### Alkylation of Adenine with t-Propargyl Chlorides: Acetylene/Allene Ratio and N9/N7 Regionelectivity.

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Alkylation of adenine (6) with dimethyl- or diethylpropargyl chloride 3a, 3b and 1-bromo-3,3-dimethylallene (10a) gave  $N^9$ - and  $N^7$ -acetylenes (7a, 7b, 9a and 9b) accompanied by  $N^9$ -allenes (8a, 8b).

Tetrahedron, 1993, 49, 2361

# SELF-ASSOCIATION OF DIPYRRINONES OBSERVED BY 2D-NOE NMR AND DIMERIZATION CONSTANTS CALCULATED FROM <sup>1</sup>H-NMR CHEMICAL SHIFTS

Daniel F. Nogales, Jin-Shi Ma and David A. Lightner Department of Chemistry, University of Nevada, Reno and The Institute of Photographic Chemistry, Academia Sinica, Beijing, China

Dipyrrinone analogs of bilirubin form intermolecularly hydrogen-bonded dimers in nonpolar solvents such as CHCl<sub>3</sub>. Such dimers are observed by  $^1\text{H-NMR}$  NOE between the C(2)-CH<sub>3</sub> and C(9)-R. Self-association constants are determined from analysis of concentration and temperature-dependent N- $^{\prime\prime}$  chemical shifts.

1: Methyl xanthobilirubinate (R=CH<sub>3</sub>)
2: Methyl neoxanthobilirubinate (R=H)

Tetrahedron, 1993, 49, 2373

#### A COMPARATIVE STUDY OF SOLID STATE AND

SOLUTION ALDOL ADDITION REACTIONS OF THE LITHIUM ENOLATE OF METHYL 3,3-DIMETHYLBUTANOATE: STEREOCHEMISTRY AND MECHANISTIC IMPLICATIONS

Yen Wei\* and R. Bakthavatchalam

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We report the first systematic study of the solid state aldol reactions of the title enolate with aldehydes. The same reacting species and transition state might be involved in both the solid state and solution reactions.

### HYMENAMIDES A AND B, NEW PROLINE-RICH CYCLIC HEPTAPEPTIDES FROM THE OKINAWAN MARINE SPONGE HYMENIACIDON SP.

Jun'ichi Kobayashi\*, Masashi Tsuda, Takemichi Nakamuraa, Yuzuru Mikamib, and Hideyuki Shigemori

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan, <sup>a</sup>Analytical and Metabolic Laboratories, Sankyo Co., Ltd., Tokyo 140, Japan, and bResearch Center for Pathogenic Fungi and Microbial Toxicoses, Chiba University, Chiba 280, Japan

Two new cyclic heptapeptides, hymenamides A (1) and B (2), have been isolated from the Okinawan marine sponge Hymeniacidon sp.

Tetrahedron, 1993, 49, 2391

Pro-Pro-Val-Pro-Phe-Trp-Arg 1

Pro-Pro-Asn-Phe-Val-Glu-Phe

2

Tetrahedron, 1993, 49, 2403

### REACTIONS OF UNSTABLE DIALKYLCARBAMOYL LITHIUMS WITH SULFUR COMPOUNDS

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$$\begin{array}{c|c}
O \\
\parallel \\
R_2NCSR'
\end{array}$$

$$\begin{array}{c|c}
O \\
\parallel \\
R_2NC^TLi^+
\end{array}$$

$$\begin{array}{c|c}
O \\
R_2NCSR'
\end{array}$$

$$\begin{array}{c|c}
O \\
\parallel \\
R_2NCSR'
\end{array}$$

$$\begin{array}{c|c}
O \\
R'SSR'
\end{array}$$

$$\begin{array}{c|c}
R'SSR'
\end{array}$$

$$\begin{array}{c|c}
O \\
\parallel \\
R_2NCSR'
\end{array}$$

$$\begin{array}{c|c}
O \\
R_2NCSR'
\end{array}$$

#### NEW TOTAL SYNTHESIS OF (+)-M-METHYLANISOMYCIN BY ANODIC CYCLIZATION OF 8-ALKENYLAMINE

Tetrahedron, 1993, 49, 2413

Masao Tokuda,\* Hirotake Fujita, Tohru Miyamoto and Hiroshi Suginome Organic Synthesis Division, Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

