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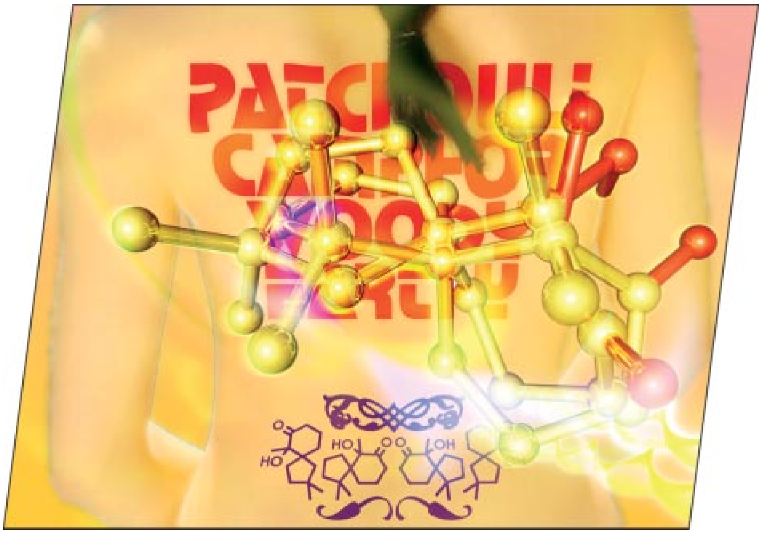
The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic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

COVER PICTURE

The cover picture shows the superposition of two spirocyclic target molecules, modeled on a recently discovered high-impact patchouli odorant by ring-reversal and structural simplification. Yet, despite omission of two methyl substituents, these sterically congested structures proved to be synthetically challenging targets. The synthesis of the first and principal target features a $TiCl_4$-mediated spiroannulation of the TMS-enolate of cyclohexanone with 1-bromo-4-chloro-4-methylpentane, subsequent dehydration by Appel–Lee bromination with concomitant dehydrohalogenation, and the elegant ketohydroxylation reaction of Plietker. Key odor descriptors for "*patchouli*" are "*camphor*", "*woody*" and "*earthy*", and depending on the molecular shape of the odorants, these are more or less balanced; the first target structure, for instance, is more shifted towards the camphoraceous, in principle an anti-erogenous, attribute. Yet patchouli oil always had a sensual connotation, and since Indian girls ritually used to perfume their backs with patchouli oil to bewitch a lover, these molecules shine in front of a female back bearing their structural formulae in a lower backpiece fashion tattoo. The molecular design, synthesis and olfactory properties of these new odorants are discussed in the article by P. Kraft and A. Bruneau on p. 2257 ff.



CONTENTS

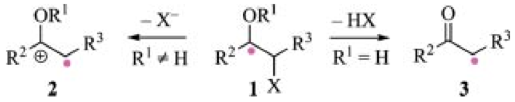
MICROREVIEWS

Radical Reactions

P. Wessig,* O. Muehling 2219–2232

Spin-Center Shift (SCS) – A Versatile Concept in Biological and Synthetic Chemistry

Keywords: Photochemistry / Radical reactions / Cyclization / Enzymes / DNA



Radicals of type **1** undergo very rapid elimination either to radical cations **2** or to oxoallyl radicals **3** depending on the functional group $-OR^1$ at the radical center. In both cases the spin density is shifted to the adjacent atom (spin-center shift). Reactions of this type are important key steps in several radical-induced biological processes. Various synthetic applications of this concept are known and will be presented.

Iminium Salts

P. Langer* 2233–2238

Synthesis of Bridged and Nonbridged N-Heterocycles by Cyclocondensation of Bis(silyl enol ethers) with Iminium Salts

Keywords: Cyclizations / Iminium salts / N-Heterocycles / Silyl enol ethers

The cyclization of bis(silyl enol ethers) with iminium salts allows the synthesis of a variety of bridged and nonbridged N-heterocycles.

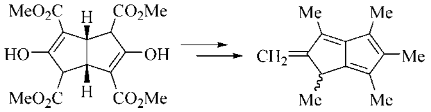
SHORT COMMUNICATIONS

Pentalene Chemistry

A. E. Ashley, A. R. Cowley,
D. O'Hare* 2239–2242

Permethylpentalene Chemistry

Keywords: Pentalenes / Fulvenes / Ligand design / Aromaticity / Organocerium



The large-scale synthesis of an exocyclic isomer of the anti-aromatic hexamethylpentalene (C_8Me_6; Pn*) has been achieved from readily available starting materials, which is a precursor for entry into organometallic permethylpentalene chemistry.

