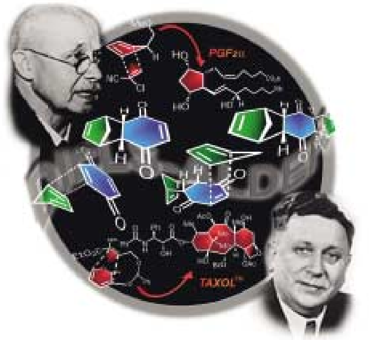
ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker
INTERNATIONAL EDITION

2002
41/10
Pages 1629–1808

COVER PICTURE

The cover picture shows portraits of Otto Diels (top left) and Kurt Alder together with the original Diels–Alder reaction between cyclopentadiene and *p*-quinone. Also illustrated are the key Diels–Alder reactions that enabled the total synthesis of prostaglandins and taxol as they were carried out by the research groups of Corey and Nicolaou, respectively. This year marks the centennial anniversary of Alder's birth—and this date will be celebrated at Alder's University, the Universität Köln, by a symposium on the 27th May—while last year was the 125th anniversary of the birth of Diels and next year will signify the 75th anniversary of the first publication of Diels and Alder on the reaction of 1,3-dienes with olefins. The Diels–Alder reaction, as it has become known, is without doubt one of the most important reaction of organic syntheses, and thus it is a bonanza that Corey and Nicolaou et al. have written appropriate reviews, which can be found on pp. 1650–1667 and 1668–1698, respectively.

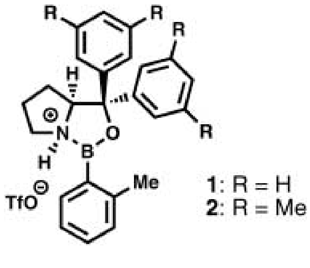


REVIEWS

Contents

One century after the birth of Kurt Alder and 75 years after the discovery of his famous reaction, research on the Diels–Alder process continues to surprise, excite, and delight the chemical community. The reader is taken on an exciting journey into how chiral Lewis acids, including the new cationic Lewis acids **1** and **2**, have transformed the Diels–Alder reaction into a highly enantioselective process.

Angew. Chem. **2002**, *114*, 1724–1741



E. J. Corey* 1650–1667

Catalytic Enantioselective Diels–Alder Reactions: Methods, Mechanistic Fundamentals, Pathways, and Applications

Keywords: asymmetric catalysis · chiral ligands · cycloaddition · Lewis acids · transition states

On the occasion of the 100th anniversary of Alder's birth, the authors tell, in a didactic style and through a series of stunning examples of natural-product syntheses, including some from their own laboratories, the thrilling story of how the venerable Diels–Alder reaction enabled and shaped the art and science of total synthesis (see scheme) in the last half century.

Angew. Chem. **2002**, *114*, 1742–1773

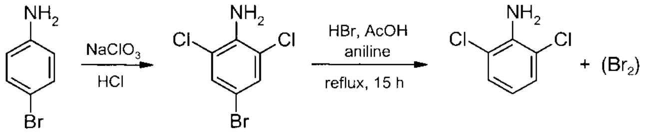
K. C. Nicolaou,* S. A. Snyder,
T. Montagnon,
G. E. Vassilikogiannakis 1668–1698

The Diels–Alder Reaction in Total Synthesis

Keywords: biomimetic synthesis · cascade reaction · cycloaddition · Diels–Alder reaction · total synthesis

HIGHLIGHTS

The reversibility of electrophilic bromination of aromatic compounds has been known for a long time, but the possibility of using bromine as a protecting group in aromatic or heterocyclic chemistry has now been shown for the first time (see scheme for an example). Compared with typical protective groups (SO_3H, COOH, NH_2, $CHMe_2$, CMe_3) bromine offers many advantages; a decisive aspect for its successful application is the choice of optimized reaction conditions which are predictable from the reaction mechanism.



Angew. Chem. **2002**, *114*, 1775–1776

F. Effenberger* 1699–1700

How Attractive is Bromine as a Protecting Group in Aromatic Chemistry?

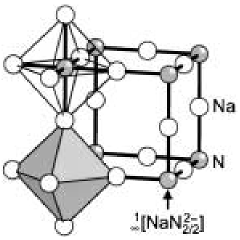
Keywords: arenes · bromine · electrophilic subsitution · protecting groups · reversibility

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

The First Method for Achieving Palladium-Catalyzed Cross-Couplings of Simple Alkyl Chlorides: Suzuki Reactions Catalyzed by $[Pd_2(dba)_3]/PCy_3$	J. H. Kirchhoff, C. Dai, G. C. Fu* ◆
Catalytic Activity and Poisoning of Specific Sites on Supported Metal Nanoparticles	J. Hoffmann, V. Johánek, J. Hartmann, J. Libuda,* H.-J. Freund
Understanding Zeolite Catalysis: Inverse Shape Selectivity Revised	M. Schenk, S. Calero, T. L. M. Maesen, L. L. van Benthem, M. G. Verbeek, B. Smit*
Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids	L. C. Branco, J. G. Crespo, C. A. M. Afonso*
Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids	D. Yang,* S. Gu, H.-W. Zhao, N.-Y. Zhu

The game of hide and seek is over: The existence of a binary sodium nitride Na_3N (see structure) has been the subject of speculation for a long time. Recently, through a novel experimental method, the synthesis and structural characterization of this compound has been successful. The compound crystallizes in the unexpected anti-Re_3O structure type.



