Biosynthesis of the Benz[a]anthraquinone Antibiotic PD 116198

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Tetrahedron, 1993, 49, 11145

POTENTIALLY TAUTOMERIC 1,2,3,4-TETRAHYDRO-1,4-DIOXO-5*H*-PYRIDAZINO[4,5-*b*]INDOLE

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At equilibrium in water, the ratio of the four possible tautomeric forms 1a, 1b, 1c, and 1d of 1,2,3,4-tetrahydro-1,4-dioxo-5H-pyridazino[4,5-b]indole is 10^{4.93}:10^{8.03}:10^{3.61}:1.

Tetrahedron, 1993, 49, 11155

Characterization and Synthesis of a New Calcium Antagonist from the Venom of a Fishing Spider

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A new calcium antagonist, CNS 2103, is isolated from the venom of a fishing spider, *Dolomedes okefinokensis*. The structure of this compound is derived from spectroscopic data, including tandem mass spectrometry. A flexible, convergent synthesis of CNS 2103 is described.

STEREOSELECTIVE REDUCTION OF 2-METHYL-3-OXO ESTERS (OR AMIDES) WITH SODIUM BOROHYDRIDE CATALYZED BY MANGANESE(II) CHLORIDE OR TETRABUTYLAMMONIUM BOROHYDRIDE. A PRACTICAL PREPARATION OF ERYTHRO AND THREO-3-HYDROXY-2-METHYL ESTERS (OR AMIDES)

Masahiko Taniguchi, Hideaki Fujii, Koichiro Oshima,* and Kiitiro Utimoto* Division of Material Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

$$R^{1} \xrightarrow{O} OR^{3} \xrightarrow{NaBH_{4}/MnCl_{2}} OR^{3} \xrightarrow{R^{2}} OR^{3} + R^{1} \xrightarrow{QH} OR^{3}$$

Tetrahedron, 1993, 49, 11183

Toxadocials B, C and Toxadocic acid A: Thrombin-Inhibitory Aliphatic Tetrasulfates from the Marine Sponge, Toxadocia cylindrica

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Abstract: Three new thrombin-inhibitory metabolites, toxadocial B (2), toxadocial C, and toxadocic acid A have been isolated from the marine sponge *Toxadocia cylindrica*. The structures of these compounds were determined by spectroscopic and chemical methods.

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Tetrahedron, 1993, 49, 11189

TOTAL SYNTHESIS OF (±)-HIRSUTENE VIA Pd²⁺-PROMOTED CYCLOALKENYLATION REACTION

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Acid catalyzed conjugate addition (1 \rightarrow 2) and Pd²⁺-promoted cycloalkenylation (3 \rightarrow 4) are used as key steps in the synthesis of (\pm)-hirsutene(5)

A short, practical synthesis of the ant venom alkaloid, three (3R,5S,8aS)-3-alkyl-5-methylindolizidines

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Sugitani 2630, Toyama 930-01, Japan

A short, practical and diastereoselctive method for preparing the ant venom alkaloid, three (3R,5S,8aS)-3-alkyl-5-methyl-indolizidines (1-3), has been developed.

Tetrahedron, 1993, 49, 11213

NEW HALOGENATED FURANONES FROM THE MARINE RED ALGA DELISEA PULCHRA (cf. FIMBRIATA)

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Tetrahedron, 1993, 49, 11221

TRANSITION METAL-DIENE COMPLEXES IN ORGANIC SYNTHESIS - 16. IRON-MEDIATED TOTAL SYNTHESIS OF 1-OXYGENATED CARBAZOLE ALKALOIDS

H.-J. Knölker* and M. Bauermeister

Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, D-76131 Karlsruhe, Germany Using a methodology of consecutive iron-induced C-C and C-N bond formation we describe the total synthesis of murrayafoline A, murrayaquinone A, koenoline, murrayanine, mukoeic acid, and mukonine.

SYNTHESIS OF PURINE-ACRIDINE HYBRID MOLECULES RELATED TO ARTIFICIAL ENDONUCLEASES

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The synthesis of a new series of hybrid molecules in which a purine is linked to an acridine nucleus by an aliphatic chain including amido and amino groups is described. The key intermediates are different α-halo-ω-amino polyaza chains.

S_{DN}1 REACTIONS OF ANTHRAQUINONE ALKYLATING AGENTS

Tetrahedron, 1993, 49, 11253

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Radicaux Libres et Synthèse, URA CNRS N°1412, BP 562, 13397 Marseille Cedex 20, France

The C-alkylation reaction of three anthraquinone alkylating agents by 2-nitropropane and 1-methyl-3-nitropyrrolidin-2-one anions is shown to proceed by the $S_{\rm RN}1$ mechanism.

