#### **GRAPHICAL ABSTRACTS**

Tetrahedron, 1993, 49, 8311

REACTION OF TRIALKYLBORANES WITH SODIUM

DIETHYLDIHYDROALUMINATE IN THE PRESENCE OF

1,4-DIAZABICYCLO[2.2.2]OCTANE. A CONVENIENT,

GENERAL METHOD FOR PREPARATION OF SODIUM TRIALKYLBOROHYDRIDES

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NaEt<sub>2</sub>AlH<sub>2</sub> (toluene solution) + R<sub>3</sub>B + DABCO NaR<sub>3</sub>BH +

DABCO • Et<sub>2</sub>AlH<sub>1</sub>

Tetrahedron, 1993, 49, 8317

Phomaligols and Phomaligadiones: New Metabolites From The Blackleg Fungus.

M. Soledade C. Pedras\*, Victor M. Morales, and Janet L. Taylor, Plant Biotechnology Institute, National Research Council of Canada, Saskatoon, Saskatchewan, S7N 0W9, Canada

The isolation and structure elucidation of four new metabolites (1-4) from *Phoma lingam* (Leptosphaeria maculans) are described. The structures were determined employing 2D NMR spectroscopy.

Tetrahedron, 1993, 49, 8323

# HIGHLY STEREOCONTROLLED ASYMMETRIC SYNTHESES OF TAXOL AND TAXOTÈRE C-13 SIDE CHAIN ANALOGUES

Chisato Mukai, In Jong Kim, Etsuko Furu, and Miyoji Hanaoka Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa 920, JAPAN The title compounds were synthesized in enantiomerically pure form on the basis of *anti*-selective aldol reaction of a chiral chromium(0)-complexed benzaldehyde derivative with titanium enolate of *S-tert*-butyl benzyloxyethanethioate.

TMS

$$RNH O$$

OMe  $R = Bz$ 
 $Cr(CO)_3$ 

# Two New Polycyclic Aromatic Alkaloids from the Okinawan Marine Sponge Biemna sp.

Chun-min Zeng, Masami Ishibashi, Keita Matsumoto<sup>a</sup>, Shiro Nakaike<sup>a</sup>, and Jun'ichi Kobayashi\*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan and <sup>a</sup>Research Center, Taisho Pharmaceutical Co. Ltd., Yoshino, Omiya 330, Japan

Two new polycyclic aromatic alkaloids, biemnadin (1) and 8,9-dihydro-11-hydroxyascididemin, have been isolated from the Okinawan marine sponge Biemna sp. The X-ray diffraction analysis of 1 has established its octacyclic structure.

Tetrahedron, 1993, 49, 8343

### REACTION OF ACYLSILANES WITH SULFUR YLIDES.

SELECTIVE FORMATION OF SILYL ENOL ETHERS OR  $\beta\textsc{-}KETOSILANES.$ 

Tadashi Nakajima,\* Masahito Segi, Fumitosi Sugimoto, Reiko Hioki, Seiko Yokota, and Kiyoshi Miyashita

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Kanazawa University, 2-40-20 Kodatsuno, Kanazawa 920, Japan

The reaction of acylsilanes (1) with sulfur ylides in THF results in the formation of the corresponding silyl enol ethers (2) or  $\beta$ -keto-silanes (3). The relative ratio of these products can be controlled with the ylide conditions and the stability of ylide used.

Sulfur ylide: DMSY: R"= H, Z= Me,S(O), DTSY: R"=H, Z=p-tolyi-S(O)NMe, DPSY: R"= H or Me,Z=Ph,S

Tetrahedron, 1993, 49, 8359

Theoretical Studies of Substituent Effects on  $S_N1$  Reactivities of Benzyl- and Benzhydryl Systems.

Dong Soo Chung, Chang Kon Kim, Bon-Su Lee and Ikchoon Leee Department of Chemistry, Inha University, Inchon 402-751, Korea

**AM1-MO Studies** 

 $Ar = YC_6H_4$ :  $Y = NH_2$ ,  $CH_3O$ , H, CN or  $NO_2$ .

I. R = H

 $\Pi$ .  $R = C_6H_8$ 

 $\overline{\mathbf{II}}$ .  $R = Y'C_6H_4$ 

a. Y(and Y') at para position.

b. Y(and Y') at meta position.

### New Synthesis of Orelline by Metalation of Methoxypyridines François Trécourt, Marc Mallet, Olivier Mongin, Bruno Gervais and Guy Quéguiner\*.

Laboratoire de Chimie Organique Fine et Hétérocyclique de l' IRCOF, URA 1429, INSA de Rouen, BP 08, 76131 Mont-Saint-Aignan Cedex (France)

A new total synthesis in five steps of the alkaloid Orelline is reported. The methodology involves metalation of methoxypyridines to afford 2-halo-3,4-dimethoxypyridine on which an homocoupling reaction is performed to build the 2,2'-bipyridyl stucture of the alkaloid.

Tetrahedron, 1993, 49, 8381

## SYNTHESIS OF $3\alpha\text{-Alkoxy-}4\beta\text{-substituted-2-azetidinones}$ from L(+)- Tartaric acid

Derek H. R. Barton<sup>a</sup>, Jeanine Cléophax<sup>b</sup>, Alice Gateau-Olesker<sup>b</sup>, Stephan D. Géro<sup>\*b</sup> and Catherine Tachdjian<sup>a</sup>.

a) Department of Chemistry, Texas A&M University, College Station, Texas 77843.b) Institut de Chimie des Substances Naturelles, C.N.R.S., 91198 Gif-sur-Yvette, France.

