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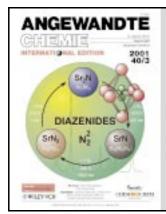
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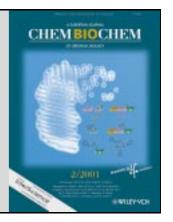
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ChemBioChem 2/2001 is bound in this issue of Angewandte Chemie.



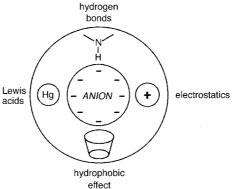
COVER PICTURE

The cover picture shows schematically the conditions for preparation and decomposition of strontium diazenides. The crystal structures of the diazenides, which were obtained as single-phase products under high N₂ pressure (up to 5500 bar), were determined by neutron diffraction. The background is provided by a section of the powder diffraction pattern of SrN₂, and the coordination of the diazenide ions is shown top right. The N–N bond length in the diazenide ions is 122 pm in both compounds. Details of the preparation and characterization of the Sr diazenides are reported by G. Auffermann, Y. Prots, and R. Kniep on p. 547 ff.



REVIEWS

Since the birth of anion coordination chemistry in the late 1960s, anion recognition is today an established area of supramolecular chemistry. This review gives an overview of the state of the art of inorganic and organic anion receptors which can selectively bind and detect relevant anionic guest molecules by a variety of interactions (see picture). The most recent developments are in the areas of self-organization by anionic templates, ion-pair recognition, and the function of anions in



tion, and the function of anions in supramolecular catalysis. Clearly this shows that the chemistry of anion recognition at the start of the new millennium is exciting, surprisingly rich, and

Angew. Chem. 2001, 113, 502-532

Keywords: anions • molecular

recognition • self-assembly • sensors •

supramolecular chemistry

P. D. Beer,* P. A. Gale * 486-516

Anion Recognition and Sensing:

The State of the Art and Future

Perspectives

 ${\bf CO_2}$, the solvent of choice! Whether it is compressed as a liquid or as a supercritical fluid the properties of ${\bf CO_2}$ are, in principle, ideal to make it the solvent of the future. One of the main problems, the low solubility in ${\bf CO_2}$ of many industrially important compounds, can be overcome by the development of ${\bf CO_2}$ soluble surfactants. The broad application spectrum of this new technology is presented with examples of dispersion polymerization, polycarbonate synthesis, stone protection, and spin coating for microelectronics.

a continually growing interdisciplinary field of coordination chemistry.

Angew. Chem. 2001, 113, 534-544

S. L. Wells, J. DeSimone * 518 – 527

CO₂ Technology Platform: An Important Tool for Environmental Problem Solving

Keywords: carbon dioxide • micelles • polymers • supercritical fluids • surfactants

VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Synthesis and Structure of a $Ga_{84}R_{20}^{4-}$ Cluster—A Link between Metalloid Clusters and Fullerenes?

From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality

Heterogeneous Dinuclear Rhodium(II) Hydroformylation Catalysts—Performance Evaluation and Silsesquioxane-Based Chemical Modeling

Formation of Super Wires of Clusters by Self-Assembly of Transition Metal Cluster Anions with Metal Cations

Synthesis of Conformationally Locked Carbohydrates: A Skew-Boat Conformation of L-Iduronic Acid Governs the Antithrombotic Activity of Heparin

Highly Efficient and Ultrafast Phototriggers for cAMP and cGMP by Using Long-Wavelength UV/Vis Activation

A. Schnepf, H. Schnöckel*

E. Solari, J. Hesschenbrouck, R. Scopelliti, C. Floriani,* N. Re

M. Nowotny,* T. Maschmeyer, B. F. G. Johnson, P. Lahuerta, J. M. Thomas, J. E. Davies

T. Nakajima, A. Ishiguro, Y. Wakatsuki*

S. K. Das, J.-M. Mallet, J. Esnault, P.-A. Driguez, P. Duchaussoy, P. Sizun, J.-P. Hèrault, J.-M. Herbert, M. Petitou,* P. Sinaÿ*

V. Hagen,* J. Bendig, S. Frings, T. Eckardt, S. Helm, D. Reuter, U. B. Kaupp Can a simple amino acid act like an enzyme? This question is reviewed and discussed herein. In addition, new contributions in which simple organic molecules are used as efficient chiral catalysts in asymmetric synthesis (see scheme) are highlighted.

