GRAPHICAL ABSTRACTS

Tetrahedron, **1992**, *48*, 1407

TRIFUNCTIONAL REAGENTS FOR SUBSTRATE-PROTEIN CONJUGATION: APPLICATION TO PYRROLIZIDINE ALKALOID ANALOGUES

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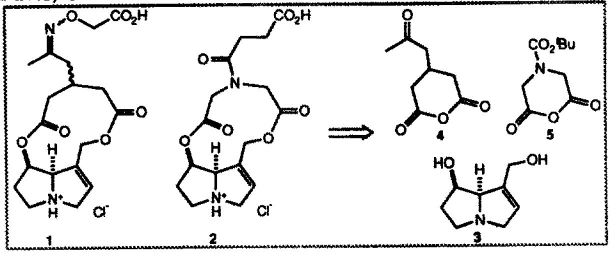
Pyrrolizidine alkaloid (PA) analogues **1** and **2** are prepared from retronecine (**3**) and the novel substrate-protein coupling reagents **4** and **5**. These analogues provide the targeted macrocyclic diester substructural unit, possess a handle for protein conjugation, and potentially maintain the conformational integrity of macrocyclic PAs.



Tetrahedron, **1992**, *48*, 1417

Mn(III)-BASED OXIDATIVE FREE-RADICAL CYCLIZATIONS OF γ,γ-BIS(ALLYLIC) ACETOACETATES

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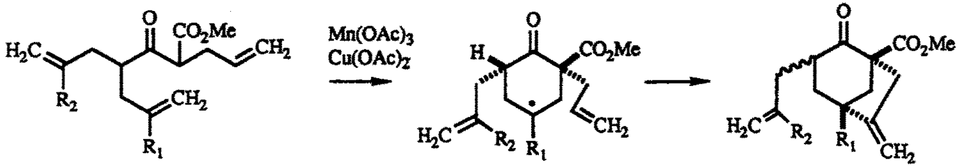
Oxidative free-radical cyclizations of γ,γ-bis(allylic)acetoacetates give monocyclic radicals that cyclize through a transition state with a boat cyclohexane to the allyl group attached to the α-carbon.

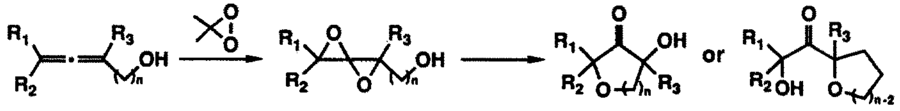


Tetrahedron, **1992**, *48*, 1427

ALLENE EPOXIDATION. HIGHLY FUNCTIONALIZED TETRAHYDROFURANS AND TETRAHYDROPYRANS FROM THE OXIDATIVE CYCLIZATION OF ALLENIC ALCOHOLS.

Jack K. Crandall,* David J. Batal, Feng Lin, Thierry Reix, Gregory S. Nadol, and Raymond A. Ng
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

The dimethyldioxirane oxidation of various allenic alcohols yields highly functionalized tetrahydrofuran and tetrahydropyran derivatives *via* intramolecular nucleophilic addition of the hydroxy group to an intermediate allene diepoxide.



Tetrahedron, **1992**, *48*, 1449

DISTANNOXANE-CATALYZED ACETALIZATION OF CARBONYLS

J. Otera, N. Dan-oh, and H. Nozaki
Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan

Actalization of carbonyls, particularly α,β-unsaturated derivatives, is catalyzed by the title compound.

$$RR'C{=}O \xrightarrow{R''OH/X\text{-}Bu_2SnOSnBu_2\text{-}Y} RR'C(OR'')_2$$

Tetrahedron, **1992**, *48*, 1457

NEW AMINO ACIDS FROM THE POISONOUS MUSHROOM *CLITOCYBE ACROMELALGA*

Kimiaki Yamano and Haruhisa Shirahama*
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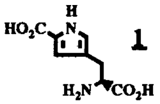
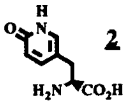
Sapporo 060, Japan

New amino acids, L-3-(2-carboxy-4-pyrrolyl)-alanine (1) and L-3-(2-oxo-5-pyridyl)-alanine (2), were isolated from *Clitocybe acromelalga* and their structures were deduced by spectral data and biogenesis and confirmed by syntheses.



1



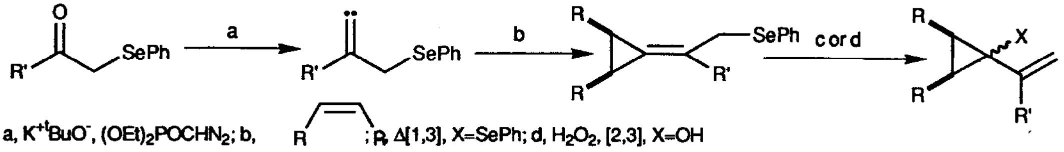
2

Tetrahedron, **1992**, *48*, 1465

SOME NOVEL ROUTES TO 1-HETERO-SUBSTITUTED 1-VINYLCYCLOPROPANES

Richard T. Lewis and William B. Motherwell,* Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.

