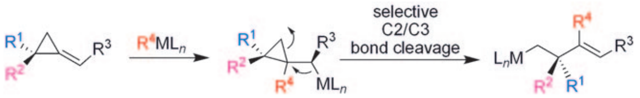
CONTENTS

CONCEPTS

Cyclopropanes

*A. Masarwa, I. Marek** ..... 9712 – 9721

Selectivity in Metal-Catalyzed Carbon−Carbon Bond Cleavage of Alkylidenecyclopropanes



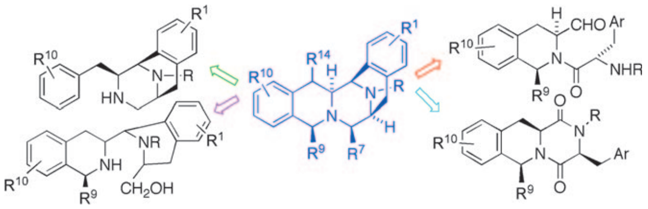
Complex, but still simple: The ring-opening of strained three-membered rings such as methylene- and alkylidenecyclopropanes generally lead to several products. If one starts with a more functionalized carbon skeleton, a selective reaction is now observed and rationalization as well as synthetic applications are described in this Concept article. This methodology could be used in the preparation of challenging structural motifs possessing quaternary carbon stereocenters in acyclic systems.

MINIREVIEWS

Antitumor Analogues

*C. Avendaño,**
E. de la Cuesta .... 9722 – 9734

Recent Synthetic Approaches to 6,15-Iminoisoquino[3,2-*b*]3-benzazocine Compounds



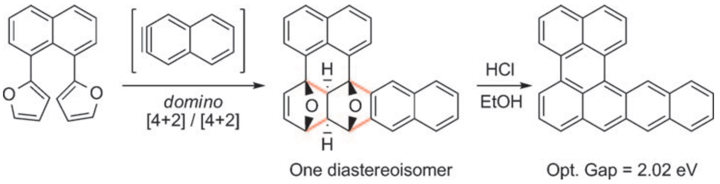
New perspectives: This minireview is intended to update the synthetic contributions to obtain saframycin analogues. These compounds constitute the largest subgroup among the tetrahydroisoquinoline antitumor antibiotics. A brief description of the different strategies has been organized according to the order of bonding events that will link the precursors (see scheme).

COMMUNICATIONS

Domino Reactions

A. Criado, D. Peña, A. Cobas,*
*E. Guitián** .... 9736 – 9740

Domino Diels–Alder Cycloadditions of Arynes: New Approach to Elusive Perylene Derivatives

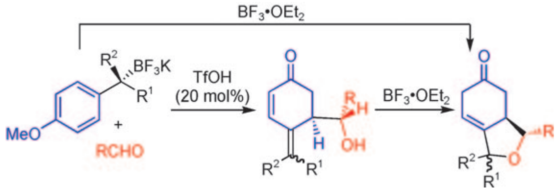


A game of dominos: Domino [4+2]/[4+2] cycloadditions between 1,8-difurylnaphthalene and arynes provide the corresponding adducts in a highly diastereoselective manner. This new synthetic methodology enables the preparation of elusive perylene derivatives with a remarkable reduced HOMO–LUMO gap, a crucial feature for organic semiconductors.

Asymmetric Catalysis

A. Ros, A. Bermejo,
*V. K. Aggarwal** .... 9741 – 9745

Benzylic Boron Reagents Behaving as Allylic Boron Reagents towards Aldehydes: A New Asymmetric Reaction Leading to Homoallylic Alcohols with Concomitant Dearomatisation

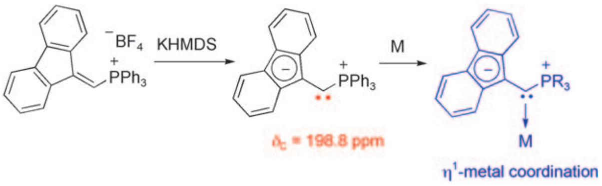


Retention of stereochemistry: *p*-Methoxybenzylic trifluoroborate salts react with aldehydes in the presence of Lewis or Brønsted acids to give homoallylic alcohols with concomitant dearomatisation of the aromatic ring (see scheme). Using enantioenriched benzylic trifluoroborate salts leads to adducts with >98 % retention of the stereochemistry in most cases.

