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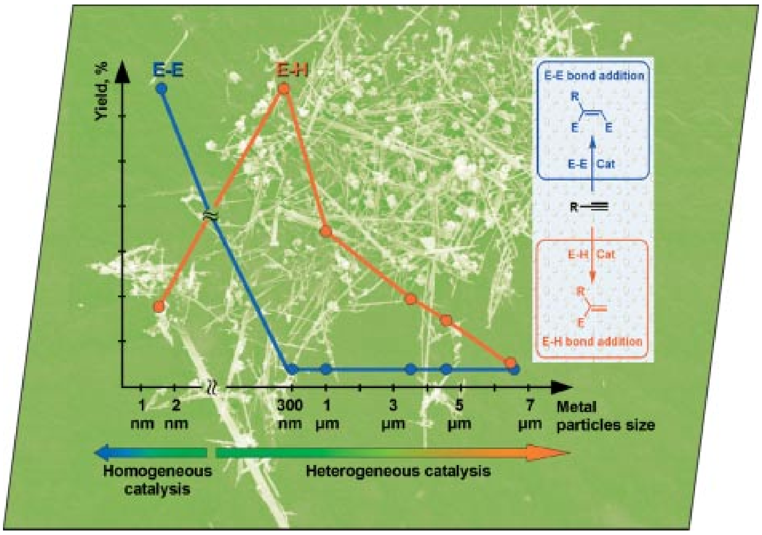
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows that tuning the size of the catalyst particles provides a powerful synthetic tool for controlling not only the selectivity and yield, but also the direction of the chemical transformation. Soluble mononuclear and dinuclear phosphine complexes of palladium are excellent catalysts for stereoselctive E−E (E = S, Se) bond addition to alkynes. However, these complexes are poor catalysts for E−H bond addition to alkynes. Increasing the size of the catalyst particles changes the reactivity: polymeric species of nickel and palladium become efficient catalysts of E−H bond addition under heterogeneous conditions, while they are totally inactive in E−E bond addition. The unique self-organized catalytic system shown in the background (magnified by scanning electron microscopy) combines the best features on the polynuclear metal complex and supported catalyst. Details are presented in the Microreview by I. P. Beletskaya and V. P. Ananikov on p. 3431 ff.



CONTENTS

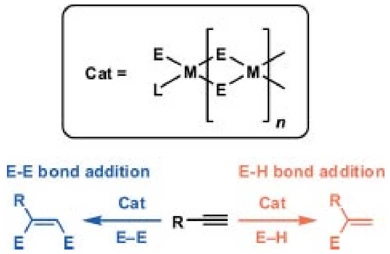
MICROREVIEW

Transition Metal Catalysis

I. P. Beletskaya,*
V. P. Ananikov .... **3431−3444**

Unusual Influence of the Structures of Transition Metal Complexes on Catalytic C−S and C−Se Bond Formation Under Homogeneous and Heterogeneous Conditions

Keywords: Synthetic methods / Homogeneous catalysis / Heterogeneous catalysis / Selectivity / Nanosized catalysts



In the presence of transition metal catalysts, hydrothiolation and hydroselenation reactions, as well as bisthiolation and bisselenation reactions, have been successfully carried out with high selectivities and yields. New transition metal-catalyzed synthetic methods have been developed for the preparation of vinyl sulfides and vinyl selenides of various types.

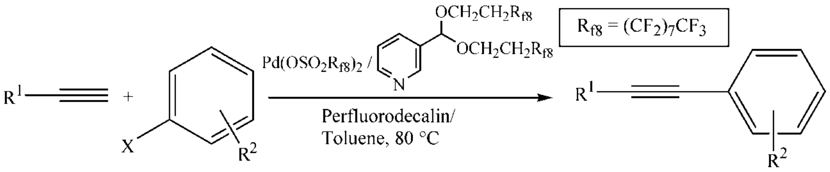
SHORT COMMUNICATION

[F]-Pd-Catalyzed Reactions

W.-B. Yi,* C. Cai,
X. Wang .... **3445−3448**

A Palladium/Perfluoroalkylated Pyridine Catalyst for Sonogashira Reaction of Aryl Bromides and Chlorides in a Fluorous Biphasic System

Keywords: Cross-coupling / Palladium / Fluorinated ligand / Heterogeneous catalysis



R^1 = aryl, alkyl; R^2 = H, Me, OMe, NO_2, CF_3, CHO, $COCH_3$, F; X = Cl, Br

$[Pd(OPf)_2]$ catalyses the Sonogashira reaction of aryl bromides and chlorides in the presence of a catalytic amount of perfluoroalkylated pyridine as a ligand in a fluorous biphasic system (FBS) composed of toluene and perfluorodecalin. The reaction can be performed under phosphane-, copper- and DMF-free conditions in an air atmosphere.

