Efficient synthesis of unsymmetrically disubstituted ferrocenes: towards electrochemical dipentide-Fc-biosensors

Tetrahedron Letters 42 (2001) 2601

Yiming Xu and Heinz-Bernhard Kraatz*

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Unsymmetrically disubstituted ferrocenes **1a** and **1b**, which may serve as precursors to electrochemical dipeptide-Fc-biosensors, were synthesized by a from 1,1'-ferrocenedicarboxylic acid. In addition, an efficient solution synthesis of pentapeptide (**2**) was reported.

HO Val-Val-Sta-Ala-Sta-OH
$$\mathbf{1a: n = 3}$$

$$\mathbf{1b: n = 4}$$

Allenes from ynals

Tetrahedron Letters 42 (2001) 2605

Marcus A. Tius* and Subrata K. Pal

Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, HI 96822, USA

Hydrosilylation of ynals with triethylsilane is catalyzed by $RhCl(PPh_3)_3$ and leads to α -triethylsilyl enals. Addition of aryl Grignard reagents takes place to give secondary allylic alcohols, which are easily converted to 1,3-disubstituted allenes.

$$R^1$$
 CHO \longrightarrow R^1 SiEt₃ \longrightarrow R^1 OH

Novel chiral phosphines derived from limonene: the synthesis and structure of 4,8-dimethyl-2-phosphabicyclo[3.3.1]nonane

Tetrahedron Letters 42 (2001) 2609

Al Robertson,^a Christine Bradaric,^a Christopher S. Frampton,^b James McNulty^c and Alfredo Capretta^{c,*}

^aCytec Canada Inc., PO Box 240, Niagara Falls, Ontario, Canada L2E 6T4

^bRoche Products Ltd, 40 Broadwater Road, Welwyn Garden City, Herts AL7 3AY, UK

^cInstitute of Molecular Catalysis, Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1

PH

The radical addition of PH_3 to limonene results in the formation of 4,8-dimethyl-2-phosphabicyclo-[3.3.1]nonane, which has been characterized by X-ray crystallographic analyses of its oxidation products.

Novel photorearrangement of a 4-chloromethylazulene

Tetrahedron Letters 42 (2001) 2613

Carlos A. A. Ruiz, Vicente G. Toscano, Daisy de Brito Rezende and Wilhelm J. Baader*

Instituto de Química, Universidade de São Paulo, Cx. Postal 26077, 05599-970 Sao Paulo, SP, Brazil

Measurement of enantiomeric excess of amines by mass spectrometry following kinetic resolution with solid-phase chiral acylating agents

Tetrahedron Letters 42 (2001) 2617

David D. Díaz, Sulan Yao and M. G. Finn*

Department of Chemistry and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA

Synthesis of 3,3-bis(difluoramino)octahydro-1,5,7,7-tetranitro-1,5diazocine (TNFX), a diversified energetic heterocycle

Tetrahedron Letters 42 (2001) 2621

Theodore Axenrod, a,* Xiao-Pei Guan, Jianguang Sun, Lida Qi, a

Robert D. Chapman^{b,*} and Richard D. Gilardi^c

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^bNaval Aviation Science and Technology Office (Code 4T4200D),

Naval Air Warfare Center Weapons Division, China Lake, CA 93555, USA ^cLaboratory for the Structure of Matter (Code 6030),

Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375, USA

 NO_2 NH₂ NH₂ 10 steps N-NO2 OH

Tetrahedron Letters 42 (2001) 2625

TNFX

Synthesis of peptide-diazenium diolate conjugates: towards enzyme activated antitumor agents

Xiaoping Tang, Ming Xian, Mohit Trikha, Kenneth V. Honn and Peng George Wanga,*

^aDepartment of Chemistry, Wayne State University, Detroit, MI 48202, USA

^bDepartment of Radiation Oncology and Pathology, Wayne State University, Detroit, MI 48202, USA

Model studies on total synthesis of the chartellines, spirocyclic β-lactam alkaloids from a marine bryozoan

Tetrahedron Letters 42 (2001) 2631

Xichen Lin and Steven M. Weinreb*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

Starting from an isatin imine, an efficient route has been developed to construct a model system containing the \(\beta \)-lactam and α,β -unsaturated imine substructures found in the chartelline marine bryozoan metabolites.

