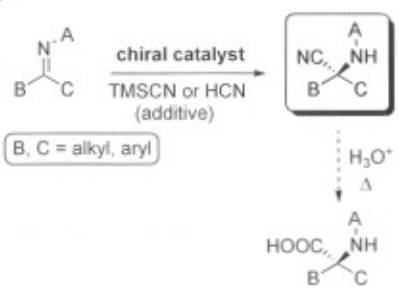
VIP ***The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:***

Obituary

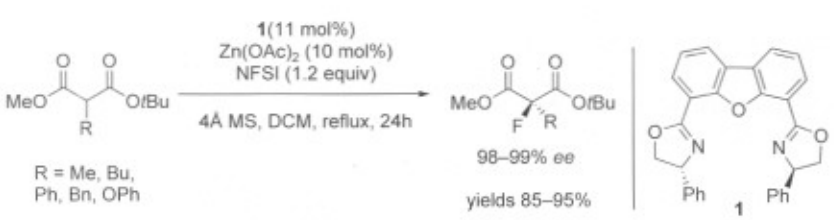
Books

Highlights

Picking up the gauntlet: The challenge of developing highly effective catalyst systems for the enantioselective Strecker reaction to convert ketimine substrates (see scheme, red; A denotes protecting group) into α-amino nitriles (blue) and ultimately α-amino acids has been met by several recent developments.



Strecker Reaction

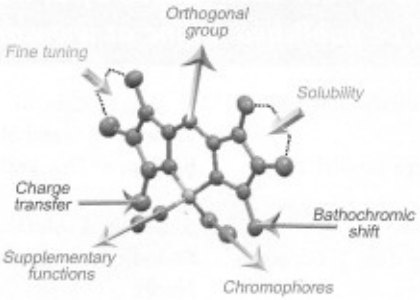


Gimme an F: Ever since the first asymmetric fluorination reagents were reported in 1988, the enantioselective introduction of a C–F bond at a stereogenic center has emerged as a major objective in organic chemistry. Newly published results on the enantioselective fluorination of malonates (see scheme) are put into context in this Highlight. NFSI = *N*-fluorodibenzenesulfonimide.

Asymmetric Fluorination

Contents

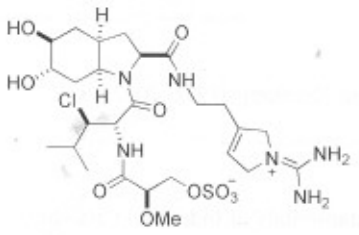
Minireviews



Unexpected adaptability: The properties of dipyrromethene boron difluoride (F-Bodipy) dyes can be modified in many ways (see picture, B pink, N blue, C gray). This versatility has allowed new uses to be developed for this molecule. Emphasis is given to synthetic considerations, optical properties, and applications as chemical sensors, luminescent devices, and molecular materials.

Reviews

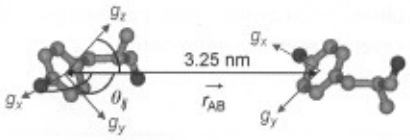
Oceans apart: With sources ranging from the marine sponges in North Queensland, Australia, to the cyanobacterial water-blooms of Lake Kasumigaura, Japan, and the blue-green algae found in Hula Valley, Israel, the aeruginosin family of linear peptides exhibit potent inhibition against serine proteases such as the medically relevant thrombin, as well as other proteins involved in the blood coagulation cascade.



Chlorodysinosin A

Communications

Paramagnetic centers rigidly embedded in proteins serve as a probe in structural studies of macromolecular complexes. Pulse EPR at high frequencies allows the determination of not only the distance but also the relative orientation of these centers (see tyrosyl radicals; C gray, O red, N blue). The method has considerable potential for studying the assembly of protein complexes.



