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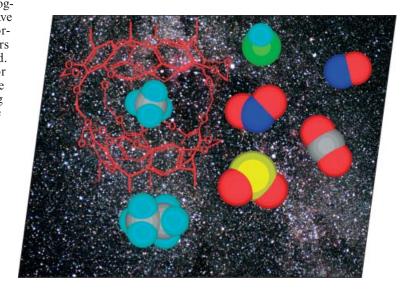




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows a star field filled with molecules of environmentally important gases. Gases are very interesting for molecular recognition. Supramolecular complexes with gases have been obtained by utilizing dynamic, reversible forces. On this basis, supramolecular, optical sensors for the detection of gases have been introduced. Studies on molecules and molecular materials for gas entrapment, separation, storage and release that involve synthetic containers, self-assembling capsules and even nanotubes and fullerenes have been well in progress. Moreover, supramolecular fixation of gases has yielded stable and selective chemical reagents for preparative organic chemistry. Gases have also been used as building blocks for supramolecular nanostructures. Dynamic, switchable polymers that can be used as storing and separating materials have been constructed from gases. The current progress in supramolecular chemistry and molecular recognition of gases is presented in the Microreview by D. M. Rudkevich on p. 3255 ff. The star field picture is a courtesy of Joe Eakin, Director, The Planetarium at The University of Texas at Arlington.



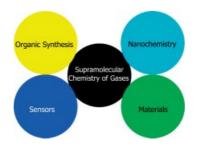
MICROREVIEW

Supramolecular Chemistry

D. M. Rudkevich* 3255-3270

Progress in Supramolecular Chemistry of Gases

Keywords: Calixarenes / Complexation / Gases / Host-guest systems / Molecular recognition / Supramolecular chemistry



The progress in supramolecular chemistry of gases is presented. Novel sensors for gases are introduced. Molecules and materials for gas entrapment, separation, storage and release that involve synthetic containers and nanotubes are overviewed. It is shown that supramolecular fixation of gases may lead to stable and selective chemical reagents, as well as novel polymers and dynamic nanostructures.

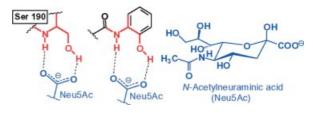
SHORT COMMUNICATIONS

Artificial Carbohydrate Receptors

M. Mazik,* A. König 3271-3276

Mimicking the Binding Motifs Found in the Crystal Structures of Protein-Carbohydrate Complexes: An Aromatic Analogue of Serine or Threonine Side Chain Hydroxyl/Main Chain Amide

Keywords: Molecular Recognition / Receptors / Carbohydrates / Hydrogen Bonds / Supramolecular Chemistry



The recognition unit consisting of the main chain amide group and the side chain hydroxyl group of Ser or Thr was successfully mimicked with an aromatic analogue, which was used for the construction of acyclic receptors incorporating only neutral recognition sites. The receptors can distinguish between two anionic sugars with remarkable selectivity.

Taxoid Synthesis

S. P. Chavan,* S. P. Chavan, H. R. Sonawane, U. R. Kalkote,

S. G. Sudrik, R. G. Gonnade,

M. M. Bhadbhade 3277-3280



Utilization of the Versatility of Sulfur in C-C Bond Formation and Cleavage: Synthesis of ABC Taxoid Skeletons

Keywords: Rearrangement / C-C coupling / Metalation / Ring expansion / Isomerization

Sulfur as a vehicle for the synthesis of complex fused ring systems of taxoids is described.



FULL PAPERS

R¹ R^2 CO_2H $\frac{I^*(N\text{-methylephedrine})_2 \text{ SbF}_6}{Ag^*(N\text{-methylephedrine})_2 \text{ SbF}_6}$ CH_2Cl_2 , $-78 ^{\circ}C$

Enantioselective lactonization of 4-substituted but-3-enoic acids at low temperatures is reported. The presence of bis(*N*-methylephedrine)silver(I) hexafluoroantimonate

in the reaction mixture is crucial for the success of this reaction. The different parameters of this cyclization reaction are examined.