Solid phase synthesis of chiral 2-amino-benzimidazoles

Tetrahedron Letters 42 (2001) 2635

Jinbo Lee,* Amanda Doucette, Noel S. Wilson and John Lord

Boehringer Ingelheim Pharmaceuticals, Inc., Research & Development Center/PO Box 368, 900 Ridgebury Rd, Ridgefield, CT 06877, USA

A regioselective PCl_5 mediated dehydration for preparing $\Delta^{9,11}$ corticosteroids

Tetrahedron Letters 42 (2001) 2639

Xiaoyong Fu,* Chou-Hong Tann, T. K. Thiruvengadam, Junning Lee and Cesar Colon Synthetic Chemistry, Schering-Plough Research Institute, 1011 Morris Ave., Union, NJ 07083, USA

A regioselective PCl_5 -induced dehydration of 11α -hydroxyl corticosteroids was invented to provide the corresponding $\Delta^{9,11}$ double bond trienes in excellent yield (>90%) with 99:1 regioisomeric ratio to the $\Delta^{11,12}$ isomers.

On the bromination of methyl 2-methyl-3-furoate

Tetrahedron Letters 42 (2001) 2643

Haripada Khatuya*

Department of Chemistry (0506), University of California-San Diego, La Jolla, CA 92093, USA

CO₂Me NBS (2.2), Bz₂O₂,
$$O$$
 NBS (2.3), DMF O Rr CCl₄, reflux, 63 % O O C to rt, 41 % O Rr

Enantioselective total synthesis of salicylihalamides A and B

Tetrahedron Letters 42 (2001) 2645

Denis Labrecque,* Sylvie Charron, Rabindra Rej, Charles Blais and Serge Lamothe

Department of Medicinal Chemistry, Biochem Pharma Inc., 275 Armand-Frappier Blvd, Laval, Québec, Canada H7V 4A7

A sterically hindered optically active pentamethine dye

Tetrahedron Letters 42 (2001) 2649

Guido Nuding, Edgar Zimmermann and Volker Buss*

Institute of Physical and Theoretical Chemistry, Gerhard-Mercator-University, D-47048 Duisburg, Germany

Two approaches to α,α -bis-Mannich salts of N-monosubstituted amides

Tetrahedron Letters 42 (2001) 2653

Andreas Brunschweiger and Dieter Heber*

Department of Pharmaceutical Chemistry, University of Kiel, Gutenbergstr. 76, D-24118 Kiel, Germany

1. POCl₃/EtOEt 2. 2 CH₂=NMe₂Cl 3. (Me)₂CHOH/HClO₄

Synthesis of E- and Z-substituted methylene-3,4-dihydro-2H-1-benzopyrans by regio- and stereocontrolled palladium-catalyzed intramolecular cyclization

Tetrahedron Letters 42 (2001) 2657

France R = H A =

Olivier Barberan, Mouâd Alami* and Jean-Daniel Brion

Laboratoire de Chimie Thérapeutique associé au CNRS (ESA 8076, BIOCIS), Faculté de Pharmacie, rue J.B. Clément, 92296 Châtenay Malabry Cedex, France

Carbohydrate mimics: analogues of aza-di-(or tri-)saccharides

Tetrahedron Letters 42 (2001) 2661

Yves Le Merrer,* Michèle Sanière, Isabelle McCort, Catherine Dupuy and Jean-Claude Depezay Université René Descartes, Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR 8601 CNRS, 45, rue des Saints-Pères, 75270 Paris Cedex 06, France

Four enantiopure pseudo-aza-di-(or tri-)saccharides have been synthesized by aminocyclization of a C_2 -symmetrical D-manno-bis-epoxide either with a primary amine having a polyhydroxylated tetrahydrofuran skeleton or with a polyhydroxylated piperidine or azepan.