(+)-N-Methylanisomycin

# NEW AMINO ACIDS FROM *CLITOCYBE ACROMELALGA*. POSSIBLE INTERMEDIATES IN THE BIOGENESIS OF MUSHROOM TOXINS, ACROMELIC ACIDS

Kimiaki Yamano and Haruhisa Shirahama\*

Department of Chemistry, Faculty of Science, Hokkaido University,

Sapporo 060, Japan

Structures of new amino acids (1~3) which were isolated from poisonous mushroom, Clitpcybe acromelalga were determined. Their occurrences support the previously proposed biogenesis of acromelic acids.

SYNTHESIS AND CONFORMATIONAL STUDY OF 1,1'-ETHANO-9,9'-BIFLUORENYL. ANTI AND GAUCHE CONFORMERS OF A 9,9'-BIFLUORENYL DERIVATIVE AND CHAIR AND TWIST CONFORMERS

OF A DIBENZO-1,5-CYCLOOCTADIENE DERIVATIVE

Y.-H. Lai\*, S.-M. Lee, S.-Y. Lee and M Yi, Department of Chemistry, National University of Singapore, Kent Ridge, Republic of Singapore 0511

The kinetically controlled dimerization of (1) gave regioselectively (2a) and (2b) which were readily characterized by <sup>1</sup>H NMR spectroscopy. The results observed were supported by a semiempirical MO PM3 calculation. Dynamic <sup>1</sup>H NMR studies indicated an interconversion process (2a) • (2b) involving a conformational barrier estimated at 65.2 kJ moi<sup>-1</sup>.

Tetrahedron, 1993, 49, 2447

Tetrahedron, 1993, 49, 2437

AN EFFICIENT SYNTHESIS OF TETRAARYL PORPHYRINS SUB-STITUTED WITH ESTER GROUPS BEARING LONG ALKYL CHAINS Hermann K. Hombrecher\* and Stefan Ohm

Institut für Chemie der Medizinischen Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1, Germany The Synthesis of tetraaryl porphyrins substituted with long chain ester groups is described.

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# SYNTHESIS OF AN ADVANDED FORSKOLIN INTERMEDIATE

Tetrahedron, 1993, 49, 2457

St. Bick, S. Zimmermann, H. Meuer, W. S. Sheldrick, and P. Welzel\*
Falvillit für Chemie der Puhr. Heinerick Profest 100140

Fakultät für Chemie der Ruhr - Universität, Postfach 102148, D - 4630 Bochum (Germany)

2 X Y a OH OH c H H

En route to forskolin (2a) via 1,9 - dideoxyforskolin (2c) tricylic labdane derivative rac - 19 has been prepared in eight steps from (E,E) - farnesol (8).

#### SYNTHESE D' \alpha-HYDROXYSULFINATES

Tetrahedron, 1993, 49, 2469

Michel Mulliez et Carole Naudy

URA 454, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

α hydroxysulfinates 1 of limited stability are synthetized, starting from sodium dithionite 4, and are characterized:

Tetrahedron, 1993, 49, 2477

A NEW SYNTHESIS OF UNSYMMETRICAL DIALKYL PEROXIDES FROM TERTIARY ALCOHOLS Marie-Josèphe BOURGEOIS <sup>a</sup>, Evelyne MONTAUDON <sup>a\*</sup> et Bernard MAILLARD <sup>b\*</sup>