Enantioselective Lactonization

An Approach to Enantioselective 5-endo Halo-Lactonization Reactions

Keywords: N ligands / Iodine / Cyclization / Enantioselectivity / Lactones

Fungal Phenylpropanoids

Two novel phenylpropanoid-derived polyketides (8, 9) that feature an unprecedented mode of bis(styrylpyrone) fusion were

isolated from the saprotrophic tree fungi *Pholiota squarrosa* and *Phellinus pini* and identified as potent XO inhibitors.

Squarrosidine and Pinillidine: 3,3'-Fused Bis(styrylpyrones) from *Pholiota squarrosa* and *Phellinus pini*

Keywords: Fungi / Natural products / Phenylpropanoids / Pyrones / Xanthine oxidase

The efficient synthesis of polyhydroxy-tetrahydropyrano-pyrroles from acetylenic carbohydrate precursors in three to four steps is described. The methodology involves, as key steps, the ring contraction of pyridazine intermediates obtained by an inverse-demand Diels—Alder reaction and subsequent intramolecular lactonization.

N-Heterocycles from Carbohydrates

S. Naud, M. Pipelier, G. Viault, A. Adjou, F. Huet, S. Legoupy, A.-M. Aubertin, M. Evain, D. Dubreuil* 3296-3310

Synthesis of Polyhydroxylated Pyrano-Pyrrole Derivatives from Carbohydrate Precursors

Keywords: Cycloaddition / Ring contraction / Pyridazine / Pyrrole / α -Pyrone / Carbohydrates

Hydroamination

LiN(SiMe₃)₂/TMEDA is an efficient catalyst for the anti-Markovnikov addition of primary and secondary amines to vinylarenes. Reactions proceed readily at 120 °C

in the absence of solvent. The mechanism of the lithium-catalyzed hydroamination and the influence of TMEDA was studied with DFT methods.

P. Horrillo-Martínez, K. C. Hultzsch,*
A. Gil, V. Branchadell 3311-3325

Base-Catalyzed Anti-Markovnikov Hydroamination of Vinylarenes — Scope, Limitations and Computational Studies

Keywords: Phenethylamines / Hydroamination / Homogeneous catalysis / Lithium / Density functional calculations / Reaction mechanisms

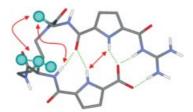
CONTENTS

Intramolecular Ion Pairing

C. Schmuck,* J. Dudaczek 3326-3330

Ion Pairing Between the Chain Ends Induces Folding of a Flexible Zwitterion in Methanol

Keywords: Ion pairing / Guanidinium cations / Supramolecular chemistry / Foldamers / Amino acids



Flexible zwitterion 10 folds into a stable loop due to directed charge interactions between the two chain ends. This loop is stable even in polar protic solvents (methanol) as shown by NMR studies.

Bile Acids

Nonappa, U. Maitra* 3331-3336

First Chemical Synthesis, Aggregation Behavior and Cholesterol Solubilization Properties of Pythocholic Acid and 16α-Hydroxycholic Acid

Keywords: Pythocholic acid / Oxidation / Critical micellar concentration / Regio and chemoselective / Remote functionalization

First chemical synthesis of pythocholic acid and 16α -hydroxycholic acid were achieved using a remote functional strategy

as a key step. Unusually low CMC and high cholesterol solubilization ability was observed for pythocholic acid.

Asymmetric Homoaldol Reactions

Asymmetric Homoaldol Reactions with Cyclohex-2-enyl *N,N*-Diisopropylcarbamate: Kinetic Resolution, Elucidation of the Stereochemical Course and Applications in the Synthesis of Hexahydroisobenzofuran-4-(1*H*)-ones

Keywords: Asymmetric synthesis / Kinetic resolution / Metallated allyl carbamates / Homoaldol reactions / Tetrahydrofuran synthesis

1-Carbamoyloxy allylstannane was synthesized by stereospecific deprotonation and kinetic resolution of cyclohex-2-enyl *N,N*-diisopropylcarbamate with up to 97 % *ee.* The stereospecific TiCl₄-mediated homo-

aldol reaction with aldehydes leads to *syn*-configured 3-(1-hydroxyalkyl)-cyclohex-1-enyl carbamates which were converted to *all-cis*-configured hexahydroisobenzofuran-4-(1*H*)-ones with up to 96 % *ee*.