Angew. Chem. 2001, 113, 545-548

H. Gröger,* J. Wilken 529 – 532

The Application of L-Proline as an Enzyme Mimic and Further New Asymmetric Syntheses Using Small Organic Molecules as Chiral Catalysts

Keywords: aldol reactions • amino acids · asymmetric catalysis · enzyme mimics · homogeneous catalysis

Diamond Surfaces: Just Big Organic Molecules?

Does a diamond surface react like a large organic molecule or does the underlying bulk material affect its behavior? Fascinating work by the groups of Bent and Hamers suggests that the (100) diamond surface has a very strong organic character (a model Diels-Alder reaction is depicted), which is less affected by the underlying material than silicon or germanium.



Angew. Chem. 2001, 113, 548-550

Keywords: cycloaddition · diamond · germanium · silicon · surface chemistry

Functional group tolerance and accessibility of unique microstructures are attractive features of olefin polymerization by late transition metal catalysts. Recent discovery of several new classes of highly active catalysts provide access to a range of new materials.

diamond

S. Mecking* 534 – 540

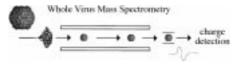
Olefin Polymerization by Late Transition Metal Complexes—A Root of Ziegler Catalysis Gains New Ground

Keywords: homogeneous catalysis • polymerization · polymers · transition metals

Angew. Chem. 2001, 113, 550-557

COMMUNICATIONS =

The simultaneous measurement of the time-of-flight and the number of charges on each electrosprayed ion provides a new way to determine the mass of a whole intact virus. The



diamond

weights of an icosahedral virus (rice yellow mottle virus) consisting of a singlestranded RNA surrounded by a homogeneous protein shell with a mass of $6.5 \times$ 10^6 Da, and a rod-shaped RNA virus (tobacco mosaic virus) with a mass of $40.5 \times$ 10⁶ Da were measured with this technique.

Angew. Chem. 2001, 113, 560-562

S. D. Fuerstenau, W. H. Benner,* J. J. Thomas, C. Brugidou, B. Bothner, G. Siuzdak* 541 – 544

Mass Spectrometry of an Intact Virus

Keywords: mass spectrometry • noncovalent interactions . RNA structures · viruses



Correct additions make a difference: Asymmetric deactivation and asymmetric amplification concepts coupled with a high-throughput screening technique provided a successful strategy for designing a highly enantioselective catalytic system by simple combination of a racemic amino alcohol (rac-DB) and a nonracemic additive (AA). The example in the scheme shows the conversion of 1 into 2 with up to 92.7% ee.

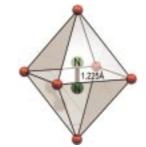
Angew. Chem. 2001, 113, 562-565

J. Long, K. Ding * 544 – 547

Engineering Catalysts for Enantioselective Addition of Diethylzinc to Aldehydes with Racemic Amino Alcohols: Nonlinear Effects in Asymmetric Deactivation of Racemic Catalysts

Keywords: asymmetric catalysis • asymmetric deactivation • high-throughput screening . nonlinear effects · zinc

Nitride and/or diazenide ions in the octahedral holes of nearly close-packed arrangements of Sr²⁺ ions (see picture) characterize the new compounds described herein. They were obtained as singlephase products by oxidation of Sr₂N with molecular nitrogen under high pressure.



G. Auffermann, Y. Prots, R. Kniep* 547 – 549

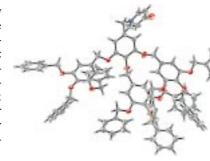
SrN and SrN₂: Diazenides by Synthesis under High N₂-Pressure

Keywords: diazenides • high-pressure chemistry . neutron diffraction · nitrides · redox chemistry

Angew. Chem. 2001, 113, 565-567



Passivation of the metal surface by dendrons bearing a focal 4-pyridone functionality (the second-generation dendron is shown; C: gray, N: blue, O: red) allows controlled nucleation and growth of gold nanoclusters. The particle size is a direct function of the generation number of the dendritic ligands, with higher generation dendron producing larger particles.