The synthesis of  $3\alpha$ -alkoxy-2-azetidinones from L(+)-tartaric acid is described. Regionelective saponification (a) and methylation (c) along with a stereoselective radical decarboxylative alkylation (b) are the key steps leading to optically pure trans- $\beta$ -lactams.

Tetrahedron, 1993, 49, 8397

# SYNTHESE DU SYSTEME CYCLIQUE DE L'AZA-TRIQUINANE LINEAIRE PAR TROIS CYCLISATIONS RADICALAIRES EN CASCADE

Doug Boate<sup>(a)</sup>, Catherine Fontaine<sup>(b)</sup>, Eric Guittet<sup>(b)</sup> et Lucien Stella<sup>(a)\*</sup>, (a)Laboratoire de Chimie Organique B - Associé au CNRS, Faculté des Sciences de Saint-Jérôme, Université d'Aix-Marseille III, Avenue Normandie-Niemen - 13397 Marseille Cédex 13 - France (b) Institut de Chimie des Substances Naturelles - CNRS - 91198 - Gif sur Yvette - France

Treatment of the trienic N-chloroamine 5 by TiCl<sub>3</sub> induces a chain process including three consecutive regio- and stereo-selective homolytic cyclisations affording, as the major product the new cis-syn-cis aza-triquinane 10c

### STEREOELECTRONIC EFFECT IN EQUILIBRATION AND METHOXY EXCHANGE OF CYCLIC METHOXYSULFONIUM

SALTS

I. Jalsovszky, F. Ruff and A. Kucsman:

Department of Organic Chemistry, Eötvös University, PO Box 32, H-1518 Budapest 112, Hungary

Cis- and trans-methoxythiolanium and -thianium salts show equilibration and methoxy exchange in deuteromethanol containing chloride ions. The greater reactivity of the trans isomers is explained by stereoelectronic effect of  $\sigma(C-H)$ - $\sigma^*(S-X)$  type with X = OMe or Cl.

$$R^{2} \xrightarrow{\text{CCH}_{2}} \begin{array}{c} \text{CCH}_{2})_{n} \\ \text{S-OCH}_{3} \end{array} \xrightarrow{\text{CD}_{3}\text{CD}} \qquad R^{2} \xrightarrow{\text{CCD}_{3}} + R^{2} \xrightarrow{\text{CCD}_{3}} + R^{2} \xrightarrow{\text{CCD}_{3}} \\ \text{S-OCD}_{3} \end{array} + R^{2} = \iota \text{C}_{4}\text{H}_{9} \text{ or } \text{H}_{2}$$

cis- or transmethoxysulfonium salts cis- and trans-deuteromethoxysulfonium salts equilibrium mixture

### STEREOSELECTIVE TOTAL SYNTHESIS OF (±)-PAULOWNIN AND (±)-ISOGMELINOL THROUGH RADICAL ANNULATION ROUTE

Tetrahedron, 1993, 49, 8415

Subhas Chandra Rov and Sankar Adhikari

Indian Association for the Cultivation of Science. Department of Organic Chemistry, Jadavpur, Calcutta - 700 032, India.

A highly stereocontrolled synthesis of  $(\pm)$ -(1a) and (±)-isogmelinol (1b) is paulownin described involving intramolecular radical cyclisation reaction as a key step.

a, Ar=3,4-methylenedioxophenyl

b, 3,4-dimethoxyphenyl

Tetrahedron, 1993, 49, 8423

C-ALKYLATION of NITRILES: a USEFUL ROUTE to 2-ETHOXYALKYL

DERIVATIVES of CADAVERINE PLANNED for ENZYME STUDY

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<sup>3</sup>Dipartimento di Chimica, Università della Calabria, Italy

The cadaverine derivatives 1-4 designed for the diamine oxidase active site study, were synthesized and characterized.

## CHEMOENZYMATIC SYNTHESIS OF PURE ENANTIOMERIC 2-ARYL-PROPIONIC ACIDS

M.García, C. del Campo, E.F.Llama, J.M.Sánchez-Montero and J.V.Sinisterra\*
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Tetrahedron, 1993, 49, 8441

# HETEROAROMATICITY.8. THE INFLUENCE OF N-OXIDE FORMATION ON HETEROCYCLIC AROMATICITY

Clive W. Bird

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A recently described aromaticity index has been used to examine the changes in the aromaticity of nitrogen heterocycles accompanying their  $\underline{N}$ -oxidation. Some instances are noted where there is an unforeseen increase in aromatic character. The aromaticity indices of isomeric furoxans can be a useful indication as to their relative stabilities.

Tetrahedron, 1993, 49, 8449

### SYNTHESIS AND CONJUGATE AND 1, 2 ADDITION REACTIONS OF A STERICALLY HINDERED ALLYLIC SULFOXIMINE

Stephen G. Pyne\* and Gernot Boche, Department of Chemistry, University of Wollongong, Wollongong, NSW, 2522, Australia and Fachbereich Chemie, Philipps Universitat, Marburg, 3350, Germany.

The synthesis and reactions of lithiated allylic sulfoximine 4 with electrophiles is described.

#### ENOLIC RADICAL DERIVED FROM ACETIC ACID: A USEFUL RADICAL ALTERNATIVE TO ACETATE ENOLATE IN MICHAEL-TYPE REACTIONS

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Z=CO<sub>2</sub>Me, CO<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, CO<sub>2</sub>Bu<sup>t</sup>, CONMe<sub>2</sub>, CONPr<sup>i</sup><sub>2</sub>, CN, Cl R=H, Me, Cl Reagents: i, Bu<sup>n</sup><sub>3</sub>SnCl, NaBH<sub>4</sub>, AIBN, EtOH; ii, NaF, H<sub>2</sub>O

X