Carbenes

*M. Alcarazo, R. M. Suárez, R. Goddard, A. Fürstner** . . 9746 – 9749

A New Class of Singlet Carbene Ligands

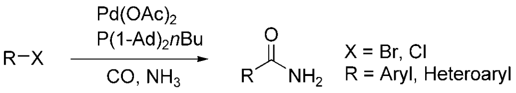


What are you? Deprotonation of fluorenylidene phosphonium salts generates reactive intermediates that can be described as push–pull cumulenes or singlet carbenes (see scheme). Whereas the NMR data are ambiguous, the coordination behavior shows the ready availability of a lone pair at the central C atom. The donor ability of singlet carbene ligands of this new class exceeds that of the commonly used N-heterocyclic carbenes (NHCs).

Amide Synthesis

*X.-F. Wu, H. Neumann, M. Beller** . . . . 9750 – 9753

Selective Palladium-Catalyzed Aminocarbonylation of Aryl Halides with CO and Ammonia

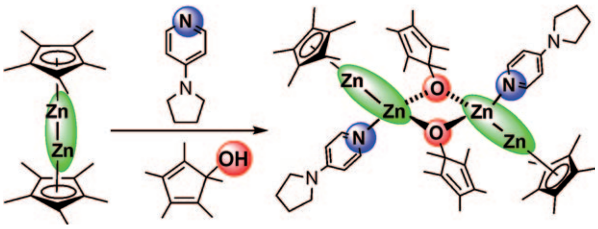


Wake up and smell the ammonia! A palladium-catalyzed aminocarbonylation of aryl halides with CO and ammonia has been developed (see scheme). Primary amides are accessible, under mild reaction conditions, in moderate to excellent yields.

Metallocenes

*M. Carrasco, R. Peloso, A. Rodríguez, E. Álvarez, C. Maya, E. Carmona** . . . . 9754 – 9757

Zn–Zn-Bonded Compounds that Contain Monoanionic Oxygen-Donor Ligands

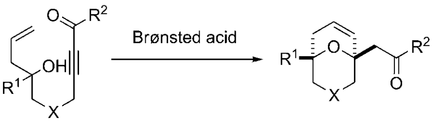


The zinc connection! Reaction of bulky alcohols with $[Zn_2Cp^*_2]$ in the presence of a Lewis base allowed the isolation of the first zinc–zinc bonded complexes containing a Zn−O bond (see scheme).

Cyclisation Reactions

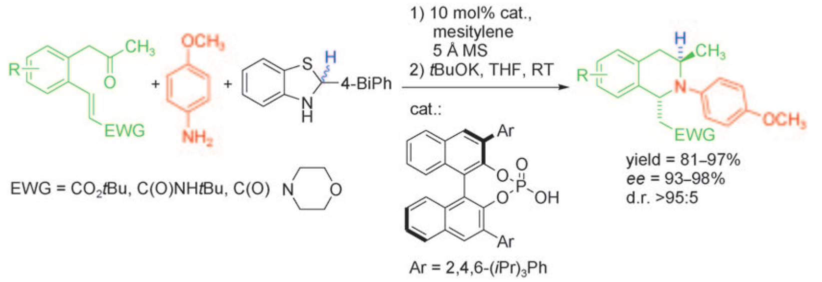
A. Mendoza, P. Pardo, F. Rodríguez, F. J. Fañanás** . . . . 9758 – 9762

Synthesis of [3.3.1] Bicyclic Compounds by a Brønsted Acid Catalysed Double Intramolecular Michael Addition



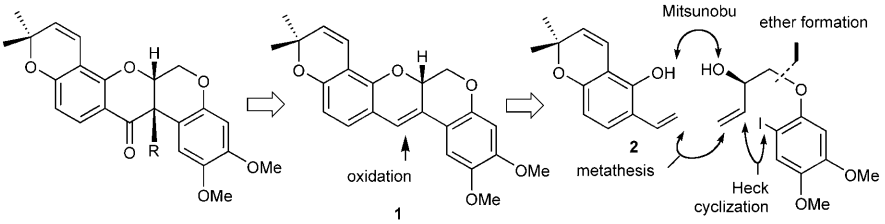
Cyclisation sequence: An efficient method for the synthesis of [3.3.1] bicyclic compounds from easily available ynone derivatives has been developed. The reaction is based on an unprecedented double intramolecular Michael addition (DIMA) of an oxygen-centred and a carbon-centred nucleophile to the ynone (see scheme).