Angew. Chem. **2002**, *114*, 1777 – 1778

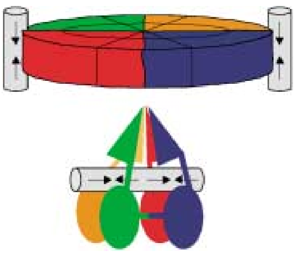
R. Niewa* .... 1701 – 1702

Na_3N—An Original Synthetic Route for a Long Sought After Binary Nitride

Keywords: alkali metals · nitrides · solid-state reactions · structure elucidation

---

Despite the high pharmaceutical relevance of the important tumor-suppressor protein p53, its mechanism of activation is still unclear. A recent paper now sheds light on some of the structural features associated with the activation of p53 and its binding to DNA. On the basis of these results, a “sandwich” model for the interaction of p53 with DNA was proposed (top) to replace the long-favored “clamp model” (bottom).



Angew. Chem. **2002**, *114*, 1778 – 1780

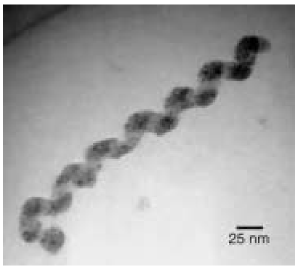
P. Chene, W. Jahnke* .... 1702 – 1704

Oligomerization of p53 upon Cooperative DNA Binding: Towards a Structural Understanding of p53 Function

Keywords: DNA recognition · NMR spectroscopy · protein – protein interactions · tumor suppression

COMMUNICATIONS

Helices on helices: Nanohelices of polycrystalline cadmium sulfide (see transmission electron micrograph) have been made by the mineralization of helical self-assembled objects shaped like twisted ribbons. The coiled morphology of the inorganic helices apparently results from growth on only one face of the organic ribbon template.



Angew. Chem. **2002**, *114*, 1781 – 1785

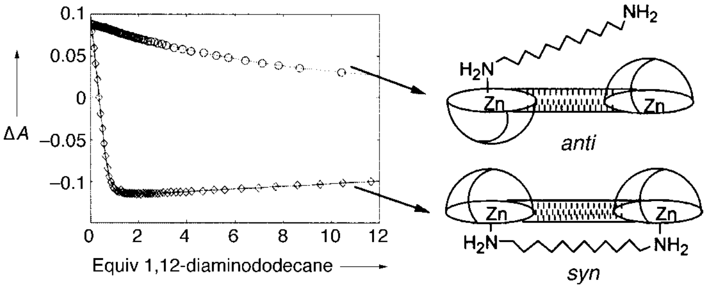
E. D. Sone, E. R. Zubarev,
S. I. Stupp* .... 1705 – 1709

Semiconductor Nanohelices Templated by Supramolecular Ribbons

Keywords: cadmium sulfide · mineralization · nanostructures · self-assembly · template synthesis

---

The power of supramolecular chemistry to solve problems in structural chemistry where conventional techniques such as NMR, UV, and IR spectroscopy failed is demonstrated in the differentiation of the *syn*- and *anti*-bis(capped porphyrin) isomers (obtained after condensation of a capped porphyrin monomer) by simple UV/Vis binding studies using bidentate ligands that act as “molecular rulers” (see picture).



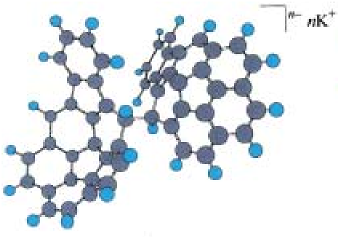
Angew. Chem. **2002**, *114*, 1785 – 1788

M. J. Crossley,*
P. Thordarson .... 1709 – 1712

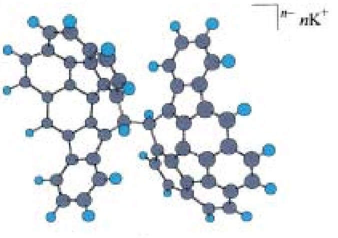
Assignment of Stereochemistry of Facially Protected Bis-porphyrins by Use of a “Molecular Ruler”

Keywords: bridging ligands · capped porphyrins · configuration determination · molecular recognition · porphyrinoids

A reduction cascade: The reduction of indenocorannulene by potassium leads to the formation of the diastereomeric dimers **1** and/or **2**; this is the first case of reductive dimerization of a large nonplanar polycyclic aromatic hydrocarbon. The twofold formation of these dimers, and their dissociation to the monomeric species, was monitored by NMR spectroscopic methods.



1 $n = 2,6$



2 $n = 2,6$

Angew. Chem. **2002**, *114*, 1788–1791

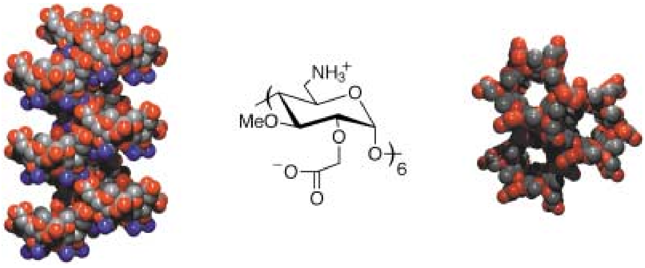
I. Aprahamian, R. E. Hoffman,
T. Sheradsky, D. V. Preda, M. Bancu,
L. T. Scott, M. Rabinovitz* 1712–1715

A Four-Step Alternating Reductive Dimerization/Bond Cleavage of Indenocorannulene

Keywords: dimerization • NMR spectroscopy • polyanions • polycycles • reduction

---

A zwitterionic α-cyclodextrin amino acid (picture, middle) undergoes solid-state self-assembly to give a novel helical column architecture (left), which is cross-linked by hydrogen bonds into an array of parallel straight channels (right). Surprisingly, no hydrogen bonds are formed between proximate cyclodextrin units in the individual channels.



