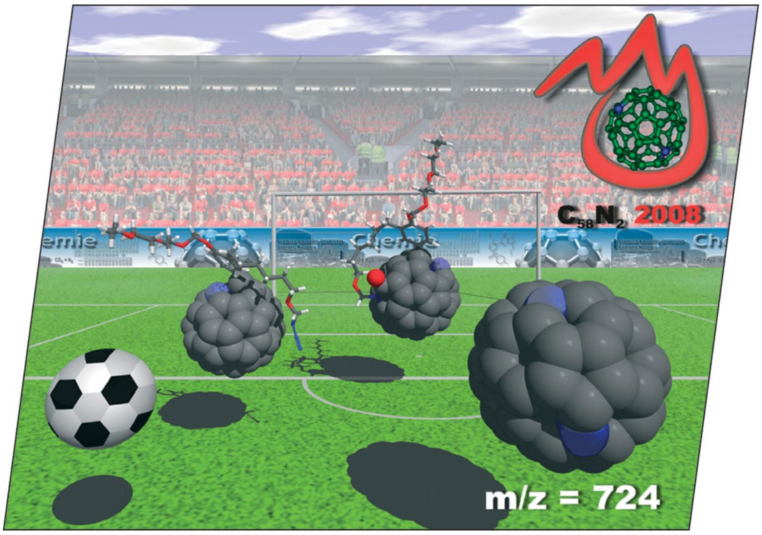
COVER PICTURE

The cover picture shows the synthetic pathway for the substitution of two carbon atoms of the fullerene C_{60} framework with two nitrogen atoms, bringing the new heterofullerene football $C_{58}N_2$ into play. The easily accessible $(C_{59}N)_2$ is used as a starting material for a tether-based functionalization sequence leading to a direct $C_{58}N_2$ precursor. The chemical transformation of this precursor molecule under the same conditions used for the introduction of one nitrogen atom leads to a reaction product that, according to FAB mass spectroscopic analysis, contains up to 20% of a $C_{58}N_2$ species. This represents the first strategic chemical synthesis of the $C_{58}N_2$ cage. Details are discussed in the article by A. Hirsch et al. on p. 4109ff. The authors acknowledge the support of this work by Dipl. Chem. Benjamin Gebhardt, who designed the cover page.



CONTENTS

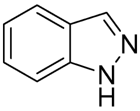
MICROREVIEW

Heterocyclic Chemistry

A. Schmidt,* A. Beutler,
B. Snovydovych 4073–4095

Recent Advances in the Chemistry of Indazoles

Keywords: Indazole alkaloids / Biological activities / Syntheses of indazoles / Functionalizations of indazoles / Indazol-3-ylidene / Indazolium salts



Indazoles are of great current interest which is due to their broad spectrum of biological activities. This review summarizes not only structures of pharmacologically interesting indazoles published during the last decade, but also syntheses, reactions and functionalizations. Recent advances in the field of derived *N*-heterocyclic carbenes, indazol-3-ylidenes, and indazolium salts are also reported.

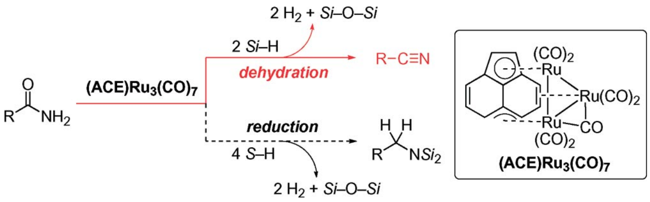
SHORT COMMUNICATIONS

Hydrosilanes for Dehydration

S. Hanada, Y. Motoyama,
H. Nagashima* 4097–4100

Hydrosilanes Are Not Always Reducing Agents for Carbonyl Compounds but Can Also Induce Dehydration: A Ruthenium-Catalyzed Conversion of Primary Amides to Nitriles

Keywords: Amides / Dehydration / Cyanides / Hydrosilanes / Ruthenium



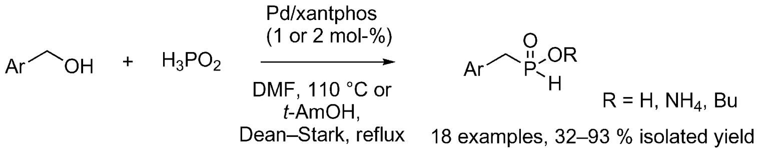
A practical procedure for production of nitriles is offered by the triruthenium carbonyl cluster catalyzed dehydration of primary carboxamides with hydrosilanes under neutral conditions. This is the first example that a transition-metal-catalyzed activation of Si–H bonds does not lead to the reduction of carbonyl compounds but to dehydration.