Carbohydrate-Based Surfactants

Z. D. Wang,* S. O. Sheikh, S. Cox,
Y. Zhang, K. Massey 2243–2247

Direct Preparation of N-Glycosidic Bond-Linked Nonionic Carbohydrate-Based Surfactant (NICBS) via Ritter Reaction

Keywords: Ritter reaction / Carbohydrates / Surfactants / Carbocations / Acylation

The Ritter reaction has been successfully extended to the direct preparation of N-glycosidic bond-linked nonionic carbohydrate-based surfactants from carbohydrates and nitriles in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and silver perchlorate ($AgClO_4$) on a high-speed mechanical shaker. The new surfactant molecules have the features of low toxicity, environmental compatibility and biodegradability.

Enantioenriched Ferrocenes

A shortcut in ferrocene chemistry! The direct reaction of enantioenriched ferrocenyl alcohols with a variety of nucleophiles is efficiently catalyzed by $InBr_3$ at room temperature under very mild conditions, and the reaction proceeds with retention of stereochemistry.

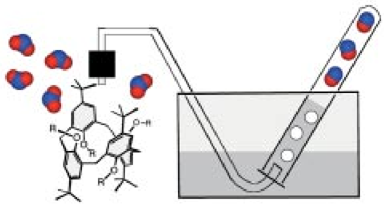
P. Vicennati, P. G. Cozzi* 2248–2253

Facile Access to Optically Active Ferrocenyl Derivatives with Direct Substitution of the Hydroxy Group Catalyzed by Indium Tribromide

Keywords: Ferrocene / Alcohols / Indium tribromide / Catalysis

Supramolecular Reactivity

Calixarenes convert NO_2/N_2O_4 gases into nonvolatile NO^+ and encapsulate it. In a one-electron reduction scheme with simple hydroquinone, the NO^+ transforms into NO gas. NO is released. Calixarenes are regenerated and can be loaded again. Supramolecular materials for generation, storage and release of NO gas can be potentially created, with high-capacity calixarene nanotubes holding a special promise.



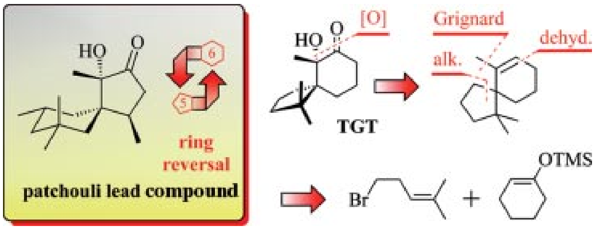
E. Wanigasekara, A. V. Leontiev, V. G. Organo, D. M. Rudkevich* 2254–2256

Supramolecular, Calixarene-Based Complexes That Release NO Gas

Keywords: Calixarenes / Complexes / Molecular recognition / Nitrogen dioxide / Supramolecular chemistry

FULL PAPERS

Patchouli Odorants



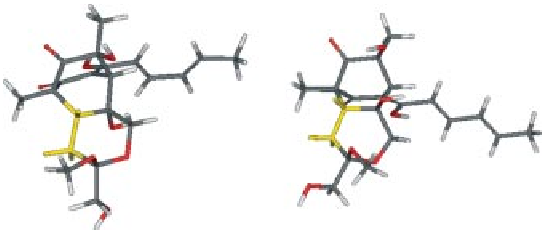
Does "*twisted rings*" mean "*twisted odors*"? Not quite so! – Though accentuated differently, all three attributes, "*camphoraceous*", "*woody*", and "*earthy*", are retained after ring reversal of the spirocyclic patchouli lead compound, and the structure can even be simplified. The synthetic challenge was tackled by $TiCl_4$-mediated enolate spiroannulation, Appel–Lee dehydration, and Plietker ketohydroxylation.

P. Kraft,* A. Bruneau 2257–2267

Ring Reversal of a Spirocyclic Patchouli Odorant: Molecular Modeling, Synthesis, and Odor of 6-Hydroxy-1,1,6-trimethylspiro[4.5]decan-7-one

Keywords: Ketohydroxylation / Olfactory properties / Patchouli / Spiro compounds / Structure–activity relationships

Natural Products from Marine Fungi



Chemical investigation of the fungus *Trichoderma* sp., isolated from the Caribbean sponge *Agelas dispar* led to four novel sorbicillinoid polyketide derivatives with an unprecedented tricyclic ring system, the Trichodermanones A–D. The structures of all compounds, including the absolute configuration, were determined and a proposal for the biosynthesis was made.

