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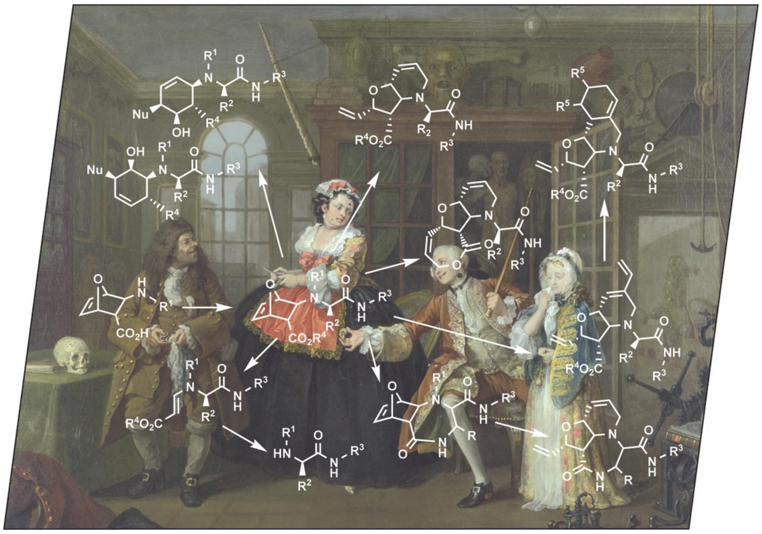
COVER PICTURE

The cover picture shows one of the six paintings of *Marriage à-la-mode* (©National Gallery, London) created by William Hogarth in 1743–1745 and portrays a pointed skewering of upper-class 18th century society. This moralistic warning shows the disastrous results of an ill-considered marriage for money. However, the authors of this Microreview demonstrate that the marriage of convenience between the Ugi reaction and the norbornenyl scaffold is not to be blamed. Details are presented in the Microreview by A. Basso et al. on p. 1831ff.



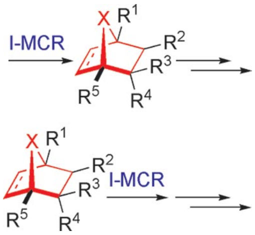
MICROREVIEW

Multicomponent Reactions

**A. Basso,* L. Banfi,
R. Riva 1831–1841**

A Marriage of Convenience: Combining the Power of Isocyanide-Based Multicomponent Reactions with the Versatility of (Hetero)norbornene Chemistry

Keywords: Multicomponent reactions / Molecular diversity / Fused-ring systems / Oxygen heterocycles / Nitrogen heterocycles



Norbornanyl building blocks can be employed as constituents in isocyanide-based multicomponent reactions (I-MCRs), and norbornene derivatives can also be assembled through multicomponent condensations. In both cases the products can be further elaborated very efficiently and straightforwardly, due to the peculiar reactivity of the norbornenyl moiety, leading to highly valuable final molecules.

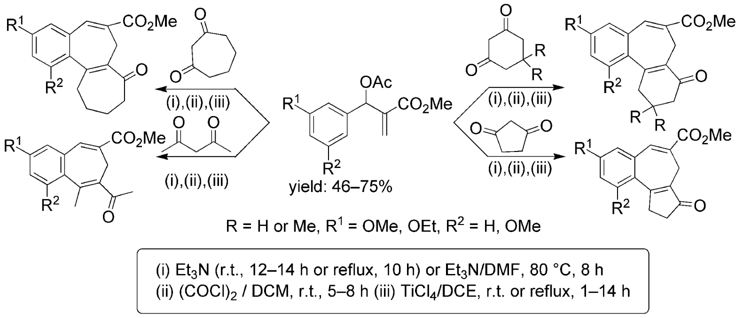
SHORT COMMUNICATIONS

Carbocyclic Chemistry

**D. Basavaiah,* K. Aravindu, K. S. Kumar,
K. R. Reddy 1843–1848**

Simple, One-Pot, and Facile Synthesis of Angularly Fused [6-7-5], [6-7-6], [6-7-7], and [6,7] Ring Systems Using Baylis–Hillman Acetates