<sup>a</sup> Institut du Pin- Laboratoire de Chimie Appliquée- <sup>b</sup> Laboratoire de Chimie Organique et Organométallique, associé au CNRS URA 35 - Université Bordeaux I, 351 cours de la Libération, 33405 Talence Cedex, France.

$$R_3COH \xrightarrow{CCl_3CN} R_3CO-C \xrightarrow{NH} \xrightarrow{R'OOH} R_3COOR' \qquad R': 1^{ary}, 2^{ary}, 3^{ary} \text{ alkyl}$$

## SYNTHESIS OF A TRITIATED 3-DEHYDROECDYSTEROID, PUTATIVE PRECURSOR OF ECDYSTEROID BIOSYNTHESIS.

F. DOLLE¹, C. HETRU², B. ROUSSEAU³, F. SOBRIO³, C. BLAIS⁴, R. LAFONT⁴, M. DESCAMP⁵ & B. LUU¹.

¹Laboratoire de Chimie Organique des Substances Naturelles, associé au CNRS, 5 rue Blaise Pascal, 67084 Strasbourg, France; ²Laboratoire de Biologie Générale, associé au CNRS, 12 rue de l'Université, 67000 Strasbourg, France; ³Service des Molécules Marquées, Departement de Biologie Cellulaire et moléculaire, CE de Saclay, 91191 Gif-sur-Yvette, France; ⁴Laboratoire de Biochimie et Physiologie du Développement, associé au CNRS, ENS, 46 rue d'Ulm, 75230 Paris, France; ⁵Laboratoire de Biologie Animale, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France. [Tritiated]-5β-cholest-7-ene-3,6-dione (1) have been synthesized with high specific activity (9.2 TBq/mmol) in ten steps from deoxychenocholic acid (2) with labelling by tritiation into both the side chain and the nucleus at the last step. It does not seem to be an intermediate in ecdysone biosynthesis in Pieris Brassicae or Lithobius forficatus.

# FIRST SYNTHESIS OF TWO NATURALLY OCCURRING OXETANE LACTONES: CLEMENTEIN AND CLEMENTEIN B

Tetrahedron, 1993, 49, 2499

Francisco A. Macías, José María G. Molinillo and Guillermo M. Massanet.

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain.

Clementein and clementein B have been synthesized from the  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone cynaropicrin. Conjugated photoaddition, stereoselective  $\alpha$ -hydroxylation and mild cyclization to form the exetane ring using THP as leaving group have been employed in this transformation.

Tetrahedron, 1993, 49, 2509

### ACYLOXY TRI(ISOPROPOXY)TITANIUM REAGENTS FOR REGIOSELECTIVE CLEAVAGE OF 2,3-EPOXYALCOHOLS. A SYNTHESIS OF 2-DEOXY-D-RIBOSE.

Yuri E. Raifeld, Antonia Nikitenko, Boris M. Arshava

Joint Laboratory of Carbohydrates and Nucleoside Synthesis,

Moscow Institute of Fine Chemical Technology and JV "Angarex", Vernadsky Ave., 86,

Moscow 117571, RUSSIA

The synthesis of 2-deoxy-D-ribose by acyloxy tri(isopropoxy)titanium reagent mediated cleavage of 2,3-epoxyalcohols under mild conditions is reported. Mechanistic aspects of these reactions are also described.

## HOMOGENEOUS HYDROGENATION OF SUBSTITUTED (Z)-ENE-DICARBAMATES WITH Rb(1) PHOSPHINE COMPLEXES

Janina Altman and Dov Ben-Ishai

Department of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel Evelina Berkovich

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Homogeneous hydrogenation of substituted (Z)-ene-1,2-dicarbamates with Rh(1) complexes containing (+)DIOP or (-)DIOP as ligands affords the saturated products with de of 47 and 40% when R' = (-)-menthyl, and ee of 21 and 18% when R' = iso-Bu.