K. Neumann, A. Abdel-Lateff, A. D. Wright, S. Kehraus, A. Krick, G. M. König* 2268–2275

Novel Sorbicillin Derivatives with an Unprecedented Carbon Skeleton from the Sponge-Derived Fungus *Trichoderma* Species

Keywords: Natural products / Sorbicillin derivatives / Structure elucidation / Trichodermanones / Configuration determination

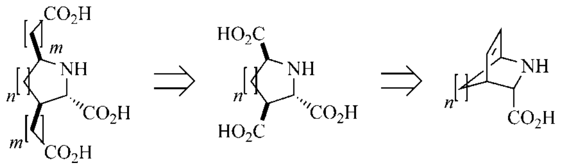
CONTENTS

Glutamate Mimetics

W. Maison* 2276–2284

Azabicycloalkenes as Synthetic Intermediates – Synthesis of Conformationally Constrained Glutamate Analogues

Keywords: Glutamate mimetics / Amino acids / Tumour marker / Peptidomimetics / Neurotransmitter



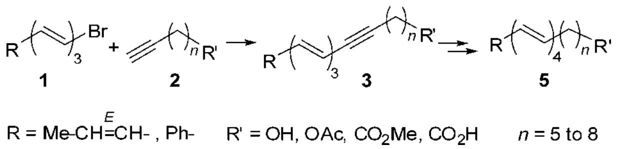
The stereoselective synthesis of conformationally constrained glutamate mimetics is reported. Key intermediates are azabicycloalkenes which are synthesized via diastereoselective or enantioselective *imino*-Diels–Alder protocols. The versatility of the route is demonstrated with the synthesis of Asp, Glu and *H*Glu-mimetics based on proline or pipecolic acid scaffolds.

Amphiphilic Fluorescent Polyenes

E. Quesada, J. Delgado,
V. Hornillos, A. U. Acuña,*
F. Amat-Guerri* 2285–2295

Synthesis and Spectral Properties of Amphiphilic Lipids with Linear Conjugated Polyene and Phenylpolyene Fluorescent Groups

Keywords: Amphiphiles / Polyenes / Cross-coupling / Enynes / Fluorescent probes



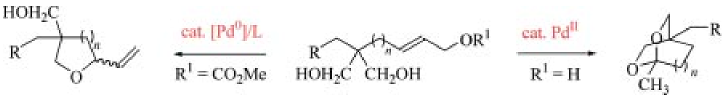
A Songashira–Hagihara cross-coupling reaction is the key step in the synthesis of amphiphilic linear compounds that contain the conjugated chromophores pentaene, tetraenyne, ω-phenyltetraene, or ω-phenyltrienyne coupled to a hydrophilic head-group through a polymethylene chain. These lipidic structures show absorption and fluorescence spectral properties suitable for a number of applications in lipidomics.

Intramolecular C–O Bond Formation

A. Zawisza, B. Fenêt,
D. Sinou* 2296–2309

Palladium-Catalyzed Formation of Cyclic Ethers – Regio-, Stereo- and Enantioselectivity of the Reaction

Keywords: Cyclization / Palladium / Oxygen heterocycles / Diastereoselectivity / Enantioselectivity



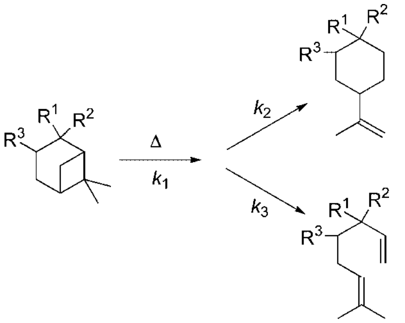
The Pd^0-catalyzed cyclization of the methyl carbonates of ω,ω-bis(hydroxymethyl)-α,β-unsaturated alcohols efficiently and stereoselectively afforded 3-alkyl-3-hydroxymethyl-5-vinyltetrahydrofurans. The use of chiral ligands gave the corresponding tetrahydrofuran derivatives in low to moderate enantiomeric ratios. The Pd^{II}-catalyzed cyclization of ω,ω-bis(hydroxymethyl)-α,β-unsaturated alcohols afforded 1-methyl-4-alkyl-2,6-dioxobicyclo[2.2.2]octanes as the main products.

