

























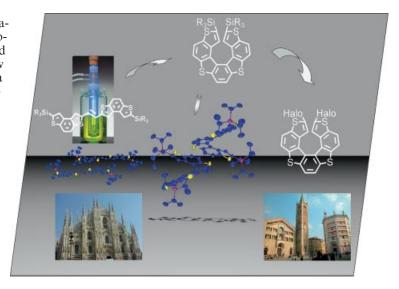




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

COVER PICTURE

The cover picture shows the photochemical cyclization of silyl-substituted trans-1,2-bis(benzodithiophen-2-vl)ethenes into the corresponding silvlated helicenes and the transformation of these into new halogenated helicenes. The picture underlines a peculiar aspect of the paper, that is, the high solubility of the above silvlated trans alkenes, which is a consequence of the presence of the two silyl groups and results in a very fast and easy photocyclization that can be performed in solution by using a glass reactor with an immersion Hg lamp. The molecular packing of the trans alkenes in solution shows a long interplanar distance between two molecules, which accounts for its high solubility. The work is a collaboration between Milan and Parma Universities, whose Cathedrals are shown. Details are discussed in the article by E. Licandro et al. on p. 4499ff.



MICROREVIEW

Carbonylation of Amines

D. J. Díaz, A. K. Darko, L. McElwee-White* 4453-4465

Transition Metal-Catalyzed Oxidative Carbonylation of Amines to Ureas

Keywords: Carbonylation / Homogeneous catalysis / Green chemistry

Synthesis of ureas from amines traditionally involves stoichiometric reactions of phosgene or its derivatives, which are associated with environmental and waste disposal issues. Because of the prevalence of urea moieties in molecules of interest, alternative catalytic routes for the oxidative conversion of amines to ureas using CO as the carbonyl source have been developed. This microreview discusses recent developments in transition metal-catalyzed oxidative carbonylation of amines to ureas.

SHORT COMMUNICATIONS

Organoborane C-Alkylation

M. Valpuesta,* C. Muñoz, A. Díaz, R. Suau, G. Torres* 4467-4470

Organoborane Reagents in the C-Alkylation of Aromatic Aldimines

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

The reaction of an aldimine with dicyclohexylboron chloride in the presence of hydrogen peroxide gives *N*-[cyclohexyl(aryl)methyl]arylamines **2** in good yields via oxidized imine—borane complexes. The

amines can also be obtained by a threecomponent reaction involving an arenecarbaldehyde, an arylamine and a dialkylchloroborane reagent.

Hydroamination

BiCl₃-Catalyzed Hydroamination of Norbornene with Aromatic Amines

Keywords: Hydroamination / Lewis acids / Bismuth / Catalysis

A BiCl₃-catalyzed hydroamination of norbornene, in which different electron-withdrawing groups were tolerated on amines, was presented. This process represents a

rare system for main group Lewis acid catalyzed intermolecular hydroamination of unactivated alkenes.



Hypervalent Iodine

Phenyliodine(III) sulfate, which has a complex polymeric structure of the trimeric iodosylbenzene units linked by sulfate anions, was prepared; this sulfate can find practical application as a readily available, stable, and water-soluble hypervalent iodine reagent with a reactivity pattern similar to that of iodosylbenzene. Preparation and Structure of Oligomeric Iodosylbenzene Sulfate (PhIO)₃·SO₃: Stable and Water-Soluble Analog of Iodosylbenzene

Keywords: Iodine / Hypervalent compounds / Iodosylbenzene / Oxidation / X-ray diffraction

[2+2] Cycloadditions

OBn +
$$R^1$$
 CN 1 atm OBn R^1 CN R^2 CN R^2 CN R^2 CN

The reaction of (benzyloxymethylene)cyclopropane with alkylidenemalononitriles at ambient pressure afforded the corresponding cyclobutane derivatives in good-tohigh yields. Control experiments proved that the reaction proceeds via a well-stabilized zwitterionic intermediate. Thermally Induced [2+2] Cycloadditions of (Benzyloxymethylene)cyclopropane with Alkylidenemalononitriles

Keywords: Cycloaddition / Cyclobutanes / Enols / Cyclopropanes

Ambiphilic Ligands

Lithiation of 2-bromo-2'-diphenylphosphanyl diphenyl ether in toluene prevents the undesirable cyclization observed in THF and allows access to a phosphane—borane and an unsymmetrical diphosphane featuring a flexible diphenyl ether tether.

