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Two Novel Alkaloids with a Unique Fused Hexacyclic Skeleton from Daphniphyllum s ubverticillatum

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On the Cover: Alkali enediolates from carboxylic acids are important synthetic reagents. For a dicesium salt, the small amount of monomer in equilibrium with dimer is the active alkylating reagent. The dilithium salt is aggregated so tightly that only the dimer reacts. Mixed aggregates are also formed. Ab initio calculations suggest structures as shown. See Streitwieser and co-workers, p 7937.

Articles

7937 Aggregation and Reactivity of the Dilithium and Dicesium Enediolates of 1-Naphthylacetic

M = Li, Cs

Aggregation Mixed Aggregates Alkylation Kinetics Theoretical Models

Andrew Streitwieser,* Marc Husemann, and Yeong-Joon Kim

7943 Spiro-Fused (C2)-Azirino-(C4)-pyrazolones, a

■ New Heterocyclic System. Synthesis,
Spectroscopic Studies and X-ray Structure
Analysis

Wolfgang Holzer,* Rosa M. Claramunt,* Marta Pérez-Torralha, Davide Guggi, and Thomas H. Brehmer

7951 Photolysis of α-Azidoacetophenones: Direct

■ Detection of Triplet Alkyl Nitrenes in Solution

Pradeep N. D. Singh, Sarah M. Mandel, Rachel M. Robinson, Zhendong Zhu, Roberto Franz, Bruce S. Ault, and Anna D. Gudmundsdóttir*

7961 Two Novel Alkaloids with a Unique Fused

Hexacyclic Skeleton from Daphniphyllum subverticillatum

Sheng-Ping Yang and Jian-Min Yue*

7967 Regulated-Stereoselective Construction of

■ Thirteen Stereogenic Centers Necessary for the Frame of (+)-Discodermolide, Based on **Iterative Lewis Acid-Promoted Aldol Reactions**

Syun-ichi Kiyooka,* Kazi Abdus Shahid, Fumitaka Goto, Momotoshi Okazaki, and Yoshihiro Shuto

a enantioselective aldol reaction

ⁿ diastercoselective aldol reaction (when R has chiral centers)

divergent diastereosolective radical reductions

7979 Highly Efficient Peterson Olefination Leading

to Unsaturated Selenoamides and Their Characterization

Me₃Si
$$NR_2$$
 BuLi $Ar \leftarrow n$ H Se $Ar \leftarrow n$ NR_2 $Ar \leftarrow n$ NR_2 $Ar \leftarrow n$ NR_2

Toshiaki Murai,* Akinori Fujishima, Chigusa Iwamoto, and Shinzi Kato

7983 Total Synthesis of Mappicine Ketone

(Nothapodytine B) by Means of Sulfur-Directed 5-exo-Selective Aryl Radical Cyclization onto Enamides

Issei Kato, Masayuki Higashimoto, Osamu Tamura, and Hiroyuki Ishibashi*

7990 Complete and Remarkable Reversal of

Chemoselectivity in [4 + 2] Cycloadditions Involving Electron-Poor Indoles as Dienophiles. Diels-Alder versus Hetero-Diels-Alder Processes

Antony Chrétien, Isabelle Chataigner, Nathalie L'Hélias, and Serge R. Piettre*

8003 P(i-BuNCH2CH2)3N: An Efficient Ligand for the

Direct a-Arylation of Nitriles with Aryl **Bromides**

Jingsong You and John G. Verkade*

8008 Synthesis of Aryl- and Heteroaryl[a]pyrrolo[3,4-c]carbazoles

Concha Sanchez-Martinez,* Margaret M. Faul,* Chuan Shih, Kevin A. Sullivan, John L. Grutsch, Jeremy T. Cooper, and Stanley P. Kolis

8015 Tandem Double Intramolecular [4+2]/[3+2]

Cycloadditions of Nitroalkenes. The Fused/ **Bridged Mode**

COX
$$(H_2C)$$

$$(H_2C)$$

$$(H_2C)$$

$$(CH_2)$$

Scott E. Denmark* and Laurent Gomez

8025 Spin Exchange Interaction through

■ Phenylene-Ethynylene Bridge in Diradicals Based on Iminonitroxide and Nitronylnitroxide Radical Derivatives. 1. Experimental Investigation of the Through-Bond Spin **Exchange Coupling**