Keywords: Carbocycles / Cyclization / Fused-ring systems / Michael addition



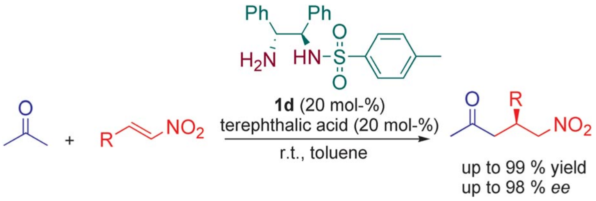
A simple, convenient, and one-pot synthesis of angularly fused [6-7-5], [6-7-6], [6-7-7], and [6,7] carbocyclic ring systems from Baylis–Hillman acetates through a strategy involving alkylation, formation of a vinyl chloride, and intramolecular cyclication (Friedel–Crafts or Michael reaction) is described.

Organocatalysis

**L. Peng, X.-Y. Xu, L.-L. Wang, J. Huang,
J.-F. Bai, Q.-C. Huang,
L.-X. Wang* 1849–1853**

Noyori's Ts-DPEN Ligand: Simple yet Effective Catalyst for the Highly Enantioselective Michael Addition of Acetone to Nitroalkenes

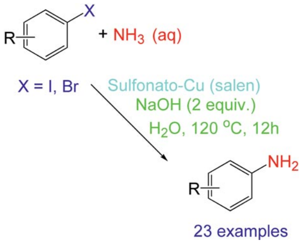
Keywords: Organocatalysis / Michael addition / Asymmetric synthesis / Amines



A series of simple and commercially available primary amine bifunctional catalysts represented by Noyori's Ts-DPEN ligand were used in the highly enantioselective Michael addition of acetone to a variety of nitroalkenes in excellent yields (84–99%) and enantioselectivities (93–98%*ee*).

Aqueous Catalysis

A simple, highly efficient, and environmentally friendly protocol for coupling aryl halides with aqueous ammonia in water catalyzed by the sulfonato–Cu(salen) complex was developed. Substituted 1*H*-benzimidazole was prepared easily by coupling aqueous ammonia with 2-iodoacetanilide in one pot with this catalytic system.



Z. Wu, Z. Jiang, D. Wu, H. Xiang, X. Zhou* **1854–1857**

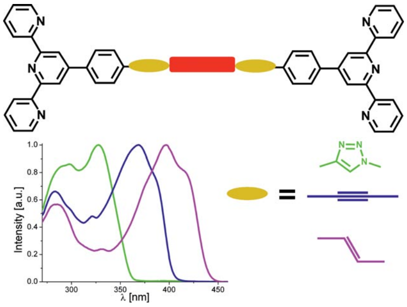
A Simple and Efficient Catalytic System for Coupling Aryl Halides with Aqueous Ammonia in Water

Keywords: Amination / Cross-coupling / Copper / Nitrogen heterocycles / Water chemistry

FULL PAPERS

Band-Gap Tuning

By varying both the spacer unit and the linker in conjugated bis(terpyridines), a library of π-conjugated bis(terpyridines) has been synthesized, enabling structure–property relationships of these materials to be studied. With the same conjugated backbone, the absorption and emission maxima can be tuned over a range of about 80 nm just by varying the connecting unit.

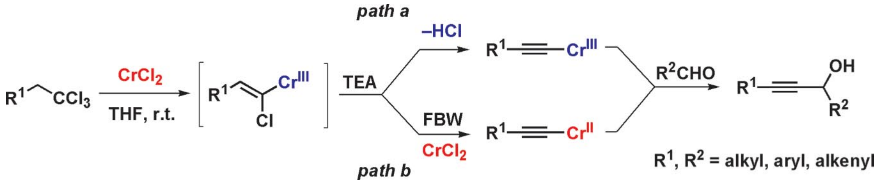


A. Wild, C. Friebe, A. Winter, M. D. Hager, U.-W. Grummt, U. S. Schubert* **1859–1868**

π-Conjugated 2,2′:6′,2′′-Bis(terpyridines): Systematical Tuning of the Optical Properties by Variation of the Linkage between the Terpyridines and the π-Conjugated System