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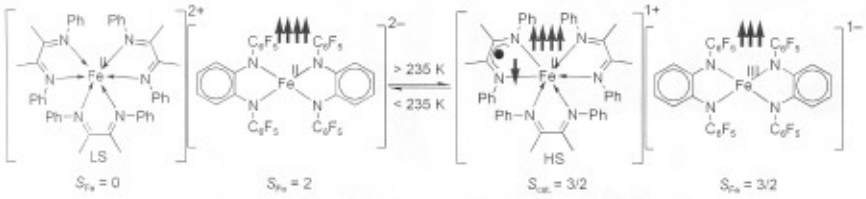
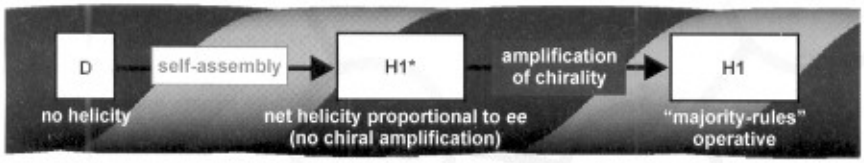


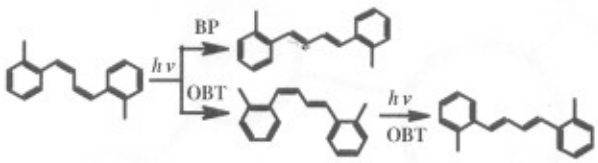
A rad. dad: The electronic structure of $[Fe(dad)_3][Fe(pda)_2]$ was investigated by X-ray crystallography, Mössbauer spectroscopy, and magnetic susceptibility measurements as a function of the temperature. Reversible one-electron transfer from the dianion (high-spin Fe^{II}) to the dication (low-spin Fe^{II}) generates a monoanion (intermediate-spin Fe^{III}) and a monocation (high-spin Fe^{II} and α-diimine π radical anion) above 235 K.

Spin Crossover



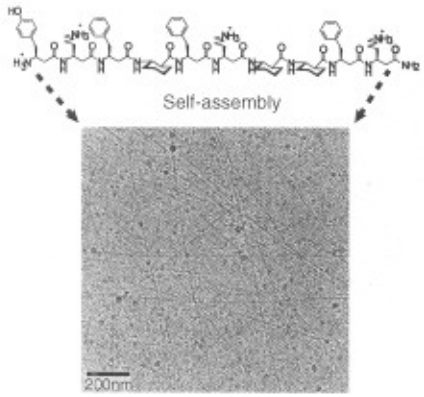
Chiral amplification in action: Kinetic studies on the self-assembly of bis(merocyanine) dyes reveal that two phenomena that have been suggested to be of importance for natural homochirogenesis, namely, autocatalysis and the "majority-rules" effect, are both involved in the evolution of homochiral helical dye nanorods (see picture, **D** = supramolecular oligomer species; **H1** = kinetically self-assembled nanorods; **H1*** = **H1**-type aggregate precursors).

Chiral Amplification



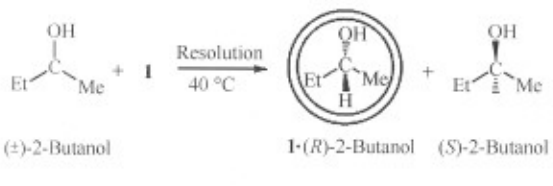
Let's twist again: In the isomerization of *cis,cis*-1,4-di-*o*-tolyl-1,3-butadiene in isopentane glass at 77 K, hula-twist pathways are eliminated, because unstable photoproduct conformers do not form. Instead, the isomerization is found to proceed by bicycle-pedal (BP) and one-bond-twist (OBT) mechanisms (see scheme).

Photoisomerization



More than a pretty phase: A class of helical β-peptides has been discovered that form lyotropic liquid-crystalline (LC) phases in water. The β-peptide sequence strongly affects the mode of assembly and ultimately whether a LC phase is formed. For a non-globally amphiphilic β-peptide that can form a LC phase, cryo-TEM revealed thin fibers several micrometers in length, consistent with Onsager theory.

