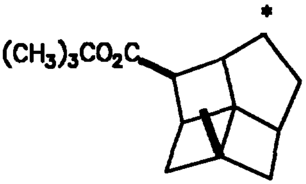
GRAPHICAL ABSTRACTS

Tetrahedron, **1992**, *48*, 6757

CATION, CARBENE, AND RADICAL CENTERS IN A [4.4.4.5]FENESTRANE

D.Venugopal and William C. Agosta*
Laboratories of The Rockefeller University
New York, New York 10021-6399
U.S.A.

Cation, carbene, and radical centers at * in this [4.4.4.5]fenestrane ester react without skeletal rearrangement despite the availability of thermodynamically favorable pathways.

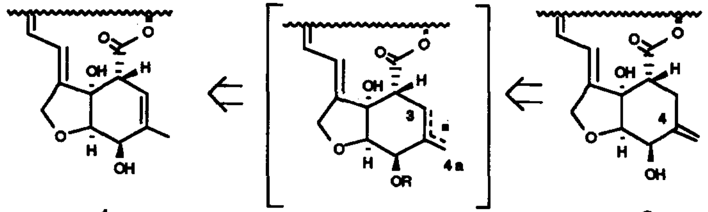


Tetrahedron, **1992**, *48*, 6763

THE C4-EXO METHYLENE ISOMER OF AVERMECTIN B_{1a}: SYNTHESIS VIA AN ALLYLIC RADICAL AND BIOACTIVITY.

Bert Fraser-Reid*, J. Cristóbal López and Ramin Faghih
Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706

Avermectin B_{1a} $\Delta^{4,4a}$, **2**, has been obtained from avermectin B_{1a}, **1**, and its bioactivity evaluated. The key step of the transformation is the reduction of an intermediate allylic radical with tributyltin hydride.



1

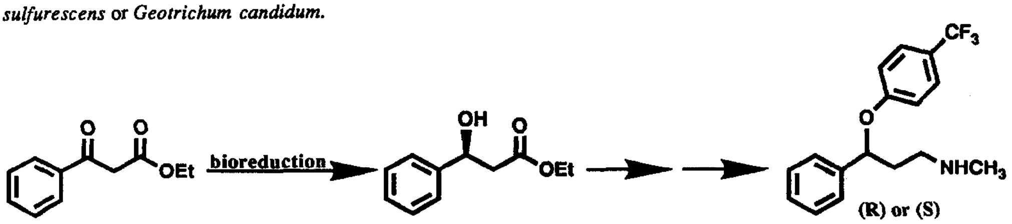
2

Tetrahedron, **1992**, *48*, 6769

ASYMMETRIC SYNTHESIS OF BOTH ENANTIOMERS OF FLUOXETINE VIA MICROBIOLOGICAL REDUCTION OF ETHYL BENZOYLACETATE.

Robert Chênevert*, Geneviève Fortier and Rachid Bel-Rhlid, Département de Chimie, Faculté des Sciences et de Génie, Université Laval, Québec, Canada G1K 7P4.

Both enantiomers of fluoxetine were prepared via the reduction of ethyl benzoylacetate by bakers' yeast, *Beauveria sulfurescens* or *Geotrichum candidum.*

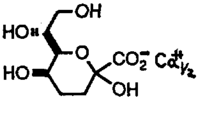


Tetrahedron, **1992**, *48*, 6777

ENANTIOSPECIFIC SYNTHESES OF 3,4-DIDEOXY-OCT-2-ULOSONIC ACIDS

Tony K. M. Shing
Department of Chemistry, The Chinese University of Hong Kong,
Shatin, Hong Kong.

Bisacetonated aldehydo-D-arabinose has been converted by three consecutive reactions (Wittig reaction, catalytic hydrogenation, and hydrolysis) into 3,4-dideoxy-D-arabino-oct-2-ulosonic acid (4-deoxy-KDO), isolated as its calcium salt 2 in an overall yield of 37% from D-arabinose. Likewise reactions of D-xylose gave calcium 3,4-dideoxy-D-xylo-oct-2-ulosonate 3 in an overall yield of 34%. Other routes attempted are also described.



