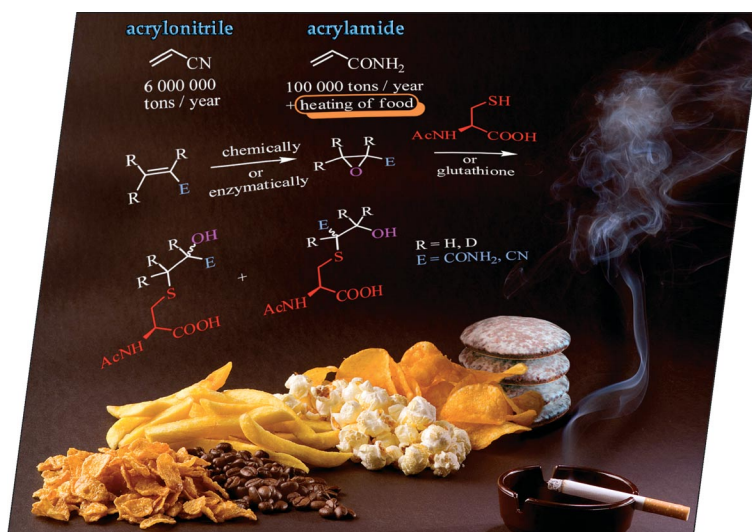




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further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

COVER PICTURE

The cover picture shows data on the total worldwide industrial production of acrylonitrile and acrylamide. These monomers were found to be carcinogenic in rats, mutagenic in *E. coli*, harmful to blood and to the liver, as well as to the immuno, neuro, reproductive and respiratory systems. Their enzymatic epoxidation to even more poisonous oxiranes is believed to be responsible for the carcinogenic activity. In vivo, cyano- or carbamoyloxiranes readily react with glutathione and at the end of this metabolic path yield two regioisomeric *S*-alkylated *N*-acetylcysteines (see cover picture). Both acrylonitrile and acrylamide are present in cigarette smoke. Acrylamide has also been found in various starchy foods such as the ones shown, which have been roasted or baked. Though the possible risk of such food to public health is unclear, dietary intake of acrylamide contributes a lot to overall human exposure. For quantification of the oxidative metabolites of acrylonitrile and acrylamide in humans, two sets of the regioisomeric reference compounds were synthesized with deuterium labels. They may be used as “ideal” internal standards in all toxicological studies aimed at quantitative determination and product distribution of oxidative urinary metabolites of acrylonitrile and acrylamide. Details are discussed in the article by A. de Meijere et al. on p. 4417ff. The authors acknowledge the support of this work by Irene Böttcher-Gajewski (Göttingen), who provided the photographical content of the cover picture.



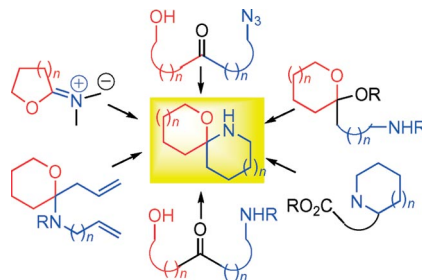
MICROREVIEW

Spiroaminals

M.-E. Sinibaldi,* I. Canet* ... 4391–4399

Synthetic Approaches to Spiroaminals

Keywords: Nitrogen heterocycles / Oxygen heterocycles / Spiro compounds / Synthetic methods



This review covers general strategies for the synthesis of spiroaminal frameworks.

SHORT COMMUNICATIONS

Catalytic Glycosylation

C. Lucas-Lopez, N. Murphy,
X. Zhu* 4401–4404



Catalytic Glycosylation with Glycosyl Thioimide Donors

Keywords: Glycosylation / Sulfur / Catalytic activation / Carbohydrates



A new class of glycosyl thioimides, glycosyl *N*-phenyl-trifluorothioacetimidates, were readily prepared and activated with catalytic amounts of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Their

reactions with acceptors gave the corresponding glycosidation products in very good to excellent yields.