Angew. Chem. **2002**, *114*, 1791–1793

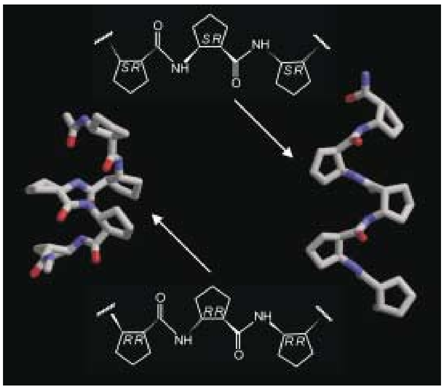
T. Kraus,* M. Buděšínský, I. Císařová,
J. Závada* 1715–1717

Per(6-amino-2-*O*-carboxymethyl-6-deoxy-3-*O*-methyl)-α-cyclodextrin: Helical Self-Assembly of a Polyionic Amino Acid into Nanotubes

Keywords: amino acids • cyclodextrins • helical structures • hydrogen bonds • self-assembly

---

Rational control over helix and strand secondary structures is possible when conformationally restricted cyclic β-amino acid residues are incorporated in the β-peptides. Inversion of the relative configuration of these residues enables the preferred periodic structure to be switched from a helix to a single nonpolar strand (see picture).



Angew. Chem. **2002**, *114*, 1794–1797

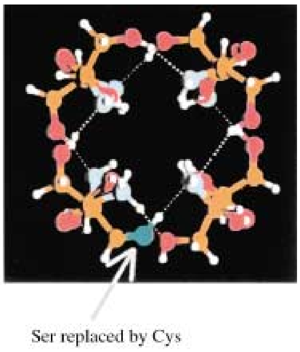
T. A. Martinek, G. K. Tóth, E. Vass,
M. Hollósi, F. Fülöp* 1718–1721

cis-2-Aminocyclopentanecarboxylic Acid Oligomers Adopt a Sheetlike Structure: Switch from Helix to Nonpolar Strand

Keywords: amino acids • chirality • conformation analysis • NMR spectroscopy • peptides

---

Chiral exchange: Substitution of cysteine for serine in the homochiral serine octamer (see calculated structure) occurs in a chirally dependent fashion and may represent an example of transfer of chirality between primitive biological molecules. The findings are supported by HF/6-31G calculations.



Angew. Chem. **2002**, *114*, 1797–1800

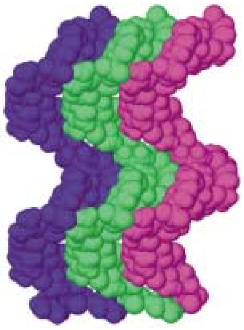
K. J. Koch, F. C. Gozzo, S. C. Nanita,
Z. Takats, M. N. Eberlin,
R. G. Cooks* 1721–1724

Chiral Transmission between Amino Acids: Chirally Selective Amino Acid Substitution in the Serine Octamer as a Possible Step in Homochirogenesis

Keywords: amino acids • chirality • mass spectrometry • molecular evolution • supramolecular chemistry

Like spiral staircases connecting the floors of a building, twisted chiral organic "pillars" link hydrogen-bonded guanidinium sulfonate sheets and produce extended supramolecular helices (see picture) that wind through crystals with predictable three-dimensional architectures.

Angew. Chem. **2002**, *114*, 1800–1804



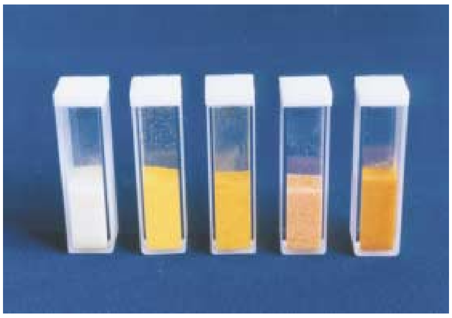
R. Custelcean, M. D. Ward* 1724–1728

Hydrogen-Bonded Helices in Crystals with Prescribed Organization

Keywords: crystal engineering · helical structures · hydrogen bonds · inclusion compounds · self-assembly

---

A combination of nucleophilic aromatic substitution of fluorine by amino groups with a sol–gel process leads to the synthesis of organic-functionalized hybrid gels by a one-pot method based on silicates. The sol–gel reaction is catalyzed by hydrofluoric acid formed after addition of ethanol and water. The picture shows a selection of the dried gels.



Angew. Chem. **2002**, *114*, 1805–1808

S. Spange,* A. Seifert, H. Müller,
S. Hesse, C. Jäger 1729–1732

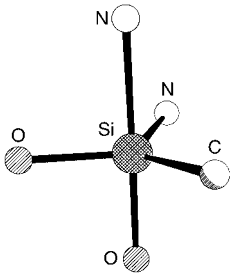
A One-Pot Synthesis of Chromophoric Silicate-Based Xerogels

Keywords: fluoroarenes · nucleophilic substitution · silicates · sol–gel processes · synthetic methods

---

Ligands with enamine structures can be surprisingly well stabilized in pentacoordinate silicon complexes. These novel coordination complexes contain a central Si atom in a trigonal-bipyramidal coordination environment, surrounded by a threefold-deprotonated salen ligand (2 × N, 2 × O, see structure). The complexes are starting materials for the synthesis of novel compounds containing hexacoordinate Si atoms by acid-addition reactions.