Nanostructured Materials



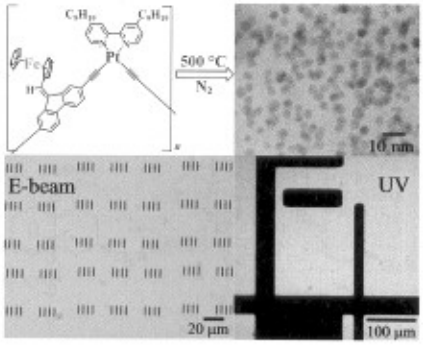
Only half may enter: A homochiral porous nanoscale metallacycle has been efficiently self-assembled from semiflexible enantiopure metallosalen complexes with complementary coordination motifs. Single crystals of the macromolecule (see structure; C gray, Zn purple, O red, N blue) show a reversible and controllable dynamic behavior. Particularly, the metallacycle can be used to resolve small racemic alcohols with high enantioselectivity (over 99.0% *ee*).

Porous Assemblies

The benefits of separation: For homologous polymers having similar backbone composition and charge/tail ratios, placing the charge and alkyl tail on spatially separated centers results in a higher membrane-disrupting ability, as evident from the increased antibacterial and hemolytic activities. The spatial separation particularly amplifies mammalian cell toxicity (see picture).

Antimicrobial Polymers

Micropatterns of arrays of ferromagnetic face-centered tetragonal FePt nanoparticles can be fabricated from thin films of a novel air- and moisture-stable bimetallic polyferroplatinyne precursor, which can be utilized directly as a negative resist in both electron-beam lithography and UV photolithography.

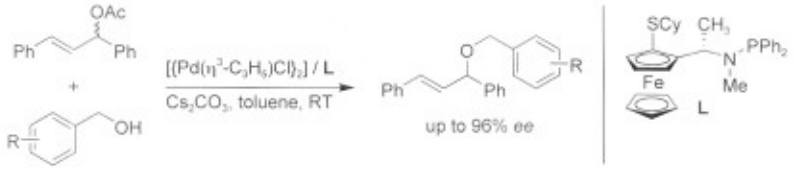


Metallopolymers

A new concept for fabricating nanocarriers carrying free DNA for gene delivery to overcome the intracellular dissociation barrier of cationic polymer/DNA complexes is presented. Free DNA plasmids (shown in green) are encapsulated in a nanocapsule core, which is protected by a hydrophobic membrane (purple) with a poly(ethylene glycol) outer layer (blue). The nanocapsules can release free DNA into the cells and have high in vitro and in vivo transfection efficiency.

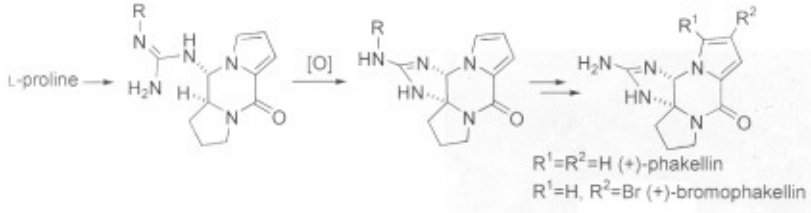
Gene Delivery

Contents



Asymmetric Catalysis

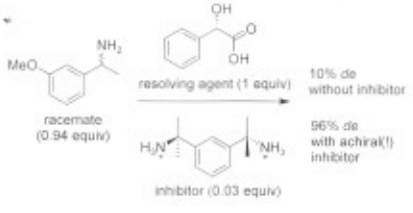
An enantioselective C–O bond-forming reaction proceeds well under palladium catalysis with newly developed N–P,S ligands with a ferrocene motif (see scheme). Nonconjugated substituents on the benzylic alcohol substrate lead to an increase in enantioselectivity with increasing electron-donating ability in the title reaction with racemic 1,3-diphenyl-2-propenyl acetate. Cy = cyclohexyl.



