Synthesis of Glycofuranosides

by J. Bogusiak

Faculty of Pharmacy, Silesian Medical School, Pl 41-200 Sosnowiec, Poland
FAX: 048 (032) 266 78 60, E-mail: jbogusiak@farmant.slam.katowice.pl

(Received May 28th, 2001; revised manuscript November 9th, 2001)

Glycofuranosides are ubiquitous in biological structures, playing important functions in immunological response and bacterial or viral infection [1,2]. To elucidate their biological functions and their possible use in therapy, there are more and more attempts to synthesize smaller or bigger structures (glycosides, oligosaccharides, glycoconjugates) containing furanosyl units. This article describes recent advances in the development of efficient synthesis methods for glycofuranosides.
Synthesis, Characterization and Magnetic Studies of μ-Oxamido-Bridged Cu(II)–Mn(II) Heterobinuclear Complexes

by Y.-T. Li\textsuperscript{1}, C.-W. Yan\textsuperscript{2} and X.-C. Yin\textsuperscript{3}

\textsuperscript{1}Department of Chemistry, Qufu Normal University, Qufu, Shandong, 273165, P. R. China
\textsuperscript{2}Department of Biology, Qufu Normal University, Qufu, Shandong, 273165, P. R. China
\textsuperscript{3}Department of Chemistry, Jining Teacher’s College, Jining, Shandong, 272125, P. R. China

(Received January 19th, 2001; revised manuscript September 17th, 2001)

Four new μ-oxamido-bridged copper(II)–manganese(II) heterobinuclear complexes described by the overall formula \([\text{Cu}(\text{dmoxpn})\text{MnL}_2](\text{ClO}_4)_2\), where \text{dmoxpn} denotes \(N,N'\)-bis[3-(dimethylamino)propyl]oxamido dianion, \(L\) represents 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine (Me\textsubscript{2}-bpy); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), have been synthesized and characterized. Based on elemental analyses, IR and electronic spectra studies and molar conductivity measurements, these complexes are proposed to have oxamido-bridged structures and to consist of the copper(II) ion in a planar environment and the manganese(II) ion in an octahedral environment. The electronic reflectance spectrum indicates the presence of exchange-coupling interaction between bridging copper(II) and manganese(II) ions. The \([\text{Cu}(\text{dmoxpn})\text{Mn}(\text{bpy})_2](\text{ClO}_4)_2\) complex has been further characterized by variable temperature susceptibility (4.2–300 K) and the observed data were least-square fitted to the susceptibility equation derived from the spin Hamiltonian, \(H = -2JS_1S_2\), giving the exchange integral \(J = -27.8\ \text{cm}^{-1}\). The results are commensurate with antiferromagnetic interaction between the adjacent manganese(II) and copper(II) ions through the oxamido-bridge within the complex. The influence of structural variation of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

The binary system YPO$_4$ –– Ba$_3$(PO$_4$)$_2$ has been examined by differential thermal analysis, X-ray and microscopy in reflected light. Its phase diagram has been proposed. The initial orthophosphates react at a 1:1 and 2:1 molar ratio to give two intermediate compounds: Ba$_3$Y(PO$_4$)$_3$ and Ba$_3$Y$_2$(PO$_4$)$_4$. It has been established that Ba$_3$Y(PO$_4$)$_3$ melts congruently at 1950 ± 20°C. Ba$_3$Y$_2$(PO$_4$)$_4$ melts incongruently at 1800°C and is stable at high temperature only; it decomposes into YPO$_4$ and Ba$_3$Y(PO$_4$)$_3$ at about 1150°C.