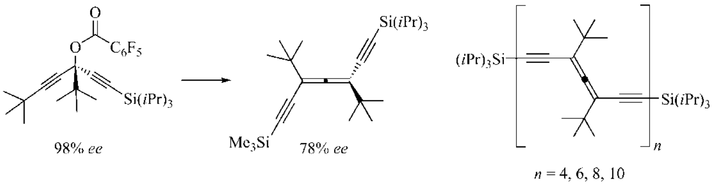
FULL PAPERS

Allene Chemistry

M. K. J. ter Wiel, S. Odermatt, P. Schanen,
P. Seiler, F. Diederich* .... **33449−3462**

1,3-Diethynylallenes: Stable Monomers, Length-Defined Oligomers, Asymmetric Synthesis, and Optical Resolution

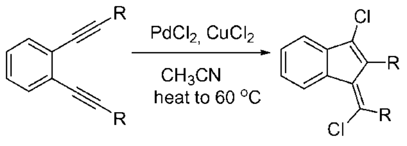
Keywords: Allenes / Carbon-rich scaffolds / Enynes / Oligomerization / Stereoselective synthesis



1,3-Diethynylallenes (DEAs) with polar functionalities were prepared to explore their challenging optical resolution. Asymmetric synthesis from optically pure bispropargylic precursor opens another promising route to optically active 1,3-diethynylallenes. A series of length-defined oligomers were prepared by end-capping oligomerization using an “expanded monomer”.

Enediyne Cyclizations

Palladium-catalyzed cyclization of enediynes for the synthesis of indenes **2** in yields of 59–76 % was accomplished by treatment of dialkynylbenzenes **1** with $PdCl_2$ and $CuCl_2$ in acetonitrile at 60 °C for 2 h.



1 **2**

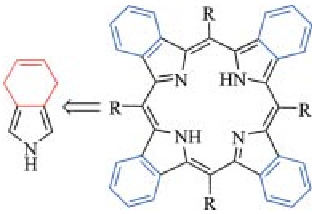
C.-Y. Lee, M.-J. Wu* 3463–3467

Synthesis of Benzofulvenes by Palladium-Catalyzed Cyclization of 1,2-Dialkynylbenzenes

Keywords: Benzofulvenes / Palladium / Cyclization / Enediynes

π-Extended Porphyrins

Aromatization of annelated rings, which is the most serious bottleneck in the synthesis of tetrabenzoporphyrins, was dramatically facilitated and allowed these compounds to be prepared from 4,7-dihydroisoindole. The capabilities of the new method are illustrated by the synthesis and unambiguous characterization of 5,15-diphenyltetrabenzoporphyrin.

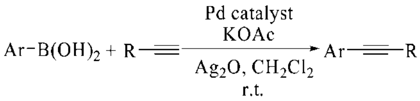


M. A. Filatov, A. V. Cheprakov,*
I. P. Beletskaya 3468–3475

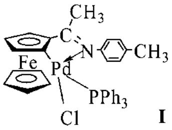
A Facile and Reliable Method for the Synthesis of Tetrabenzoporphyrin from 4,7-Dihydroisoindole

Keywords: Porphyrinoids / Nitrogen heterocycles / Tetrabenzoporphyrins / π-Extended porphyrins / Dipyrromethanes

Synthetic Strategies



$$\mathrm{Ar{-}B(OH)_2 + R{-}{\equiv}} \xrightarrow[\mathrm{Ag_2O,\ CH_2Cl_2}\ \text{r.t.}]{\text{Pd catalyst}\ \ \text{KOAc}} \mathrm{Ar{-}{\equiv}{-}R}$$



I

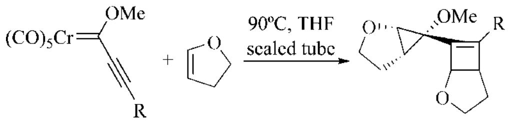
An efficient and convenient catalytic system for the cross-coupling of aryl boronic reagents with terminal alkynes was described by using cyclopalladated ferrocenylimine (**I**)/silver oxide as the catalyst at room temperature. The substrates could be extended to electron-poor alkynes, for which the traditional Sonogashira reaction does not proceed.