Organocatalysis



Benzothiazoline better than Hantzsch: A stereoselective Brønsted acid catalyzed reductive amination/aza-Michael approach towards the important class of tetrahydroisoquinolines is presented (see scheme). A biphenyl-substituted benzothiazoline is used as the reducing agent and leads to superior yields and enantiomeric excesses compared with the frequently used Hantzsch ester. The cyclization of the amine intermediate occurs smoothly with potassium *tert*-butoxide as the base and affords the *trans*-1,3-disubstituted tetrahydroisoquinolines.

Natural Products



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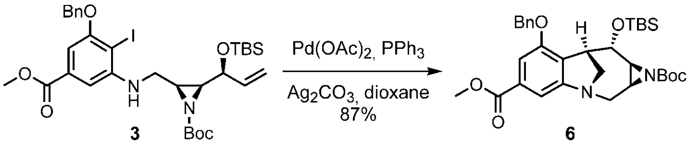
The concise nature and modularity of the synthesis described for deguelin and tephrosin (retrosynthetic analysis depicted) should facilitate access to labeled analogues to dissect the mechanism of action of this important pharmacophore.

Domino Heck Reaction



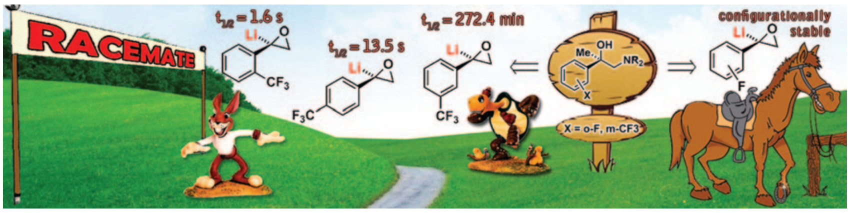
Unexpected Heck: During efforts toward the synthesis of FR900482, an unexpected domino Heck product was isolated (see scheme). Although this pathway was ultimately not productive for the aforementioned natural product synthesis, efforts were made to extend the methodology to the synthesis of amurensinine. To our knowledge this domino reaction was the first such tandem Heck-alkylation pathway in the presence of a geometrically favorable β-hydrogen elimination.

FULL PAPERS

Lithiated Compounds

V. Capriati, S. Florio,* F. M. Perna, A. Salomone* 9778–9788

Lithiated Fluorinated Styrene Oxides: Configurational Stability, Synthetic Applications, and Mechanistic Insight

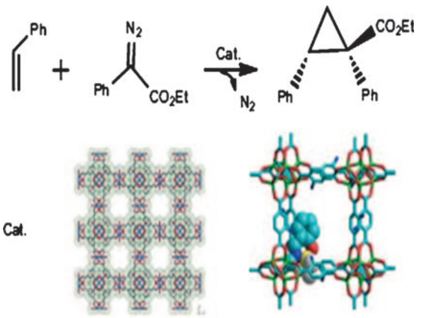


Where is the boundary between configurational stability/instability of lithiated fluorinated styrene oxides? It depends upon both the type of fluorinated group and its relative position on the phenyl ring (see figure). Barriers of inversion, activation parameters, and mechanisms of racemization have been discussed for configurationally unstable intermediates, as well the synthesis.

Metal–Organic Frameworks

A. Corma, M. Iglesias, F. X. Llabrés i Xamena, F. Sánchez* 9789–9795

Cu and Au Metal–Organic Frameworks Bridge the Gap between Homogeneous and Heterogeneous Catalysts for Alkene Cyclopropanation Reactions



Transfer of fragments: Metal–organic framework (MOF) materials containing either Cu or Au centers can act as catalysts (i.e., $[Cu_3(BTC)_2]$ (BTC = benzene-1,3,5-tricarboxylate), and IRMOF-3-SI-Au) for the cyclopropanation of alkenes with diazoacetates (see scheme). This example is the first use of these materials to induce the carbene transfer reactions from diazo compounds.