Pascale Wautelet, Jacques Le Moigne, Vladimira Videva, and Philippe Turek*

8037 Asymmetric Synthesis of Fused Bicyclic

■ α-Amino Acids Having a Hexahydro-cyclopenta[c]pyridine Skeleton via Intramolecular Pauson-Khand Reaction of 1-Sulfonimidoyl-Substituted 5-Azaoct-1-en-7-ynes

Markus Günter and Hans-Joachim Gais*

8042 Synthesis of Both Possible Isomers of the

■ Northwest Quadrant of Altromycin B

Paolo Pasetto and Richard W. Franck*

8061 Asymmetric Synthesis of the Quinolizidine Alkaloid ()-Epimyrtine with Intramolecular Mannich Cyclization and N-Sulfinyl δ-Amino β-Ketoesters

Franklin A. Davis,* Yulian Zhang, and Gopinathan Anilkumar

8065 Rearrangements of Bicyclic Nitrones to Lactams: Comparison of Photochemical and Modified Barton Conditions

Yibin Zeng, Brenton T. Smith, John Hershberger, and Jeffrey Aubé*

8068 Novel Synthesis of Carbapenam by Intramolecular Attack of Lactam Nitrogen toward η¹-Allenyl and η³-Propargylpalladium Complex

Yuji Kozawa and Miwako Mori*

8075 Synthesis of a Tritium-Labeled, Fipronil-Based, Highly Potent, Photoaffinity Probe for the GABA Receptor

Robert E. Sammelson and John E. Casida*

8080 Lasonolide A: Structural Revision and Total ■ Synthesis

Ho Young Song, Jung Min Joo, Jung Won Kang, Dae-Shik Kim, Cheol-Kyu Jung, Hyo Shin Kwak, Jin Hyun Park, Eun Lee,* Chang Yong Hong, ShinWu Jeong, Kiwan Jeon, and Ji Hyun Park

8088 Asymmetric Synthesis of Cyclic Hydroxy

Ketones Derived from Enol Ethers via
Sharpless Asymmetric Dihydroxylation. A
Study in the Correlation of the Enol Ether
Chain Length and Enantioselectivity

Benjamin F. Marcune,* Sandor Karady, Paul J. Reider, Ross A. Miller, Mirlinda Biba, Lisa DiMichele, and Robert A. Reamer

8092 General Method for the Palladium-Catalyzed

■ Allylation of Aliphatic Alcohols

$$R_{2} = 1^{\circ} \text{ to } 3^{\circ} \text{ alkyl}$$

$$R_{2} = R_{2} = R_{2$$

Anthony R. Haight,* Eric J. Stoner, Matthew J. Peterson, and Vandana K. Grover

$R_2 = aryl, H$

8097 Epimerization of 2'-Carbonylalkyl-C-Glycosides via Enolation, β-Elimination and Intramolecular Cycloaddition

Zerong Wang, Huawu Shao, Edith Lacroix, Shih-Hsiung Wu, Harold J. Jennings, and Wei Zou*

8106 Application of Silicon-Based Cross-Coupling

Technology to Triflates

Shaundra Riggleman and Philip DeShong*

8110 Synthesis, Electrochemistry, and Gas-Phase

Photoelectron Spectroscopic and Theoretical Studies of 3,6-Bis(perfluoroalkyl)-1,2-dithiins

Edward D. Lorance, Richard S. Glass,* Eric Block,* and Xiaojie Li

8115 An Efficient Route for the Synthesis of Glycosyl

■ Phosphinic Acids

Charla A. Centrone and Todd L. Lowary*

8120 Synthesis of Nanostructures Based on 1,4- and 1,3,5-Ethynylphenyl Subunits with π -Extended Conjugation. Carbon Dendron Units

$$\begin{array}{c|c} \text{SiMe}_{2} \\ \\ \text{Ne}_{3}\text{Si} \\ \\ \text{X=} & \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \text{SiMe}_{2} \\ \\ \text{SiMe}_{3} \\ \\ \text{SiMe}_{3} \\ \end{array}$$

J. Gonzalo Rodríguez,* Jorge Esquivias, Antonio Lafuente, and Cristina Díaz

8129 A Formal Total Synthesis of the Salicylihalamides

Christian Herb and Martin E. Maier*

8136 Using a Lipase as a High-Throughput Screening
■ Method for Measuring the Enantiomeric Excess
of Allylic Acetates

M. Burak Onaran and Christopher T. Seto*

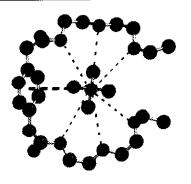
8142 Influence of the 4,6-O-Benzylidene,