F. Yang, Y. Wu* 3476–3479

Facile Synthesis of Substituted Alkynes by Cyclopalladated Ferrocenylimine Catalyzed Cross-Coupling of Arylboronic Acids/Esters with Terminal Alkynes

Keywords: Palladium / Cross-coupling / Arylboronic acids / Alkynes / Silver

Diastereoselective Cyclopropanation



Tandem [2+2]/[2+1] (or [3+2]/[2+1]) sequences take place involving alkynyl(alkoxy) Fischer carbene complexes, 2,3-dihydrofuran (or trimethylsilyldiazomethane), and one unit of a second olefin to produce the diastereoselective formation of three-component adducts in moderate yields.

A. Pérez-Anes, P. García-García,
Á. L. Suárez-Sobrino,
E. Aguilar* 3480–3487

Domino [2+2]/[2+1] and [3+2]/[2+1] Reaction Sequences of Alkynyl(alkoxy) Chromium Fischer Carbene Complexes

Keywords: Carbenes / Domino reactions / Cyclopropanation / Oxygen heterocycles

CONTENTS

Dendritic Fluorophores

A. Ebel, W. Donaubauer, F. Hampel, A. Hirsch* 3488–3494

Amphiphilic Pyrene-Functionalized Dendrons: Synthesis and Intermolecular Interactions

Keywords: Dendrons / Pyrene / Crystal engineering / Intermolecular interactions / Micelles

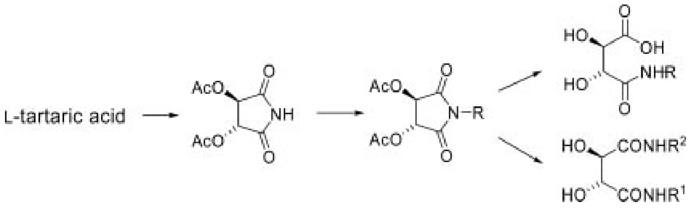
The supramolecular organization of new water-soluble amphiphiles bearing a fluorescent pyrene unit connected to Newkome dendrons was investigated by X-ray crystallography and NMR as well as optical spectroscopy. The amphiphiles form small micelles in water which are able to encapsulate apolar perylene molecules.

Chiral Amphiphiles

S. Villa Gonzalez, P. Carlsen* 3495–3502

Tartaric Acid Amides by the Gabriel Route

Keywords: Amphiphiles / Functional surfactants / Ketene / Cyclic imides / Alkylation / Amides / Optical activity



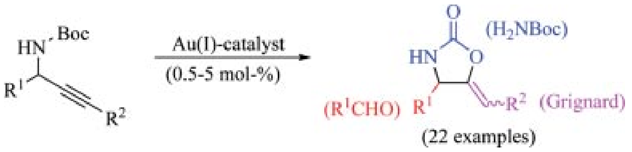
Optically active cyclic imides were prepared from the tartaric acids, which upon alkylation were further transformed into optically active amphiphilic tartramides and tartradiamides. The formation of the cyclic imide is proposed to proceed by competing mechanisms, including a proposed ketene intermediate.

Gold Catalysis

E.-S. Lee, H.-S. Yeom, J.-H. Hwang, S. Shin* 3503–3507

A Practical Gold-Catalyzed Route to 4-Substituted Oxazolidin-2-ones from *N*-Boc Propargylamines

Keywords: Gold / Oxazolidinones / 1,3-Allylic interactions / Isomerization



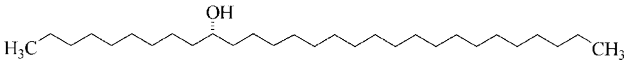
Substitution effects of the gold-catalyzed modular assembly of 4-substituted oxazolidin-2-ones, as well as the intriguing isomerization mechanism, are discussed. This approach is characterized by low catalyst loading, mild conditions, and operational simplicity. This method also allows the oxazolidinones to be sterically and electronically fine-tuned.

Plant Wax Synthesis

A. Dommisse, J. Wirtz, K. Koch, W. Barthlott, T. Kolter* 3508–3511

Synthesis of (*S*)-Nonacosan-10-ol, the Major Component of Tubular Plant Wax Crystals

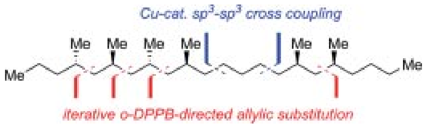
Keywords: Alcohols / Biosynthesis / Lipids / Plants / Racemic resolution / Waxes



The major component of tubular wax crystals found on plant leaves, (*S*)-nonacosan-10-ol, is prepared together with its enantiomer.