### Tetrahedron, 1993, 49, 2521

### REACTION OF DIANION β-ENAMINO KETONES WITH

electrophiles. Part. 4. Synthesis of  $\beta$ '- and  $\delta$ -hydroxy- $\beta$ -enamino ketones.

Giuseppe Bartoli, <sup>a\*</sup> Marcella Bosco, <sup>b</sup> Cristina Cimarelli, <sup>a</sup> Renato Dalpozzo, <sup>b</sup> Gianni Palmieri<sup>a</sup>, <sup>a</sup> Dipartimento di Scienze Chimiche, Via S. Agostino 1, I-62032 Camerino, Italy, <sup>b</sup>Dipartimento di Chimica Organica "A. Mangini", V.le Risorgimento 4, I-40136, Bologna, Italy.

Selective generation tecniques of  $\alpha'$ - and  $\gamma$ -diamions of  $\beta$ -enamino ketones allows an almost complete regiocontrol in the reaction with aldehydes and ketones for the synthesis of  $\beta'$ - and  $\delta$ -hydroxy- $\beta$ -enamino ketones. The reaction gives good to high yields even with enolizable carbonylic compounds.

#### Tetrahedron, 1993, 49, 2533

#### BASE-MODIFIED PYRIMIDINE NUCLEOSIDES. EFFICIENT ENTRY TO 6-DERIVATIZED URIDINES BY Sn-Pd TRANSMETALLATION-COUPLING PROCESS

Giovanni Palmisano\* and Marco Santagostino Dipartimento di Chimica Organica e Industriale, Università degli Studi di Milano, Milano, Italy

#### PREPARATION OF 1-SUBSTITUTED-3,4-DIHYDRONAPHTHALENE-2-CARBOXALDEHYDE N,N-DIMETHYLHYDRAZONES BY PALLADIUM(0) COUPLING, AND THEIR ELECTROCYCLIC RING CLOSURE

Thomas L. Gilchrist and Maureen A. M. Healy Chemistry Department, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, U. K.

The synthesis of fused pyridines from several 1-vinyl, 1-aryl- and 1-heteroaryl-3,4-dihydronaphthalene-2-carboxaldehyde N,N-dimethylhydrazones is described.

Tetrahedron, 1993, 49, 2557

## HOMOLYTIC SUBSTITUTION AT SELENIUM: RING CLOSURE OF $\omega$ -(BENZYLSELENO)ALKYL RADICALS

Lynda, J. Benjamin, Carl H. Schiesser\* and Katarina Sutej Department of Chemical Sciences, Deakin University, Geelong, Victoria, Australia, 3217.

The ring closure of a series of  $\omega$ -(benzylseleno)alkyl radicals (1) has been studied. Thiohydroxamic esters derived from  $\omega$ -(benzylseleno)alkanoic acids decompose smoothly, upon irradiation, with the loss of carbon dioxide to afford 5- and 6- membered selenium-containing rings in 78 - 95% yield. The thiohydroxamic ester derived from 7-(benzylseleno)heptanoic acid affords the 7-membered heterocycle, selenopane, in approximately 50% yield. The 5-(benzylseleno)hex-2-yl radical (1: R = R' = Me, n = 1) appears to ring close without stereoselectivity to give a 1:1 mixture of cia- and rang-2,4-dimethyltertahydroselenophene, a finding in keeping with MM2 calculations.

$$Ph \stackrel{R'}{\searrow} O - N \stackrel{hv}{\searrow} Ph \stackrel{R'}{\searrow} O - N \stackrel{R'}{\searrow} O - N \stackrel{hv}{\searrow} Ph \stackrel{R'}{\searrow} O - N \stackrel{N}{\searrow} O -$$

Tetrahedron, 1993, 49, 2567

Predominant Conformations of N<sub>4</sub>-Boc-deformyl-Z- and N<sub>4</sub>-Boc-deformyl-E-geissoschizine, the Latter a Possible Synthetic Intermediate in the Preparation of Sarpagan and Ajmalan Ring Systems

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