Keywords: Conjugation / Supramolecular chemistry / UV/Vis spectroscopy / Density functional calculations

Chromium Acetylides



Mixed, low-valent chromium(II) and chromium(III) acetylides are generated from the smooth reduction of primary 1,1,1-trichloroalkanes with chromium(II) chloride in the presence of triethylamine. A mechanism for the formation of these nucleophilic alkynylating agents was proposed. Both species were used in the *one-pot* synthesis of functionalized propargyl alcohols.

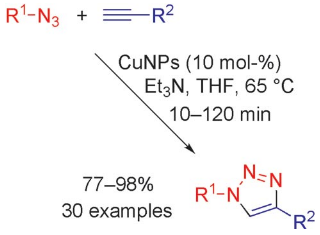
D. Kashinath, S. Tisserand, N. Puli, J. R. Falck,* R. Baati* **1869–1874**

Generation of Nucleophilic Chromium Acetylides from *gem*-Trichloroalkanes and Chromium Chloride: Synthesis of Propargyl Alcohols

Keywords: Chromium / Carbenoids / Rearrangement / Alkynes / Alcohols

Click Chemistry

The 1,3-dipolar cycloaddition of terminal alkynes and azides catalysed by readily generated copper nanoparticles is reported. Reactions are fast and lead to the corresponding triazoles in good-to-excellent yields. A reaction mechanism involving copper(I) acetylides is proposed on the basis of different reactivity studies and deuteration experiments.



F. Alonso,* Y. Moglie, G. Radivoy, M. Yus* **1875–1884**

Unsupported Copper Nanoparticles in the 1,3-Dipolar Cycloaddition of Terminal Alkynes and Azides

Keywords: Click chemistry / Cycloaddition / Alkynes / Azides / Copper / Nanoparticles

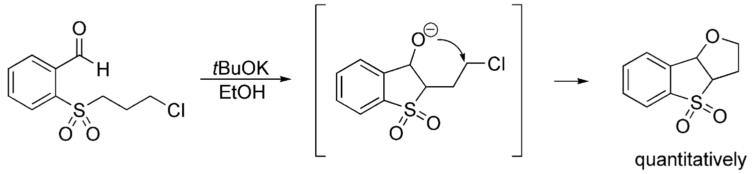
CONTENTS

Reactions of γ-Halo Carbanions

A. Wojtasiewicz, M. Barbasiewicz,
M. Mąkosza* 1885–1894

Intramolecular Addition of γ-Chloro Carbanions to Electrophilic Groups: Synthesis of Tricyclic Tetrahydrofurans, Pyrrolidines, and Cyclopentanes

Keywords: Carbanions / Aldol reactions / Cyclization / Nucleophilic substitution / Polycycles



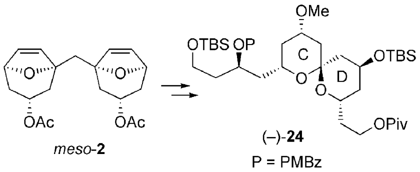
Precursors of γ-chloro carbanions with electrophilic multiple bonds undergo two-step reactions under basic conditions. Aldol-type addition and subsequent cyclization leads to tricyclic derivatives of tetrahydrofurans, pyrrolidines, and cyclopentanes with good to excellent yields.

