

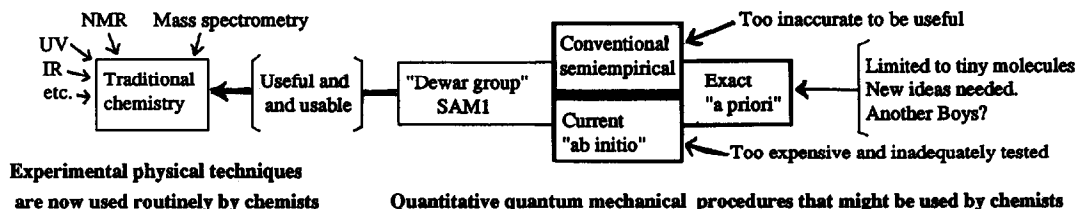
*Tetrahedron*, 1993, 49, 5003

**SAM1; THE FIRST OF A NEW SERIES OF GENERAL PURPOSE QUANTUM MECHANICAL MOLECULAR MODELS**

Michael J. S. Dewar\*, Caoxian Jie, and Jianguo Yu

Department of Chemistry, The University of Florida, Gainesville, Florida 32611, USA

SAM1 is the latest "Dewar group" procedure. Calculations for 512 molecules, ions, and radicals, and for 11 chemical reactions, show its superiority to AM1. Its development also opens the way to a new generation of progressively better "semi-ab-initio" treatments.



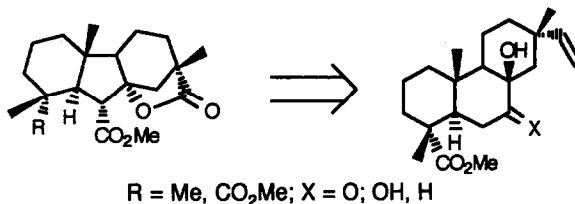
*Tetrahedron*, 1993, 49, 5039

**SYNTHESIS OF ENANTIOMERIC GIBBERELLIN ANALOGS FROM NATURAL ISOPIMARENES**

Angelo C. Pinto\*, Rosângela de A. Epifanio<sup>1</sup> and Wilson Camargo

Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, Ilha do Fundão, 21910, Rio de Janeiro, RJ, Brasil.

We report the synthesis of 15-oxa-giberellanes, enantiomeric analogs of gibberellins, from natural isopimarenes.

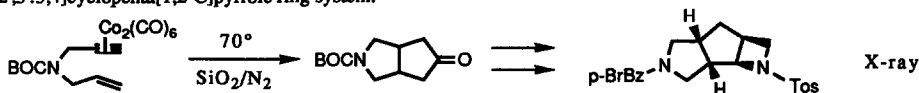


*Tetrahedron*, 1993, 49, 5047

**Synthesis of N-BOC-3-Azabicyclo[3.3.0]octan-7-one via Reductive Pauson-Khand Cyclization and Subsequent Conversion to a Novel Diazatricyclic Ring System**

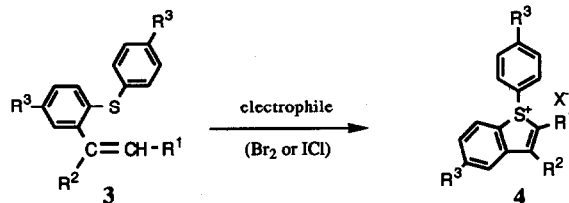
Daniel P. Becker\* and Daniel L. Flynn, Searle Research & Development, 4901 Searle Parkway, Skokie, IL 60077

A reductive intramolecular Pauson-Khand cyclization under dry-state adsorption conditions and inert atmosphere directly afforded the saturated N-BOC-3-azabicyclo[3.3.0]octan-7-one which was converted to the novel octahydro-1-azeto[2'3':3,4]cyclopenta[1,2-C]pyrrole ring system.