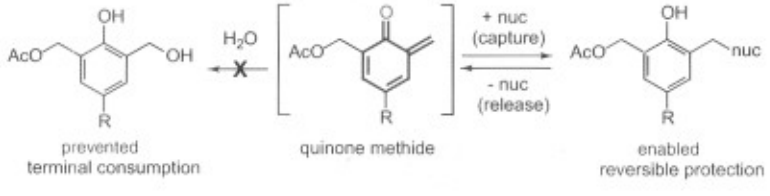
Alkaloid Synthesis

A unique oxidative cyclization of a tricycle bearing a guanidine aminal provides a concise route to the enantioselective synthesis of (+)-phakellin and (+)-monobromophakellin in nine and ten steps, respectively, starting from L-proline (see scheme). This sequence provides a simple annulation strategy applicable to the preparation of more complex members of this family of marine sponge-derived alkaloids including palau'amine.

You say you want a resolution: Nucleation inhibitors for the resolution of diastereomers by selective crystallization have been designed and tested. The resolution of racemic 3-methoxyphenylethylamine was optimized with (*S*)-mandelic acid as the resolving agent (see scheme). Multifunctional inhibitors are particularly effective.



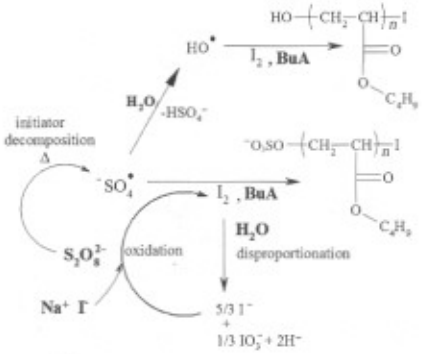
Resolution of Diastereomers



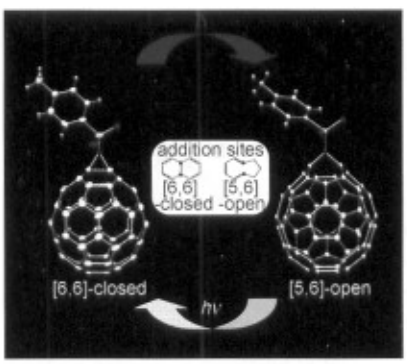
Quinone Methides

Who wants to live forever? Compounds that act as strong nucleophiles and good leaving groups repeatedly capture and release a transient quinone methide to extend its effective lifetime under aqueous conditions and promote DNA cross-linking (see scheme). This finding may expand the biological and therapeutic activity of quinone methides.

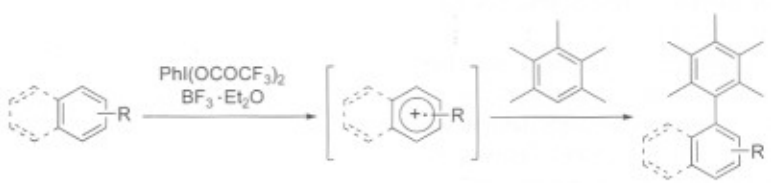
Contents



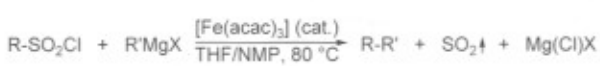
Iodide does the job: Water-soluble, harmless, cheap, and nonhazardous NaI was used in combination with $K_2S_2O_8$ instead of I_2 itself to produce an uncolored living poly(butyl acrylate) latex of controlled molecular weight by a single-step polymerization process (see scheme for one polymerization pathway). Reactivation of the polymer then yielded a block-copolymer latex. BuA = butyl acrylate.



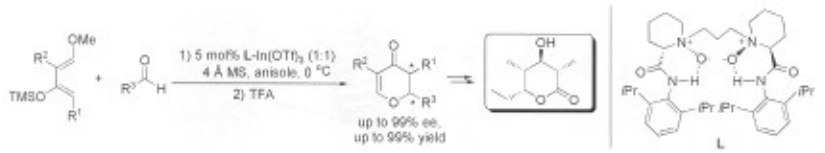
An open and closed case: The reversible interconversion of a [1,2]aziridinofullerene and a [1,6]azafulleroid represents the first such example for a monosubstituted fullerene. While the [1,2]aziridinofullerene rearranges thermally to the [1,6]azafulleroid, the [1,6]azafulleroid rearranges photochemically to the [1,2]aziridinofullerene in high yield (see picture).