Angew. Chem. **2002**, *114*, 1825–1827



J. Wagler, U. Böhme,
G. Roewer* 1732–1734

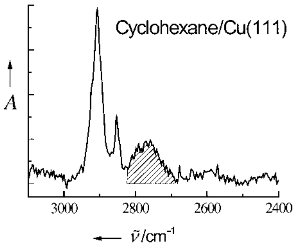
Silicon–Enamine Complexes: Pentacoordinate Silicon Compounds

Keywords: chelates · hypervalent compounds · N,O ligands · Schiff bases · silicon

---

On contact with transition metals, saturated hydrocarbons reveal pronounced red shifts in the C–H stretching region in their IR spectra (shaded region in picture), which are discussed in connection with C–H activation. Detailed ab initio calculations for cyclopropane and cyclohexane on a Cu surface suggest that this anomaly is caused by an unexpected chemical interaction.

Angew. Chem. **2002**, *114*, 1811–1814

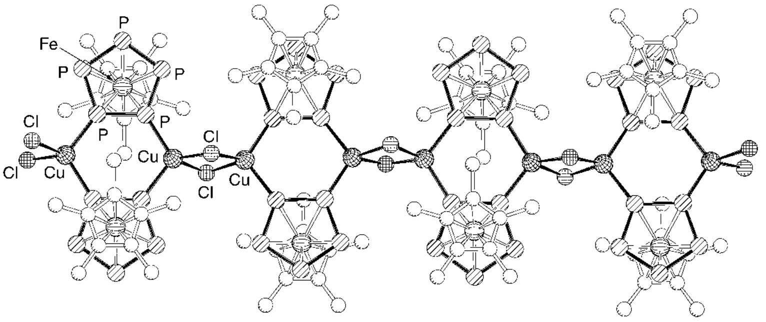


K. A. Fosser, R. G. Nuzzo, P. S. Bagus,
C. Wöll* 1735–1737

The Adsorption of Cyclopropane and Cyclohexane on Cu(111): An Experimental and Theoretical Investigation on the Nature of the CH–Metal Interaction

Keywords: ab initio calculations · adsorption · alkanes · IR spectroscopy · surface chemistry

Different copper halide, different copper product: The *cyclo*-P_5-ligand complex $[Cp^*Fe(\eta^5-P_5)]$ (**1**; $Cp^* = C_5Me_5$) reacts with CuBr and CuI to give two-dimensional networks in which **1** is the linking unit. However, a novel one-dimensional-chain coordination polymer (see picture) is formed with CuCl.



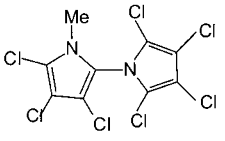
Angew. Chem. **2002**, *114*, 1808–1811

J. Bai, A. V. Virovets,
M. Scheer* 1737–1740

Pentaphosphaferrocene as a Linking Unit for the Formation of One- and Two-Dimensional Polymers

Keywords: coordination polymers • copper • iron • phosphorus • P ligands

Which organism produces it? The natural product Q1 is 64 % chlorine and every third atom is a halogen, but the source of Q1 is unknown. Synthetic Q1, made for the first time, has identical chromatographic and spectroscopic properties to those of Q1 extracted from environmental samples.



Q1

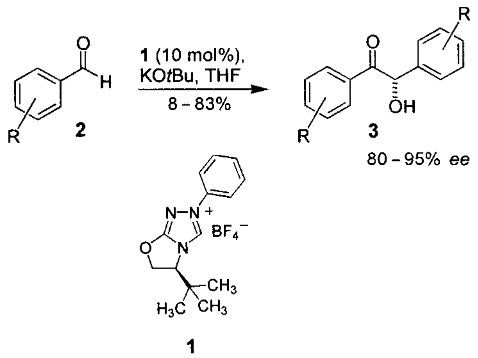
Angew. Chem. **2002**, *114*, 1814–1817

J. Wu, W. Vetter,* G. W. Gribble,*
J. S. Schneekloth, Jr., D. H. Blank,
H. Görls 1740–1743

Structure and Synthesis of the Natural Heptachloro-1′-methyl-1,2′-bipyrrole (Q1)

Keywords: chlorine • halogenation • natural products • nitrogen heterocycles • structure elucidation

The chiral bicyclic triazolium salt 1 is currently the most efficient precatalyst for the asymmetric benzoin condensation. The substituted acyloins **3** are obtained in moderate to good yields and with very good enantiomeric excesses from the corresponding aldehydes **2**. The high asymmetric induction is presumably based on the conformational rigidity of the bicyclic nucleophilic carbene catalyst and on the steric hindrance of the *tert*-butyl group in the Breslow intermediate.