Cross-Coupling Reactions

L. Coudray,
J.-L. Montchamp* 4101–4103

Green, Palladium-Catalyzed Synthesis of Benzylic *H*-Phosphinates from Hypophosphorous Acid and Benzylic Alcohols

Keywords: Phosphorus / Cross-coupling / Organophosphorous compounds / Alcohols / Palladium / Homogeneous catalysis



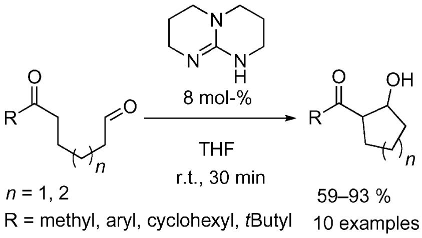
A green, PCl$_3$-free access to benzylic-*H*-phosphinic acids was developed from benzylic alcohols and H$_3$PO$_2$ by using Pd/xantphos. A range of benzylic alcohols react successfully to give moderate to good yields in *t*-AmOH at reflux with a Dean–Stark trap or in DMF at 110 °C. The preparation of phosphinic and phosphonic acids and the asymmetric reaction of a secondary alcohol are also demonstrated.

enolexo Aldolizations

C. Ghobril, C. Sabot, C. Mioskowski,
R. Baati* 4104–4108

TBD-Catalyzed Direct 5- and 6-*enolexo* Aldolization of Ketoaldehydes

Keywords: Aldol reactions / Carbocycles / Organocatalysis / Alcohols / Aldehydes

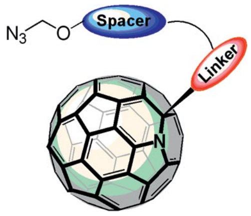


1,5,7-Triazabicyclo[4.4.0]dec-5-ene represents a new and very active class of organocatalysts for the direct 5-and 6-*enolexo* aldolization of unfunctionalized acyclic ketoaldehydes. The aldol addition products are obtained in good-to-excellent yields.

FULL PAPERS

From Mono- to Diaza[60]fullerenes

A new approach towards the synthesis of the elusive heterofullerene $C_{58}N_2$ is presented. The synthetic strategy is based on the intramolecular [3+2] addition of a spacer-linked azide to a monoazaheterofullerene ($C_{59}N$) core. One-pot experiments gave promising mass spectrometric results. Although isolation could not be achieved in this case, a major step forward towards this fascinating compound has been achieved.



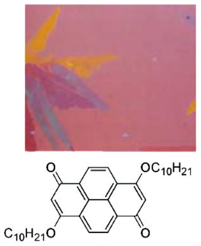
M. von Delius, F. Hauke, A. Hirsch* 4109–4119

Evaluation of an Intramolecular Approach for the Synthesis of the Elusive $C_{58}N_2$ Heterofullerene Family

Keywords: Fullerenes / Heterofullerenes / Azides / Molecular modelling / 1,3-Dipolar cycloaddition

Liquid Crystals

Discotic liquid crystalline π-acceptor compounds were synthesized by using *anti-* and *syn*-pyrenediones. The liquid crystalline phases were assigned to be D_{L2} from POM, DSC, and XRD measurements and single-crystal study of the model crystalline compounds.



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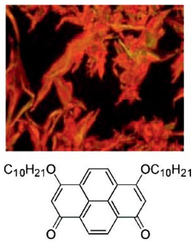


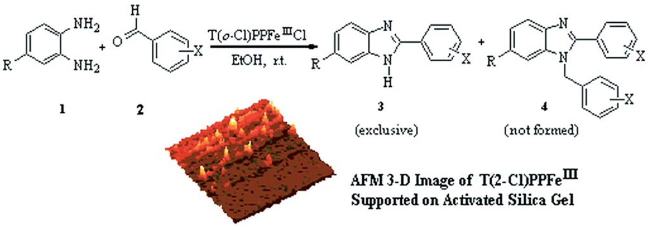
5c

M. Yasutake, T. Fujihara, A. Nagasawa, K. Moriya, T. Hirose* 4120–4125

Synthesis and Phase Structures of Novel π-Acceptor Discotic Liquid Crystalline Compounds Having a Pyrenedione Core

Keywords: Liquid crystals / Lamellar phase / Arenes / Fused-ring systems / Semiconductors

"Green" Oxidation Catalyst



AFM 3-D Image of T(2-Cl)PPFe^III Supported on Activated Silica Gel

A facile, one-pot, selective synthesis of 2-arylbenzimidazoles using immobilized (*meso*-tetrakis(*o*-chlorophenyl)porphyrinato)iron(III) on activated silica as a new heterogeneous and reusable catalyst in the presence of atmospheric air as a "green" oxidant at ambient temperature is described.