Cross-coupling goes green: The direct oxidative cross-coupling reaction of naphthalenes and other electron-rich arenes with mesitylenes has been achieved in high yields using hypervalent iodine(III) reagents. The key for reaction success is the exclusive generation of cation radical intermediates of naphthalenes and the use of mesitylenes as the reactive and less dimerizable nucleophiles. R = alkyl, aryl, halogen, ester, alkoxy, etc.

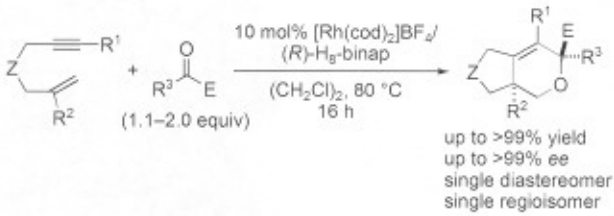


A friendly couple: Conditions have been uncovered that allow the desulfinylative C–C cross-coupling reaction of inexpensive sulfonyl chlorides and Grignard reagents (see scheme, acac = acetylacetonate, NMP = *N*-methylpyrrolidone). The reactions rely on environmentally friendly iron catalysts and do not require expensive and/or toxic ligands.



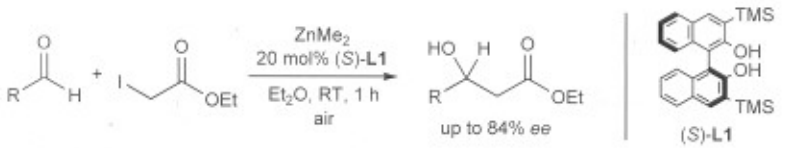
Asymmetric Catalysis

In-teresting catalyst: An asymmetric hetero Diels–Alder reaction between Danishefsky's dienes and various aldehydes using an *N*,*N*'-dioxide/In(OTf)$_3$ complex affords highly substituted chiral dihydropyranones with up to 99% *ee* (see scheme). The catalyst was applied to the synthesis of triketide from propionaldehyde in 72% yield and with 97% *ee*.



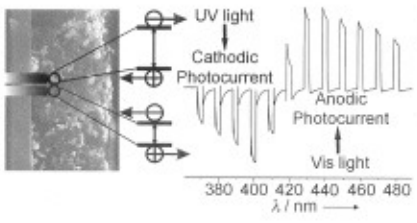
Asymmetric Catalysis

Two quaternary carbon centers are created in the title reaction to form fused dihydropyrans (see scheme). The same catalyst promotes the *ortho* functionalization of aryl ketones with 1,6-enynes with excellent regio- and enantioselectivity. Z = amide, C(CO$_2$Me)$_2$, O; E = CO$_2$Et, Ac; R^1 = Me, aryl, CO$_2$Me; R^2 = Me; R^3 = Me, CO$_2$Et.



Asymmetric Catalysis

120 years after the discovery of the Reformatsky reaction, the first effective catalytic enantioselective Reformatsky reaction with aldehydes using a binol derivative as a chiral catalyst is presented (see scheme; TMS = trimethylsilyl). The reaction is performed with ethyl iodoacetate and Me$_2$Zn. The presence of air is found to be crucial to reach high conversions and selectivities.



Photoelectrochemistry

A light switch: A nanocrystalline hybrid photoelectrode consisting of nitrogen-modified titanium dioxide (an n-type semiconductor) and copper(I) iodide (a p-type semiconductor) on conducting glass shows wavelength-controlled switching of the photocurrent in the narrow range from 410 to 420 nm (see picture).

Contents

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

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

There was a small error in the second sentence on page 8576 of this Communication. This sentence should read: "The ratio of intensities of acetylene to aromatic peaks was calculated using variable-contact-time ^{1}H–^{13}C CP/MAS NMR spectra with the following results: CMP-1 0.27 (expected value 0.40); CMP-2 0.18 (expected value 0.25); CMP-3 0.10 (expected value 0.18)."
The authors apologize for this error and wish to note that none of the interpretations in the paper are affected by this change.

Conjugated Microporous Poly(aryleneethynylene) Networks

J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper* **8574–8578**

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Vacancy