Natural Product Synthesis

S. Favre, S. Gerber-Lemaire,*
P. Vogel 1895–1903

Synthetic Studies toward the CD Spiroketal of Spongistatins

Keywords: Spiro compounds / Polyketides / Natural products / Desymmetrization / Alcoholysis



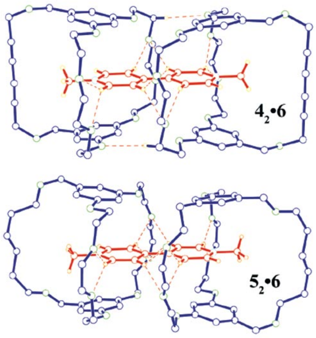
Stereoselective functionalization of *meso*-methylenebis(8-oxabicyclo[3.2.1]oct-6-ene-1,3-diyl) diacetate has allowed the asymmetric synthesis of a direct precursor of the CD spiroketal of spongistatins. This pathway makes use of the early desymmetrization of the starting bicyclic template and relies on the careful choice of protecting groups to achieve the targeted spiroketal in 3% overall yield from *meso* diketone **1**.

Host–Guest Systems

Z. Xu, X. Huang, J. Liang, S. Zhang,
S. Zhou, M. Chen, M. Tang,
L. Jiang* 1904–1911

Efficient Syntheses of Novel Cryptands Based on Bis(*m*-phenylene)-26-crown-8 and Their Complexation with Paraquat

Keywords: Cryptands / Macrocycles / Host–guest systems



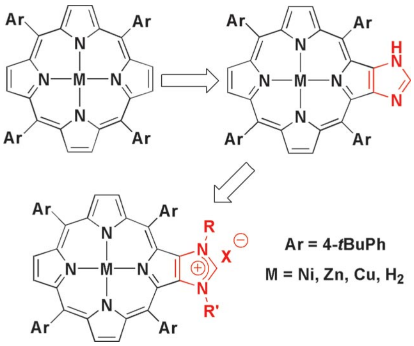
The two novel cryptands **4** and **5**, based on bis(*m*-phenylene)-26-crown-8, were synthesized in excellent yields through the use of copper(II)-mediated Eglinton coupling and (for **5**) subsequent Pd/C-catalyzed reduction. These new cryptands bind paraquat **6** more strongly than the corresponding crown ether, forming [3]pseudorotaxane-like complexes both in solution and in the solid state.

Porphyrin Chemistry

J.-F. Lefebvre, D. Leclercq,
J.-P. Gisselbrecht,
S. Richeter* 1912–1920

Synthesis, Characterization, and Electronic Properties of Metalloporphyrins Annulated to Exocyclic Imidazole and Imidazolium Rings

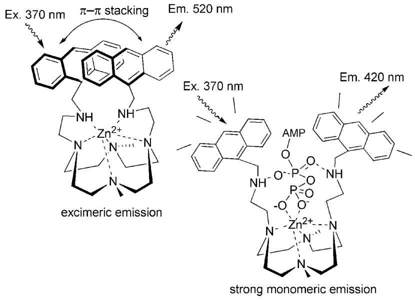
Keywords: Porphyrinoids / Cyclization / Alkylation / Fused-ring systems / Electrochemistry



Porphyrins containing one pyrrole that is annulated to an imidazole or an imidazolium ring have been prepared and studied by electrochemistry.

Fluorescent Chemosensors

The macrocycle complex **1**-Zn^{II} shows obvious excimer emission, resulting from intramolecular π–π stacking interactions. After adding ATP, the two anthracene units were forced to separate and extend, resulting in decreased excimer emission and increased monomer emission. Insertion of ATP occurs so that the adenosine adopts a sandwich-type disposition between the two anthryl ring systems of the receptor.



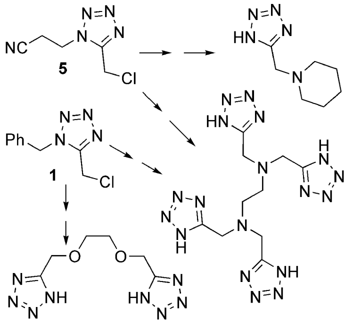
X.-h. Huang, Y. Lu, Y.-b. He,*
Z.-h. Chen **1921–1927**

A Metal–Macrocycle Complex as a Fluorescent Sensor for Biological Phosphate Ions in Aqueous Solution

Keywords: Fluorescence / Excimers / Sensors / Macrocycles / Supramolecular chemistry

Tetrazole Synthons

Both, the newly synthesized β-cyanoethyl-protected synthon **5** and its benzylated analogue **1** alkylate very efficiently, but the different polarity of both protecting groups and the conditions of their removal can be regarded as so diverging that both can be found attractive for specific challenges of introducing the tetrazolylmethyl group. Deprotection of the BCE group is supremely effective, but in selected cases the benzyl group has its merits, too.