Double orthophosphate, Ba$_3$Y(PO$_4$)$_3$, has a cubic unit cell (eulytite structure) with the parameter a = 10.4655 Å.
Crystal Structure, Spectroscopy and Thermal Study of Manganese(II) Complex with Sarcosine

by Z. Rzączyńska, R. Mrozek and M. Sikorska-Iwan

Faculty of Chemistry, Maria Curie-Skłodowska University,
M.C. Skłodowska Sq. 2, 20-031 Lublin, Poland

(Received June 19th, 2001; revised manuscript September 25th, 2001)

A polymeric manganese(II) complex of sarcosine [Mn(sar)_2(H_2O)_2]Cl_2 (where sar = sarcosine) has been prepared and characterized by elemental, spectroscopic, thermal, magnetic and X-ray investigations. X-ray crystallographic study shows that the octahedral-coordinated manganese(II) ion is situated in the crystallographic center of symmetry and is bound to four carboxylate oxygen atoms of different sarcosine molecules and two water molecules. Two non-coordinated chloride ions are located between the chains. IR spectra of the free ligand and the complex have been discussed. This complex is stable up to 378 K, later loosing water and transforming into oxides. The gas-phase products of decomposition have been analyzed by FTIR spectra.
Novel Rearrangement of Tertiary Fenchyl Alcohols with Sulfuric Acid in Acetonitrile

by M. Welniai

Faculty of Chemistry, Nicolaus Copernicus University, 87-100 Toruń, Poland

(Received April 20th, 2001; revised manuscript July 6th, 2001)

The influence of steric hindrance on rearrangements of tertiary 2-fenchyl cations under the Ritter reaction conditions (CH₃CN/H₂SO₄) has been described. Depending on the branching of alkyl substituents at the C-2 position, the reaction time and temperature, different reaction courses have been observed. After 10 minutes at –20 to –15°C alcohol 2 (R = iso-Am) gave alkenes 7, whereas a pair of amides 8 and 9 for 24 hours at ambient temperature as a result of successive exo-3,2-methyl shift, Wagner-Meerwein rearrangement and endo-6,2-hydride shift. Alkene 10 was obtained as a primary product from alcohol 3 (R = iso-Bu) after 10 minutes at –20 to –15°C. When the same reaction was continued for 24 hours at room temperature, amide 12 has been obtained as the only product. It was explained by the operation of endo-6,2-hydride shift after protonation of alkene 10 and further reaction with acetonitrile. In the case of alcohols 4–6 with bulky isopropyl, sec-butyl and 2-sec-amyl substituents, a novel rearrangement to tetrasubstituted alkenes containing the bicyclo[3.1.1]heptane skeleton have been notified. The mechanistic proposals for the investigated reaction are presented.
Ipso and cine Substitution of Bromine in Pyridazinones

by A.A. Katrusiak¹, A. Katrusiak², S. Baloniak¹ and K. Zielińska¹

¹Department of Organic Chemistry, Karol Marcinkowski University of Medical Sciences, Grunwaldzka 6, 60-780 Poznań, Poland
²Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

(Received May 31st, 2001; revised manuscript August 22nd, 2001)

Nucleophilic ipso and cine substitution of bromine in pyridazine derivatives has been investigated in several solvents, such as dry DMF, anhydrous ethanol and dry THF. The structures of obtained isomeric products have been monitored by chemical methods, X-ray diffraction and ¹H NMR spectra.
New Galanin Analogues with Contractile Activities on Rat Gastric Smooth Muscles

by J. Ruczyński¹, A. Sawula¹, Z. Konstański², R. Korolkiewicz² and P. Rekowski¹

¹Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland
²Department of Pharmacology, Medical University of Gdańsk, Do Studzienki 38, 80-227 Gdańsk, Poland

(Received September 3rd, 2001; revised manuscript October 15th, 2001)

We synthesized new 15-amino-acid-residue analogues of porcine galanin modified in positions 2, 6, 8 or 14 and studied their activity on isolated rat gastric smooth muscles. Thus, we intended to characterize the molecular domains of GAL responsible for binding to its receptors and biological activity in the gastric fundus. All peptides were synthesized by the solid phase peptide synthesis with the use of Fmoc strategy. All galanin analogues contracted rat gastric fundus strips in a concentration-dependent manner with significantly increased or decreased activities as compared to GAL(1–15)NH₂. As expected, the modifications introduced into the amino acid sequence of galanin caused changes in the interaction of GAL(1–15)NH₂ with its receptors. Thus, residues: Trp², Ser⁶, Gly⁸ and His¹⁴ in the amino acid sequence of GAL(1–15)NH₂ play an important roles in the high-affinity binding of GAL to its receptors and biological activity in rat gastric smooth muscle cells.
Convenient Synthesis of 1-(1,3-Dihydroxy-2-propyl)-4-nitroimidazoles

by J. Wengel\textsuperscript{1} and K. Walczak\textsuperscript{2}

\textsuperscript{1}Department of Chemistry, University of Southern Denmark, 5230-Odense M, Campusvej 55, Denmark
\textsuperscript{2}Institute of Organic Chemistry and Technology, Silesian Technical University, 44-100 Gliwice, Poland
E-mail: walczak@zeus.polsl.gliwice.pl