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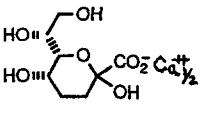


3

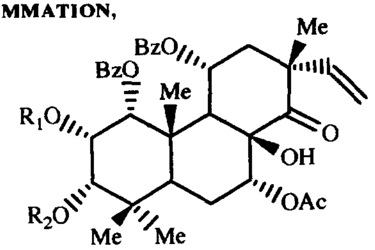
Tetrahedron, **1992**, *48*, 6787

ORTHOSIPHOL A AND B, NOVEL DITERPENOID INHIBITORS OF TPA (12-*O*-TETRADECANOYLPHORBOL-13-ACETATE)-INDUCED INFLAMMATION, FROM *ORTHOSIPHON STAMINEUS*

Toshiya Masuda, Kazuyo Masuda, Shizuno Shiragami, Akiko Jitoe, and Nobuji Nakatani

Laboratory of Food Chemistry, Faculty of Science of Living, Osaka City University, Sumiyoshi, Osaka 558, Japan

Two anti-inflammatory substances were isolated from *Orthosiphon stamineus*, an anti-inflammatorily active plant. Their structures were determined to be highly oxygenated pimarane diterpenoid structures.

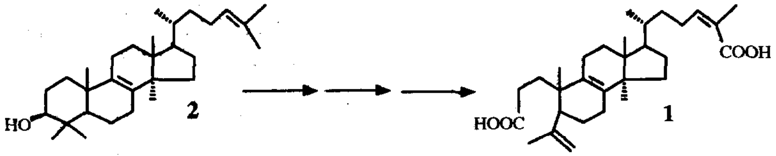


1: R_1=Ac, R_2=H; 2: R_1=H, R_2=Ac

Tetrahedron, **1992**, *48*, 6793

Synthesis of Manwuweizic Acid, An Anticancer Triterpenoid

Jia-Sen Liu* and Yong Tao
Shanghai Institute of Materia Medica, Academia Sinica;
319 Yueyang Rd., Shanghai 200031, China

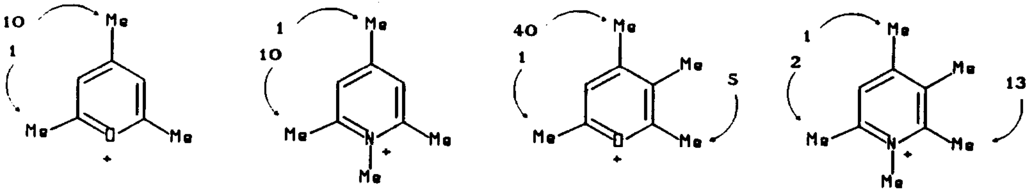


$$\text{R-COOH} \xrightarrow[\text{r.t.}]{\text{DMSO, DCC, TFA}} \text{R-COOCH}_2\text{SCH}_3$$

Tetrahedron, **1992**, *48*, 6799

Relative Stabilities of Pyrylium Anhydrobases (α/γ-Methylene-pyrans) and their N-Methylpyridinium Congeners

F.Hampel[a], D. Wilhelm[a], P.v.R. Schleyer[a] and A.T. Balaban[b], [a]Institut für Organische Chemie, Universität Erlangen-Nürnberg, (FRG), [b]Polytechnic Institute Bucharest, (Romania).



preferred positions for H/D exchange

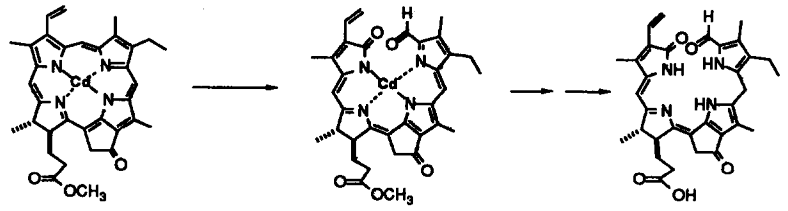
Counterion = ClO_4^-

Tetrahedron, **1992**, *48*, 6807

A Biomimetic Partial Synthesis of the Red Chlorophyll-a Catabolite from *Chlorella Protothecoides*

José Iturraspe and Albert Gossauer
Institut für Organische Chemie der Universität Freiburg i. Ue., rte. du Musée, CH-1700 Fribourg

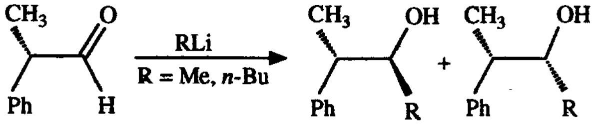
The recently established structure of a chlorophyll-a catabolite isolated from the microalgae *Chlorella protothecoides* has been confirmed by a six-step synthesis starting from chlorophyll-a.