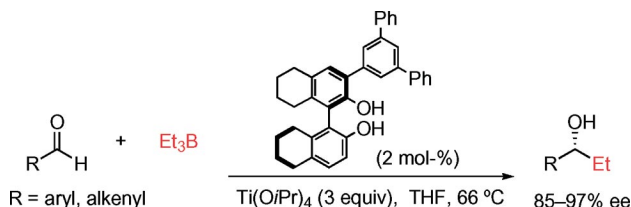
Asymmetric Catalysis

T. Ukon, T. Harada* 4405–4407



Catalytic Asymmetric Alkylation of Aldehydes by Using Trialkylboranes

Keywords: Asymmetric catalysis / Alkylation / asymmetric synthesis / Boron / Titanium



Triethylborane can be used in the asymmetric alkylation of aldehydes by using a 3-(3,5-diphenylphenyl)- H_8 -BINOL-derived titanium(IV) catalyst in the presence of an excess amount of titanium tetraisopropoxide.

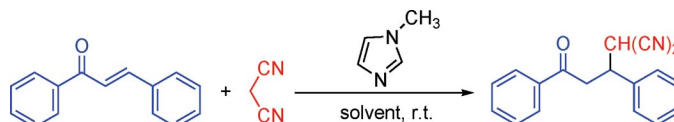
The reaction proceeds with a low catalyst loading (2 mol-%), exhibiting high enantioselectivity for aromatic and unsaturated aldehydes.

Kinetics in Ionic Liquids

M. Mečiarová,* M. Cigán,* Š. Toma,
A. Gáplovský 4408–4411

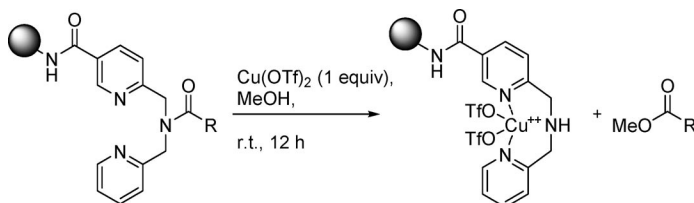
Kinetic Study of Michael Addition Catalyzed by *N*-Methylimidazole in Ionic Liquids: Residual *N*-Methylimidazole in Ionic Liquids as a Strong Base

Keywords: Ionic liquids / Michael addition / Basicity / Kinetics



The reaction rate for the Michael addition of malonodinitrile to chalcone was found to be higher in some common imidazolium-based ionic liquids than in conventional organic solvents. The catalytic

activity of *N*-methylimidazole as a basic catalyst was much more expressive in the studied imidazolium ionic liquids than in molecular solvents.



Cu²⁺ complexation of a bispicolylamide entity leads to weakening of the N–C–amide bond, which can then be cleaved by methanolysis. On the basis of this principle, we developed a versatile and robust linker

for solid-phase chemistry that was evaluated for its utility in peptide synthesis and in reductive amination, Pd-mediated C–C–coupling, and metathesis reactions.

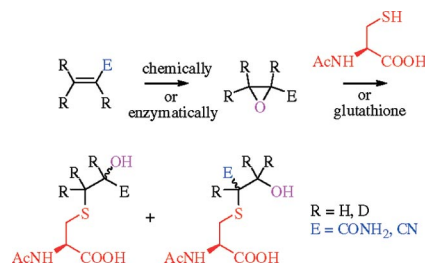
M. C. Bröhmer,
W. Bannwarth* 4412–4415

Forced Complexation of Nitrogen Leading to a Weakening of Amide Bonds: Application to a New Linker for Solid-Phase Chemistry

Keywords: Solid-phase synthesis / Linkers / Amides / Cleavage reactions / Copper

FULL PAPERS

Practical syntheses of all four oxidative metabolites of acrylamide and acrylonitrile in their unlabelled and deuterium-labelled forms make it possible to clarify the metabolism of and quantify human exposure to these toxic electrophiles. An approach to compounds with the rare structural fragment R¹OCH₂CH(SR²)CN [R¹ = protecting group or H, R² = (functionally substituted) alkyl or aryl group] has been developed.

