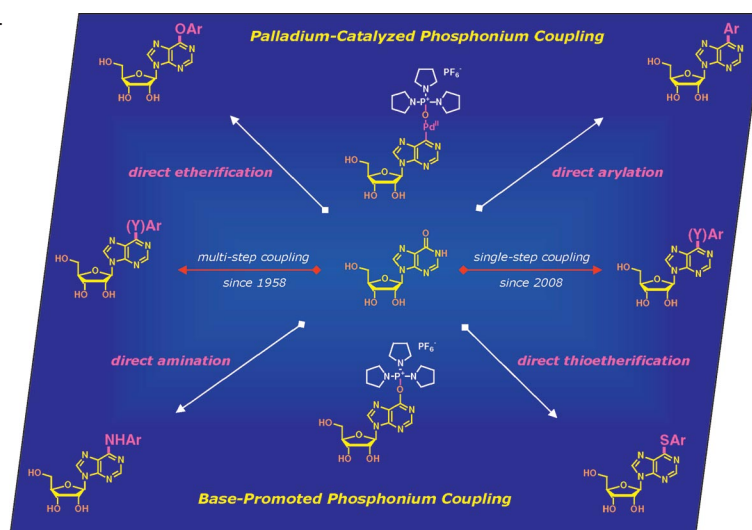


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows the single-step direct transformations of inosine into C6-functionalized nucleosides by base-promoted or palladium-catalyzed phosphonium couplings. Since the pioneering work by Fox et al. in 1958, the functionalization of nucleosides has been routinely carried out in a multi-step sequence including protection, activation, functionalization, and deprotection. As the first direct bond formation through C–OH bond activation of tautomerizable heterocycles with PyBroP, this new, mild, efficient, chemoselective, and versatile phosphonium coupling methodology has solved a long-standing synthetic challenge in nucleoside chemistry. Details of the discovery, mechanism, scope, and application of this technology are presented in the Microreview by F.-A. Kang et al. on p. 461ff.



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## MICROREVIEW

### Phosphonium Coupling

F.-A. Kang,\* Z. Sui,  
W. V. Murray ..... 461–479

Phosphonium Coupling in the Direct Bond Formations of Tautomerizable Heterocycles via C–OH Bond Activation

**Keywords:** Phosphonium coupling / Phosphonium salts / Direct bond formation / C–OH bond activation / Nucleosides / Tautomerizable heterocycles



A long-standing synthetic challenge of a single-step transformation in nucleoside chemistry has been eventually overcome by phosphonium coupling. It is a new mild efficient chemoselective and versatile methodology for the direct C–C, C–N, C–O, and C–S bond formations of *unactivated* and

*unprotected* tautomerizable heterocycles that proceeds via C–OH bond activation of a tautomerizable heterocycle with a phosphonium salt (PyBroP), and subsequent functionalization with either a nucleophile or an organometallic compound.

## IN MEMORIAM

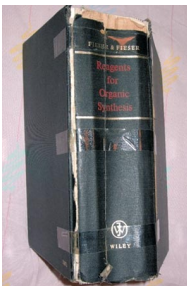
### Chemical History

D. Lenoir, T. T. Tidwell\* ..... 481–491



Louis Fieser: An Organic Chemist in Peace and War

**Keywords:** Reminiscences / History of organic chemistry / Louis and Mary Fieser / Cancer and smoking / Napalm / Chemical education / Organic synthesis



Louis Frederick Fieser (1899–1977) was a prominent figure among organic chemists of the mid-20<sup>th</sup> century, remembered today mainly for *Reagents for Organic Synthesis*, co-authored with his wife Mary. Fieser was known for his prolific research efforts, and was also a leading educator and public servant. His activities included cancer research and cancer prevention but also enthusiastic participation in war research and the invention of napalm, which tend to darken his memory.

## FULL PAPERS

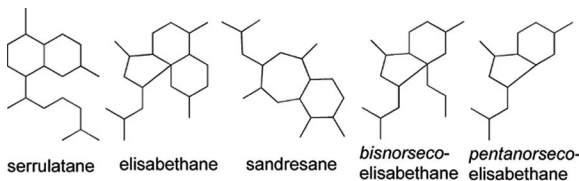
### Marine Natural Products

Y.-P. Shi, X. Wei, I. I. Rodríguez,  
A. D. Rodríguez,\*  
A. M. S. Mayer ..... 493–502



New Terpenoid Constituents of the Southwestern Caribbean Sea Whip *Pseudopterogorgia elisabethae* (Bayer), Including a Unique Pentanorditerpene