Tetrahedron, **1992**, *48*, 6813

CRAM SELECTIVITY IN THE REACTION OF 2-PHENYLPROPANAL WITH ALKYLLITHIUM REAGENTS: MYTH AND REALITY

Manfred T. Reetz*, Stephan Stanchev and Helmut Haning
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 4330 Mülheim/Ruhr

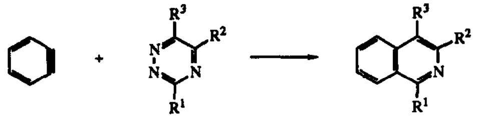


ds = 90 - 94%

Tetrahedron, **1992**, *48*, 6821

Synthesis of Isoquinolines by Cycloaddition of Arynes to 1,2,4-Triazines. António M. d'A. Rocha Gonsalves and Teresa M. V. D. Pinho e Melo, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Portugal
Thomas L. Gilchrist, Chemistry Department, University of Liverpool, Liverpool L69 3BX, U.K.

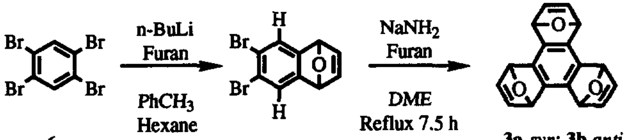
Reaction of benzyne and methylbenzyne with 1,2,4-triazines leads to the formation of isoquinolines.



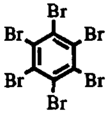
Tetrahedron, **1992**, *48*, 6827

THE REGIOSELECTIVE GENERATION OF ARYNES FROM POLYHALOGENOBENZENES. AN IMPROVED SYNTHESIS OF *SYN*- AND *ANTI*-1,4,5,8,9,12-HEXAHYDRO-1,4:5,8:9,12-TRIEPOXYTRIPHENYLENE
Françisco Raymo, Franz H. Kohnke, and Francesca Cardullo - Dipartimento di Chimica Organica e Biologica, Università di Messina, Salita Sperone 31, 98166 - S. Agata - Messina, Italy
Ulrich Girreser and J. Fraser Stoddart - School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

The halogenated benzenes, 1,2,4,5-tetrabromobenzene **6**, hexabromobenzene **9**, *p*-dichlorotetrabromobenzene **11**, and 1,2-dibromo-4,5-dichlorobenzene **12**, were investigated as 1,3-bis-, 1,4-bis-, and 1,3,5-tris-aryne precursors by using alkyllithiums and alkali metal amides as metalating reagents. The arynes were trapped in Diels-Alder reactions with furan as the diene. The title compounds **3a/b** are now readily available in two steps in 7% overall yield from 1,2,4,5-tetrabromobenzene **6**.



6 **3a** *syn*; **3b** *anti*



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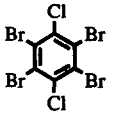

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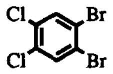

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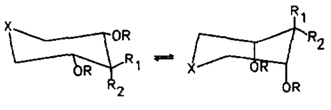
Tetrahedron, **1992**, *48*, 6839

CONFORMATIONAL ANALYSIS ON CYCLOHEXANE, OXANE, AND THIANE DERIVATIVES BEARING TWO GEMINAL ELECTRON-WITHDRAWING GROUPS AND ACETOXY SUBSTITUENTS AT THE β AND β' CARBONS.

F. Santoyo-González[a,*], J. Molina-Molina[a], D. Portal-Olea[a], A. Vargas-Berenguel[a], J. D. Martín-Ramos[b], and J. Romero-Garzón[b].
[a]*Departamento de Química Orgánica, and* [b]*Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain.*

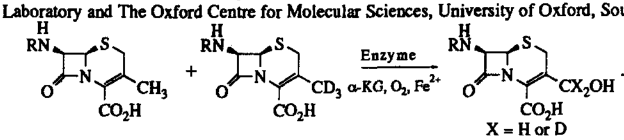
A qualitative conformational analysis on cyclohexane, oxane, and thiane structures bearing two geminal electron-withdrawing groups and having two acetoxy substituents at the β and β' positions has been performed. The predominant conformation depends on X, and the R_1 and R_2 bulks.