**Intramolecular Cyclization of [*o*-(Arylthio)phenyl]ethenes. Synthesis and Crystal Structure of 1-Arylbenzo[*b*]thiophenium Salts**

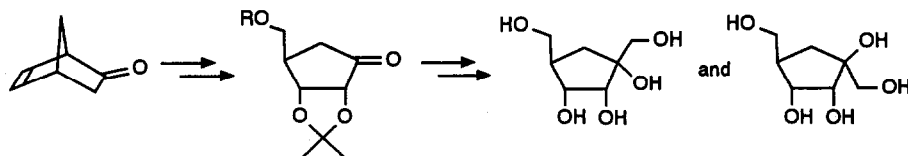
Tsugio Kitamura,\* Shin-ichi Soda, Hironobu Kawasato, and Hiroshi Taniguchi\*,  
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu  
University 36, Hakozaki, Fukuoka 812, Japan; Motoo Shiro, Rigaku Corporation, Matsubara-cho 3-9-12, Akishima, Tokyo 196,  
Japan


**SYNTHESIS OF  $\alpha$ - AND  $\beta$ -D,L-*ribo*-CARBAHEX-2-ULOFURANOSE**

Ch. Marschner, G. Penn and H. Griengl\*

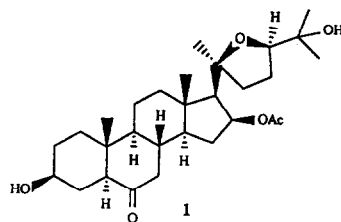
Institute of Organic Chemistry, Graz University of Technology, Stremayrgasse 16, A-8010 Graz

Racemic  $\alpha$ - and  $\beta$ -isomers of D,L-*ribo*-carbahex-2-ulofuranose have been synthesized. An unexpected stereochemical course in the reaction of sulfur ylides with  $\alpha$ -alkoxy ketones has been observed.


**Hemisynthesis of (20S,24R)-20,24-Epoxy-3 $\beta$ ,16 $\beta$ ,25-Trihydroxy-6-Oxo-5 $\alpha$ -Cholestane 16-Acetate from Diosgenin.**

Regina Tavares, Thierry Randoux, Jean-Claude Braekman, and Désiré Daloze.  
Laboratory of Bio-organic Chemistry, Faculty of Sciences, University of Brussels,  
Av. F.D. Roosevelt, 50, B-1050 Brussels - Belgium.

The title compound **1** which was isolated as its 3 $\beta$ -sophoroside from the defensive secretion of *Chrysolina varians* (Coleoptera: Chrysomelidae) has been synthesized from diosgenin in 8 steps.

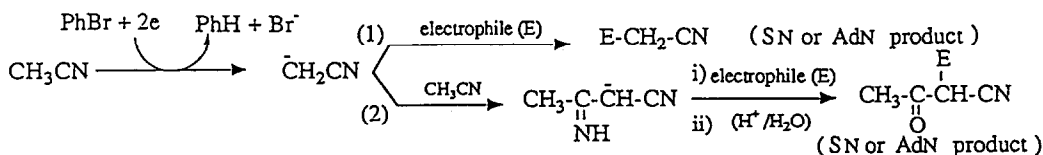


# Aryl Halides as Precursors of Electrogenerated Bases. Utilization in Coupling Reactions of Acetonitrile with various Electrophilic Compounds.

Rachid Barhdadi, Jacques Gal, Monique Heintz, Michel Troupel\* and Jacques Périchon.

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (UMR 28), C.N.R.S., 2, rue Henri Dunant, 94320 Thiais, France.

Cyanomethylation reactions are performed using bases electrogenerated from aryl halides. Different products are obtained depending on the procedure utilized.

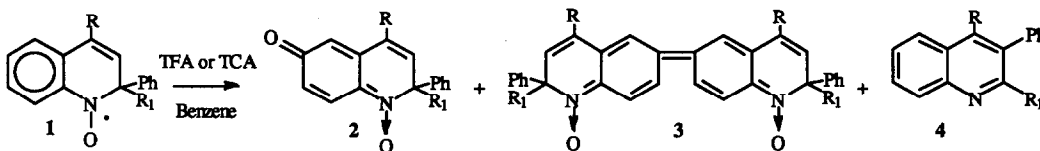


(1): one-pot procedure (2): two steps-procedure E = ester, carbonyl-, alkylchloride, acylchloride.

# OXIDATIVE DIMERIZATION OF QUINOLINIC NITROXIDE WITH TRIFLUORO- AND TRICHLORO- ACETIC ACID. CRYSTAL STRUCTURES OF 6,6'-BIS-(1-OXIDE-1,2,6,8A-TETRAHYDROQUINOLINE)YLIDENE AND OF 2,3-DIPHENYLQUINOLINE.