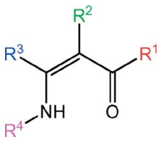
H. Sharghi,* M. H. Beyzavi, M. M. Doroodmand 4126–4138

Reusable Porphyrinatoiron(III) Complex Supported on Activated Silica as an Efficient Heterogeneous Catalyst for a Facile, One-Pot, Selective Synthesis of 2-Arylbenzimidazole Derivatives in the Presence of Atmospheric Air as a "Green" Oxidant at Ambient Temperature

Keywords: Iron / Porphyrinoids / Benzimidazoles / Heterogeneous catalysis / Activated silica gel / Oxidation

Bidentate Chelate Ligands

A highly modular route towards substituted β-enaminones is presented. Thus obtained N,O-chelating ligands play an important role in the nickel-catalysed copolymerisation of ethene and CO.



U. Beckmann,* E. Eichberger, M. Lindner, M. Bongartz, P. C. Kunz 4139–4147

Modular Routes Towards New N,O-Bidentate Ligands Containing an Electronically Delocalised β-Enaminone Chelating Backbone

Keywords: Polyketones / β-Enaminones / N,O ligands / Bidentate chelate ligands

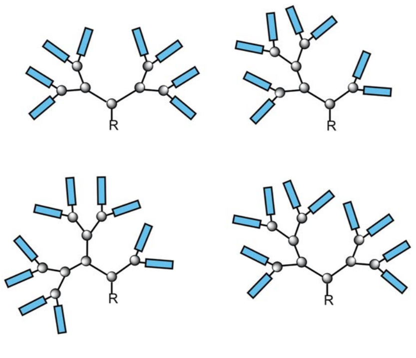
CONTENTS

Dendritic Molecules

D. Schubert, M. Corda, O. Lukin,*
B. Brusilowskij, E. Fiškin,
C. A. Schalley 4148–4156

A Topological View of Isomeric Dendrimers

Keywords: Dendrimers / Topology / Sulfonimides / Mass spectrometry / Isomers



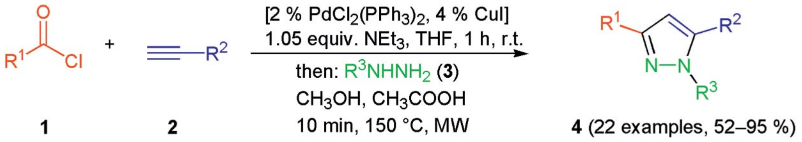
Purposely designed and synthesized isomeric dendrimers provide a good benchmark for separation science and mass spectrometry. A handy topological view of the isomerism of dendrimers is proposed and used to analyze their properties.

One-Pot Synthesis of Pyrazoles

B. Willy, T. J. J. Müller* 4157–4168

Regioselective Three-Component Synthesis of Highly Fluorescent 1,3,5-Trisubstituted Pyrazoles

Keywords: C–C coupling / Cyclocondensation / Fluorescence / Microwave reactions / Multi-component reactions / Pyrazoles



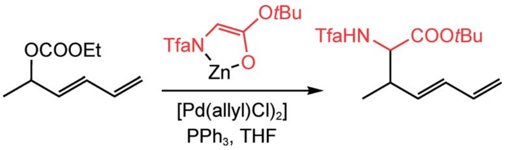
Highly fluorescent 3,5-disubstituted and 1,3,5-trisubstituted pyrazoles are synthesized by a regioselective one-pot three-component Michael addition/cyclocondensation sequence in good yields. According to UV/Vis, fluorescence and computational data, the excited state is highly polar and allows fine-tuning of the absorption and emission properties.

Amino Acid Synthesis

S. Basak, U. Kazmaier* 4169–4177

Palladium-Catalyzed Dienylations of Chelated Enolates

Keywords: Allylations / Amino acids / Chelates / Dienylations / Enolates / Palladium



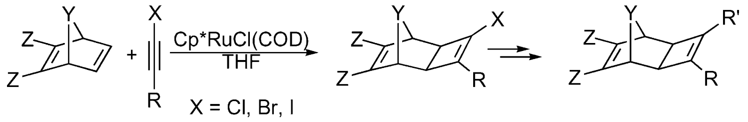
Isomerization-free reactions of dienyl carbonates with chelated amino acid ester enolates at −78 °C provide important information concerning the mechanism of these dienylations.