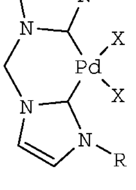
Angew. Chem. **2002**, *114*, 1822–1824

D. Enders,* U. Kallfass 1743–1745

An Efficient Nucleophilic Carbene Catalyst for the Asymmetric Benzoin Condensation

Keywords: acyloins • asymmetric catalysis • benzoin condensation • carbenes • triazolium salts

Palladium complexes with N-heterocyclic carbenes, such as in the biscarbene chelate ligands shown (R = *t*Bu, Me; X = Br, I), have proved to be stable in strongly acidic media and were tested in the catalytic conversion of methane into methanol. The prominent influence of the halogenide ligand is shown since, in contrast to the bromo complex, the iodo complex does not catalyze the reaction. The steric bulk of the substituents R also influences the catalytic activity.



Angew. Chem. **2002**, *114*, 1817–1819

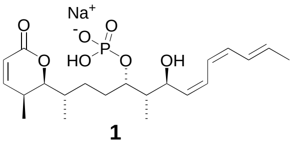
M. Muehlhofer, T. Strassner,*
W. A. Herrmann 1745–1747

New Catalyst Systems for the Catalytic Conversion of Methane into Methanol

Keywords: alkanes • carbenes • C–H activation • homogeneous catalysis • oxidation

1433-7851/02/4110-1637 $ 20.00+.50/0

Reagent-controlled reactions are key to the introduction of the stereocenters in the total synthesis of the cytostatin isomer **1**. The stereochemical flexibility of the synthesis allows efficient and convenient access to other isomers.



1

Angew. Chem. **2002**, *114*, 1819 – 1822

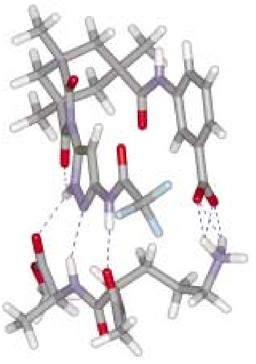
L. Bialy, H. Waldmann* .... 1748 – 1751

Synthesis of the Protein Phosphatase 2A Inhibitor (4*S*,5*S*,6*S*,10*S*,11*S*,12*S*)-Cytostatin

Keywords: inhibitors · natural products · phosphorylation · total synthesis

---

A toolkit of tailor-made peptide receptors contains building blocks for polar, aromatic, and cationic amino acids. Dipeptides are stabilized in the β-sheet conformation by complexation with an aminopyrazole which carries a U-shaped substituent with a properly placed binding site at its tip (see picture). The additional interaction with the amino acid side chain leads to a tenfold increase in the association constant.



Angew. Chem. **2002**, *114*, 1827 – 1831

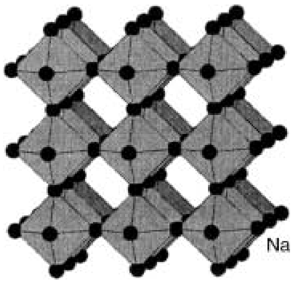
M. Wehner, T. Schrader* ... 1751 – 1754

Modular Building Blocks for Amino Acid Recognition in Peptides

Keywords: amino acids · host – guest systems · molecular recognition · peptides · receptors

---

After a long search the elusive compound Na_3N (see structure) has been synthesized for the first time, starting from the elements dispersed on an atomic level, by a solid-state reaction at extremely low temperatures. The metastable compound crystallizes in the anti-ReO_3 structure type and decomposes into the elements at 360 K.



Angew. Chem. **2002**, *114*, 1831 – 1833

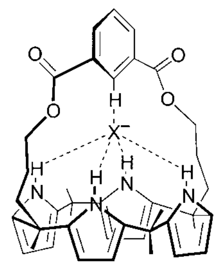
D. Fischer, M. Jansen* ...... 1755 – 1756

Synthesis and Structure of Na_3N

Keywords: alkali metals · nitrides · solid-state reactions · structure elucidation

---

Enhanced affinity and selectivity for halide anions is seen for the strapped calix[4]pyrrole (see picture, $X^- = F^-$, Cl^-) relative to normal calix[4]pyrroles. The encapsulated binding site differentiates the anions on the basis of size, and the existence of hydrogen-bonding interactions between the aromatic proton and halide anions has been verified by ^1H NMR spectroscopy. A binding constant of approximately 3.87×10^6 M was found for the fluoride complex.



Angew. Chem. **2002**, *114*, 1835 – 1837

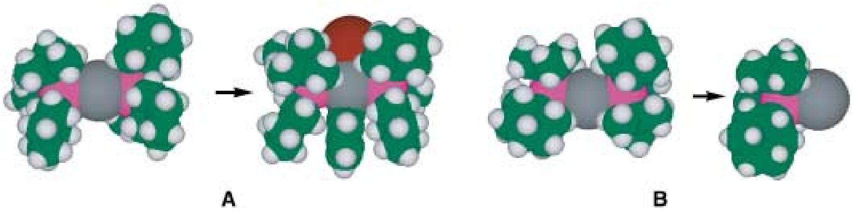
D.-W. Yoon, H. Hwang,
C.-H. Lee* .... 1757 – 1759

Synthesis of a Strapped Calix[4]pyrrole: Structure and Anion Binding Properties

Keywords: anions · calixpyrroles · hydrogen bonds · macrocycles · molecular recognition

---

The steric bulk of the phosphane ligand determines the mechanism of the ArX addition to zero-valent $[PdL_2]$ complexes. This effect has been studied by variation of ligands (catalyst: $[Pd(PCx_ntBu_{3-n})_2]$; $n = 0-3$, Cx = cyclohexyl) in Pd couplings of unsaturated electrophiles, and different reaction pathways (A = associative, B = dissociative) identified, depending on the size of the ligand.