Terpenoid Pyrolysis

A. Stolle, B. Ondruschka,*
W. Bonrath 2310–2317

Comprehensive Kinetic and Mechanistic Considerations for the Gas-Phase Behaviour of Pinane-Type Compounds

Keywords: Terpenoids / Pyrolysis / Reaction mechanisms / Rearrangement / Radical reactions / Kinetic modelling



The thermal behaviour of selected pinane-type compounds, α-pinene, β-pinene, pinane and nopinone, has been investigated. Experimental evidence for the formation of pyrolysis products by a biradical pathway is discussed. In addition to these results a kinetic model describing the isomerisation of the bicyclic compounds to their acyclic and monocyclic isomers is presented.

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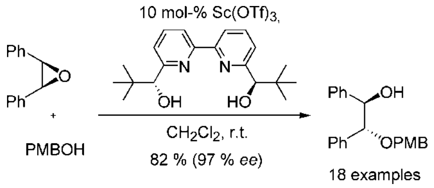
Asymmetric Catalysis

Chiral 1,2-diol monoethers are obtained in good yields and partly excellent enanantioselectivities by the nucleophilic ring-opening of *meso*-epoxides with aliphatic alcohols. A C_2-symmetric scandium-bipyridine catalyst is employed to effect this desymmetrization reaction.

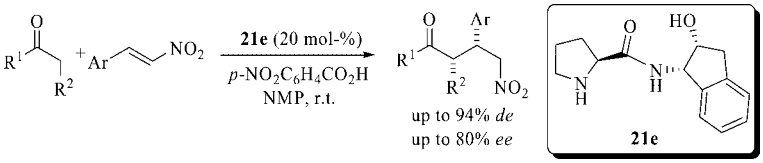


A. Tschöp, A. Marx, A. R. Sreekanth, C. Schneider* 2318–2327

Scandium-Bipyridine-Catalyzed, Enantioselective Alcoholysis of *meso*-Epoxides

Keywords: Alcohols / Asymmetric catalysis / Desymmetrization / Epoxide / Scandium-bipyridine

Asymmetric Michael Addition



Prolinamide **21e** exhibits excellent activities in the conjugate addition of ketones to nitrostyrenes, leading to products in good yields and diastereo-, and enantioselectivities in the presence of an equimolar amount of *p*-nitrobenzoic acid. ESI-MS studies are used to characterize the intermediates assumed for the catalytic cycle. Transition-state energies for the rate-limiting C–C bond-forming step have been calculated.

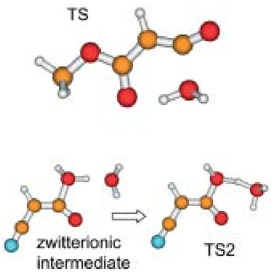
D. Almaşi, D. A. Alonso,* E. Gómez-Bengoa, Y. Nagel, C. Nájera* 2328–2343

Asymmetric Conjugate Addition of Ketones to β-Nitrostyrenes by Means of 1,2-Amino-Alcohol-Derived Prolinamides as Bifunctional Catalysts

Keywords: Asymmetric catalysis / Michael addition / Ketones / Amino acids

Reaction Mechanisms

A DFT study of the nucleophilic addition of water to methylcarboxyketene and cyanoketene was conducted. The results agree with the experimental data, according to which the addition to methylcarboxyketene occurs by a concerted mechanism and the addition to cyanoketene occurs via a zwitterionic intermediate.

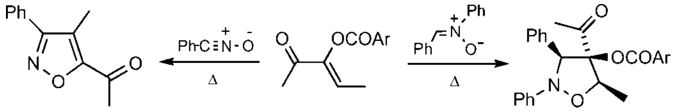


J. M. Hermida-Ramón, J. Rodríguez-Otero,* E. M. Cabaleiro-Lago 2344–2351

DFT Study of the Nucleophilic Addition of Water to Ketenes

Keywords: Density functional calculations / Reaction mechanisms / Solvent effects / Nucleophilic addition / Ketenes

Pericyclic Reactions



The regioselectivity in 1,3-dipolar cycloadditions of captodative olefins 1-acetylvinyl carboxylates substituted with alkyl groups at the β position with nitrones is opposite to that observed for their unsubstituted analogs. This effect of the β substituent is rationalized in terms of DFT calculations of the transition states.

R. Herrera, J. A. Mendoza, M. A. Morales, F. Méndez, H. A. Jiménez-Vázquez,* F. Delgado, J. Tamariz* 2352–2364

Selectivity in 1,3-Dipolar Cycloadditions of β-Substituted Captodative Olefins – An Experimental and DFT Transition State Study

Keywords: Cycloadditions / Nitrones / Regioselectivity / Density functional calculations / Transitions states

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If not otherwise indicated in the article, papers in issue 13 were published online on April 10, 2007