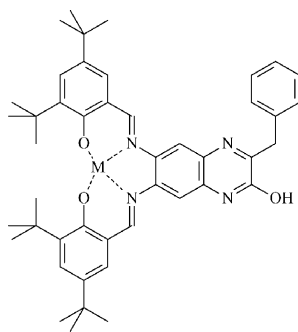
**Keywords:** Terpenoids / Natural products / Structure elucidation / Biological activity / *Pseudopterogorgia elisabethae*



Coral terpenoids: Fractionation of an organic extract of a southwestern Caribbean gorgonian, *Pseudopterogorgia elisabethae*, resulted in the discovery of seven new structurally diverse terpenes. The structures

of seven compounds were determined by 1D and 2D NMR, IR, UV, and MS data analysis. A number of the compounds isolated have significant biological activity.

A copper(II) complex of the 2-quinoxalinol salen ligand has been tested for use in catalysis. Here, an optimized method for oxidation of aryl methylenes, and its potential applications are described. This presents an opportunity for more environmentally friendly or “green” chemistry in a single-phase system.

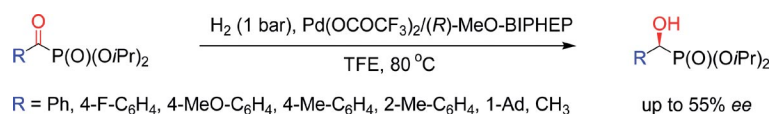


X. Wu, A. E. V. Gorden\* ..... 503–509

2-Quinoxalinol Salen Copper Complexes for Oxidation of Aryl Methylenes

**Keywords:** Salen / Copper / Catalysts / Methylene / Oxidation / Chelates / Homogeneous catalysis

## Asymmetric Catalysis



The first example of the catalytic asymmetric hydrogenation of  $\alpha$ -keto phosphonates is disclosed. The method appears to be

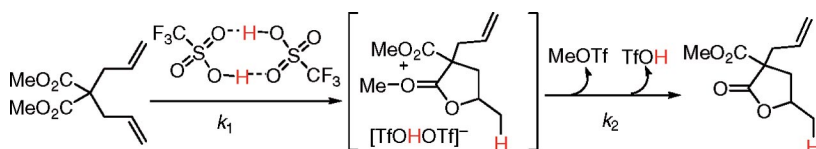
particularly promising for the preparation of optically active  $\alpha$ -hydroxy phosphonates containing the quaternary  $\beta$ -carbon atom.

N. S. Goulioukina,\* G. N. Bondarenko,  
A. V. Bogdanov, K. N. Gavrilov,  
I. P. Beletskaya\* ..... 510–515

Asymmetric Hydrogenation of  $\alpha$ -Keto Phosphonates with Chiral Palladium Catalysts

**Keywords:** Asymmetric catalysis / Hydrogenation / Phosphonates / Palladium

## Lactonisation Mechanism



Dealkylative lactonisation of allylmalonates is mediated by TfOH and occurs via an oxonium triflate intermediate, detected by NMR spectroscopy.  $^2\text{H}$ -labelling experiments suggest intramolecular transfer of

the proton from a carbonyl-protonated ester. Carbocations are involved in the formation and isomerisation of the oxonium intermediates.

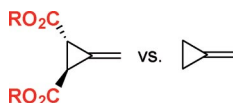
M. Paz Muñoz,\*  
G. C. Lloyd-Jones ..... 516–524

Triflic Acid Mediated Dealkylative Lactonisation via NMR-Observable Alkyl-oxonium Intermediates

**Keywords:** Lactones / Triflic acid / Allylmalonates / Intermediates / Kinetics

## Methylenecyclopropane Chemistry

Combined data demonstrate the significant difference of electronic structure and reactivity between ring-acceptor-substituted Feist's esters and unsubstituted methylenecyclopropanes. In particular, Feist's esters show the inverse regioselectivity and decreased reactivity in cycloadditions with nitrones and considerable lowering of the HOMO energy.