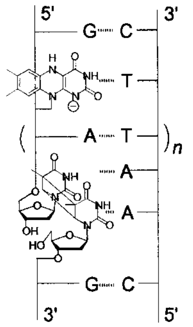
Angew. Chem. **2002**, *114*, 1838 – 1841

E. Galardon, S. Ramdeehul,
J. M. Brown,* A. Cowley,
K. K. (Mimi) Hii, A. Jutand 1760 – 1763

Profound Steric Control of Reactivity in Aryl Halide Addition to Bisphosphane Palladium(0) Complexes

Keywords: cross-coupling · palladium · phosphane ligands · reaction mechanisms · steric hindrance

Remote reductive repair of thymine dimers in a DNA duplex by transfer of excess electrons over a distance of up to roughly 24 Å ($n = 7$) has been attributed to thermally activated hopping (see scheme). Possible consequences for humans: the harmful effect of UV irradiation responsible for the development of skin cancer could potentially be reduced by compounds that bind to DNA and trigger long-range electron transport.



Angew. Chem. **2002**, *114*, 1841–1844

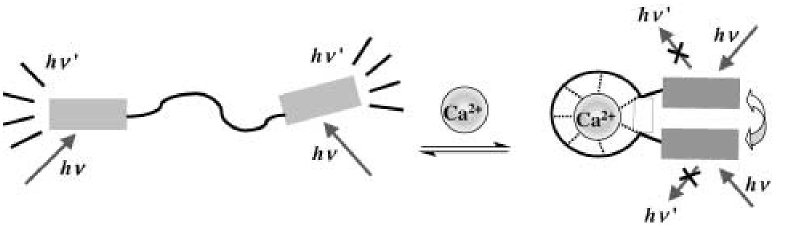
C. Behrens, L. T. Burgdorf, A. Schwögler, T. Carell* 1763–1766

Weak Distance Dependence of Excess Electron Transfer in DNA

Keywords: bioorganic chemistry • DNA repair • electron transfer • photolyase

---

Selective, sensitive cation capture: A bichromophoric "H"-foldamer (rigid-flexible-rigid) demonstrates a cation-steered exciton interaction (see figure; the interaction is denoted by the double-headed arrow) and thereby allows the selective signaling of Ca^{2+}-ion binding among Na^+, K^+, and Mg^{2+} ions. The binding can be observed with the naked eye, as well as by absorption, emission, and ^1H NMR spectral changes. An analogous monochromophore (flexible-rigid-flexible) failed to signal any of the binding events.



Angew. Chem. **2002**, *114*, 1844–1847

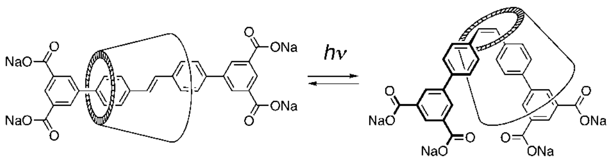
A. Ajayaghosh,* E. Arunkumar, J. Daub 1766–1769

A Highly Specific Ca^{2+}-Ion Sensor: Signaling by Exciton Interaction in a Rigid–Flexible–Rigid Bichromophoric "H" Foldamer

Keywords: aggregation • calcium • chromophores • host–guest systems • sensors

---

Up and down the dumbbell: Photoisomerization of a stilbene rotaxane results in relocation of the cyclodextrin macrocycle in just one direction (see scheme). This behavior, and that of related rotaxanes, sheds light on the mechanism of shuttling in molecular machines.



Angew. Chem. **2002**, *114*, 1847–1850

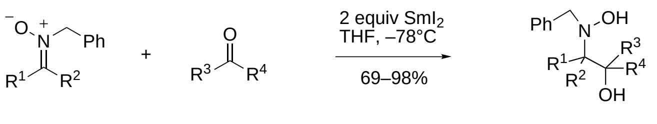
C. A. Stanier, S. J. Alderman, T. D. W. Claridge, H. L. Anderson* 1769–1772

Unidirectional Photoinduced Shuttling in a Rotaxane with a Symmetric Stilbene Dumbbell

Keywords: cyclodextrins • molecular devices • photoisomerization • rotaxanes • stilbene

---

Highly substituted amino alcohols or *N*-hydroxyamino alcohols can be prepared in good yield through a novel reductive cross-coupling of nitrones with aldehydes or ketones (see scheme). The reactions are fast and highly chemoselective, that is, no homocoupling or reduction products are formed.



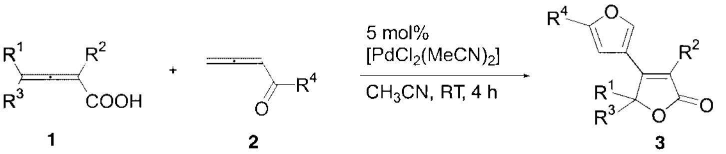
Angew. Chem. **2002**, *114*, 1850–1853

G. Masson, S. Py,* Y. Vallée* 1772–1775

Samarium Diiodide-Induced Reductive Cross-Coupling of Nitrones with Aldehydes and Ketones

Keywords: amino alcohols • C–C coupling • cross-coupling • nitrones • samarium

The active Pd^{II} catalyst in the efficient oxidative cyclization/dimerization reaction between 2,3-allenoic acids **1** and 1,2-allenyl ketones **2** to give 4-(3′-furanyl)-butenolide derivatives **3** may be regenerated from Pd^0 after a cyclometalation/protonolysis step in the catalytic cycle.