Tetrahedron, 1993, 49, 11263

ADDITIVE PUMMERER REACTIONS OF VINYLIC SULFOXIDES. SYNTHESIS OF γ -HYDROXY- α , β -UNSATURATED ESTERS, α -HYDROXYKETONES, AND 2-PHENYLSULFENYL ALDEHYDES AND PRIMARY ALCOHOLS

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Additive Pummerer reactions of vinylic sulfoxides 1 and 3 give respectively thioethers 6 and acylals 14. Some derivatization reactions of 6 and 14 are described.

OH
$$R^{2}$$
 O' S^{2} Ar R^{2} O' S^{2} Ar R^{2} O' S^{2} Ar S^{2} O' S^{2} Ar S^{2} O' S^{2} Ar S^{2} O' S^{2} Ar S^{2} Ar S^{2} Ar S^{2} O' S^{2}

REACTION OF N-VINYLINDAZOLIUM AND N-VINYLBENZOTRIAZOLIUM SALTS WITH NUCLEOPHILES.

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The reaction of salts 6, 11 and 13 with nucleophiles (HO-, H- and CH3OH) is studied and a general mechanism is proposed.

Tetrahedron, 1993, 49, 11321

A STEREOSELECTIVE SYNTHESIS OF 3(R)-HYDROXY-2(S)-ORNITHINE

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Tetrahedron, 1993, 49, 11329

ADDITION OF A REFORMATSKY REAGENT TO N-ANTHRACENE-9-SULFONYL AND RELATED IMINES:

SYNTHESIS OF PROTECTED β-AMINO ACIDS Andrew J. Robinson and Peter B. Wyatt*, Department of Chemistry, Queen Mary and Westfield College, University of London, Mile End Road, London, El 4NS, UK.

$$R^{1}CHO \xrightarrow{R^{2}SO_{2}NH_{2}} R^{1} \xrightarrow{NSO_{2}R^{2}} R^{1} \xrightarrow{(i) BrZnCH_{2}CO_{2}t \cdot Bu} R^{1} \xrightarrow{CH_{2}CO_{2}t \cdot Bu} R^{1} \xrightarrow{(ii) H'} CH_{2}CO_{2}t \cdot Bu} \xrightarrow{(ii) Al/H_{2}} R^{1} \xrightarrow{NH_{2}O} R^{1$$

e.g. R^1 = Ph, 4-FC₆H₄, 4-MeOC₆H₄, 4-NCC₆H₄, 2-furyl, (*E*)-styryl; R^2 = 4-MeC₆H₄, 4-MeO₂CC₆H₄, 9-anthryl.

Oligodeoxynucleotide Analogues Containing 3'-Deoxy-3'-C-threohydroxymethylthymidine: Synthesis, Hybridization Properties and Enzymatic Stability.

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Molecular Biology, Odense University, DK-5230 Odense M, Denmark.

3'-Deoxy- 3'-C-threo-hydroxymethyl nucleoside 4 was stereoselectively synthesized in three steps from 5'-O-(4,4'-dimethoxytrityl)thymidine (1) and subsequently incorporated into oligodeoxynucleotides. Hybridization and enzymatic stability experiments are reported.

Tetrahedron, 1993, 49, 11353

REGIO- AND STEREOSELECTIVITY OF ADDITIONS OF ORGANOMETALLICS TO ENDO- AND EXO-TRICYCLO[5.2.1.0^{2,6}]DECA-4,8-DIEN-3-ONES

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In order to evaluate the use of tricyclodecadienones 1, 2 and 3 for the stereo- and enantioselective synthesis of cyclopentenoid natural products, 1,2- and 1,4-additions of organometallics were investigated. Both for 1 and 3 stereospecific addition from the convex face takes place. For 2 1,4-addition leads to mixtures of syn- and anti-addition products.







Tetrahedron, 1993, 49, 11373

HALOGEN ADDITION TO ENDO- AND EXO-TRICYCLO[5,2,1,0^{2,6}]DECA-4,8-DIEN-3-ONES

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The electrophilic addition of bromine and iodine to endo- and exo-tricyclodecadienones 1 and 2 was investigated.

<u>a</u>: $R_1 = R_2 = H$ <u>b</u>: $R_1 = Me$, $R_2 = H$ <u>c</u>: $R_1 = H$, $R_2 = Me$

Chemistry of Ethanediyl S,S-Acetals 6 - An Example of Vicarious

Nucleophilic Substitution of Hydrogen in 1,4-Benzodithians

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Quantum mechanical semiempirical calculations suggest the very fast bromination of 1,4-benzodithians to proceed likely via a vicarious nucleophilic substitution of hydrogen rather than an aromatic electrophilic substitution.

Tetrahedron, 1993, 49, 11389

Relative Thermodynamic Stabilities of Isomeric

Alkyl Allyl and Alkyl (Z)-Propenyl Ethers

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