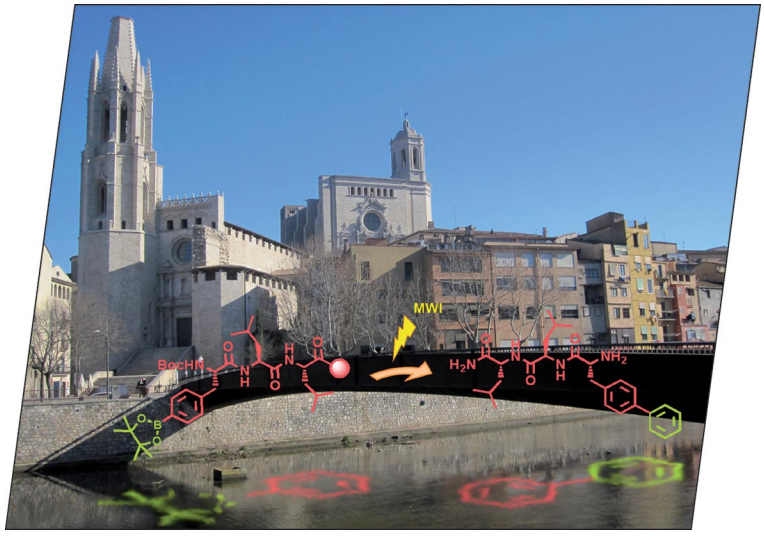
COVER PICTURE

The cover picture shows the skyline of the old part of Girona in northeast Catalonia, Spain. In the foreground is one of the many bridges that span the river Onyar from the new part of the town to the Jewish quarter. This bridge, named the Pont de Sant Feliu, is the usual starting point for visiting this quarter. It offers a nice view of the narrow colourful houses that back onto the river and allows an impressive view of the Cathedral and the Sant Feliu church. Built in different styles (11th−17th century AD), the Cathedral preserves a Gothic nave with the widest arched span in the world. In this picture, the Pont de Sant Feliu serves as a means to depict the synthesis of a 4-arylphenylalanine tripeptide from a resin-bound phenylalanine boronate. Details can be found in the article by L. Feliu et al. on p. 1461ff, and results on the formation of the boronate through a solid-phase Miyaura borylation are also discussed.



CONTENTS

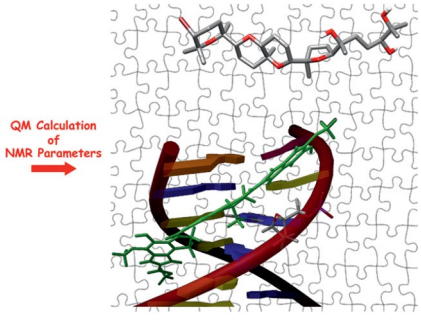
CONFERENCE REPORT

An overview of the *Chimie Supramoléculaire Journées Scientifiques en l'honneur de Jean-Pierre Sauvage*, organized by the Institut de Science et d'Ingénierie Supramoléculaires (ISIS) at the University of Strasbourg, held on November 26 and 27, 2009 in Strasbourg is presented.

MICROREVIEW

QM Calculation of NMR Parameters

Keywords: Natural products / NMR spectroscopy / Stereochemistry / Quantum chemistry / Drug-Macromolecule interactions

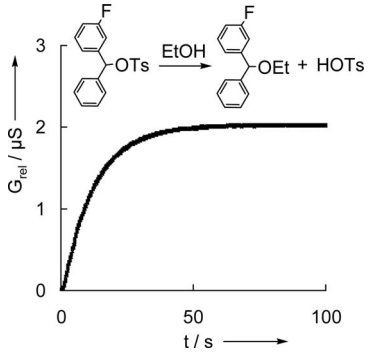


The present microreview highlights the recent goals reached by the application of quantum mechanical calculation of NMR properties for structural studies of natural products. It is also shown how this method can lead the total synthesis of complex natural compounds and its potential application in ligand–macromolecule interaction studies.

SHORT COMMUNICATIONS

Nucleofugality Scales

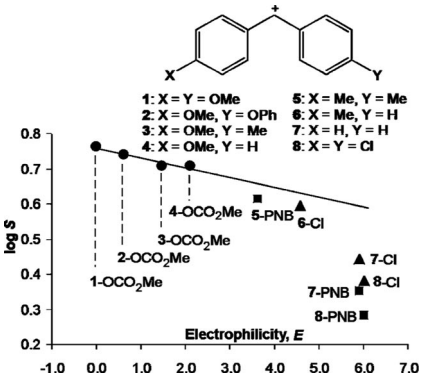
Keywords: Carbocations / Kinetics / Nucleophilic substitution / Linear free relationships / Solvent effects



Solvolysis rate constants of *m*-fluoro-substituted benzhydryl derivatives with good leaving groups have been determined in different solvents. The rate constants were subjected to a least-squares fit to the correlation $\log k_s = s_f(N_f + E_f)$ for determining the electrofugality parameters E_f of destabilized benzhydrylium ions.