P. Carloni,<sup>a</sup> E. Damiani,<sup>a</sup> L. Greci,<sup>\*,a</sup> P. Stipa,<sup>a</sup> C. Rizzoli,<sup>b</sup> P. Sgarabotto,<sup>\*,b</sup> F. Uguzzoli.<sup>b</sup> <sup>a</sup> Dip. Scienze Materiali e Terra, Università, Via Breccia Bianche, I-60131 Ancona, Italy; <sup>b</sup> Istit. Strutt. Chimica, Università, Viale delle Scienze, I-43100 Parma, Italy.

Quinolinic nitroxides 1a-c react with trichloro- and trifluoro-acetic acid to give dimers 3a-c and quinolines 4a-c as the main products.



# CHEMOSELECTIVITY OF RHODIUM CARBENOID. A COMPARISON OF THE SELECTIVITY FOR O-H INSERTION REACTIONS OR CARBONYL YLIDE FORMATION VERSUS ALIPHATIC AND AROMATIC C-H INSERTION AND CYCLOPROPANATION

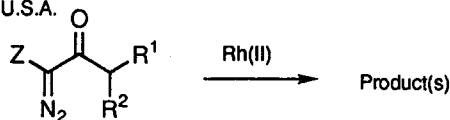
Geoffrey G. Cox and Christopher J. Moody\*

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, U.K.

David J. Austin and Albert Padwa\*

Department of Chemistry, Emory University, Atlanta, Georgia 30522, U.S.A.

A range of diazocarbonyl compounds containing two different functional groups (within R<sup>1</sup> and R<sup>2</sup>) has been prepared, and their rhodium(II) catalysed decomposition studied as a means of probing the chemoselectivity of carbenoid intermediates.

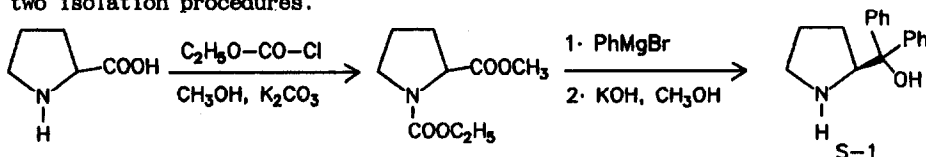


# CONVENIENT METHOD FOR THE SYNTHESIS OF CHIRAL $\alpha$ , $\alpha$ -DIPHENYL-2-PYRROLIDINEMETHANOL

J.V.Bhaskar Kanth and Mariappan Periasamy\*

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

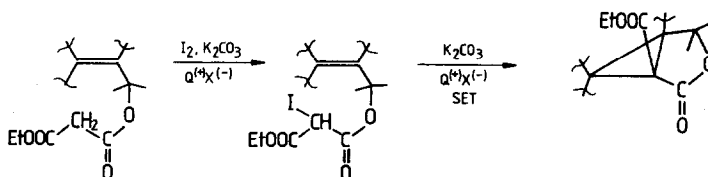
Chiral  $\alpha$ ,  $\alpha$ -diphenyl-2-pyrrolidinemethanol S-1, is synthesised from S-proline utilizing inexpensive reagents, following a method involving only two isolation procedures.



# SINGLE ELECTRON TRANSFER INDUCED ELEMENTAL STEPS IN THE TRANSFORMATION OF IODOMALONIC ESTERS AND RELATED CH- ACIDS UNDER SOLID-LIQUID PTC CONDITIONS. PREPARATION OF ELECTROPHILIC CYCLOPROPANES

L. Tóke, Z. Hell, G.T. Szabó, M. Bihari, A. Rockenbauer  
Dept. of Org. Chem. Techn. Technical University, Budapest, Hungary

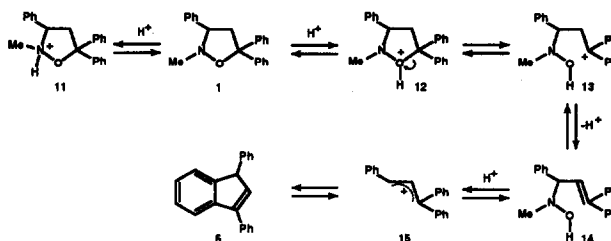
Malonic esters react with olefins under PTC-conditions in the presence of iodine to give cyclopropane derivatives. The mechanism of the reaction is also discussed.