Asymmetric Homoaldol Reaction

Stereoselective Synthesis of Hexahydroisobenzofuran-4(1*H*)-ones from Chiral Substituted Cyclohex-2-enyl Carbamates via Asymmetric Homoaldol Reaction and THF Cyclocondensation

Keywords: Asymmetric synthesis / Heterocycles / Metallated allyl carbamates / Homoaldol reactions / Tetrahydrofuran synthesis

CbO Ti(NEt₂)₃

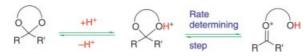
$$R^3$$
CHO
 R^2
 R^3 CHO
 R^3
 R^4 CHO
 R^3
 R^4 CHO
 R^4
 R^4

Enantiopure cyclohex-2-enyl carbamates, synthesized from (*R*)-(-)-carvon and (*R*)-(-)-crypton, were lithiated and then transmetallated with CITi(NEt₂)₃ to yield *anti*-configured 3-(1-hydroxy-alkyl)-cyclohex-1-

enyl carbamates after homoaldol reaction with aldehydes. These were transferred into *cis,trans,cis*-configured hexahydroisobenzo-furan-4(1*H*)-ones in excellent diastereo-selectivities.



Cyclic Acetal Hydrolysis



The rates of hydrolysis of 5- and 6-ring acetals are controlled by ring conformational stereoelectronic effects, and resonance

effects depending upon the substituents on the parent ketone; an A1 mechanism of hydrolysis explains the observed effects.

The Effects of Ring Size and Substituents on the Rates of Acid-Catalysed Hydrolysis of Five- and Six-Membered Ring Cyclic Ketone Acetals

Keywords: Acetal / Hydrolysis / Cleavage reactions / Kinetics / Reaction mechanism

Tetraketide Lactones

Synthesis of the tetraketide lactones, which are likely to be produced with a model pikromycin polyketide synthase (PKS), has been investigated. The tetraketide lactones

were synthesized by the asymmetric aldol reaction, allylation, and the Reformatsky reaction.

the Pikromycin Biosynthetic Pathway **Keywords:** Polyketide / Pikromycin / Bio-

Keywords: Polyketide / Pikromycin / Biosynthesis / Lactones / Asymmetric synthesis

Bisphosphonate Prodrugs

O OH O

$$RO - P \rightarrow P \rightarrow OR'$$
 OR''
 O

Several synthetic pathways for obtaining phosphonic esters of the amino bisphosphonic acids (NBPs) pamidronate, alendronate and neridronate were investigated. Phthalimide *N*-protected amino acids allowed access to alkyl or aryl mono-, disymmetric or not) and triesters of these three NBPs in high yields.

E. Guénin, M. Monteil, N. Bouchemal, T. Prangé, M. Lecouvey* 3380-3391

Syntheses of Phosphonic Esters of Alendronate, Pamidronate and Neridronate

Keywords: Phosphonic ester / Alendronate / Pamidronate / Neridronate / Arbusov reaction

Glycosylation Reactions

Thioglucosaminides with different *N*-protecting groups could selectively be benzoylated at the 3- and 6-hydroxy groups in good yields without the requirement for low-

temperature techniques. The efficacy of these thioglycosides both as donors and acceptors for the construction of chitosans

S. Grann Hansen, T. Skrydstrup* 3392–3401

Studies Directed to the Synthesis of Oligochitosans — Preparation of Building Blocks and Their Evaluation in Glycosylation Studies

Keywords: Benzoylation / Glucosamine / Chitosan / Glycosylation

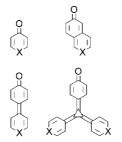
was evaluated

CONTENTS

Carbonyl Bases and Superbases

Design of Brønsted Neutral Organic Bases and Superbases by Computational DFT Methods: Cyclic and Polycyclic Quinones and [3]Carbonylradialenes

Keywords: Proton affinity / Basicity / Aromaticity / Cationic resonance / Relaxation effects



 $X = C=O, N-Me, C=C(NMe_2)_2$

A combination of quinoid/[3]radialene backbones and judiciously chosen "tails" leads to high oxygen basicity in molecules possessing a carbonyl "spearhead".

If not otherwise indicated in the article, papers in issue 19 were published online on June 18, 2007