Angew. Chem. **2002**, *114*, 1853–1856

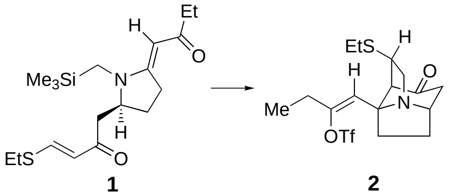
S. Ma,* Z. Yu 1775–1778

Oxidative Cyclization–Dimerization Reaction of 2,3-Allenoic Acids and 1,2-Allenyl Ketones: An Efficient Synthesis of 4-(3′-Furanyl)butenolide Derivatives

Keywords: allenes · butenolides · carboxylic acids · cyclization · dimerization

---

An important precursor to the bridged pyrrolizidine core **2** of asparagamine A is vinylogous amide **1**. The key reaction in the synthesis of **2** is an intramolecular 1,3-dipolar cycloaddition of an azomethine ylide derived from the sulfonylation of **1**. A variety of highly functionalized pyrrolidines, pyrrolizidines, and indolizidines can be prepared from vinylogous amides such as **1**. Tf = trifluoromethanesulfonyl.



Angew. Chem. **2002**, *114*, 1856–1858

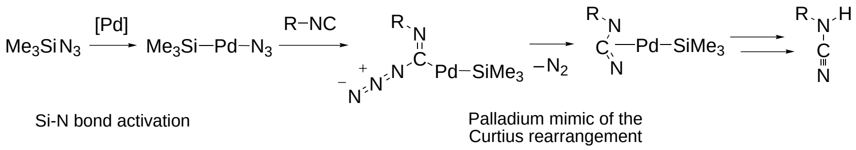
M. T. Epperson, D. Y. Gin* 1778–1780

Enantiospecific Synthesis of the Bridged Pyrrolizidine Core of Asparagamine A: Dipolar Cycloadditions of Azomethine Ylides Derived from the Sulfonylation of Vinylogous Amides

Keywords: amides · azomethine ylides · cycloaddition · natural products · synthetic methods

---

A palladium mimic of the Curtius rearrangement and a palladium-catalyzed geminal addition of a Si–N bond occurs in the high-yielding synthesis of cyanamides from isocyanides and trimethylsilyl azide in the presence of a palladium catalyst (see scheme). A wide range of functional groups are tolerated in the reaction.



Angew. Chem. **2002**, *114*, 1858–1860

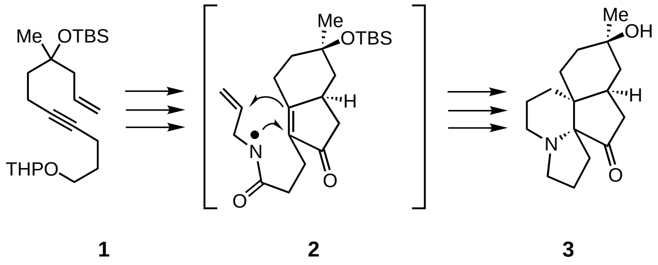
S. Kamijo, T. Jin, Y. Yamamoto* 1780–1782

Cyanamide Synthesis by the Palladium-Catalyzed Cleavage of a Si–N Bond

Keywords: cyanamides · homogeneous catalysis · isocyanides · palladium · rearrangement

---

A short and efficient total synthesis of (±)-13-deoxyserratine (**3**) features a highly stereoselective intramolecular Pauson–Khand reaction of **1** and a cascade of radical cyclizations starting with the amidyl radical **2**. The desired alkaloid **3** was thus obtained in ten steps in an overall yield of 12%. THP = tetrahydropyranyl, TBS = *tert*-butyldimethylsilyl.



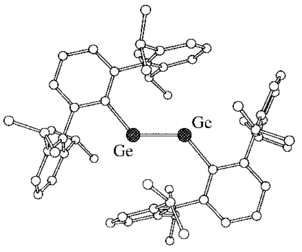
Angew. Chem. **2002**, *114*, 1861–1863

J. Cassayre, F. Gagosz, S. Z. Zard* 1783–1785

A Short Synthesis of (±)-13-Deoxyserratine

Keywords: alkaloids · indolizidines · Pauson–Khand reaction · radical reactions · total synthesis

Multiple Ge–Ge bonds: The title compound, which has a *trans*-bent structure (see structure; Ge-Ge-C = 128.67(8)°) and a short Ge–Ge bond (2.2850(5) Å), is the first stable digermanium analogue of an alkyne.



Angew. Chem. **2002**, *114*, 1863 – 1865

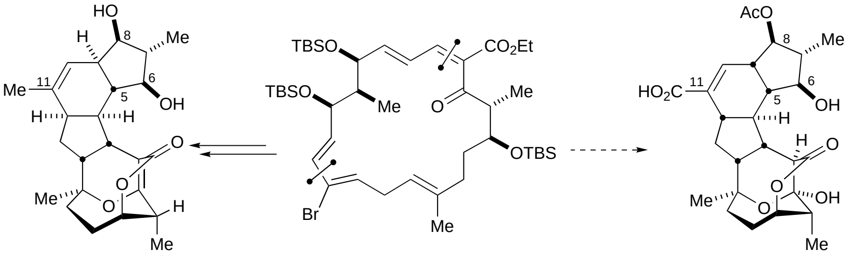
M. Stender, A. D. Phillips, R. J. Wright, P. P. Power* .... 1785 – 1787

Synthesis and Characterization of a Digermanium Analogue of an Alkyne

Keywords: alkynes · digermyne · germanium · multiple bonds · structure elucidation

---

A tandem transannular [4+2] cycloaddition strategy is presented for the synthesis of the class of natural products containing FR182877 (**1**) and hexacyclinic acid (**2**). As part of this program, a tandem transannular [4+2] cycloaddition reaction has been employed in the enantioselective synthesis of (−)-FR182877 (**1**) via the macrocyclic precursor (**3**).