[3,3]-Sigmatropic rearrangement of allyl (or propargyl) fluorovinyl ethers. Synthesis of α -trifluoromethyl unsaturated acids and derivatives

Tetrahedron Letters 42 (2001) 2665

Frédérique Tellier, a,* Max Audouinb and Raymond Sauvêtrec

^aUnité de Phytopharmacie et Médiateurs Chimiques, INRA, Route de Saint-Cyr, 78026 Versailles Cedex, France ^bLaboratoire de Synthèse Organique et Organométallique, associé au CNRS, Université P. et M. Curie, boîte 181,

4 place Jussieu, 75252 Paris Cedex 05, France

^cLaboratoire de Chimie des Organoéléments, associé au CNRS, Université P. et M. Curie, boîte 183, 4 place Jussieu, 75252 Paris Cedex 05, France

A one pot synthesis of α -trifluoromethyl unsaturated acids and derivatives via a [3,3]-sigmatropic rearrrangement of allyl (or propargyl) fluorovinyl ethers is described.

$$R^1$$
 R^2
 R^2

A new alkaloid from the purple Indian Ocean tunicate *Eudistoma bituminis*

Isabelle Viracaoundin,^a Robert Faure,^b Emile Marcel Gaydou^b and Maurice Aknin^{a,*}

^aLaboratoire de Chimie des Substances Naturelles et des Sciences des Aliments, Université de la Réunion, Saint-Denis Messag Cedex 9, France

bLaboratoire de Phytochimie de Marseille-UMR 6171 et ESA 6009, Faculté des Sciences de Saint-Jérôme, Université d'Aix-Marseille III, Marseille Cedex 20, France

A new alkaloid, segoline C 1 possessing the benzo 1,6-diazaphenanthroline ring system has been isolated from the Indian Ocean tunicate *Eudistoma bituminis*. The structure of this compound was elucidated on the basis of spectroscopic data. The relative configuration of the chiral compound 1 is proposed on the basis of comparative circular dichroism (CD) measurements with segolines A and B.

Tetrahedron Letters 42 (2001) 2669

Synthesis of novel pentacyclic pyrrolothiazolobenzoquinolinones, analogs of natural marine alkaloids

Tetrahedron Letters 42 (2001) 2673

Valérie Bénéteau and Thierry Besson*

Laboratoire de Génie Protéique et Cellulaire, UPRES EA3169, Groupe de Chimie Organique, U.F.R. Sciences Fondamentales et Sciences pour l'Ingénieur, Université de La Rochelle, Avenue Michel Crépeau, F-17042 La Rochelle cedex 1, France

Multistep synthesis (12 steps) of new pentacyclic compounds, which are structurally very close to natural marine alkaloids, was performed.

(S)
$$NH_2$$
 NH_2 $NH_$

Dithio-phospholipids for oriented immobilization of proteins to gold surfaces

Tetrahedron Letters 42 (2001) 2677

Gerald Kada, Christian K. Riener and Hermann J. Gruber*

Institute for Biophysics, Johannes Kepler University of Linz, Altenbergerstr. 69, A-4040 Linz, Austria

Quantitative solvent extraction from neutral aqueous nitrate media of silver(I) against lead(II) with a new calix[4]arenebased bipyridine podand

Jean-Bernard Regnouf-de-Vains, a,* Jean-Olivier Dalbavie, Roger Lamartine and B. Fenet

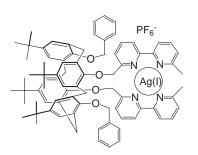
^aGEVSM, UMR 7565 CNRS-UHP, Faculté de Pharmacie,

5 rue Albert Lebrun, F-54001 Nancy Cedex, France

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^cCentre Commun de RMN, UCBL, La Doua, F-69622 Villeurbanne Cedex, France

Tetrahedron Letters 42 (2001) 2681



Visible light promoted organic reaction on a solid support

Tetrahedron Letters 42 (2001) 2685

Gemma Arsequell,^{a,*} Asensio González^b and Gregorio Valencia^a

^aUnit of Glycoconjugate Chemistry, IIQAB-CSIC, E08034 Barcelona, Spain

^bLaboratory of Organic Chemistry, Faculty of Pharmacy, University of Barcelona, E08028 Barcelona, Spain

A novel *cis-trans* photoisomerization of vinylidenecyclopropanes via an electron-transfer chain process

Tetrahedron Letters 42 (2001) 2689

Kazuhiko Mizuno,* Koji Nire, Hikaru Sugita and Hajime Maeda

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

 \mathbf{a} ; Ar = p-MeOC₆H₄

b; Ar = p-MeC₆H₄

 \mathbf{c} ; Ar = Ph

Structure of pittosporumxanthins A1 and A2, novel C₆₉ carotenoids from the seeds of *Pittosporum tobira*

Tetrahedron Letters 42 (2001) 2693

Yasuhiro Fujiwara* and Takashi Maoka

Kyoto Pharmaceutical University, Yamashina-ku, Kyoto 607-8414, Japan

Two novel C_{69} carotenoids containing an α -tocopherol moiety, named pittosporumxanthins A1 (1) and A2 (2), have been isolated from the seeds of *Pittosporum tobira*.

