizing the bicyclic 1,2-oxazine intermediate.

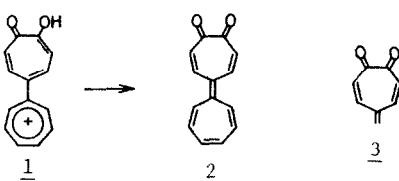


HEPTAFULVALENE-3,4-DIONE, A NOVEL p-TROPOQUINONE METHIDE-TYPE COMPOUND

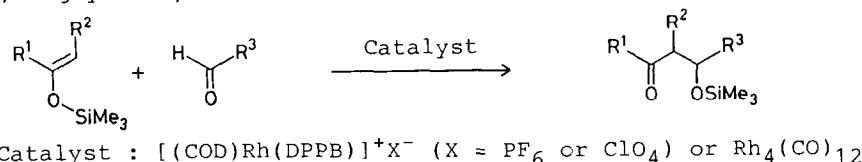
Kazuko Takahashi, \* Norio Namekata, and Kahei Takase

Department of Chemistry, Faculty of Science,  
Tohoku University, Sendai 980, Japan

The title compound 2 has been synthesized from 1 by deprotonation and physico-chemical properties of 2 have been clarified, providing valuable informations to characterize p-troponone methide 3.



THE FIRST EXAMPLE OF ALDOL REACTIONS BETWEEN  
TRIMETHYLSILYL ENOL ETHERS AND ALDEHYDES BY THE AID OF RHODIUM COMPLEX  
Susumu Sato, Isamu Matsuda, \* and Yusuke Izumi  
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University,  
Chikusa, Nagoya 464, JAPAN

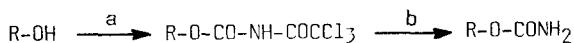


Catalyst : [(COD)Rh(DPPB)]<sup>+</sup>X<sup>-</sup> (X = PF<sub>6</sub> or ClO<sub>4</sub>) or Rh<sub>4</sub>(CO)<sub>12</sub>

CARBAMATES : A METHOD OF SYNTHESIS AND  
SOME SYNTHETIC APPLICATIONS

Pavel Kočovský  
Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences  
16610 Prague 6, Czechoslovakia

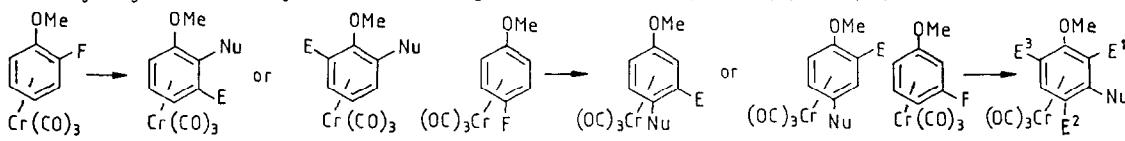
Alcohols are converted into unsubstituted carbamates by treatment with trichloroacetyl isocyanate (TAI, a) followed by hydrolysis on Al<sub>2</sub>O<sub>3</sub> (b). This mild procedure tolerates various labile functional groups. The carbamate moiety can function as a control element in epoxidation and in epoxide opening.



FLUORINE DIRECTED LITHIATION IN TRICARBONYLARENENECHROMIUM(0) COMPLEXES:

THE REGIOSPECIFIC SYNTHESIS OF POLYSUBSTITUTED ARENES.

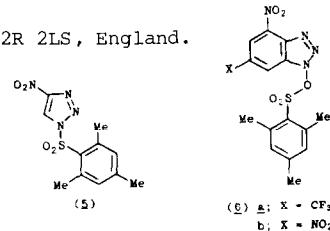
John P. Gilday and David A. Widdowson\*  
Chemistry Department, Imperial College, London SW7 2AY      Summary: Lithiation/electrophilic quenching of the  
isomeric tricarbonylfluoroanisole chromium(0)  
complexes in combination with nucleophilic displacement of the fluorine by amine and thiolate allows the  
totally regiocontrolled synthesis of a range of 1,2,3-, 1,2,4-, and 1,2,3,4,5-polysubstituted arenes.