Pheromone Total Synthesis

Total synthesis of the hexamethyldocosane from the cuticula of the Australian cane beetle allowed to establish the absolute configuration of the natural product.



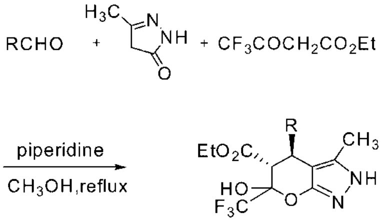
C. Herber, B. Breit* 3512–3519

Enantioselective Total Synthesis and Determination of the Absolute Configuration of the 4,6,8,10,16,18-Hexamethyldocosane from *Antitrogus parvulus*

Keywords: Asymmetric synthesis / Total synthesis / Pheromones / *Antitrogus parvulus* / C–C coupling / Grignard reaction / Organocopper reagents

Fluorine-Containing Heterocycles

One-pot syntheses of ethyl (4*S**,5*R**)-4-aryl-6-hydroxy-3-methyl-6-(trifluoromethyl)-2,4,5,6-tetrahydropyrazolo[3,4-*b*]pyran-5-carboxylate derivatives are described.



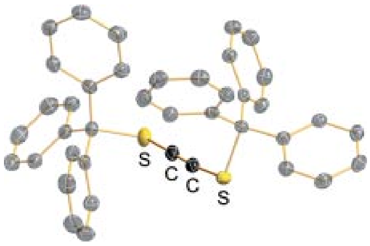
D.-M. Li, L.-P. Song,* X.-F. Li, C.-H. Xing, W.-M. Peng, S.-Z. Zhu* 3520–3525

Simple Synthesis of 6-(Trifluoromethyl)-2,4,5,6-tetrahydropyrazolo[3,4-*b*]pyran Derivatives by One-Pot, Three-Component Reactions

Keywords: Aldehydes / Oxygen heterocycles / Cyclization / Hydrogen transfer

Sulfur-Substituted Alkynes

Acetylenedithiolate is an interesting building block in coordination chemistry but unfortunately an elusive beast. The synthesis and reactivity of acetylene disulfides, which are furnished with thiol protection groups is described.

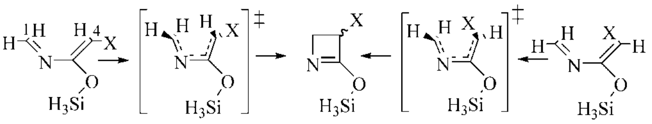


W. W. Seidel,* M. J. Meel, M. Schaffrath, T. Pape 3526–3532

In Pursuit of an Acetylenedithiolate Synthesis

Keywords: Alkynes / Thiol protection groups / Synthesis / Structure determination

Azadiene Cyclizations



Electrocyclization of 4-substituted-3-silyloxy-2-azadienes to β-lactams was shown to be dependent on the (*Z*) configuration and the electron-donor capabilities of the substituent.

A. Bongini,* Z. Xia, M. Panunzio 3533–3538

An Ab Initio Study of Substituent Effects on the Electrocyclization of Silyloxyazadienes

Keywords: Azadienes / β-Lactams / Ab initio calculations / Electrocyclization / Nitrogen heterocycles

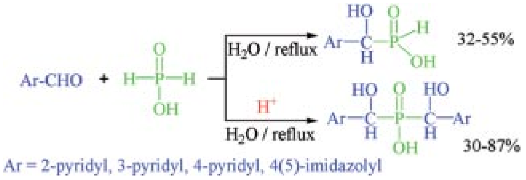
CONTENTS

Hydroxyphosphinic Acids

T. K. Olszewski, J. Gałęzowska,
B. Boduszek,* H. Kozłowski 3539–3546

New Heterocyclic Mono- and Bis(α-hydroxymethyl)phosphinic Acids: Synthesis and Cu^{II} Binding Abilities

Keywords: Hypophosphorous acid / H-Phosphinic acids / Pyridine / Imidazole / Coordination ability



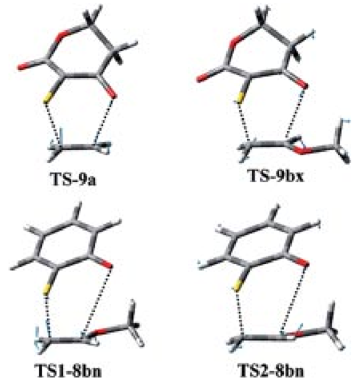
A simple and efficient method for the synthesis of mono- and bis(α-hydroxymethyl)phosphinic acids in a pyridine and imidazole series from their corresponding aldehydes and aqueous hypophosphorous acid was developed. The coordination properties of these compounds towards Cu^{II} ions were determined.

