

## GRAPHICAL ABSTRACTS

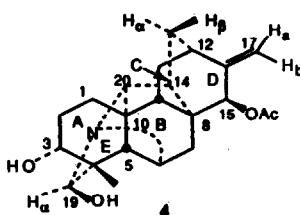
*Tetrahedron*, 1994, 50, 12283

**THE STRUCTURE OF ANDERSOBINE, A NEW DITERPENOID ALKALOID FROM *DELPHINIUM ANDERSONII* GRAY**

Balwami S. Joshi,<sup>1</sup> Mohinder S. Puri,<sup>2</sup> Yili Bai,<sup>1</sup> A. Mukundi Panne,<sup>1</sup> and S. W. Pelletier<sup>1</sup>

<sup>1</sup>Institute for Natural Products Research & Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, U.S.A.; <sup>2</sup>Schering-Plough Research Institute, 2015 Galloping Hill Road, Kenilworth, New Jersey 07033, U.S.A.

The structure of andersobine (4), a new diterpenoid alkaloid from *Delphinium andersonii* Gray, has been determined by <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H homonuclear COSY, HETCOR, one dimensional <sup>1</sup>H NMR, 2D <sup>1</sup>H NMR, and selective INEPT NMR spectral studies.

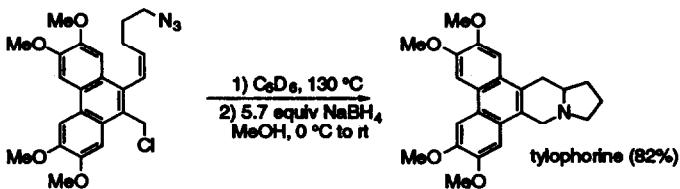


*Tetrahedron*, 1994, 50, 12293

**SYNTHESIS OF ( $\pm$ )-TYLOPHORINE BY THE INTRAMOLECULAR CYCLOADDITION OF AN AZIDE WITH AN  $\alpha$ -CHLOROALKENE.**

William H. Pearson\* and Rajesh Walavalkar

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055



*Tetrahedron*, 1994, 50, 12305

**Mechanism of the Rearrangement of 2-(Vinyloxy)alkyl to 4-Ketobutyl Radicals**

D. Crich\* and Q. Yao, Dept. of Chemistry, Univ. Illinois at Chicago, 845 W. Taylor St., Chicago, IL 60607-7061.

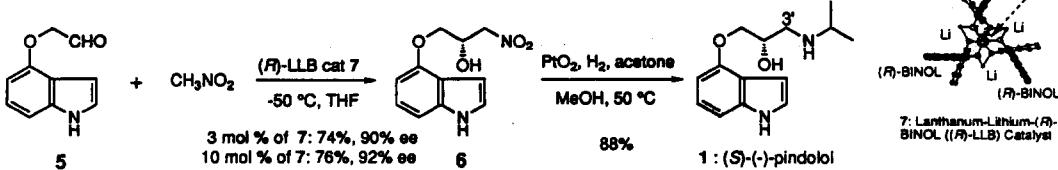


The title rearrangement is shown to occur via a stepwise mechanism involving closure to a tetrahydrofuran radical, which can be trapped, followed by a fragmentation step.

*Tetrahedron*, 1994, 50, 12313

**Syntheses of (*S*)-(-)-Pindolol and [ $^{3'}\text{-}^{13}\text{C}$ ]-(*R*)-(-)-Pindolol Utilizing a Lanthanum-Lithium-(*R*)-BINOL ((*R*)-LLB) Catalyzed Nitroaldol Reaction**

Hiroaki Sasai, Yoichi M. A. Yamada, Takeyuki Suzuki, and Masakatsu Shibasaki\*  
Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

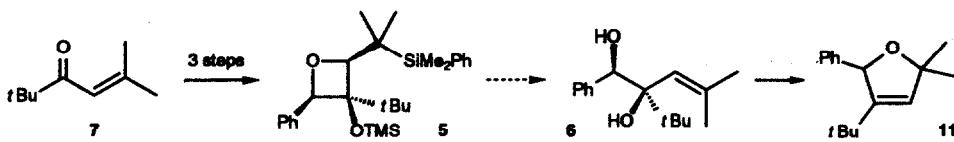


**THE  $\beta$ -SILICON EFFECT AS A CONTROL ELEMENT  
FOR THE REGIOSELECTIVE RING OPENING OF OXETANES**

*Tetrahedron*, 1994, 50, 12319

Thorsten Bach\* and Kristian Kather, Organisch-Chemisches Institut der Universität, Orleansring 23, D-48149 Münster, Germany

The silyl substituted oxetane 5 was prepared from ketone 7 in order to evaluate the effect of the silicon group on a projected ring opening to the diol 6. Regioselective ring opening occurred, but 6 underwent a subsequent ring closure to the dihydrofuran 11.