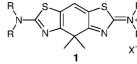
R. Wang, J. Yang, Z. Zheng,* M. D. Carducci, J. Jiao, S. Seraphin 549 – 552

Dendron-Controlled Nucleation and Growth of Gold Nanoparticles

Angew. Chem. 2001, 113, 567-570

Keywords: dendrimers • electron microscopy · gold · nanostructures · steric hindrance

The fluorescence-enhancing effect of the oxygen bridge in pyronine and rhodamine di- or triphenylmethane dyes, is connected to a significant hypsochrome shift of the absorption bands. This shift is absent when the bridge is an alkylene unit. While



H. Hartmann,* A. Noack 552-554

the preparation of such compounds is difficult, that of the heterocyclic analogues 1 is relatively simple and gives rise to intensely fluorescent dyes with absorptions

Alkylene-bridged N,N,N'N' – Tetrasubstituted Bis(2-amino-5thiazolyl)methinium Salts—A New Class of Strongly Fluorescent Dyes

Angew. Chem. 2001, 113, 597-599

at long wavelength.

Keywords: chromophores • fluorescence · heterocycles · methine dyes · thiazoles

As valuable chiral building blocks for the syntheses of natural products and pharmacologically active substances, especially of carbohydrate mimetics, functionalized cyclohexadiene-trans-diols such as (2S,3S)-dihydroxy-2,3-dihydrobenzoic acid (1) can be prepared easily in 17% yield starting from glucose by using metabolically deregulated, recombinant microorganisms such as the Escherichia coli strain AN193 (see scheme).

AN193

Synthesis of Functionalized Cyclohexadiene-trans-Diols with Recombinant Cells of Escherichia coli

Angew. Chem. 2001, 113, 578-581

Keywords: asymmetric synthesis • bioorganic chemistry . biotransformations · shikimic acid



Pericyclic or pseudopericyclic? Although both mechanisms lead to the same product, they are deeply different in nature. The ring-current model proves to be a useful tool to define different kinds of aromaticity and to distinguish between pericyclic and pseudopericyclic reactions (see scheme).

A. R. de Lera,* R. Alvarez, B. Lecea, A. Torrado, F. P. Cossío * 557 – 561

On the Aromatic Character of Electrocyclic and Pseudopericyclic Reactions: Thermal Cyclization of (2Z)-Hexa-2,4,5-trienals and Their Schiff Bases

Angew. Chem. 2001, 113, 570-574

Keywords: ab initio calculations . allenes · aromaticity · electrocyclic reactions · heterocycles

A fulvene-type coupling results from the reduction of acenaphthylene by activated samarium or ytterbium in THF. This leads exclusively to the formation of the respective C_2 -symmetric trans-rac-ansa-lanthanocene complexes $[(\eta^5 - \eta^5 - \eta^$ $C_{12}H_8$ ₂ $Ln(thf)_2$ [Eq. (1); Ln = Sm, Yb].

Angew. Chem. 2001, 113, 584-586

I. L. Fedushkin,* S. Dechert, H. Schumann* 561 – 563

Stereoselective Formation of C_2 -Symmetric ansa-Lanthanocenes by Reductive Coupling of Acenaphthylene with Activated Ytterbium or Samarium

Keywords: ansa compounds • C-C coupling • lanthanides • metallocenes · polycycles

Areas of $80-3500 \mu m^2$ are displayed by gold single-crystal ultramicroelectrodes, which were fabricated from gold single crystals grown electrolytically in silicate gels. According to their cyclic voltammograms in 0.01M HCl, these ultramicroelectrodes behave similarly to electrodes of more normal dimensions with the same crystallographic orientation of the surface.