4,6-O-Phenylboronate, and
4,6-O-Polystyrylboronate Protecting Groups on
the Stereochemical Outcome of
Thioglycoside-Based Glycosylations Mediated
by 1-Benzenesulfinyl Piperidine/Triflic
Anhydride and N-Iodosuccinimide/
Trimethylsilyl Triflate

Y-X = Ph-CH, Ph-B, or polystyryl-B. Stereochem = galacto-, gluco, or manno-

David Crich,* Marco de la Mora, and A. U. Vinod

8149 Binding of Tetramethylammonium to Polyether
■ Side-Chained Aromatic Hosts. Evaluation of the
Binding Contribution from Ether Oxygen
Donors



Sandra Bartoli, Gina De Nicola, and Stefano Roelens*

8157 Kinetic Investigation of the Reactions of S-4-Nitrophenyl 4-Substituted Thiobenzoates with Secondary Alicyclic Amines in Aqueous Ethanol

O

$$Ar - \overset{\square}{C} - SPN + \overset{\square}{\longrightarrow} \overset{k_1}{\longrightarrow} \overset{k_1}{\longrightarrow} \overset{k_1}{\longrightarrow} \overset{Ar - \overset{\square}{C} - SPN} \overset{k_2}{\longrightarrow} \overset{O}{\longrightarrow} \overset{\square}{\longrightarrow} \overset{+ - SPN}{\longrightarrow} \overset{$$

Enrique A. Castro,* Jorge Bessolo, Raul Aguayo, and José G. Santos

8162 Total Synthesis of (+)-Geldanamycin and (-)-o-Quinogeldanamycin: Asymmetric Glycolate Aldol Reactions and Biological **Evaluation**

Merritt B. Andrus,* Erik L. Meredith, Erik J. Hicken, Bryon L. Simmons, Russell R. Glancey, and Wei Ma

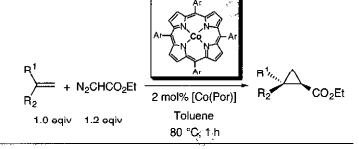
8170 A Theoretical Study of the Mechanism of

Selective Fluorination of Saturated Hydrocarbons by Molecular Fluorine. Participation of CHCl₃ Solvent Molecules in the **Ionic Process**

Haruhiko Fukaya and Koiji Morokuma*

8179 Diastereoselective and Enantioselective Cyclopropanation of Alkenes Catalyzed by Cobalt Porphyrins

Lingyu Huang, Ying Chen, Guang-Yao Gao, and X. Peter Zhang*



8185 Synthesis of Orthogonally Protected ■ Lanthionines

M. Firouz Molid Mustapa, Richard Harris, Nives Bulic-Subanovic, Susan L. Elliott, Sarah Bregant, Marianne F. A. Groussier, Jessica Mould, Darren Schultz, Nathan A. L. Chubb, Piers R. J. Gaffney, Paul C. Driscoll, and Alethea B. Tabor*

COOAllyl

NHFmoc

HO.

8193 Synthesis of a Cyclic Peptide Containing

■ Norlanthionine: Effect of the Thioether Bridge on Peptide Conformation

M. Firouz Mohd Mustapa, Richard Harris, Diego Esposito, Nathan A. L. Chubb, Jossica Mould, Darren Schultz, Paul C. Driscoll, and Alethea B. Tabor*

8199 Synthesis of Cyclic Hexameric Porphyrin

Arrays. Anchors for Surface Immobilization and Columnar Self-Assembly

Kin-ya Tomizaki, Lianhe Yu, Lingyun Wei, David F. Bocian,* and Jonathan S. Lindsey* 8208 The Nicotinic Pharmacophore:

 Thermodynamics of the Hydrogen-Bonding Complexation of Nicotine, Nornicotine, and Models

Jérôme Graton, Michel Berthelot, Jean-François Gal, Christian Laurence,* Jacques Lebreton, Jean-Yves Le Questel, Pierre-Charles Maria, and Richard Robins

8222 Chiral Hydroperoxides as Oxygen Source in the

■ Catalytic Stereoselective Epoxidation of Allylic

Alcohols by Sandwich-Type Polyoyometalates:

Alcohols by Sandwich-Type Polyoxometalates: Control of Enantioselectivity through a Metal-Coordinated Template