Star-shaped discotic nematic liquid crystal containing 1,3,5-triethynylbenzene and oxadiazole-based rigid arms

Bong Gi Kim, Sehoon Kim and Soo Young Park*

School of Materials Science and Engineering, Seoul National University, San 56-1, Shillim-Dong, Kwanak-Ku, Seoul 151-742, South Korea

A novel three-armed discotic liquid crystal based on 1,3,5-triethynylbenzene as a core and 2,5-diphenyloxadiazole as rigid arms has been synthesized, which is the first star-shaped molecule exhibiting a discotic nematic phase.

Tetrahedron Letters 42 (2001) 2697

Total synthesis of sphingofungin E

Tetrahedron Letters 42 (2001) 2701

Tsuyoshi Nakamura and Masao Shiozaki*

Exploratory Chemistry Research Laboratories, Sankyo Co. Ltd., Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140-8710, Japan

Total synthesis of sphingofungin E from an already known D-glucose derivative in a stereocontrolled manner was described.

Catalytic enamine reaction: an expedient 1,4-conjugate addition of naked aldehydes to vinylketones and its application to synthesis of cyclohexenone from *Stevia purpurea*

Tetrahedron Letters 42 (2001) 2705

Hisahiro Hagiwara, a,* Tomoyuki Okabe, Keisuke Hakoda, Takashi Hoshi, Hiroki Ono, Vijayendra P. Kamat, Toshio Suzuki and Masayoshi Ando

^aGraduate School of Science and Technology, Niigata University, 8050, 2-nocho, Ikarashi, Niigata 950-2181, Japan ^bFaculty of Engineering, Niigata University, 8050, 2-nocho, Ikarashi, Niigata 950-2181, Japan

RCH₂CHO +
$$Et_2$$
NH (0.2 eq.) toluene, 80 °C sealed tube Et_2 NH (0.2 eq.) Et_2 NH (0.2 eq.) no aqueous work-up Et_2 NH (0.2 eq.) Et_2 NH (0

An efficient and practical method for the synthesis of mono-N-protected α, ω -diaminoalkanes

Tetrahedron Letters 42 (2001) 2709

Jae Wook Lee, Sung Im Jun and Kimoon Kim*

National Creative Research Initiative Center for Smart Supramolecules and Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, South Korea

$$N_3$$
 N_3
 N_3
 N_3
 N_4
 N_5
 N_4
 N_5
 N_6
 N_6
 N_6
 N_7
 N_8
 N_8
 N_8
 N_8
 N_8
 N_9
 N_9

Synthesis of novel (R)- and (S)-piperidazine-3-phosphonic acids and transformation into (R)- and (S)-pyrrolidine-2-phosphonic acids

Tetrahedron Letters 42 (2001) 2713

Mamoru Kaname, Yasushi Arakawa and Shigeyuki Yoshifuji*

Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa 920-1181, Japan

An easy and efficient method for the synthesis of 2,2-dialkyl-3-nitrochromene

Tetrahedron Letters 42 (2001) 2717

Ming-Chung Yan, Yeong-Jiunn Jang and Ching-Fa Yao*

Department of Chemistry, National Taiwan Normal University 88, Sec. 4, Tingchow Road, Taipei, Taiwan 116, ROC

One-pot transformation of nitriles into aldehyde tosylhydrazones

Tetrahedron Letters 42 (2001) 2723

Marietta Tóth and László Somsák*

Department of Organic Chemistry, University of Debrecen, PO Box 20, H-4010 Debrecen, Hungary

A facile synthesis of 2,5-diketopiperazines based on isocyanide chemistry

Tetrahedron Letters 42 (2001) 2727

Stefano Marcaccini,* Roberto Pepino and Ma Cruz Pozo

CNR, Centro di Studio sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, Dipartimento di Chimica Organica 'Ugo Schiff', Università di Firenze, via Gino Capponi 9, I-50121 Florence, Italy

Compounds 8 were easily cyclised to 2,5-diketo-piperazines 9 with KOH under ultrasonication.