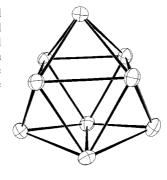
V. Komanicky, W. R. Fawcett* 563 - 566

Fabrication and Properties of Gold Single-Crystal Ultramicroelectrodes

Angew. Chem. 2001, 113, 594-596

Keywords: electrochemistry • electrodes • gold · single-crystal electrodes · ultramicroelectrodes

A simple preparative method has been employed for the synthesis of the novel cluster compound Ga₉(CMe₃)₉, which contains a tricapped trigonal prism of monovalent gallium atoms. Electron transfer processes were observed similar to those of polyboranes, leading to the the reversible formation of the corresponding radical anion.



W. Uhl,* L. Cuypers, K. Harms, W. Kaim, M. Wanner, R. Winter, R. Koch, W. Saak 566 – 568

Ga₉(CMe₃)₉, an Important New Building Block in the Structural Chemistry of the Alkylelement(I) Compounds $E_n R_n$ (E = B - In)

Keywords: cluster compounds • electron deficiency · gallium

Angew. Chem. 2001, 113, 589-591



Six at a time! Up to six stereogenic centers can be diastereoselectively formed in one step in three-component domino reactions of 4-silyloxypyrylium triflates with 2-silyloxybuta-1,3-dienes. Annulated or bridged ring systems such as 1 and 2, respectively, can be formed with high selectivity. $R^1 = \text{silyl group}$; R^2 , $R^3 = \text{organyl}$ group.

$$R^{1}O + R^{2}$$

$$R^{2}OR^{1}$$

$$R^{2}OR^{1}$$

$$R^{2}OR^{1}$$

Angew. Chem. 2001, 113, 591-594

U. Beifuss,* K. Goldenstein, F. Döring, C. Lehmann, M. Noltemeyer . . 568-570

Stereoselective Multiple Functionalization of Pyrylium Salts by Domino Reactions with 2-Silyloxybuta-1,3-dienes

Keywords: annulation • domino reactions · heterocycles · polycycles · rearrangement

In aqueous solution, the neutral radical formed by H-abstraction by ${}^{\bullet}$ OH from one of the side-chain methyl groups of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) is protonated by water to give the aromatic radical cation, TMPD ${}^{\bullet}$ + (see scheme). This reaction involves an intramolecular electron transfer from the ring to the side chain and is the reverse of the classical side-chain deprotonation reaction of radical cations.

Angew. Chem. 2001, 113, 581 - 583

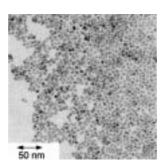
S. Steenken,* A. J. S. C. Vieira 571 – 573

Water-Assisted Intramolecular Electron Transfer from the Ring to the Side Chain in *N*,*N*,*N'*,*N'*-Tetraalkyl-*para*-phenylenediamine Radicals—The Reverse of Side Chain Deprotonation of Radical Cations

Keywords: acidity • protonations • pulse radiolysis • radical cations • radical reactions

Nanoparticles with high photoluminescence quantum yield have been recently considered as possible biolabels and as emitters in optoelectronic devices. Now gram amounts of nontoxic, chemically stable LaPO₄:Ce,Tb nanocrystals (see picture) have been obtained in a coordinating solvent. These nanoparticles can be easily redispersed in polar solvents to give scatter-free colloids that exhibit quantum yields of up to 61 %.

Angew. Chem. 2001, 113, 574-578

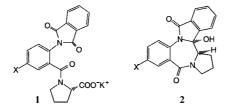


Liquid-Phase Synthesis of Colloids and Redispersible Powders of Strongly Luminescing LaPO₄:Ce,Tb Nanocrystals

Keywords: colloids • luminescence • nanostructures • rare-earth compounds

Memory of chirality in triplet 1,7-diradicals was detected for the first time and to a remarkably high degree in the decarboxylative photocyclization of the proline derivative of N-phthaloyl anthranilic acid 1 into 2 (X = H: 45 % yield, 86 % ee; X = Cl: 50 % yield, 79 % ee).

Angew. Chem. 2001, 113, 586-589



Diastereo- and Enantioselective Synthesis of Pyrrolo[1,4]benzodiazepines through Decarboxylative Photocyclization

Keywords: atropisomerism • circular dichroism • diradicals • memory of chirality • photochemistry

The intermolecular exchange coupling 2*J* for the light-induced radical pair in a crystal of 2,2'-di(*ortho*-chlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole (*o*-Cl-HABI) was measured for the first time on the basis of Curie analyses of the EPR spectral intensities. The coupling constant evaluated from density functional theory calculations compares well with the experimental value. The picture shows the distribution of spin density for the radical pair.