1 **3** **2**

Angew. Chem. **2002**, *114*, 1865 – 1868

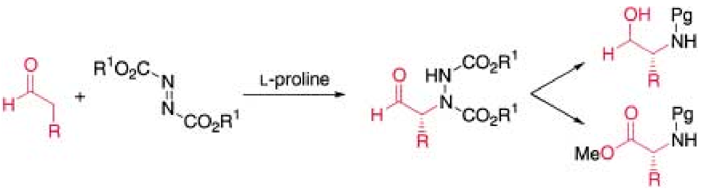
D. A. Evans,* J. T. Starr ..... 1787 – 1790

A Cascade Cycloaddition Strategy Leading to the Total Synthesis of (−)-FR182877

Keywords: asymmetric synthesis · cycloaddition · macrocycles · natural products

---

L-Proline as the catalyst: The first direct asymmetric α-amination of aldehydes using L-proline as the catalyst is presented (see scheme; Pg = protecting group). This new reaction gives easy access to optically active α-amino aldehydes, α-amino alcohols, and α-amino acids from simple and easily available starting materials and catalysts. The reactions proceed in high yields and excellent enantioselectivities with as little as 2 mol% of the catalyst.



Angew. Chem. **2002**, *114*, 1868 – 1871

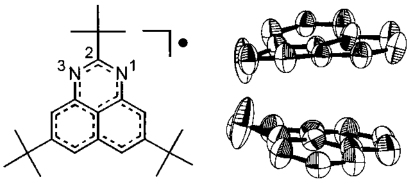
A. Bøgevig, K. Juhl, N. Kumaragurubaran, W. Zhuang, K. A. Jørgensen* .... 1790 – 1793

Direct Organo-Catalytic Asymmetric α-Amination of Aldehydes—A Simple Approach to Optically Active α-Amino Aldehydes, α-Amino Alcohols, and α-Amino Acids

Keywords: aldehydes · amino acids · amino alcohols · amino aldehydes · asymmetric catalysis

---

Stable gable radical: 1,3-Diazaphenalenyl radical, a typical example of an isoelectronic mode of modification for phenalenyl, has been isolated for the first time as a crystalline solid by introducing bulky substituents (see picture, *tert*-butyl groups are omitted from the crystal structure). The gable *syn* dimer with a column motif shows an extremely strong antiferromagnetic exchange coupling of $2J/k_B = -4.19(2) \times 10^3$ K.



Angew. Chem. **2002**, *114*, 1871 – 1874

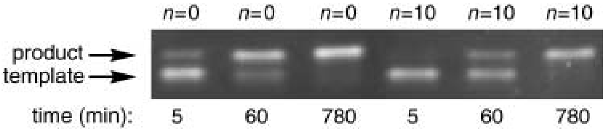
Y. Morita,* T. Aoki, K. Fukui, S. Nakazawa, K. Tamaki, S. Suzuki, A. Fuyuhiro, K. Yamamoto, K. Sato, D. Shiomi, A. Naito, T. Takui,* K. Nakasuji* .... 1793 – 1796

A New Trend in Phenalenyl Chemistry: A Persistent Neutral Radical, 2,5,8-Tri-*tert*-butyl-1,3-diazaphenalenyl, and the Excited Triplet State of the Gable *syn*-Dimer in the Crystal of Column Motif

Keywords: dimerization · magnetic properties · nitrogen heterocycles · radicals · steric hindrance

1433-7851/02/4110-1641 $ 20.00+.50/0

Powerful reactions such as Wittig olefinations, nitro-aldol additions, dipolar cycloadditions, and Heck coupling reactions can be mediated by DNA templates. The yields of several DNA-templated reaction products are independent of the number of bases ($n = 0$ or 10) separating the annealed reactive groups (as an example, the denaturing polyacrylamide gel electrophoresis of a DNA-templated Wittig reaction is shown).



Angew. Chem. **2002**, *114*, 1874–1878

Z. J. Gartner, M. W. Kanan,
D. R. Liu* 1796–1800

Expanding the Reaction Scope of DNA-Templated Synthesis

Keywords: coupling reactions · DNA · molecular evolution · synthetic methods · template synthesis

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

* Author to whom correspondence should be addressed

Accelerated publications

The cover picture was designed by Robbyn Echon and Scott Snyder.

BOOKS

WEB SITES

SERVICE

Don't forget all the Tables of Contents from 1998 onwards may be still found on the WWW under: http://www.angewandte.com

CORRIGENDUM

Note from the Editors: unfortunately the results reported in the communication “The Stable Pentamethylcyclopentadienyl Cation” by Joseph B. Lambert et al. in issue 8/2002 (pp. 1429–1431) must be corrected. Guy Bertrand et al. quickly discovered that not the pentamethylcyclopentadienyl cation but the pentamethylcyclopentenyl cation was prepared and characterized (the corresponding communication will be published in issue 13, and will appear earlier on the *Angewandte Chemie* homepage).