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Synthesis and cytotoxic properties of a series of bicyclo[3.2.1] octane α -methylene ketones

Tetrahedron Letters 42 (2001) 2729

J. A. Miller, a,* G. M. Ullah, G. M. Welsha and P. Mallonb

^aDepartment of Medicinal Chemistry, Wellcome Research Laboratories, Langley Court, Beckenham, Kent BR3 3BS, UK ^bChemistry Department, University of St. Andrews, St. Andrews, Fife, Scotland KY16 9AL, UK

[3+2] Cycloaddition to 5 gives bicyclo[3.2.1]oct-6-ene adduct 3, which has been converted into a range of bicyclic α -methylene ketones, some of which are very toxic to cells in culture.

Synthesis and X-ray crystal structure of a novel long chain acyclic phosphazene, N,N'-{dimethyl-bis(diphenylphosphinimino-phosphorane)}ethylenediamine {(PhO)₂P(O)N=PN(CH₃)CH₂}₂, obtained via a Staudinger reaction

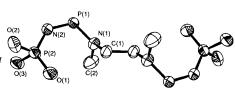
Maravanji S. Balakrishna,* Rita M. Abhyankar and

Mrinalini G. Walawalker

Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India

The novel long chain acyclic phosphazene $[(PhO)_2P(O)NPh_2PN(Me)CH_2]_2$ was synthesized by the reaction of N,N'-dimethyl-N,N'-bis(diphenylphosphino)-ethylenediamine with phosphoryl azide. The core of the structure resembles an unlocked 'handcuff'.

Tetrahedron Letters 42 (2001) 2733



Synthesis of 2,6,10,14,18,22-hexaazaspiro[11.11]tricosane, the first example of a spiro aza crown derived from 2,2-bis(aminomethyl)propane-1,3-diamine

Tetrahedron Letters 42 (2001) 2735

Qi Wang, Satu Mikkola and Harri Lönnberg*

Department of Chemistry, University of Turku, FIN-20014 Turku, Finland

2,6,10,14,18,22-Hexaazaspiro[11.11]tricosane **1** has been prepared in seven steps from pentaerythritol. The key steps include two successive cyclizations by displacement of two tosyloxy groups from the appropriate pentaerythritol derivatives with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Hydrolysis of the spiro bis(hexahydro-1*H*,4*H*,7*H*-3a,6a,9a-triazaphenalene) formed **1**.

Transition structures for the stepwise insertion of oxygen into alkane tertiary C-H bonds by dimethyldioxirane

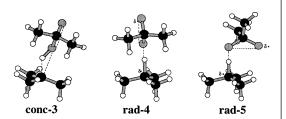
Tetrahedron Letters 42 (2001) 2739

Mauro Freccero,^a Remo Gandolfi,^a Mirko Sarzi-Amadè^{a,*} and Augusto Rastelli^b

^aDipartimento di Chimica Organica, Università di Pavia, V.le Taramelli 10, 27100 Pavia, Italy

^bDipartimento di Chimica, Università di Modena, Via Campi 183, 41100 Modena, Italy

Three TSs were located for oxygen insertion into the isobutane C–H bond by dimethyldioxirane at the B3LYP level. The two diradicaloid TSs, that according to IRC produce radical pairs, are more stable than their concerted counterpart.



Monoalcoholates of 1,3-diols as effective catalysts in the Tishchenko esterification of 1,3-dioxan-4-ols

Tetrahedron Letters 42 (2001) 2743

Olli P. Törmäkangas and Ari M. P. Koskinen*

Laboratory of Organic Chemistry, Helsinki University of Technology, PO Box 6100, FIN-02015 HUT, Finland

Strong ligand accelerated catalysis by an Arduengo-type carbene in copper-catalysed conjugate addition

Tetrahedron Letters 42 (2001) 2747

Paul K. Fraser and Simon Woodward*

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK

Aggregation behaviour and binding properties of an L-lysine appended glycoluril receptor

Tetrahedron Letters 42 (2001) 2751

Beatriu Escuder,* Alan E. Rowan, Martinus C. Feiters and Roeland J. M. Nolte

Department of Organic Chemistry, University of Nijmegen, Toernooiveld 1, NL-6525 ED Nijmegen, The Netherlands