Ambiphilic Compounds: Synthesis and Structure of a Phosphane—Borane with a Flexible Diphenyl Ether Tether

Keywords: Ambiphilic derivatives / Phosphanes / Boranes / Tethered compounds / Lithiation / Solvent effects

$\begin{array}{c} R \\ R \\ \end{array} + \begin{array}{c} O \\ R' \end{array} \qquad \begin{array}{c} PTA \ (10-30 \ mol-\%) \\ \hline MeCN, r.t. \end{array} \qquad \begin{array}{c} R \\ R_2 \\ \hline PNH \\ Ar \end{array} \qquad \begin{array}{c} Cat.: \\ \hline NNP \\ PTA \end{array}$

A novel *N*-thiophosphoryl imine based aza-Morita – Baylis – Hillman (MBH) reaction was developed. The corresponding aza-MBH adducts were obtained in fair-to-excellent yields in the presence of an efficient air-stable nucleophilic trialkyl-phosphane organocatalyst – PTA. More-

over, the *N*-thiophosphoryl moiety can be readily deprotected through acidic methanolysis in excellent yields. This protocol provides a convenient method for the synthesis of synthetically valuable α -methylene- β -amino ketone or acid derivatives.

Aza-Morita-Baylis-Hillman Reactions

The Aza-Morita—Baylis—Hillman Reaction of *N*-Thiophosphoryl Imines Catalyzed by 1,3,5-Triaza-7-phosphaadamantane (PTA) — Convenient Synthesis of α-Methylene-β-Amino Ketone or Acid Derivatives

Keywords: Imines / Alkenes / Aza-Morita—Baylis—Hillman reaction / Ketones

FULL PAPERS

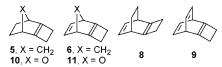
Pyramidalized Alkenes

J. A. Fernández,

S. Vázquez* 4493-4498

A Theoretical Study of Tricyclo- $[4.2.1.0^{2.5}]$ non-2(5)-ene, Tricyclo $[4.2.2.0^{2.5}]$ -dec-2(5)-ene and Related Pyramidalized Alkenes

Keywords: Ab initio calculations / Density functional calculations / Hydrocarbons / Pyramidalized alkenes / Strained molecules



Ab initio and DFT calculations showed that tricyclo[4.2.1.0^{2,5}]non-2(5)-ene (5), tricyclo[4.2.2.0^{2,5}]dec-2(5)-ene (8) and the related compounds shown are pyramidalized compounds. Triene 9, which displays a method-dependent ground state, is antiaromatic.

Tetrathia[7]helicenes

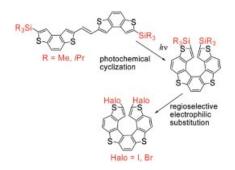
A. Bossi, S. Maiorana, C. Graiff,

A. Tiripicchio, E. Licandro* ... 4499-4509



Silyl-Substituted Tetrathia[7]helicenes: Synthesis, X-ray Characterization and Reactivity

Keywords: C-C coupling / Heterohelicenes / Sulfur heterocycles / Fused-ring systems / Olefination



The synthesis and X-ray characterization of novel silyl-functionalized helicenes, the separation into enantiomers of one of them and their regioselective transformation into dihalogenohelicenes are described.