[2+2] Cycloadditions

A. Allen, K. Villeneuve,
N. Cockburn, E. Fatila,
N. Riddell, W. Tam* 4178–4192

Alkynyl Halides in Ruthenium(II)-Catalyzed [2+2] Cycloadditions of Bicyclic Alkenes

Keywords: Ruthenium / Cycloaddition / Bicyclic alkenes / Alkynyl halides / Homogeneous catalysis

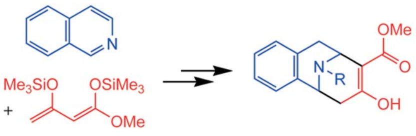


X = Cl, Br, I
Y = CH_2, O, NBoc
R = alkyl, aryl, ester, sulfone
R' = H, alkyl, $SiMe_3$, Ar, alkynyl

Alkynyl halides were found to undergo Ru-catalyzed [2+2] cycloadditions with bicyclic alkenes. The halide moiety greatly enhances the reactivity of the alkyne component in the cycloaddition and can be transformed into a variety of products that are difficult or impossible to obtain by direct cycloaddition.

Iminium Salts

Functionalized 7,8-benzo-anellated 9-azabicyclo[3.3.1]nonan-3-ones (isobenzomorphans) were prepared by cyclocondensation of isoquinolines with 1,3-bis(silyloxy)-1,3-butadienes.

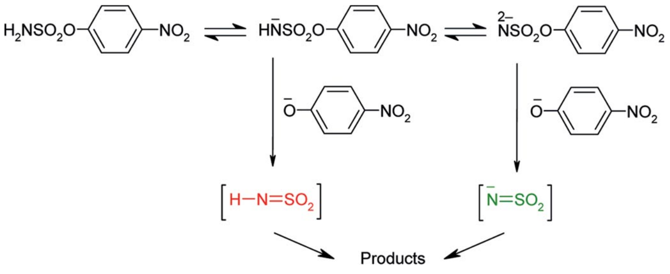


M. A. Yawer, I. Hussain, J.-P. Gütlein, A. Schmidt, H. Jiao, H. Reinke, A. Spannenberg, C. Fischer, P. Langer* 4193–4199

Synthesis of Functionalized Isobenzomorphans by Two-Step Cyclocondensation of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with Isoquinolines 💻

Keywords: Nitrogen heterocycles / Cyclizations / Iminium salts / Silyl enol ethers / Regioselectivity

Enzyme Inhibitors



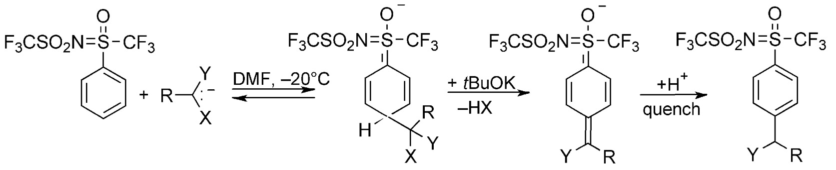
The kinetics of the reaction of 4-nitrophenyl sulfamate NH$_2$SO$_2$OC$_6$H$_4$NO$_2$-4 and other sulfamates in acetonitrile with amines have been studied. The sulfamates (models for enzyme inhibitors) and the amines (models for enzymes) react by an eliminative decomposition route involving *N*-sulfonylamines/anionic sulfonylamines.

W. J. Spillane,* A. O'Byrne, C. J. A. McCaw 4200–4205

Elimination Mechanisms in the Aminolysis of Sulfamate Esters of the Type NH$_2$SO$_2$OC$_6$H$_4$X – Models of Enzyme Inhibitors 💻

Keywords: Elimination / Enzyme models / Kinetics / Inhibitors

Substitution of Hydrogen



1,1,1-Trifluoro-*N*-[oxido(phenyl)(trifluoromethyl)-λ^4-sulfanylidene]methanesulfonamide enters a vicarious nucleophilic substitution (VNS) process. This is the first example of the VNS reaction at a benzene ring activated by an electron-withdrawing group different than the nitro group. The orientation of the substitution is exclusively *para*.

T. Lemek,* G. Groszek, P. Cmoch 4206–4209

Vicarious Nucleophilic Substitutions of Hydrogen in 1,1,1-Trifluoro-*N*-[oxido-(phenyl)(trifluoromethyl)-λ^4-sulfanylidene]-methanesulfonamide

Keywords: Carbanions / Fluorine / Sulfur / Nucleophilic substitution

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* Author to whom correspondence should be addressed.

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