Angew. Chem. 2001, 113, 600-602

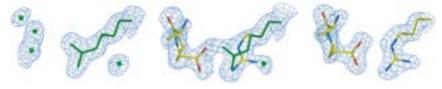


J. Abe,* T. Sano, M. Kawano, Y. Ohashi, M. M. Matsushita, T. Iyoda 580 – 582

EPR and Density Functional Studies of Light-Induced Radical Pairs in a Single Crystal of a Hexaarylbiimidazolyl Derivative

Keywords: density functional calculations • EPR spectroscopy • photochromism • radicals • through-space interactions

Crystallographic snapshots of protein-ligand complexes have been determined by soaking protein crystals in solutions of different ligand concentrations. The crystallographic refinement of ligand occupancy allows the calculation of the ligand binding constant in the crystal. The picture shows three different stages along the binding pathway: from free protein (left) to ligand-bound protein (right).



Angew. Chem. 2001, 113, 602-606

S.-y. Wu, J. Dornan, G. Kontopidis, P. Taylor, M. D. Walkinshaw* . 582 – 586

The First Direct Determination of a Ligand Binding Constant in Protein Crystals

Keywords: kinetics • noncovalent interactions · protein structures · structure elucidation

Involatile OsO₄! A tetrasubstituted olefin is immobilized on SiO₂ and reacts with OsO₄ to form a stable osmate(IV) ester (see scheme), which is a leak-proof heterogeneous catalyst for the cis-dihydroxylation of olefins.

a) SiO
$$_{2\nu_{T_{1}}}$$
 SiO $_{2\nu_{T_{1}}}$ O R , 0.2 % 1 HO R

Angew. Chem. 2001, 113, 606-609

A. Severeyns, D. E. De Vos, L. Fiermans, F. Verpoort, P. J. Grobet, P. A. Jacobs * 586 – 589

A Heterogeneous cis-Dihydroxylation Catalyst with Stable, Site-Isolated Osmium - Diolate Reaction Centers

Keywords: dihydroxylation • heterogeneous catalysis . immobilization · osmium · oxidations

A very general reaction is presented to achieve the nucleophilic transfer of "CF₃" to chiral N-(tert-butylsulfinyl)imines in high yield and high stereoselectivity (see reaction scheme). Tetrabutylammonium difluorotriphenylsilicate (TBAT) functions as a fluoride source, and aromatic, heterocyclic, and aliphatic sulfinylimines react smoothly. The high stereoselectivity suggests that the reaction proceeds through an open transition state. TMS = trimethylsilyl.

$$\begin{array}{c} O \\ \blacksquare \\ S \\ N \end{array} \begin{array}{c} H \\ \hline R1 \end{array} \begin{array}{c} TMSCF_3 \\ \hline TBAT, THF, -55^{\circ}C \end{array} \begin{array}{c} O \\ \blacksquare \\ S \\ N \end{array} \begin{array}{c} CF_3 \\ R1 \end{array} \begin{array}{c} 4N \ HCl, \ MeOH \\ RT \end{array} \begin{array}{c} CF_3 \\ \blacksquare \\ Cl \end{array} \begin{array}{c} CF_3 \\ \blacksquare \\ R1 \end{array}$$

70-95% yield, 80-99% ee

Angew. Chem. 2001, 113, 609-610

G. K. S. Prakash,* M. Mandal, G. A. Olah* 589 – 590

Stereoselective Nucleophilic Trifluoromethylation of N-(tert-Butylsulfinyl)imines by Using Trimethyl(trifluoromethyl)silane

Keywords: amines . asymmetric synthesis · imines ·

nucleophilic addition · sulfinamides

Applications of actinide chemistry, whether for energy or defense purposes, have left a legacy of potential waste hazards. The new expanded porphyrin ligand 1 forms stable complexes with both uranyl (UO_2^{2+}) and neptunyl (NpO_2^+) ions and presents a potential new avenue for waste remediation.