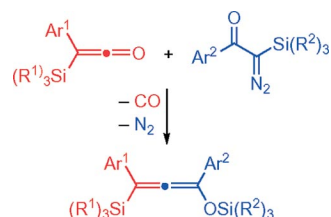


V. N. Belov, S. M. Korneev, J. Angerer,
A. de Meijere* 4417–4425

Syntheses of D-Labelled Oxidative Metabolites of Acrylamide and Acrylonitrile for the Quantification of Their Toxicities in Humans

Keywords: Isotopic labelling / Acrylonitrile / Acrylamide / Metabolism / Toxicology

Surprisingly, it was found that aryl trialkylsilyl ketenes are easily obtained from aryl-substituted α -silyl α -diazo ketones in an acid-catalyzed Wolff rearrangement. Furthermore, these ketenes react smoothly with α -silyl α -diazo ketones to form 3-silyl-1-silyloxyallenes.

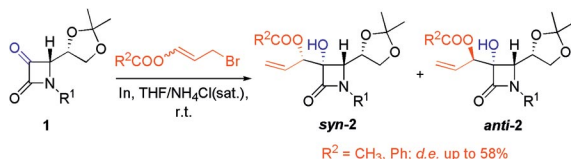


S. M. Bucher, R. Brückmann,
G. Maas* 4426–4433

Aryl Trialkylsilyl Ketenes: Acid-Catalyzed Synthesis from 1-Aryl-2-diazo-2-trialkylsilylethanones and Their Conversion into 3-Silyl-1-silyloxyallenes

Keywords: Allenes / Diazo compounds / Ketenes / Rearrangement / Silylation

Synthetic Methods



Regio- and stereoselective acyloxyallylation reactions of azetidine-2,3-diones with 3-bromopropenyl esters (acetate or benzoate), promoted by indium under Barbier

conditions in aqueous media, gave densely functionalized 3-substituted 3-hydroxy- β -lactams.

B. Alcaide,* P. Almendros, C. Aragoncillo,
G. Cabrero, R. Callejo,
M. P. Ruiz 4434–4439

Indium-Promoted Acyloxyallylation Reaction of Azetidine-2,3-diones in Aqueous Media: A New Route to Densely Functionalized 3-Substituted 3-Hydroxy- β -lactams

Keywords: Addition reactions / Ketones / C–C coupling / Heterocycles / Indium / Synthetic methods

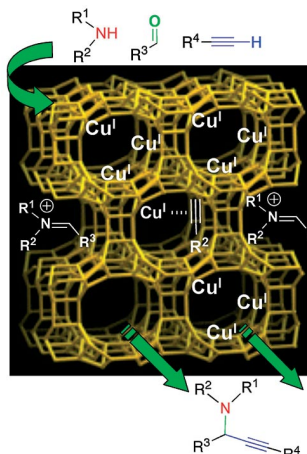
CONTENTS

Zeolite Catalysts

M. K. Patil, M. Keller, B. M. Reddy,
P. Pale,* J. Sommer* 4440–4445

Copper Zeolites as Green Catalysts for Multicomponent Reactions of Aldehydes, Terminal Alkynes and Amines: An Efficient and Green Synthesis of Propargylamines

Keywords: Zeolites / Copper / Multicomponent reactions / Amines / Alkynes



Cu^I-modified zeolites, especially Cu^I-USY, have proved to be very efficient catalysts in multicomponent reactions. Such catalysts allowed for an efficient, solvent-free synthesis of propargylamines from aldehydes, amines, and terminal alkynes.

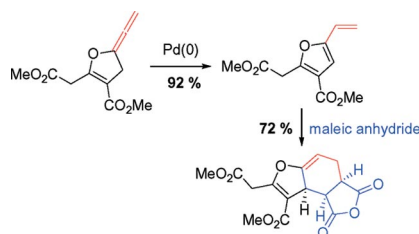
Allene Isomerisation

A. Ghobsi, S. Hacini, L. Wavrin,
A. Gaudel-Siri, A. Corbères, C. Nicolas,
D. Bonne,* J. Viala,
J. Rodriguez* 4446–4453



Palladium-Catalysed Isomerisation of 2-Vinylidenefurans to 1,3-Dienes and Some Aspects of Their Reactivity

Keywords: Palladium / Allenes / Isomerization / Diels–Alder reactions



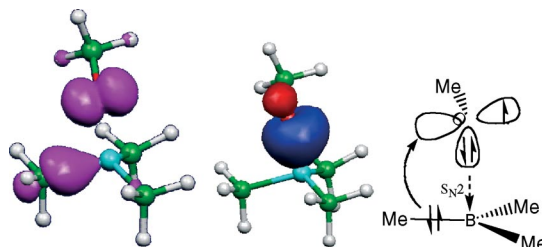
Palladium has been employed as an efficient catalyst in the isomerisation of easily synthesised vinylidenefurans to the corresponding 1,3-dienes. When treated with dienophiles, these stable compounds afforded the expected Diels–Alder adducts in good yields and high diastereoselectivities.