Tetrahedron, **1992**, *48*, 6853

CEPHALOSPORIN C BIOSYNTHESIS: ON THE MECHANISM OF HYDROXYLATION OF DEACETOXYCEPHALOSPORIN C TO DEACETYLCEPHALOSPORIN C.

Jack E. Baldwin, Robert M. Adlington, Robin T. Aplin, Nicholas P. Crouch and Roger Wilkinson
The Dyson Perrins Laboratory and The Oxford Centre for Molecular Sciences, University of Oxford, South Parks Road, Oxford, OX1 3QY



+ RECOVERED UNCONVERTED STARTING MATERIAL EXHIBITING A V_{MAX}/K_m DISCRIMINATION

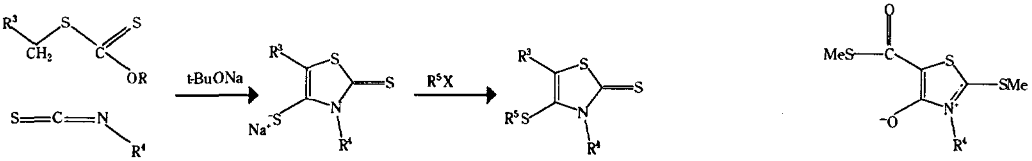
R = D-α-aminodipoyl; α-KG = α-ketoglutarate

Incubation of an equal mixture of deacetoxycephalosporin C and [3'-$^2H_3$]-deacetoxycephalosporin C with partially purified deacetoxycephalosporin C / deacetylcephalosporin C synthase from *Cephalosporium acremonium* CO728 in a mixed competitive isotope effect experiment resulted in enzymic discrimination between labelled and unlabelled substrates.

Tetrahedron, **1992**, *48*, 6863

A NOVEL CYCLOCONDENSATION OF XANTHATES CONTAINING ACTIVE METHYLENE GROUPS WITH ISOTHIOCYANATES. SPECTRAL DATA AND X-RAY STRUCTURES OF THE PRODUCTS

G.V.Tormos[1], V.Yu.Khodorkovsky[1], O.Ya.Neilands[1],* S.V.Belyakov[2]; [1]Riga Technical University, 1 Kalku St., 226355 Riga, Latvia, [2]Institute of Organic Synthesis, 21 Aizkraukles St., 226006 Riga, Latvia



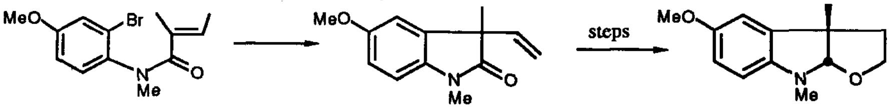
A cyclocondensation reaction of S–(alkoxycarbonylmethyl)– and S–(cyanomethyl)dithiocarbonate O–esters with isothiocyanates in the presence of sodium tert–butoxide is described.

Tetrahedron, **1992**, *48*, 6875

COBALT-MEDIATED ARYL RADICAL CYCLISATION: A FORMAL SYNTHESIS OF PHYSOVENINE

Andrew J. Clark and Keith Jones*
Department of Chemistry, King's College London, Strand, London WC2R 2LS U.K.

Cobalt-mediated radical cyclisation of (6) produces vinyloxindole (5) which has been converted into (3) a known, late intermediate in the synthesis of the calabar bean alkaloid physovenine.



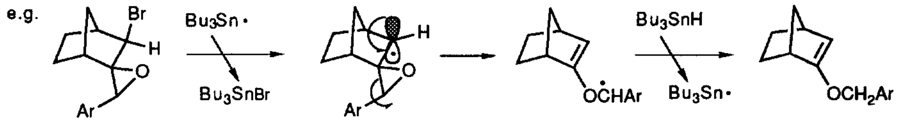
(6) (5) (3)

Tetrahedron, **1992**, *48*, 6883

RADICAL REACTIONS OF BICYCLO[2.2.1]HEPTAN-3-SPIRO-2'-OXIRANES

W. Russell Bowman*, David S. Brown, Catherine A. Burns, Brian A. Marples*, and Naveed A. Zaidi
Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU, Great Britain

Tributyltin hydride reduction of 2-bromo- and 2-keto-bicyclo[2.2.1]heptan-3-spiro-2'-oxiranes gives ring opening of the oxirane-rings *via* intermediate 3-(spiro-2'-oxiranyl)bicyclo[2.2.1]heptan-2-yl radicals, whereas reduction of the analogous 2-(thiocarbonyl)-imidazolides) [2-(O-CS-Im)] unusually yields the 2-methoxy derivatives and does not proceed by the expected normal fragmentation to yield 3-(spiro-2'-oxiranyl)bicyclo[2.2.1]heptan-2-yl radicals and subsequent ring-opening of the oxirane rings.