Selectivity of Benzhydrylium Ions

The selectivities ($S = k_E/k_W$) of stabilized benzhydrylium ions in the series of aqueous ethanols depend on solvent polarity because of different microsolvation of the transition states for hydrolysis and ethanolysis, respectively. The selectivities of ions **1**−**4** are higher than those for less stable cations **5**−**8** and do not depend on the leaving group, indicating that in given conditions free ions are formed.

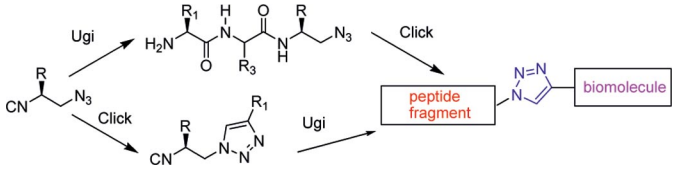


B. Denegri, M. Matić, O. Kronja* ..... 1440−1444

Selectivity of Stabilized Benzhydrylium Ions

Keywords: Kinetics / Solvolysis / Microsolvation / Stabilized benzhydrylium ions

Isocyanoazides



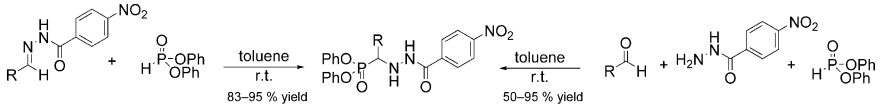
Efficient synthesis of chiral scaffolds combining isocyanide and azide groups permits the efficient construction of both amino (hydroxy) acids and triazole derivatives and the preparation of hybrid peptide molecules by Ugi/click or click/Ugi strategies.

V. G. Nenajdenko,* A. V. Gulevich, N. V. Sokolova, A. V. Mironov, E. S. Balenkova ..... 1445−1449

Chiral Isocyanoazides: Efficient Bifunctional Reagents for Bioconjugation

Keywords: Isocyanides / Azides / Multicomponent reactions / Click chemistry / Bioconjugation

Hydrophosphonylation



The uncatalyzed preparation of α-hydrazido phosphonate derivatives was achieved by playing with the pK_as of different dialkyl/diphenyl phosphites. The synthesis was conducted under mild and efficient conditions and, under an atom-economy point of view, for a variety of aliphatic aldehydes.

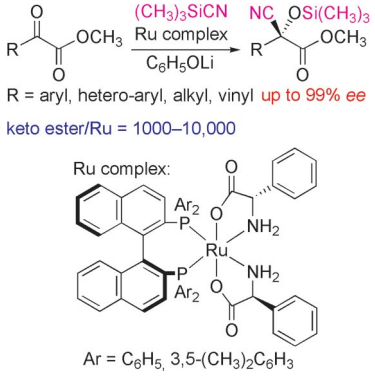
R. P. Herrera,* D. Roca-López, G. Navarro-Moros ..... 1450−1454

Uncatalyzed Three-Component Synthesis of α-Hydrazido Phosphonates

Keywords: Multicomponent reactions / Phosphonates / Hydrazones / Nucleophilic addition

Asymmetric Cyanosilylation

Asymmetric cyanosilylation of α-keto esters with the catalyst system consisting of [Ru(phgly)$_2$(binap)] and C_6H_5OLi affords the silylated cyanohydrins in high enantioselectivity (up to 99% *ee*). This catalyst is sufficiently active to complete the reaction with a substrate-to-catalyst molar ratio of 10,000 at −50 °C. A plausible reaction pathway is also proposed.



N. Kurono, M. Uemura, T. Ohkuma* ..... 1455−1459

Asymmetric Cyanosilylation of α-Keto Esters Catalyzed by the [Ru(phgly)$_2$(binap)]−C_6H_5OLi System

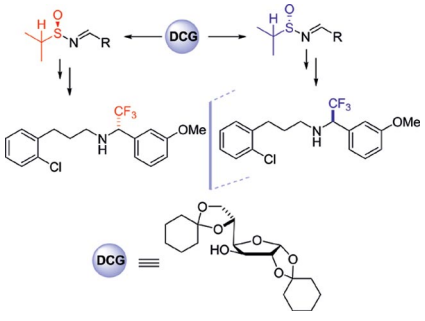
Keywords: Asymmetric catalysis / Lithium / Ruthenium / Cyanosilylation

CONTENTS

FULL PAPERS

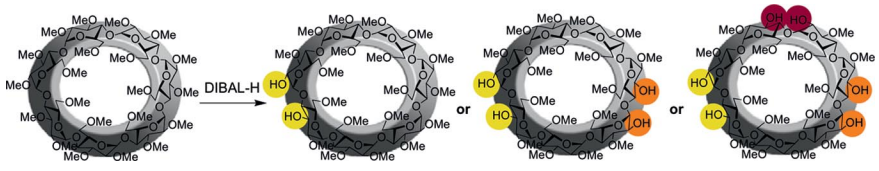
Enantiodivergent Synthesis

The first synthesis of both enantiomers of trifluoromethylated analogues of the calcimimetic NPS R-569 is reported. The method is based on the enantiodivergent synthesis of both enantiomers of *N*-(isopropylsulfinyl)imines using the "DAG methodology" and on a highly diastereoselective addition of Ruppert–Prakash's reagent to these *N*-(isopropylsulfinyl)imines.