Binding Thermodynamics

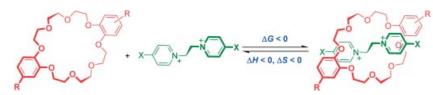
Y. Liu,* C.-J. Li, H.-Y. Zhang,

L.-H. Wang, X.-Y. Li 4510-4516



Thermodynamics of Complexes between Dibenzo-24-crown-8 Derivatives and 1,2-Bis(pyridinium)ethanes

Keywords: Crown compounds / Microcalorimetric titration / Pseudorotaxane / Thermodynamics



The binding behavior of 1,2-bis(pyridinium)ethane derivatives with dibenzo-24-crown-8 derivatives has been investigated. The results obtained indicate that the formation of [2]pseudorotaxanes is an enthalpy-driven process, and the nature of

the substituents attached to 1,2-bis(pyridinium)ethane and the catechol ring on dibenzo-24-crown-8 dramatically affects the molecular recognition behavior and the binding thermodynamics.

Azetidines

E. Banide, V. Lemau de Talancé,

G. Schmidt, H. Lubin, S. Comesse,

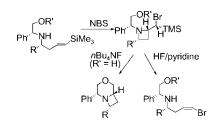
L. Dechoux, L. Hamon,

C. Kadouri-Puchot* 4517-4524



On the Synthesis and Reactivity of Enantiopure Azetidines

Keywords: Azetidines / Bromocyclization / Amino alcohols / Vinylsilane / Vinyl bromide / Cyclization



β-Amino alcohols with an (E)-vinylsilane moiety were cyclized in the presence of N-bromosuccinimide to afford diastereomerically pure azetidines. The reactivity of the azetidines towards fluorinated reagents was studied.



Indolecarboxylate Synthesis

A transition-metal-free, simple and efficient one-pot method for the synthesis of indole-2,3-dicarboxylates and 2-arylindole-3-carboxylates is described. The corresponding products are obtained by a

domino hydroamination/Fischer indole cyclization in good-to-excellent yields from easily available 1-alkyl-1-phenylhydrazines and acetylenecarboxylates.

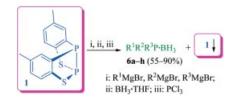
I. A. Sayyed, K. Alex, A. Tillack, N. Schwarz, D. Michalik, M. Beller* 4525–4528

A Convenient and General Method for the Synthesis of Indole-2,3-dicarboxylates and 2-Arylindole-3-carboxylates

Keywords: Alkynes / Hydroamination / Indoles

Phosphane—**Borane** Complexes

Tertiary phosphane—borane complexes containing different alkyl groups can be easily obtained by addition of different Grignard reagents to benzothiadiphosphole 1 followed by direct complexation with BH₃·THF. Treatment of the resulting mixture with PCl₃ led to the reformation of the starting reagent 1, which was quantitatively recovered from the reaction mixture by simple crystallization.



G. Baccolini,* C. Boga, M. Mazzacurati 4529-4534

General and Efficient One-Pot Synthesis of Tertiary Phosphane—Borane Complexes Containing Different Alkyl Groups and In Situ Facile Recycling of the Phosphorus Donor Reagent

Keywords: Phosphanes / Grignard reagents / Phosphorus heterocycles / Boranes / Reagent recycling

Nitrogen Macrocycles

Unsymmetrical metal-free and zinc complexes of pyrazino-quinoxalino-porphyrazines bearing eight diethylamino groups have been synthesized by statistical tetramerization of 2,3-bis(diethylamino)quinoxaline-6,7-dicarbonitrile and 5,6-bis(diethylamino)pyrazine-2,3-dicarbonitrile in lithium butanolate. The effect of the insertion of benzene rings into the tetrapyrazino-porphyrazine system is discussed.

Z. Musil, P. Zimcik,* M. Miletin, K. Kopecky, J. Lenco 4535–4542

Synthesis, Separation and UV/Vis Spectroscopy of Pyrazino-quinoxalino-porphyrazine Macrocycles

Keywords: Phthalocyanines / Asymmetric synthesis / UV/Vis spectroscopy / Nitrogen heterocycles

Selena-Aza-Payne Rearrangement

Tetraselenotungstate mediates a new selena-aza-Payne-type rearrangement of aziridinylmethyl tosylates. This rearrangement yields allylamines as the major products and cyclic five-membered diselenides as mi-

nor products with excellent regio- and stereocontrol without using any Lewis acid or base. Reasonable mechanisms have been postulated for the formation of the products. D. Sureshkumar, S. Koutha, S. Chandrasekaran* 4543–4551