HIGHLY REACTIVE CONDENSING AGENTS FOR THE SYNTHESIS  
OF OLIGONUCLEOTIDES BY THE PHOSPHOTRIESTER APPROACH

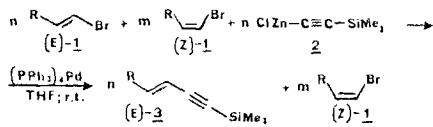
Kevin G. Devine and Colin B. Reese\*  
Department of Chemistry, King's College London, Strand, London WC2R 2LS, England.

The preparation of three new condensing agents [(5), (6a) and (6b)] that are, respectively, ca. 1.3, ca. 4 and at least 10 times more reactive than 1-(mesitylene-2-sulphonyl)-3-nitro-1,2,4-triazole (MSNT), is described.



DIASTEREOSELECTIVE SYNTHESIS OF (*E*)-1-TRIMETHYLSILYL-3-EN-1-YNES BY PALLADIUM-CATALYZED CROSS-COUPPLING REACTION BETWEEN TRIMETHYLSILYL-ETHYNYLZINC CHLORIDE AND STEREOISOMERIC MIXTURES OF 1-BROMO-1-ALKENES  
Bianca Patricia Andreini, Adriano Carpita, and Renzo Rossi. Dipartimento di Chimica e Chimica Industriale - Università di Pisa-via Risorgimento 55-56100 PISA - ITALY.

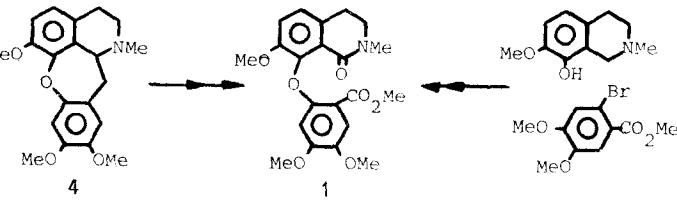
(*E*)-1-Trimethylsilyl-3-en-1-yne have been diastereoselectively synthesized starting from stereoisomeric mixtures of 1-bromo-1-alkenes. The procedure has been employed to prepare (*2E,6E*)-1-acetoxy-2,6-decadien-4-yne, a naturally occurring acetylenic compound.



## NOYAIN, THE FIRST C-RING SECOCULARARINE ALKALOID

J.M.Boente,L.Castedo,D.Dominguez and A.Rodriguez de Lera  
Departamento Química Orgánica, Facultad de Química y Sección Alcaloides del CSIC,  
Santiago de Compostela, Spain

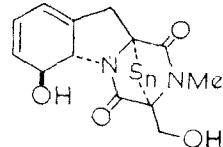
Noyaine (**1**) was isolated from *Corydalis clavicularis* (L.) DC. and its structure deduced from spectroscopic data and confirmed by synthesis from cularine (**4**) and also by total synthesis.



## PARTIAL SYNTHESIS OF GLIOTOXIN G, AN EPITETRATHIOPROXOPIPERAZINE

Gordon W. Kirby\*, Ghanakota V. Rao, David J. Robins,  
and W. Marshall Stark  
Department of Chemistry, University of Glasgow,  
Glasgow G12 8QQ

Gliotoxin (**1a**) reacts with sulphur in carbon disulphide containing a catalytic amount of thiolate to give the trisulphide (**1b**) and gliotoxin G (**1c**), a new, minor metabolite of *Aspergillus fumigatus*.



(**1a**), n = 2; (**1b**), n = 3; (**1c**), n = 4.

## PALLADIUM-CATALYZED TRIETHYLMONIUM FORMATE REDUCTION OF

## ARYL TRIFLATES. A SELECTIVE METHOD FOR THE DEOXYGENATION OF PHENOLS

Sandro Cacchi,<sup>a</sup> Pier Giuseppe Ciattini,<sup>b</sup> Enrico Morera,<sup>b</sup> and Giorgio Ortari<sup>b\*</sup>

<sup>a</sup>Istituto di Chimica Organica dell' Università, 00161 Roma. <sup>b</sup>Istituto di Chimica Farmaceutica dell' Università, 00185 Roma, Italy

Phenols can be selectively deoxygenated by reduction of the corresponding aryl triflates with triethylammonium formate in the presence of a homogeneous palladium(0) catalyst.