# RING-OPENING OF SUBSTITUTED ISOXAZOLIDINES: ONE-POT SYNTHESIS OF INDENES

F. Casuscelli,<sup>a</sup> U. Chiacchio,<sup>b</sup> A. Liguori,<sup>c</sup> G. Romeo,<sup>a</sup> G. Sindona<sup>c</sup> and N. Uccella;<sup>c</sup><sup>a</sup>Università di Messina, Italy; <sup>b</sup>Università di Catania, Italy; <sup>c</sup>Università della Calabria, Italy.

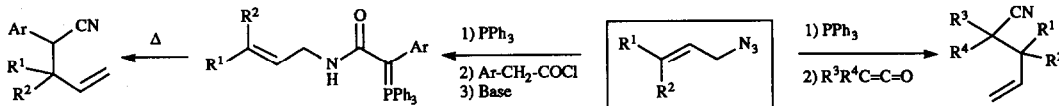
High yield conversion of 3,5,5-triaryl-isoxazolidines into indene derivatives has been achieved by 4 h refluxing in aq. H<sub>2</sub>SO<sub>4</sub>. The rearrangement pathway is interpretable on the basis of a ring-opening process where the crucial step is the protonation of the oxygen atom of the isoxazolidine nucleus.



# REACTION OF ALLYL IMINOPHOSPHORANES WITH KETENES AND ACYL CHLORIDES: ONE-POT PREPARATION OF 4-PENTENENITRILES

Pedro Molina, Mateo Alajarín, Carmen López-Leonardo, and Julian Alcántara  
Departamento de Química Orgánica, Universidad de Murcia, Campus de Espinardo, E-30071, Murcia, Spain.

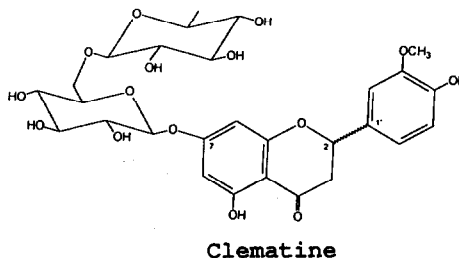
The titled iminophosphoranes react either with ketenes at r.t. or acyl chlorides and further thermal treatment of the resulting phosphoranes to give 4-pentenitriles.



# Isolation and Structure of Clematine, A New Flavanone Glycoside from *Clematis armandii* Franch

Yingfong Chen<sup>a</sup>, Jian Liu<sup>b\*</sup>, R. Stephen Davidson<sup>b</sup>, Oliver W. Howarth<sup>c</sup>; <sup>a</sup>Hunan College of Traditional Chinese Medicine, (China), <sup>b</sup>University of Kent, (UK), and <sup>c</sup>University of Warwick, (UK)

A new flavanone glycoside was isolated from Chinese crude drug "mu tong" (*Clematis armandii*). The structure was established mainly by 2D NMR methods, FAB and HREI-MS.

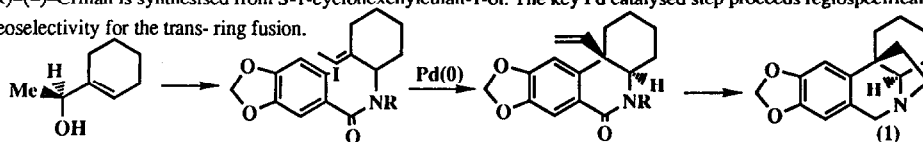


# TOTAL SYNTHESIS OF (R,R)-CRINAN VIA REGIOSPECIFIC AND STEREOSELECTIVE PALLADIUM CATALYSED CYCLISATION

R. Grigg,<sup>a</sup> V. Santhakumar,<sup>a</sup> V. Sridharan,<sup>a</sup> M. Thornton - Peu<sup>a</sup>, and A.W. Bridge<sup>b</sup>

a. School of Chemistry, Leeds University, Leeds LS2 9JT, b. Rhone - Poulenc Rorer, Rainham Road South, Dagenham RM10 7XS.

(R,R)-(-)-Crinan is synthesised from S-1-cyclohexenylethan-1-ol. The key Pd catalysed step proceeds regiospecifically and with a 20:1 stereoselectivity for the trans- ring fusion.



**NEW SYNTHESIS OF 3'-C-SUBSTITUTED NUCLEOSIDES**

N. Garg, J. Plavec and J. Chattopadhyaya\*

Department of Bioorganic Chemistry, Box 581, Biomedical Center,  
University of Uppsala, S-751 23 Uppsala, Sweden

Synthesis of 3'-C-branched thymidine **3** is described  
starting from 2',3'-dideoxy-3'-nitro-thymidine **1**.