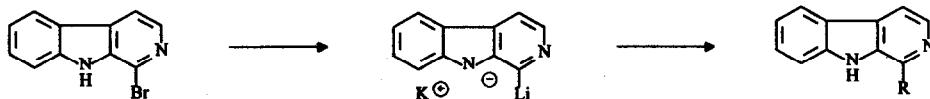


**1,9-DIMETALATED  $\beta$ -CARBOLINES.**

*Tetrahedron*, 1994, 50, 12329

**VERSATILE BUILDING BLOCKS FOR THE TOTAL SYNTHESIS OF ALKALOIDS**

Franz Bracher\*, and Dirk Hildebrand, Institut für Pharmazeutische Chemie, 38106 Braunschweig, Germany; Institut für Pharmazeutische Chemie, 35037 Marburg, Germany



Reactions of 1,9-dimetalated  $\beta$ -carbolines with electrophiles lead to various  $\beta$ -carboline alkaloids.

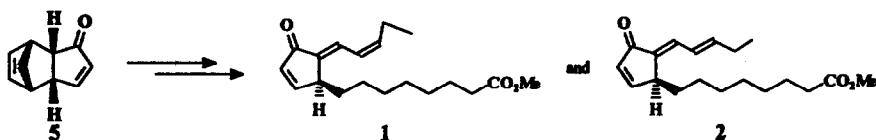
**TOTAL SYNTHESIS AND STRUCTURAL REVISION OF CHROMOMORIC**

*Tetrahedron*, 1994, 50, 12337

**ACID C-I AND C-II METHYL ESTERS** Zhi-Yu Liu\*, Hong Dong and Xin-Jie Chu

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, CHINA

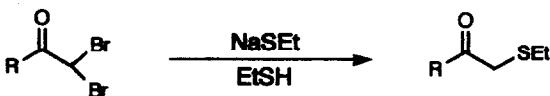
Stereospecific total synthesis of chromomoric acid C-I and C-II methyl esters (1 and 2) and a revision of original assignment were described.



*Tetrahedron*, 1994, 50, 12349

**SELECTIVE TRANSFORMATION OF  $\alpha,\alpha$ -DIBROMOMETHYL  
KETONES INTO  $\alpha$ -MONOSULFENYLATED KETONES**

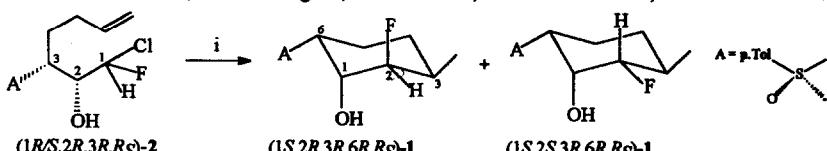
M. Boeykens and N. De Kimpe, Department of Organic Chemistry, University of Gent,  
Faculty of Agricultural and Applied Biological Sciences, Coupure Links 653, B-9000 Gent, Belgium



**ON THE SYNTHESIS OF OPTICALLY PURE MONOFLUOROCYCLO-HEXANOL DERIVATIVES BY THE FLUORINATED SULPHOXIDE CHIRON ROUTE.**

*Tetrahedron*, 1994, 50, 12361

Alberto Arnone, Pierfrancesco Bravo, Massimo Frigerio, Fiorenza Viani, Giancarlo Cavicchio, and Marcello Crucianelli



i)  $\text{Bu}_3\text{SnH}$ ,  $\text{hv}$ , benzene,  $35^\circ\text{C}$ .

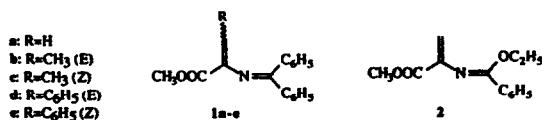
**Reactions of 3-Carbomethoxy-2-Aza-1,3-Butadiene Derivatives with Dienophiles**

Cesarino Balsamini<sup>a</sup>, Annalisa Bedini<sup>a</sup>, Roberta Galarraga<sup>a</sup>, Gilberto Spadoni<sup>a</sup>, Giorgio Tarta<sup>b</sup>, Mahmoud Hamada<sup>b</sup>.

a: Istituto di Chimica Farmaceutica - Università degli Studi - Piazza del Risascimento 6, 61029 - Urbino - Italia.

b: Glaxo Research Laboratories - Via Fleming, 4 - 37100 Verona - Italia.