Oxygen Radicals

C. Carra, J. C. Scaiano* 4454–4459

Nucleohomolytic Substitution at Boron: A Computational Approach

Keywords: Boron / Nucleophilic substitution / Density functional calculations / Radicals



Reaction of oxygen-centered radicals at the boron center is initiated by approach of a lone pair on oxygen to the empty boron p orbital, bearing close resemblance to the

mechanism for nucleophilic substitution, and it is best described as a nucleohomolytic displacement, rather than a homolytic reaction.

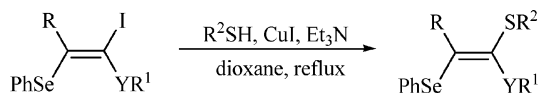
Copper-Catalyzed Cross Coupling

F. Manarin, J. A. Roehrs, E. A. Wilhelm,
G. Zeni* 4460–4465



Copper-Catalyzed Cross-Coupling of Thiols with 1-Iodo-2-chalcogenoalkenes

Keywords: Copper / Cross-coupling / Organoselenium compounds / Thiols

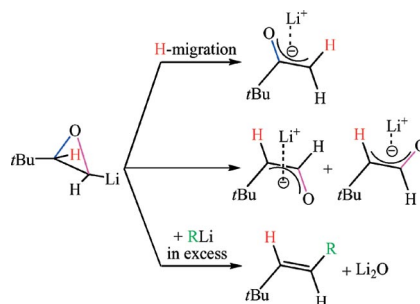


R = alkyl, aryl; YR¹ = SCH₃, SeCH₃; R² = alkyl, aryl, heteroaryl

A new method for the synthesis of densely substituted alkenes containing chalcogenide atoms by cross-coupling reactions between 1-iodo-2-chalcogenoalkenes and thiols

using copper(I) as catalyst in a ligand-free system is described. The desired cross-coupling products were obtained in good yields and with satisfactory selectivity.

No carbene found! High-level ab initio calculations carried out on the reactivity of oxiranyllithium show that no such intermediate is found on the various potential energy surfaces. The effect of solvation by MeLi was explored: the catalytic effect of an excess of MeLi is highlighted by olefin formation.

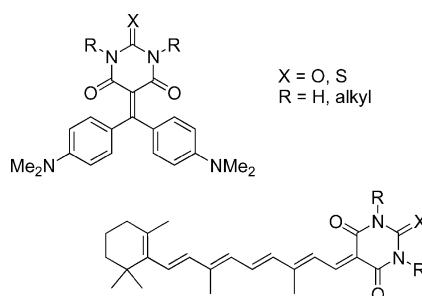


A. Bouyacoub, R. Hadjadj-Aoul, F. Volatron* 4466–4474

Reactivity of (Mono-*tert*-butyloxiranyl)-lithium: A Theoretical Ab Initio Study

Keywords: Ab initio calculations / Reaction mechanisms / Oxiranyl anion / Alkyl-lithium / Carbenes

The solvatochromism of barbiturate dyes bearing different chromophoric systems has been investigated to separate the effect of the solvent's dipolarity from its polarizability. Thus, the UV/Vis absorption maxima of these dyes in a variety of solvents have been analysed by using the Kamlet–Taft and the Catalán solvent parameter sets.