Angew. Chem. 2001, 113, 611-614

J. L. Sessler,* D. Seidel, A. E. Vivian, V. Lynch, B. L. Scott, D. W. Keogh* 591 – 594

Hexaphyrin(1.0.1.0.0.0): An Expanded Porphyrin Ligand for the Actinide Cations Uranyl (UO₂²⁺) and Neptunyl (NpO_2^+)

Keywords: actinides • coordination chemistry . macrocyclic ligands · porphyrinoids · transuranium elements

Atom transfer polymerization has been used to prepare a narrow molecular weight distribution (MWD), active ester homopolymer that acted as a precursor to prepare families of narrow MWD polymer—drug conjugates during preclinical studies (see schematic representation).

Solubilizing bydrophilic pendent chains Progression of the Polymer main chain Polymer mai

A. Godwin, M. Hartenstein, A. H. E. Müller,* S. Brocchini* 594–597

Narrow Molecular Weight Distribution Precursors for Polymer – Drug Conjugates

Angew. Chem. **2001**, 113, 614–617

Keywords: drug research • polymerization • polymers



Selective intramolecular alkane oxidations: an Rh^{II} carboxylate catalyzed C–H amination reaction facilitates the preparation of 1,2-amino alcohols from primary carbamates. The reaction is stereospecific, providing access to chiral α -branched amines from optically pure starting materials with no loss in enantiomeric excess (see scheme).

Angew. Chem. 2001, 113, 618-620

C. G. Espino, J. Du Bois * 598 – 600

A Rh-Catalyzed C-H Insertion Reaction for the Oxidative Conversion of Carbamates to Oxazolidinones

Keywords: amino alcohols • C–H insertion • cyclization • homogeneous catalysis • rhodium



Unmodified carbonyl compounds are converted in an enantioselective aldol-Tishchenko reaction directly into the chiral adduct by using catalytic amounts of a chiral base prepared in situ [Eq. (1)]. The catalyst was developed through the combination of arrayed catalyst evaluation and informed ligand design. Ad = adamantyl.

Angew. Chem. 2001, 113, 621-623

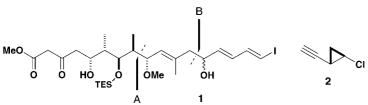
C. M. Mascarenhas, S. P. Miller, P. S. White, J. P. Morken* 601 – 603

First Catalytic Asymmetric Aldol-Tishchenko Reaction—Insight into the Catalyst Structure and Reaction Mechanism

Keywords: aldol reactions • asymmetric catalysis • lanthanides • reaction mechanisms • yttrium



Following macrolactonization, a Sonogashira coupling leads efficiently from **1** and **2** to the aglycon of the structurally unique cytotoxic macrolide callipeltoside A, isolated in tiny quantities from the lithistid sponge *Callipelta* sp. Key steps in the preparation of macrolide precursor **1** include a boron-mediated anti-aldol coupling (A) in tandem with Yamamoto's vinylogous aldol reaction (B). TES = triethylsilyl.



Angew. Chem. 2001, 113, 623-627

I. Paterson,* R. D. M. Davies, R. Marquez 603 – 607

Total Synthesis of the Callipeltoside Aglycon

Keywords: antitumor agents · boron · macrolides · natural products · total synthesis

A C-methyltransferase involved in methyl-branch formation in sugars has been characterized for the first time. TylC3, an (S)-adenosylmethylthionine(AdoMet)-dependent enzyme, catalyzes the attachment of a methyl branch [Eq. (1)] in the biosynthesis of L-mycarose, an unusual sugar found in tylosin and as its O-3-methyl derivative in erythromycin. The C-3 methylation proceeds with inversion of configuration and does not require the assistance of any cofactors. The turnover rate is $1.4 \pm 0.1 \, \text{min}^{-1}$. TDP = thymidine-5'-dihydrogenphosphate.