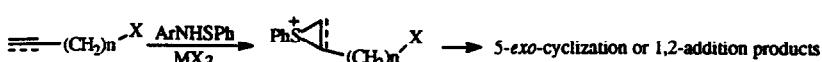
2-Azadienes 1a-e react with selected electron-poor dienophiles giving 4+2 cycloadducts; the 1-ethoxy analogue 2 undergoes Diels-Alder or Michael-type additions depending on the nature of the dienophile.



**REACTION OF 4'-NITROBENZENESULFENANILIDE (NBSA) WITH LEWIS ACIDS. A STUDY OF ITS APPLICATION IN SULFENOCYLIZATION OF ALKENES AND ALKYNES.**

Luisa Benati, Laura Capella, Pier Carlo Montevicchi<sup>a</sup> and Piero Spagnolo  
Dipartimento di Chimica Organica "A. Mangini", Viale Risorgimento 4, I-40136 Bologna, Italy

*Tetrahedron*, 1994, 50, 12395



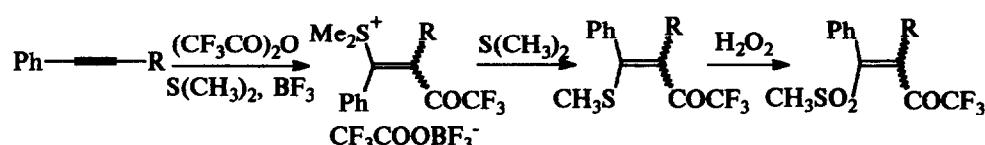
Ar = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-p; MX<sub>3</sub> = BF<sub>3</sub>, AlCl<sub>3</sub>, AlBr<sub>3</sub>; X = OH, COOH, CH=CH<sub>2</sub>; n = 1,2,3.

**PERFLUOROACYLATION OF ALKYNES**

*Tetrahedron*, 1994, 50, 12407

V.G.Nenajdenko, E.S.Balenkova\*

Department of Chemistry, Moscow State University, Moscow 119899, Russia

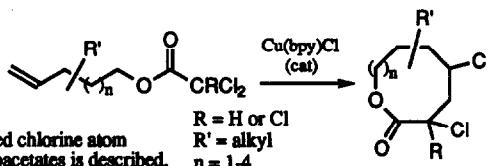


**SYNTHESIS OF MEDIUM-SIZED LACTONES BY THE COPPER(I)  
CHLORIDE/2,2'-BIPYRIDINE-CATALYZED CYCLIZATION OF  
DI- AND TRICHLOROACETATES**

*Tetrahedron*, 1994, 50, 12415

Frank O. H. Pirring, Henk Hiemstra\* and W. Nico Speckamp\*,  
Laboratory of Organic Chemistry, University of Amsterdam,  
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.  
Bernard Kaptein and Hans E. Schoemaker,  
DSM Research, P. O. Box 18, 6160 MD Geleen, The Netherlands.

The formation of 8- to 11-membered lactones by Cu(bpy)Cl catalyzed chlorine atom transfer *endo*-cyclization of (*un*)-substituted alkenyl di- and trichloroacetates is described.



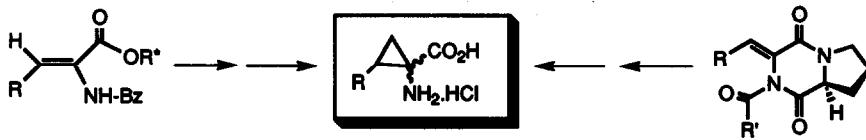
**ASYMMETRIC SYNTHESSES OF 1-AMINO-2-PHENYL(ALKYL)-  
CYCLOPROPANECARBOXYLIC ACIDS BY DIASTEREORESELECTIVE  
CYCLOPROPANATION OF HIGHLY FUNCTIONALIZED MONOCHIRAL OLEFINES**

*Tetrahedron*, 1994, 50, 12443

C. Alcaraz,\* M.D. Fernández,\* M.P. de Frutos,\* J.L. Marco,\* M. Bernabé,\* C. Foces-Foces,<sup>b</sup> F.H. Cano<sup>b</sup>

<sup>a</sup> Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006-Madrid (Spain)

<sup>b</sup> Departamento de Rayos-X, Instituto de Química Física "Rocasolano", CSIC, Serrano 119, 28006-Madrid (Spain)

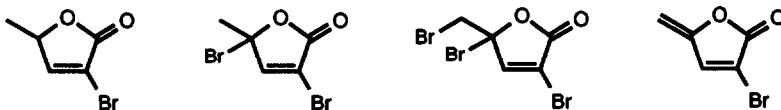


**THE BROMINATION OF  $\beta$ -ANGELICA LACTONE REVISITED:  
SYNTHESIS OF NEW 3-BROMOMETHYLENE AND  
3-BROMOMETHYL-2(SH)-FURANONES.**

*Tetrahedron*, 1994, 50, 12457

Cristina Ochoa de Echagüen and Rosa M. Ortúfio\*

Universitat Autònoma de Barcelona, Departament de Química, 08193 Bellaterra, Barcelona, Spain.