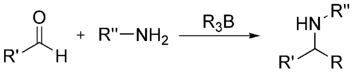
F. Touti, F. Avenier, Q. Lefebvre,
P. Maurin, J. Hasserodt* **1928–1933**

A Synthon for the Convenient and Efficient Introduction of Tetrazolylmethyl Groups into Nucleophile-Bearing Compounds

Keywords: Nitrogen heterocycles / Protecting groups / N ligands / Acidity

Multicomponent Reactions

A one-pot three-component alkylative amination reaction of an aldehyde, an amine, and a trialkylborane has been developed. The presence of hydrogen peroxide afforded the corresponding alkylated amines in good yields. The versatility of our method has been established through the use of enolizable aldehydes, alkylic amines, and cyclic imines.



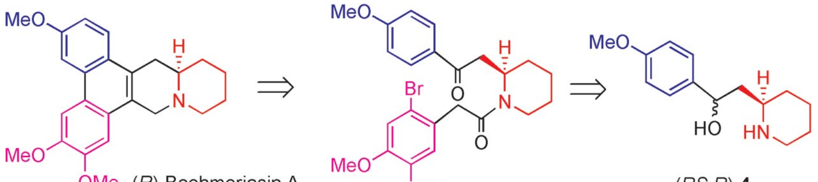
R', R'' = alkyl or aryl

M. Valpuesta,* C. Muñoz, A. Díaz,*
G. Torres, R. Suau **1934–1942**

Multicomponent *C*-Alkylation Reactions of Aromatic Aldimines with Trialkylboranes Reagents

Keywords: Boranes / Alkylation / Amines / Multicomponent reactions / Aldehydes

Asymmetric Total Synthesis



(*R*)-Boehmeriasin A

(*RS*,*R*)-**4**

The first asymmetric synthesis of (*R*)-boehmeriasin A has been achieved by sequential acylation, oxidation, aldol condensation and ultimate radical cyclization of amino alcohol **4**. Assembly of this hydroxylated piperidine was secured by combining diastereoselective 1,2-nucleophilic additions to SAMP hydrazones with ring-closing metathesis.

D. Dumoulin, S. Lebrun, A. Couture,*
E. Deniau, P. Grandclaudon ... 1943–1950

First Asymmetric Synthesis of Boehmeriasin A

Keywords: Nucleophilic addition / Diastereoselectivity / Cyclization / Ringclosing metathesis / Total synthesis

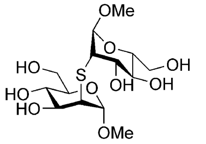
CONTENTS

Pseudodisaccharides

I. Cumpstey,* C. Ramstadius, T. Akhtar, I. J. Goldstein, H. C. Winter ... 1951–1970

Non-Glycosidically Linked Pseudodisaccharides: Thioethers, Sulfoxides, Sulfones, Ethers, Selenoethers, and Their Binding to Lectins

Keywords: Carbohydrates / Pseudodisaccharides / Glycosides / Glycomimetics / Lectins / Sulfur



Concanavalin A: K_a 59300 M^{-1}
Banana Lectin: K_a 529 M^{-1}

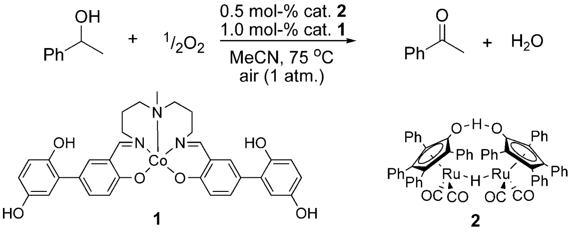
Linking two monosaccharides without using the anomeric centre gives hydrolytically stable ether or thioether pseudodisaccharides. Here we disclose our synthesis of a small library of such compounds and describe their glycomimetic properties as lectin ligands.