Stepwise Diels–Alder Reactions

L. Legnani, C. Lunghi,
F. Marinone Albini, C. Nativi, B. Richichi,
L. Toma* 3547–3554

Alternative Mechanistic Paths in the Hetero-Diels–Alder Reaction of α-Oxothiones: A Theoretical Study

Keywords: Cycloaddition / Density functional calculations / Transition states / Charge transfer



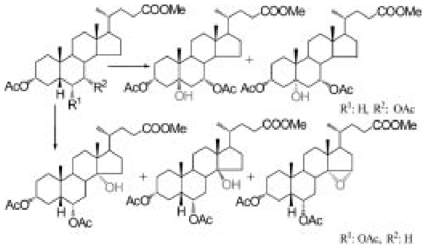
The hetero-Diels–Alder reactions of several α-oxothiones and ethylene or methyl vinyl ether were studied by DFT; the transition states and the intermediates along the reaction pathways were located, and the reaction mechanisms are discussed.

Biomimetic Oxidation

S. Ogawa, K. Hosoi, T. Iida,*
Y. Wakatsuki, M. Makino, Y. Fujimoto,
A. F. Hofmann 3555–3563

Osmiumporphyrin-Catalyzed Oxyfunctionalization and Isomerization of Natural (5β)-Bile Acids with *tert*-Butyl Hydroperoxide

Keywords: Osmium / Porphyrinoids / Bile acids / Hydroxylation / Ketones / Isomerization



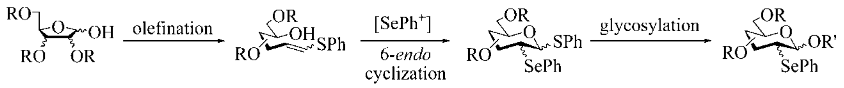
Natural (5β)-bile acids were effectively oxyfunctionalized with anhydrous TBHP catalyzed by Os(TMP)CO to cause simultaneous hydroxylation and isomerization at C-5 and C-14 and/or ketonization at C-15 and C-16 regioselectively.

2-Deoxyoligosaccharides

O. Boutureira, M. A. Rodríguez,
D. Benito, M. I. Matheu, Y. Díaz,*
S. Castillón* 3564–3572

Stereoselective Synthesis of 2-Deoxy-2-phenylselenenyl Glycosides from Furanoses: Implication of the Phenylselenenyl Group in the Stereocontrolled Preparation of 2-Deoxy-*ribo*- and 2-Deoxy-*xylo*-oligosaccharides

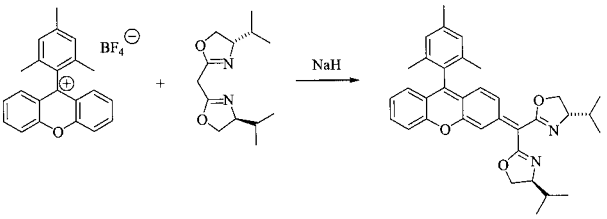
Keywords: Carbohydrates / Cyclization / Glycosylation / Selenium



2-Deoxy-2-phenylselenenyl-1-thioglycosides were evaluated as glycosyl donors to provide 2-deoxy-2-phenylselenenyl-β-D-*gulo*-glycosides and -β-D-*allo*-glycosides from furanoses. The phenylselenenyl group is necessary for the stereocontrolled preparation of 2-deoxyoligosaccharides, and the glycosylation is highly substrate dependent.

Extended π-Systems

p-Quinoid Compounds by Nucleophilic Aromatic Substitution with Hydride as Leaving Group



A simple route to functionalized *p*-quinoid π-systems from sterically shielded triarylmethylium tetrafluoroborates is presented. The reaction with CH- and NH-acidic nucleophiles proceeds readily at moderate non-oxidative conditions with hydride as leaving group.

Keywords: Triarylmethylium salts / Nucleophilic aromatic substitution / Hydride leaving group / *p*-Quinoid compounds