Chiral macrocycles

P. Rivera-Fuentes, J. L. Alonso-Gómez, A. G. Petrovic, P. Seiler, F. Santoro, N. Harada, N. Berova, H. S. Rzepa, F. Diederich** 9796–9807

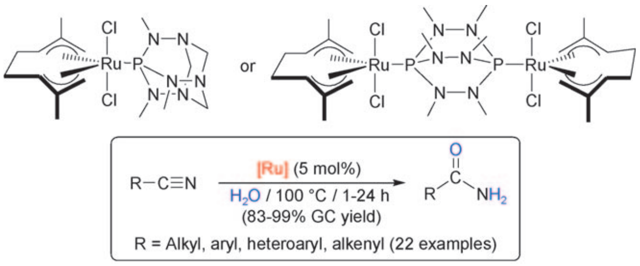
Enantiomerically Pure Alleno–Acetylenic Macrocycles: Synthesis, Solid-State Structures, Chiroptical Properties, and Electron Localization Function Analysis

Shaping up! Enantiopure, shape-persistent alleno–acetylenic macrocycles (an example of which is shown here) were prepared by oxidative homocoupling of 1,3-diethynylallenes. The synthesis and solid-state structures are reported, along with a detailed analysis of their chiroptical and electronic properties.

Homogeneous Catalysis

V. Cadierno, J. Díez, J. Francos, J. Gimeno** 9808–9817

Bis(allyl)ruthenium(IV) Complexes Containing Water-Soluble Phosphane Ligands: Synthesis, Structure, and Application as Catalysts in the Selective Hydration of Organonitriles into Amides



The power of water: Mono- and dinuclear (2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV) complexes (see picture), which contain selected water-soluble phosphanes, behave as highly efficient catalysts for the selective hydration of organonitriles into amides in pure aqueous medium under neutral conditions.

Precious-metal catalysis: 3-Propargylindoles are able to participate in 1,2-migrations under gold-catalysis. 3-(Inden-2-yl)indoles could be accessed through gold-iso-Nazarov or gold-Nazarov cyclizations, whereas 3-(1,3-dien-2-yl)indoles are generated when none of these pathways are accessible.

Gold Catalysis

R. Sanz, D. Miguel, M. Gohain,
P. García-García,
M. A. Fernández-Rodríguez,
A. González-Pérez, O. Nieto-Faza,
Á. R. de Lera,*
F. Rodríguez** 9818–9828

Synthesis of Diverse Indole-Containing Scaffolds by Gold(I)-Catalyzed Tandem Reactions of 3-Propargylindoles Initiated by 1,2-Indole Migrations: Scope and Computational Studies

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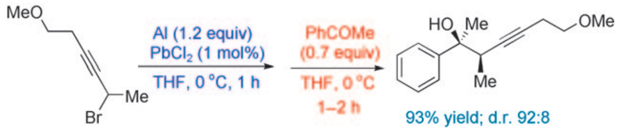

Functional group tolerance: A new and efficient preparation of allenic and propargylic aluminum reagents has been reported. These organoaluminum species react with aldehydes or ketones, giving the homopropargylic or allenic alcohols in good to excellent yields with high selectivity (see scheme). Various functional groups are tolerated in this reaction.

Diastereoselectivity

*L.-N. Guo, H. Gao, P. Mayer,
P. Knochel** 9829–9834

Preparation of Organoaluminum Reagents from Propargylic Bromides and Aluminum Activated by PbCl$_2$ and Their Regio- and Diastereoselective Addition to Carbonyl Derivatives

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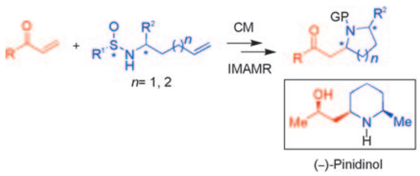
***N*-Sulfinyl amines** have been successfully employed as nitrogen nucleophiles for the asymmetric intramolecular aza-Michael reaction (IMAMR; see scheme). The synthetic strategy involves a cross-metathesis (CM) reaction followed by the Michael-type cyclization, either in a base-catalyzed two-step procedure or in a tandem fashion.