Aerobic Oxidation

E. V. Johnston, E. A. Karlsson, L.-H. Tran, B. Åkermark, J.-E. Bäckvall* 1971–1976

Efficient Aerobic Ruthenium-Catalyzed Oxidation of Secondary Alcohols by the Use of a Hybrid Electron Transfer Catalyst

Keywords: Oxidation / Alcohols / Electron transfer / Hybrid catalysts / Ruthenium



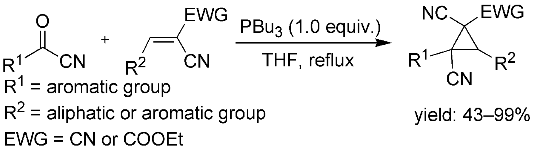
Biomimetic aerobic oxidation of secondary alcohols using bifunctional hybrid catalyst **1** and Shvo's catalyst **2** can be efficiently carried out with low catalytic loading under air at ambient pressure. A wide range of alcohols can be oxidized to their corresponding ketones under mild conditions. The efficiency is due to facile intramolecular electron transfer in hybrid catalyst **1**.

Synthesis of Novel Cyclopropanes

X.-G. Liu, Y. Wei,* M. Shi* ... 1977–1988

Probing Phosphane-Mediated [2+1] Annulation Reactions

Keywords: Cyclization / Phosphanes / Cyclopropanes / Annulation



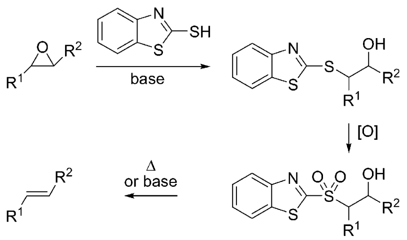
We have explored a series of phosphane-mediated [2+1] annulation reactions between acyl cyanides and methylidenemalononitriles, which provide a facile and efficient protocol for the construction of novel multiply substituted cyclopropanes.

Alkenes and Epoxides

F.-L. Wu, B. P. Ross, R. P. McGeary* 1989–1998

New Methodology for the Conversion of Epoxides to Alkenes

Keywords: Alkenes / Epoxide / Olefination / Deoxygenation / Protecting groups



Epoxides can be stereospecifically transformed into their alkene precursors. Ring-opening of mono-, di-, and trisubstituted epoxides with 2-mercaptobenzothiazole gives thioethers. Oxidation to the sulfone and either thermal- or base-promoted fragmentation then yields alkenes.

Fused Isoquinolines

A gold(I)-catalyzed process for the synthesis of a variety of fused isoquinolines starting from *o*-alkynylbenzaldehyde and aromatic amines having tethered nucleophiles was developed.

N. T. Patil,* A. K. Mutyala,
P. G. V. V. Lakshmi, P. V. K. Raju,
B. Sridhar 1999–2007

Facile Assembly of Fused Isoquinolines by Gold(I)-Catalyzed Coupling–Cyclization Reactions between *o*-Alkynylbenzaldehydes and Aromatic Amines Containing Tethered Nucleophiles

Keywords: Alkynes / Gold / Cyclization / Nitrogen heterocycles / Fused-ring systems / Polycycles

IN MEMORIAM

Michael Addition

The discovery of the Michael addition reaction, focusing on Arthur Michael, an American chemist, after whom it is named, is outlined. Some instances of the Michael addition were observed prior to Michael's crucial finding, and the validity of his credit as the discoverer is discussed.

T. Tokoroyama* 2009–2016

Discovery of the Michael Reaction

Keywords: Michael addition / History of science / Chemical creativity / Reminiscences

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* Author to whom correspondence should be addressed.

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