Angew. Chem. 2001, 113, 627-630

Insights into the Branched-Chain Formation of Mycarose: Methylation Catalyzed by an (S)-Adenosylmethionine-Dependent Methyltransferase

Keywords: alkylation · biosynthesis · carbohydrates · enzyme catalysis · transferases

Diastereomerically pure and isotopically labeled 5'-O-DMT-nucleoside-3'-O-(2-thio- and -oxo-4,4-"spiro"-pentamethylene-1,3,2-[18 O]oxathiaphospholane)s were used for stereocontrolled synthesis of P-chiral, isotopically labeled oligonucleotide phosphorothioates and phosphates, as well as "chimeric" PS^{18} O/ P^{18} O oligomers (see scheme) without loss of isotope enrichment. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DMT = 4,4'-dimethoxytrityl, ROH = 3'-O-acetylthymidine, Bz = benzoyl

Angew. Chem. 2001, 113, 630-633

Oxathiaphospholane Approach to the Synthesis of P-Chiral, Isotopomeric Deoxy(ribonucleoside phosphorothioate)s and Phosphates Labeled with an Oxygen Isotope

Keywords: oligonucleotides • phosphorothioates • isotopic labeling

Chiral recognition in organogels occurs in the coassembly of the chiral gelator 1 with the chiral guest molecule 2. The diastereomeric aggregates formed from (R,R)-2 with (R,R)-1 or (S,S)-1 were found to be truly different in structure and strength. Cooperativity makes a major contribution to the chiral recognition in this system.

$$R = C_9H_{19}$$
: $(R,R)-1$

Angew. Chem. 2001, 113, 633-636

Chiral Recognition in Bis-Urea-Based Aggregates and Organogels through Cooperative Interactions

Keywords: aggregation • chirality • cooperative effects • gels

Refixation of the CO₂ from a decarboxylation occurs in the palladium-catalyzed domino reaction of 4-methoxycarbonyloxy-2-butyn-1-ols with phenols. The reaction enables the construction of various cyclic carbonates [Eq. (1)] by efficient reincorporation of the CO_2 molecule under mild conditions, and is thus a convenient and environmentally friendly method.

HO
$$\rightarrow$$
 OCO₂Me \rightarrow OMe \rightarrow O

Angew. Chem. 2001, 113, 636-639

M. Yoshida, M. Ihara* 616-619

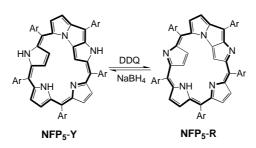
Palladium-Catalyzed Domino Reaction of 4-Methoxycarbonyloxy-2-butyn-1-ols with Phenols: A Novel Synthetic Method for Cyclic Carbonates with Recycling of CO₂

Keywords: carbon dioxide fixation • cyclization • domino reactions • palladium



From the acid-catalyzed condensation of aryl aldehyde and pyrrole a new type of fused expanded porphyrins, N-fused pentaphyrins NFP_5 -Y (24 π , yellow) and NFP_5 -R (22 π , red) were obtained in total yields of 2–19%. The two normal-type porphyrins are quantitatively interchanged through a redox reaction (see scheme). DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Angew. Chem. 2001, 113, 639-641



N-Fused Pentaphyrin

Keywords: heterocycles • macrocycles • porphyrinoids • redox chemistry



Butylation problems ironed out: 3-Pentynyl ethers react with butyllithium at -20° C in toluene, upon addition of a catalytic amount of a cheap iron(III) salt, to afford (*E*)-4-methyl-3-octenyl ethers in high yields. Stereochemically defined tetrasubstituted alkenes were also obtained by the subsequent addition of electrophiles (E⁺, see scheme; acac = acetylacetonate, Bn = benzyl).

Angew. Chem. 2001, 113, 641-643

Iron-Catalyzed Regio- and Stereoselective Carbolithiation of Alkynes

Keywords: alkenes • homogeneous catalysis • iron • lithium • nucleophilic addition

Introduction of an azido substituent at the α position of benzyl ethers can be achieved by treating them with IN₃ in refluxing acetonitrile. Some of the products obtained after $20 \, \text{min} - 5 \, \text{h}$ are given.

Angew. Chem. 2001, 113, 643-645

C. Viuf, M. Bols * 623 – 625

Radical Azidonation of Benzylic Positions with Iodonium Azide

Keywords: azides • benzyl ethers • iodine reagents • radical reactions



Supporting information on the WWW (see article for access details).

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