A New Selena-Aza-Payne-Type Rearrangement of Aziridinylmethyl Tosylates Mediated by Tetraselenotungstate

Keywords: Aziridines / Aza-Payne rearrangement / Selenium nucleophiles / Allylamines / Cyclic diselenides

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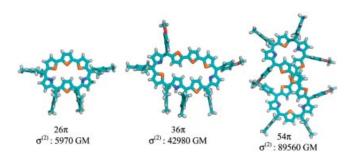
Porphyrinoids

R. Kumar, R. Misra, T. K. Chandrashekar,* A. Nag, D. Goswami, E. Suresh,

C. H. Suresh 4552-4562

One-Pot Synthesis of Core-Modified Rubyrin, Octaphyrin, and Dodecaphyrin:
Characterization and Nonlinear Optical Properties

Keywords: Expanded porphyrin / Conjugation / Porphyrinoids / Anion binding / TPA cross section



The bigger the better: three new expanded porphyrins containing 26, 36 and 54 π electrons have been synthesized in one-pot reactions using tripyrranes and terthiophene diols: the $\sigma^{(2)}$ values measured through

z scan techniques show the highest value for the 54π system, revealing the importance of the number of π electrons in conjugation for third-order NLO activity.

Natural Product Analogs

Synthesis of Highly Functionalized Anthraquinones and Evaluation of Their Antitumor Activity

Keywords: Anthraquinones / Antitumor agents / Cycloaddition / Epoxides / Natural product analogs

Highly functionalized anthraquinones which derive from the natural products mensacarcin, islandicin, and chrysophanol have been synthesized using a Diels—Alder reaction and an addition of an aryllithium species onto different aldehydes as key steps. Furthermore, the antitumor activity of these novel compounds has been studied by the in vitro growth inhibition of human lung carcinoma cells of line A549.

Pyrimidinophanes

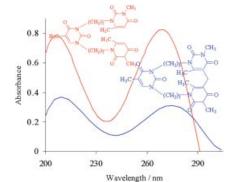
V. E. Semenov,* L. F. Galiullina,

O. A. Lodochnikova, O. N. Kataeva,

A. T. Gubaidullin, A. V. Chernova,

Yu. Y. Efremov, S. K. Latypov,

V. S. Reznik 4578-4593



A series of pyrimidinophanes and their acyclic counterparts with two 3,6-dimethyluracil or 3-methyluracil units attached to the thymine or isocyanurate fragment by polymethylene or xylylene spacers have been prepared. The mutual arrangement of the uracil moieties in the triuracils has been determined in the solid state by X-ray diffraction and in solution by NMR, UV and computational methods.

 $\label{eq:continuous} Triuracils - 1,3-Bis[\omega-(\textit{N-methyluracil-1-yl})-alkyl] thymines and Their 5,5'-Cyclic Counterparts$

Keywords: Nucleobases / Macrocycles / Structure elucidation

Spiro-β-lactams

A. Trabocchi, C. Lalli, F. Guarna, A. Guarna* 4594-4599

Diastereoselective Synthesis of Highly Constrained Spiro-β-Lactams by the Staudinger Reaction Using an Unsymmetrical Bicyclic Ketene

Keywords: Peptidomimetics / Spiro compounds / Lactams / Cycloaddition / Scaffolds

Highly constrained polycyclic spiro-β-lactams were obtained from rigid bicyclic ketenes by the Staudinger reaction. Depending on the imine component used,

high diastereoselectivity was observed in the process, and aromatic imines gave preferential formation of the *cis*-diastereoisomer.



C-N Bond Activation

In the palladium-catalyzed reaction of acrylates, C-N bond activation and acetalization occurred under different conditions. Described herein is a highly efficient palladium-catalyzed C-N bond activation

reaction and subsequent new C-N bond formation to directly construct β -amino acids from triethylamine and acrylate esters in isolated yields of up to 95 %.

Palladium-Catalyzed C-N Bond Activation: The Synthesis of β -Amino Acid Derivatives from Triethylamine and Acrylates

Keywords: Palladium / C-N bond activation / Amino acids