V. V. Diev,\* T. Q. Tung,  
A. P. Molchanov\* ..... 525–530

Esters of Feist's Acid: Some Insights into the Electronic Structure and Reactivity of Methylenecyclopropanes Ring-Substituted with Acceptor Groups

**Keywords:** Cycloaddition / Electronic structure / Methylenecyclopropane / Nitron / Substituent effects

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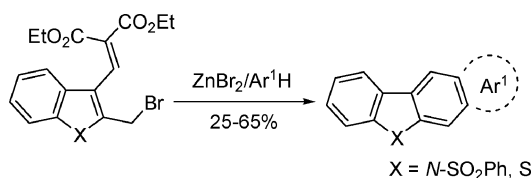
## Annulated Carbazoles

V. Dhayalan, J. A. Clement, R. Jagan,  
A. K. Mohanakrishnan\* ..... 531–546



A Versatile Synthesis of Annulated Carbazole Analogs Involving a Domino Reaction of Bromomethylindoles with Arenes/Heteroarenes

**Keywords:** Alkaloids / Sigmatropic rearrangement / Cyclization / Annulation / Arenes



A one-pot synthesis of annulated carbazole analogs was achieved and involves Lewis acid mediated arylation of bromomethylindole with arene/heteroarenes. The resulting arylated products underwent a thermal 1,5-hydrogen shift to form a triene, which upon subsequent electrocyclization followed by aromatization furnished the annulated carbazole analogs in moderate yields.

mal 1,5-hydrogen shift to form a triene, which upon subsequent electrocyclization followed by aromatization furnished the annulated carbazole analogs in moderate yields.

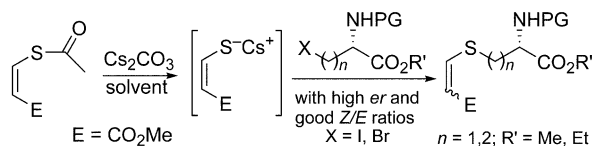
## Cesium Enethiolates

J. S. O'Donnell, S. P. Singh, T. A. Metcalf,  
A. L. Schwan\* ..... 547–553



Cesium (Z)-2-Carbomethoxyethenethiolate: A Reagent for the Preparation of (Z)-2-Carbomethoxyethenyl Thioethers Including Selected Cysteine and Homocysteine Derivatives

**Keywords:** Cesium / Amino acids / Sulfur / Synthetic methods



The cesium carbonate mediated methanalysis of (Z)-2-carbomethoxyethenyl thiolacetate at low temperature creates cesium (Z)-2-carbomethoxyethenethiolate for subsequent alkylation. The conditions were

adapted to accommodate base-sensitive cysteine derivatives, and the use of DMF permits the isolation of (Z)-2-carbomethoxyethenyl cysteinyl thioethers of high *er* (>99:1) and good *Z/E* ratios.

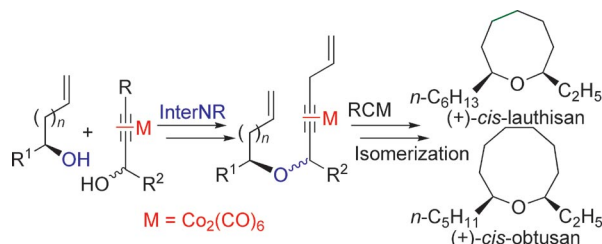
## Medium-Sized Cyclic Ethers

N. Ortega, T. Martín,\*  
V. S. Martín\* ..... 554–563



Synthesis of  $\alpha,\alpha'$ -Disubstituted Linear Ethers by an Intermolecular Nicholas Reaction – Application to the Synthesis of (+)-*cis*/(-)-*trans*-Lauthisan and (+)-*cis*/(-)-*trans*-Obtusian

**Keywords:** Cobalt / Natural products / Oxygen heterocycles / Total synthesis / Isomerization



A method for the preparation of  $\alpha,\alpha'$ -disubstituted linear ethers through an intermolecular Nicholas reaction (interNR) is described. Key steps include the ether linkage formation by interNR, RCM of the

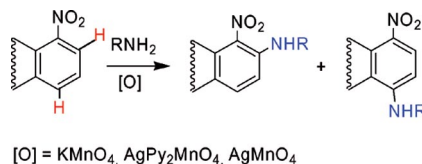
suitable acyclic dienyl ether, and isomerization of the complexed cycloalkyne. The  $\text{Co}_2(\text{CO})_6$ -cycloalkyne complex was found to act as a stereochemical modulator of the final stereochemistry.

## Nucleophilic Substitution of Hydrogen

A. V. Gulevskaya,\* S. Verbeeck,  
O. N. Burov, C. Meyers, I. N. Korbukova,  
W. Herrebout, B. U. W. Maes ..... 564–574

Synthesis of (Alkylamino)nitroarenes by Oxidative Alkylamination of Nitroarenes

**Keywords:** Aromatic substitution / Amination / Amines / Nucleophilic substitution / Nitroarenes



The viability of oxidative alkylamination for the derivatization of nitroarenes has been investigated. Nitroarenes are much more reactive than azines in this reaction.

\* Author to whom correspondence should be addressed.

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

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