**1-SUBSTITUTED 1-ETHOXY DIENES OBTAINED BY REACTION OF  
1,1-DIETHOXYBUT-2-ENE WITH ELECTROPHILES IN THE PRESENCE OF THE MIXED METAL BASE LICKOR**  
Cristina Prandi and Paolo Venturello\*- Istituto di Chimica Organica dell'Università, Via P. Giuria, 7 10125 Torino, Italy

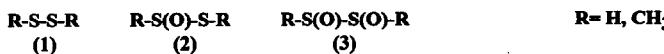
*Tetrahedron*, 1994, 50, 12463

1,4-Elimination in 1,1-diethoxybut-2-ene (1), promoted by LICKOR reagent, leads to (*E*)-1-ethoxybuta-1,3-diene (2). The obtained alkoxy diene 2 undergo further metallation and reaction with electrophiles, giving  $\alpha$ -substituted dienes 4a-e. The corresponding carbonyl compounds 5b-e can be obtained by mild acid work-up.



**AB-INITIO MCSCF STUDY OF THE HOMOLYTIC S-S BOND DISSOCIATION IN DISULPHIDES, THIOSULPHINATES AND  $\alpha$ -DISULPHOXIDES.**

Rois Benassi\*, Gian Luca Fiandri and Ferdinando Taddei  
Dipartimento di Chimica, Università, Via Campi 183, 41100 Modena, Italy

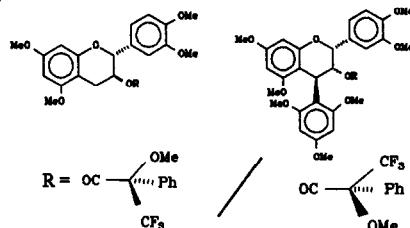


The geometrical and electronic properties of the title compounds and of the relative radicals originated from S-S cleavage were calculated with *ab-initio* MO MCSCF wavefunctions. The energy profiles for S-S bond cleavage were also determined.

**OLIGOMERIC FLAVANOIDS. PART 17. ABSOLUTE CONFIGURATION OF FLAVAN-3-OLS AND 4-ARYLFLAVAN-3-OLS VIA THE MOSHER METHOD**

W. Rossouw, A.F. Hundt, J.A. Steenkamp, and D. Ferreira  
Department of Chemistry, University of the Orange Free State, P.O. Box 339,  
Bloemfontein, 9300 South Africa

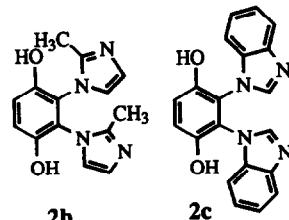
<sup>1</sup>H NMR analysis of *R*(+)- and *S*(-)-MTPA esters of flavan-3-ols and 4-arylflavan-3-ols permits assessment of the absolute configurations at C-3 of these condensed tannin structural units.



Imidazole and Benzimidazole Addition to Quinones. Formation of *meso* and *d,l* Isomers and Crystal Structure of the *d,l* Isomer of 2,3-Bis(benzimidazol-1'-yl)-1,4-Dihydroxybenzene

C. Escolástico, M.D. Santa María, R.M. Claramunt, M.L. Jimeno, I. Alkorta, C. Foces-Foces, F.H. Cano and J. Elguero, Departamento de Química Orgánica y Biología, Instituto 'Rocasolano', UNED y CSIC, E-28040 Madrid, Spain.

Compound 2b exists in the solid state as the *d,l* isomer and in solution as a 50:50 mixture of *d,l* and *meso* isomers. Both isomers of compound 2c can be isolated in the solid state and the X-ray structure of the *d,l* isomer has been determined. <sup>1</sup>H NMR (n.o.e. effects), <sup>13</sup>C CPMAS NMR and AM1 semiempirical calculations have been used to explore the potential energy surface.



*Ab Initio* Theoretical Study of the Monomer-Dimer Equilibrium in Lithium and Sodium *gem*-Dichloro Allyl and Methyl Systems.

Carlo Canepa and Giauко Tonachini\* Istituto di Chimica Organica, Università di Torino, v. P.Giuria, 7 10125 Torino, Italy  
The interaction with a discrete number of water molecules (modelling ether molecules) reverses the sign of the dimerization energy: the equilibrium is estimated to lie in favour of the monomers, in contrast with the results obtained for the fluorinated systems.