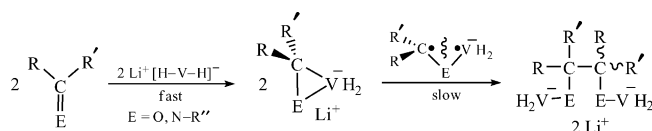


M. Bauer, A. Rollberg, A. Barth, S. Spange* 4475–4481

Differentiating Between Dipolarity and Polarizability Effects of Solvents Using the Solvatochromism of Barbiturate Dyes

Keywords: Solvatochromism / Solvent effects / Polarity / Barbiturates / Donor–acceptor systems / Polyenes

Subvalent Vanadium Salts



Subvalent vanadium(I) salts of empirical formulas, VCl, vanadium(I) chloride and LiVH₂, lithium vanadium(I) dihydride, are evaluated in their reactions with a wide

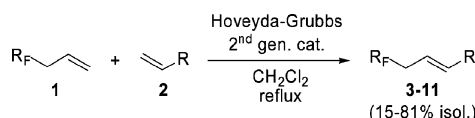
variety of π - and σ -bonded organic substrates. Compared with their chromium counterparts, these reagents are much milder and selective epimetallating agents.

J. J. Eisch,* P. O. Fregene 4482–4492

Vanadium(I) Chloride and Lithium Vanadium(I) Dihydride as Selective Epimetallating Reagents for π - and σ -Bonded Organic Substrates

Keywords: Vanadium(I) chloride / Lithium vanadium(I) dihydride / Epimetallation / Cleavage of carbon-heteroatom bonds / Reductive dimerization

Cross-Metathesis



Perfluoroalkyl groups can be easily attached to various compounds under mild reaction conditions by cross-metathesis be-

tween terminal alkenes and (perfluoroalkyl)propenes catalysed by the Hoveyda–Grubbs second-generation catalysts.

B. Eignerová, M. Dračinský, M. Kotora* 4493–4499

Perfluoroalkylation through Cross-Metathesis between Alkenes and (Perfluoroalkyl)propenes

Keywords: Perfluoroalkylation / Ruthenium / Cross-metathesis / Hoveyda–Grubbs catalysts / Alkenes

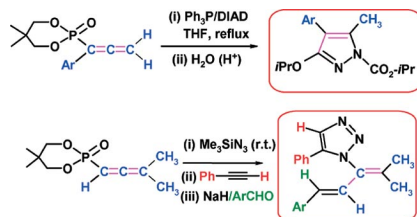
CONTENTS

Heterocyclic Chemistry

M. Chakravarty, N. N. Bhuvan Kumar,
K. V. Sajna,
K. C. Kumara Swamy* 4500–4510

Allenylphosphonates – Useful Precursors
of Pyrazoles and 1,2,3-Triazoles

Keywords: Allenes / Phosphonates / Hetero-
cycles / Pyrazoles / Triazoles



Novel pyrazoles and triazoles with or without phosphorus substituents have been synthesized from allenylphosphonates.

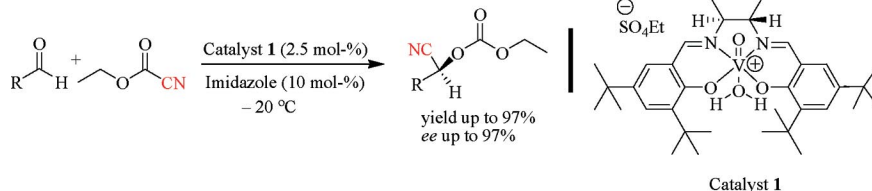
Cyanoformylation

N.-u. H. Khan,* S. Agrawal, R. I. Kureshy,
S. H. R. Abdi, K. J. Prathap,
R. V. Jasra 4511–4515



Vanadium(V) Salen Complex Catalyzed
Highly Enantioselective Cyanoformylation
of Aldehydes in the Presence of Imidazole
as a Cocatalyst

Keywords: Cyanides / Vanadium / Alde-
hydes / Nitrogen heterocycles / Asymmetric
catalysis



Cyanoformylation of aldehydes catalyzed
by V^V chiral salen complex **1** was ac-
complished in the presence of several co-
catalysts. Excellent yields and *ee* values for

the resulting cyanohydrin carbonates were
achieved when imidazole was used as a co-
catalyst at –20 °C. The *ee* values could be
improved by recrystallization.

IN MEMORIAM

H. G. Thomas* 4517–4525



Hermann Stetter (1917–1993)

Keyword: Reminiscences



* Author to whom correspondence should be addressed.

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