Waldemar Adam, Paul L. Alsters, Ronny Neumann, Chantu R. Saha-Möller, Dieter Scebach, Albert K. Beck, and Rui Zhang*

8232 Calculations of Substituent and Solvent Effects

■ on the Kinetic Isotope Effects of Menshutkin Reactions

Emilia Owczarek, Wojciech Kwiatkowski, Michał Lemieszewski, Adam Mazur, Michał Rostkowski, and Piotr Paneth*



Notes

8236 Anomalous C-C Bond Cleavage in

■ Sulfur-Centered Cation Radicals Containing a Vicinal Hydroxy Group

Zaiguo Li and Andrei G. Kutateladze*

8240 A Redox-Mediated Molecular Brake:

 Dynamic NMR Study of 2-[2-(Methylthio)phenyl]isoindolin-1-one and S-Oxidized Counterparts

Parag V. Jog, Richard E. Brown, and Dallas K. Bates*

8244 Ferromagnetic Behavior of ■ Formyl-Group-Carrying Stable Thioaminyl Radicals

Yozo Miura,* Shogo Nakamura, and Yoshio Teki*

8248 Zn(II)-Catalyzed Thiolysis of Oxiranes in Water under Neutral Conditions

Francesco Fringuelli, Ferdinando Pizzo,* Simone Tortoioli, and Luigi Vaccaro

8252 Short Synthesis of Enantiopure C₂-Symmetric ■ 1,2:4,5-Diepoxypentane and

1,2:4,5-Diepoxypentane and "Pseudo"-C₂-Symmetric 3-Azido-1,2:4,5-diepoxypentane from Arabitol

A. James Boydell, Martin J. Jeffery, Eva Bürkstümmer, and Bruno Linclau*

8256 2-Azabicyclo[2.2.2]octa-3,5-dione via a Nitrile Diels-Alder Reaction

Cynthia K. McClure* and Jeffrey S. Link

8258 Photoaddition Reactions of Acetylene and Butadiyne Derivatives to Benzodithiophene

Brigitte Wex, Bilal R. Kaafarani, Allen G. Oliver, Jeanette A. Krause Bauer, and Douglas C. Neckers*

8261 Use of Sonication for the Coupling of Sterically ■ Hindered Substrates in the Phenolic Mitsunobu Reaction

Salvatore D. Lepore* and Yuanjun He

8264 Syntheses of Regioisomerically Pure 5- or ■ 6-Halogenated Fluoresceins

Guan-Sheng Jiao, Jin Wook Han, and Kevin Burgess *

and similar compounds

8268 A Facile Asymmetric Route to

■ (-)-Aphanorphine

Honghin Zhai,* Shengjun Luo, Chengfeng Ye. and Yongxiang Ma

8272 Oxidative Aromatization of 9,10-Dihydroanthracenes Using Molecular Oxygen Promoted by Activated Carbon

Natsuki Nakamichi, Hirotoshi Kawahata, and Masahiko Hayashi*

8274 Facile One-Pot Synthesis of Aromatic and Heteroaromatic Sulfonamides

Rina Pandya, Takashi Murashima, Livio Tedeschi, and Anthony G. M. Barrett*

8277 Highly Enantioselective Conjugate Addition of Diethylzine to Acyclic Enones with Fine-Tunable Phosphite-Pyridine Ligands

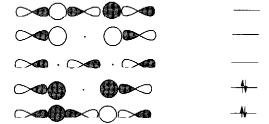
Huihui Wan, Yuanchun Hu, Yuxue Liang, Shuang Gao, Junwei Wang, Zhuo Zheng, and Xinquan Hu*

8281 Using Cyanide To Put Noble Gases inside C_{60}



R. J. Cross,* A. Khong, and M. Saunders*

8284 Evidence for 5-Center 4-Electron Bonding in (C····H····C···H····C) Array



Robert Ponec* and Gleb Yuzhakov

8287 A Novel Method for the Preparation of α,α' -Diffuoroesters and Acids Using BrF₃

Aviv Hagooly, Revital Sasson, and Shlomo Rozen*

Additions and Corrections

James A. Marshall,* Arnaud Piettre, 8290 Mikell A. Paige, and Frederick Valeriote

Total Synthesis and Structure Confirmation of the Annonaceous Acetogenins 30(S)-Hydroxybullatacin, Uvarigrandin A, and 5(R)-Hvarigrandin A (Narumicin I?)

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