The generation, trapping and adduct rearrangement of 3-phenylselenoalk-1-enylidene carbenes is described.



a, K⁺ᵗBuO⁻, (OEt)₂POCHN₂; b, ; c, Δ[1,3], X=SePh; d, H₂O₂, [2,3], X=OH

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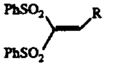
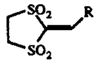
Alkyl- and Arylsubstituted Ketenedithioacetal Tetroxides: Diels-Alder Reactivity and Reductive Desulfonylation of the Adducts

Ottorino De Lucchi,*[a] Davide Fabbri,[b] and Vittorio Lucchini[c]
[a] *Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari - Italy* [b] *Istituto CNR IATCAPA, via Vienna 2, I-07100 Sassari - Italy* and [c] *Dipartimento di Scienze Ambientali, Università di Venezia, Dorsoduro 2137, I-30123 Venezia - Italy*

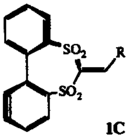
Representative ketenedithioacetal tetroxides **1A-D** react with cyclopentadiene under thermal conditions and with quadricyclane, 1-methoxy, 1- and 2-trimethylsilyloxy-1,3-butadiene and the Danishefsky diene in 5 M lithium perchlorate in ether at room temperature.



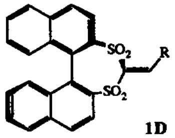
1A



1B



1C



1D

a $R = H$
b $R = CH_3$
c $R = C_6H_5$
d $R = CH{=}CH_2$

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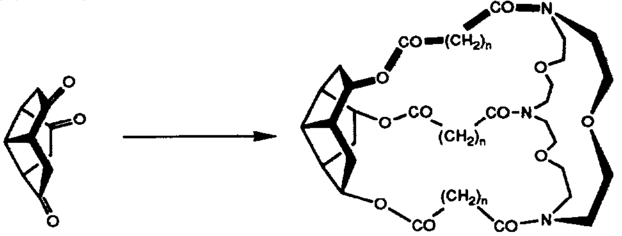
PERHYDROTRIQUINACENIC HOSTS. 2. SYNTHESIS AND COMPLEXATION PROPERTIES OF SPELEANDS OF C_3 SYMMETRY.

Carmen Almansa, Albert Moyano and Félix Serratosa. Departament de Química Orgànica, Universitat de Barcelona, Facultat de Química, C. Martí i Franquès, 1-11, E-08028 Barcelona (Spain).

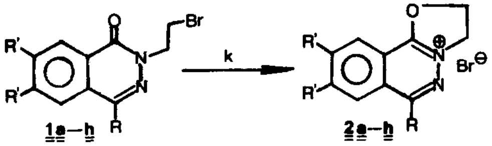
The synthesis and complexation properties of speleands of C_3 symmetry, derived from the chiral concave cap tricyclo[5.2.1.0^{4,10}]decane-2,5,8-trione, are described.

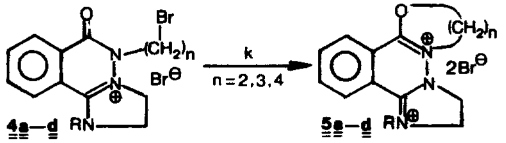


Tetrahedron, **1992**, *48*, 1507

THE EFFECT OF CONFORMATIONAL EQUILIBRIUM ON RATE OF REACTIONS INVOLVING NEIGHBOURING GROUP PARTICIPATION

A. Csámpai and Ö. Farkas, Institute of Organic Chemistry, Eötvös L. University, H-1518 Budapest 112, POB 32, Hungary





The rate of ring closures 1a–h → 2a–h is dependent on the electronic nature of ring substituents, on the other hand, cyclizations 4a–d → 5a–d are highly accelerated by an entropy effect supported by computed conformational analysis.

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ROLE OF THE MACROCYCLIC POLYETHER IN THE SYNTHESIS OF N-ALKYLCARBAMATE ESTERS FROM PRIMARY AMINES, CO_2 AND ALKYL HALIDES IN THE PRESENCE OF CROWN-ETHERS.

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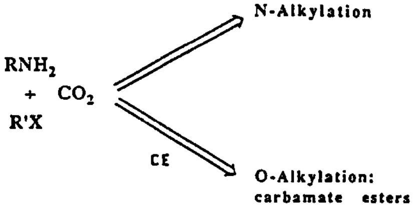
Dipartimento di Chimica, Università, Campus Universitario, 70126, Bari, Italy
Centro CNR-MISO, Via Amendola, 173, 70126, Bari, Italy.

In the presence of a suitable macrocyclic polyether (CE), primary amines and CO_2 react with alkyl halides to give carbamate esters. The role played by the macrocyclic ligand has been elucidated.



Tetrahedron, **1992**, *48*, 1531

DIOLS OBTAINED VIA CHEMO AND REGIOSELECTIVE RING OPENING OF EPOXYALCOHOLS: A STRAIGHTFORWARD SYNTHESIS OF 2S,3S OCTANDIOL

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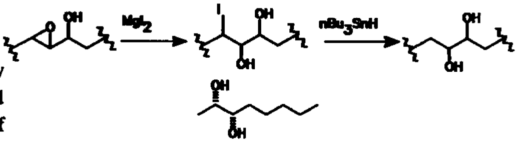
Giuliana Righi, Centro C.N.R. Sost. Nat. c/o Dipartimento di Chimica,*
Università " La Sapienza" P.le A. Moro 5, 00185 Roma

Epoxy alcohols and derivatives are regio and chemoselectively opened to the corresponding iodohydrins and then in situ reduced to vicinal (erythro or threo)diols : a short asymmentric synthesis of 2,3 octandiol, well known pheromone , is also described.



2S-3S–Octandiol