Keywords: Amines / Diastereoselectivity / Enantioselectivity / Sulfinylimines / Sulfinamides

Modified Cyclodextrins

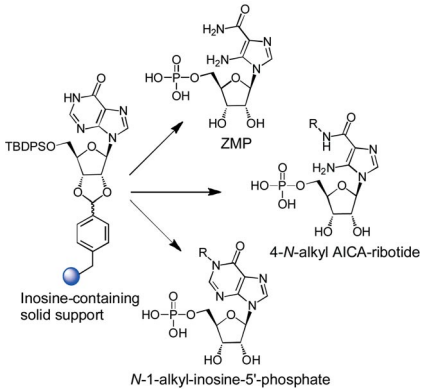


Diisobutylaluminium hydride regioselectively delivers a diol, a tetrol or an hexol from permethylated β-cyclodextrin. The mechanism for this remarkable reaction is proposed in this paper.

Keywords: Cyclodextrins / Dealkylation / Reaction mechanisms / Regioselectivity / Protecting groups

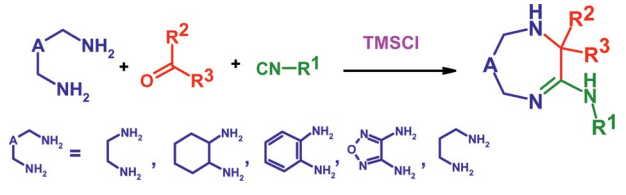
Nucleotide Analogues

5-Amino-1-(β-D-ribofuranosyl)imidazole-4-carboxamide-5′-monophosphate (ZMP), as well as collections of its 4-*N*-alkyl derivatives and *N*-1-alkylinosine-5′-phosphates, have been synthesised in high yields by a solid-phase strategy using a 5′-protected inosine connected to the solid support through the 2′,3′-positions.



Keywords: ZMP / Nucleotides / Solid-phase synthesis / Phosphorylation

Multicomponent Heterocyclization



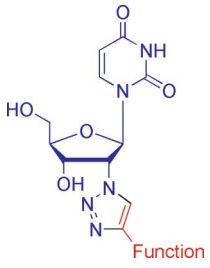
Novel multicomponent reactions based on primary 1,2- and 1,3-diamines, carbonyl compounds, and isocyanides have been developed as a general strategy for the synthesis of unique amino derivatives of various privileged azaheterocycle structures, including pyrazines, 1,4-diazepines, quinoxalines, and their fused and spirocyclic analogues.

Keywords: Multicomponent reactions / Molecular diversity / Heterocycles / Lewis acids / Cyclization

CONTENTS

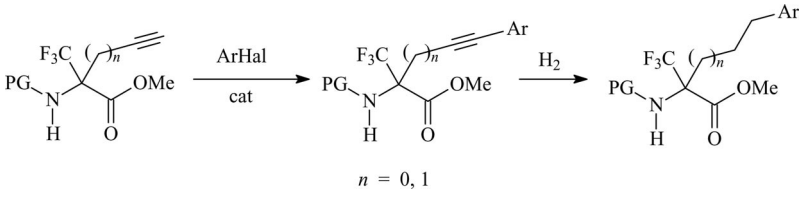
2′-Triazoyl-2′-deoxyluridines

New uridines were synthesized by Cu-catalyzed cycloaddition of 2′-azido-2′-deoxyuridine with alkynes, wherein a biochemically interesting function (lipid, fluorescent label, amino acid, glucose, or biotin) was tethered to the uridine through a 1,2,3-triazole ring. The anchoring of the cholesterol-functionalized uridines in the phospholipid membrane was studied by NMR spectroscopy.



Keywords: Cycloaddition / Nucleosides / Lipids / Membranes / NMR spectroscopy / Azides

Trifluoroalanine Derivatives



α-CF_3-α-amino acid derivatives bearing an arylalkynyl moiety at the α-carbon atom can be prepared by an efficient method based on palladium-catalyzed cross-coupling of the corresponding α-propargyl (ethynyl) α-amino esters with aryl halides to afford amino acid derivatives with an internal triple bond that is suitable for further modifications.

Keywords: Amino acids / Alkynes / Cross-coupling / Peptidomimetics / Hydrogenation

CORRECTION

Keywords: Asymmetric catalysis / Alkylation / Palladium / P ligands / Fukui function / Kinetics

* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 7 were published online on February 16, 2010