Natural Products

S. Fustero, S. Monteagudo,
M. Sánchez-Roselló, S. Flores,
P. Barrio, C. del Pozo** 9835–9845

N-Sulfinyl Amines as a Nitrogen Source in the Asymmetric Intramolecular Aza-Michael Reaction: Total Synthesis of (−)-Pinidinol

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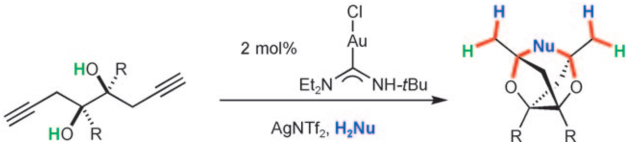


Gold closes the cage: Diyne–diols and external nucleophiles in gold-catalysed reactions deliver rigid tricyclic heterocyclic compounds in high selectivity by a domino reaction. Eight new bonds are formed by hydroalkoxylation/hydrohydroxylation or hydroamination in good overall yields (see scheme).

Heterocycles

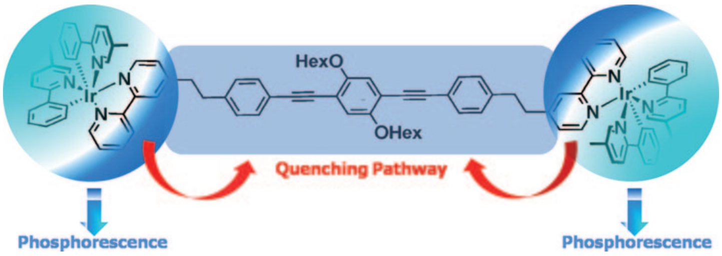
A. S. K. Hashmi, M. Bührle,
M. Wölfle, M. Rudolph, M. Wieteck,
F. Rominger, W. Frey* 9846–9854

Gold Catalysis: Tandem Reactions of Diyne–Diols and External Nucleophiles as an Easy Access to Tricyclic Cage-Like Structures

Electroluminescence

R. D. Costa, G. Fernández, L. Sánchez, N. Martín, E. Ortí,* H. J. Bolink** .... 9855 – 9863

Dumbbell-Shaped Dinuclear Iridium Complexes and Their Application to Light-Emitting Electrochemical Cells

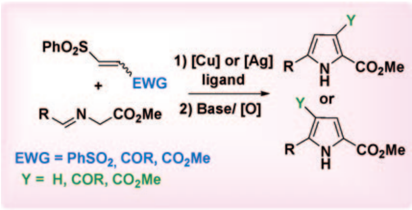


Observed quenching pathway: A novel family of dumbbell-shaped dinuclear iridium(III) complexes is presented (see figure). Theoretical and photophysical studies show that the lowest triplet state resides on the molecular spacer and constitutes an efficient quenching pathway that explains the poor photoluminescence quantum yields. Conversely, the presence of the spacer reduces the self-quenching in solid films and a near-quantitative internal electron-to-photon conversion is observed in LEC devices.

Synthetic Methods

*R. Robles-Machín, A. López-Pérez, M. González-Esguevillas, J. Adrio, J. C. Carretero** .... 9864 – 9873

Pyrrole and Oligopyrrole Synthesis by 1,3-Dipolar Cycloaddition of Azomethine Ylides with Sulfonyl Dipolarophiles

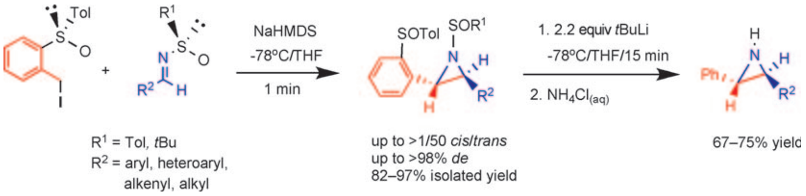


Keep y-lid-e on it! A range of pyrroles have been prepared by metal-catalyzed 1,3-dipolar cycloaddition of α-iminoesters with readily available sulfonyl dipolarophiles, followed by base-promoted sulfone elimination and aromatization (see scheme). This strategy can also be applied to the construction of *n*-oligopyrroles ($n = 2$–5).