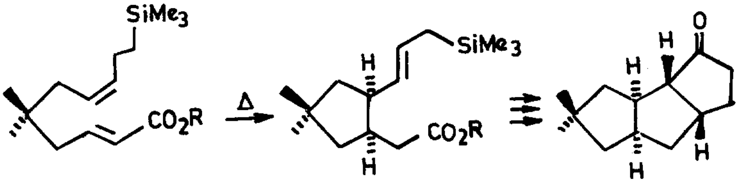


Tetrahedron, **1992**, *48*, 6897

CYCLOPENTANOID ALLYLSILANES IN SYNTHESIS OF DI- AND TRIQUINANES. A STEREOSELECTIVE SYNTHESIS OF (±)-HIRSUTENE

T.K. Sarkar,*[1] S.K. Ghosh,[2] P.S.V. Subba Rao,[1] T.K. Satapathi[1] and V.R. Mamdapur[2]

[1]Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India;
[2]Bhabha Atomic Research Centre, Bio- Organic Division, Bombay 400 085, India



Tetrahedron, **1992**, *48*, 6909

REACTIONS OF COPPER(II) β-DIKETONATES UNDER FREE RADICAL CONDITIONS. II. DIAZONIUM SALTS AS ARYL RADICALS SOURCE IN THE ARYLATION OF β-DIKETONES

María E. Lloris, Rudolph A. Abramovitch, Jorge Marquet, Marcial Moreno-Mañas;* Department of Chemistry. Universitat Autònoma de Barcelona. Bellaterra. 08193-Barcelona. Spain.

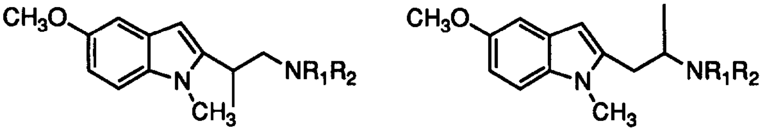
Copper complexes of 2,2,6,6-tetramethylheptane-3,5-dione and other β-diketones react with aryl radicals generated from arenediazonium tetrafluoroborates to afford α-aryl-β-diketones.

$$(R^1COCHCOR^2)_2Cu \xrightarrow[2)\ H_3O^+]{1)\ Ar\overset{+}{N_2}\ \overset{-}{BF_4}/Cu} R^1COCHArCOR^2 + R^1COCH_2COR^2$$

Tetrahedron, 1992, *48*, 6917

SYNTHESIS OF α- AND β-METHYL DERIVATIVES OF 2-[(5-METHOXY-1-METHYL)INDOL-2-YL]ETHYLAMINE AS SELECTIVE INHIBITORS OF MONOAMINE OXIDASES A AND B.

Concepción Fernández García, José L. Marco, E. Fernández Alvarez*.
Instituto de Química Orgánica General, CSIC, Juan de la Cierva, 3, 28006-Madrid, Spain.



R_1= H, 2-propynyl, 2,3-butadienyl, 2-butynyl. R_2= H, CH_3

Tetrahedron, 1992, *48*, 6929

X = Y - ZH Systems as Potential 1,3-Dipoles Part 35. Generation of Nitrones from Oximes. Class 3 Processes. Tandem Intramolecular Michael Addition (1,3 - Azaprotio Cyclotransfer) - Intermolecular 1,3-Dipolar Cycloaddition Reactions.

Ronald Grigg,*[a] Jasothara Markandu [a], Trevor Perrior [b], Sivagnanasundram Surendrakumar [a] and William J. Warnock[a].
a. School of Chemistry, Leeds University, Leeds LS2 9JT, b. I.C.I. Plant Protection, Jealotts Hill, Bracknell, Berks.

A new concerted 1,3-azaprotio cyclotransfer of oximes proceeding via a 2π+ 2σ+ 2π transition state and leading to nitrones is described.