Asymmetric Synthesis

Y. Arroyo, Á. Meana, M. A. Sanz-Tejedor,* I. Alonso, J. L. García Ruano** .... 9874 – 9883

2-(*p*-Tolylsulfinyl)benzyl Halides as Efficient Precursors of Optically Pure *trans*-2,3-Disubstituted Aziridines

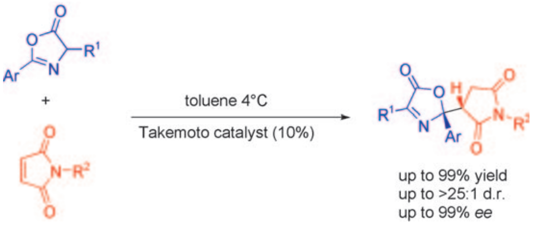


Get selective! Aziridination of (*R*)-*N*-sulfinyl aldimines (aryl, heteroaryl and alkenyl derivatives) with α-iodo-2-(*p*-tolylsulfinyl)toluene, in the presence of sodium hexamethyl disilazide (NaHMDS), takes place with almost complete control of the stereoselectivity (facial and *anti*/*syn*) and with very high yields, affording optically pure *N*-sulfinyl *trans*-2,3-disubstituted aziridines (see scheme).

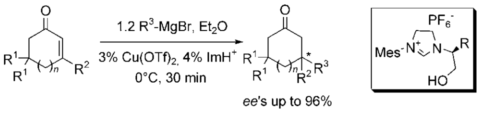
Asymmetric Organocatalysis

A.-N. R. Alba, G. Valero, T. Calbet, M. Font-Bardía, A. Moyano, R. Rios** .... 9884 – 9889

Enantioselective Organocatalytic Addition of Azlactones to Maleimides: A Highly Stereocontrolled Entry to 2,2-Disubstituted-2*H*-oxazol-5-ones



Thio-E-urea-KA! The first highly diastereo- and enantioselective organocatalytic synthesis of 2,2-disubstituted-2*H*-oxazol-5-ones is described. The addition of oxazolones to maleimides is promoted by bifunctional thiourea catalysts, which afford the corresponding 2,2-disubstituted-2*H*-oxazol-5-ones with total regio- and stereocontrol (see scheme).

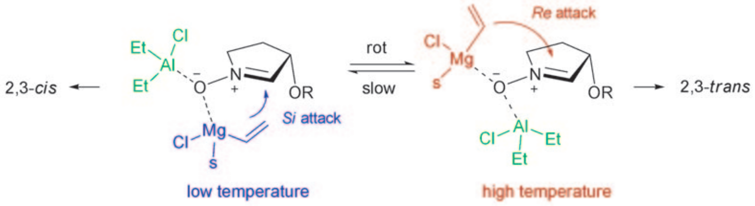


Asymmetric chemistry: The copper-catalyzed conjugate addition of Grignard reagents to 3-substituted cyclic enones allows the formation of all-carbon chiral quaternary centers (see scheme). N-Heterocyclic carbenes act as efficient chiral ligands for this transformation. High enantioselectivities (up to 96 % *ee*) could be obtained for a variety of substrates.

Copper Catalysis

Gold C−C coupling: Organogold(I) reagents (aryl, alkenyl, alkynyl, alkyl) can be used in palladium-catalyzed cross-coupling reactions with different organic electrophiles, such as aryl and alkenyl halides, aryl triflates, benzyl bromide, and benzoyl chloride (see scheme; OTf = trifluoromethane sulfonate). The reaction generally proceeds at room temperature in high yields.

Cross-Coupling Reactions



Diastereofacial discrimination: The vinylation of cyclic nitrones in the presence of diethylaluminum chloride shows a strong dependence on both temperature and steric hindrance at C3 (see scheme; s = solvent). Experimental, theoretical, and spectroscopic studies have been used for rationalizing the observed inversion of selectivity at low temperature.

Nitrogen Heterocycles

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