(Received October 4th, 2001; revised manuscript October 25th, 2001)

The title compounds have been obtained in reaction of 1,4-dinitroimidazoles with 2-amino-1,3-propanediols in water-methanol solution. 1-(1,3-Dihydroxy-2-propyl)-4-nitroimidazoles were transformed into derivatives that can be used for combinatorial oligomer synthesis.
Synthesis and Cytotoxic Properties of N-Boc-phenylisoserinates of Sesquiterpenoic Alcohols from Mushrooms of Lactarius Genus, as Analogues of Taxotere®

by A. Sarosiek¹, M. Masnyk¹, M. Gumulka¹, W.M. Daniewski¹, M. Kobus², E. Krawczyk² and M. Łuczak²

¹Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland
²Department of Medical Microbiology, Medical University of Warsaw, Chalubińskiego 5, 02-004 Warsaw, Poland

(Received October 16th, 2001; revised manuscript November 6th, 2001)

Sesquiterpenoic analogues of Taxotere® i.e., N-BOC-phenylisoserinates of sesquiterpenoic alcohols, isolated from mushrooms of Lactarius genus, were synthesized. Cytotoxicity of compounds, thus obtained, was evaluated using Vero cells.
Two potential DNA intercalators capable of cis→trans isomerization, \( 9\text{-}[2\text{(N-methylpyridinium-4-yl)viny}] \)anthracene (I) and \( 9,10\text{-bis}[2\text{(N-methylpyridinium-4-yl)viny}] \)anthracene (II), have been prepared, characterized and their spectral and photoisomerization behavior have been studied. Both ligands exhibit low fluorescence quantum yields in aqueous solution and substantial enhancement of emission in the presence of DNA. Two-way isomerization was observed for I, while trans→cis process appeared to be inefficient for ligand II. An intramolecular charge transfer excited state was suggested to explain the differences in spectral behavior and photoisomerization of ligands.
New Bis-Linked Tetrathiafulvalenes (TTFs) to [60]Fullerene: Spectral Investigations

by I. Olejniczak¹, A. Graja¹, A. Bogucki¹, P. Hudhomme², A. Gorgues², D. Kreher² and M. Cariou²

¹Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17, 60-179 Poznañ, Poland
²Laboratoire d’Ingénierie Moléculaire et Matériaux Organiques, Université d’Angers, 49045 Angers, France

(Received September 3rd, 2001; revised manuscript September 25th, 2001)

Extended spectral investigations of several new bis-linked tetrathiafulvalenes (TTFs) to [60]fullerene were performed. From VIS-NIR-IR spectra it was stated, that charge redistribution on C₆₀ and TTFs moieties in the adducts occurs after their formation. This redistribution depends not only on the nature of a substituent but also on the number of bounded donors. Vibrational features of the polyadducts were also analyzed.
Influence of 5-Sulphosalicylic Acid on Redox Reaction between Fe(III) and Sn(II)

by V. Pautienienë, G. Rozovskis and A. Survila

Institute of Chemistry, A. Goštauto 9, Vilnius LT–2600, Lithuania
E-mail: redox@ktl.mii.lt

(Received March 6th, 2001; revised manuscript October 8th, 2001)

Kinetics of Fe(III) reduction with Sn(II) in 0.5–2 M H₂SO₄ solutions involving sulphosalicylic acid (H₃Ssal) has been studied. H₃Ssal acts not only as an indicator for spectrophotometric determination of Fe(III) but also takes part in the redox reaction as an accelerator. The data are described by the kinetic equation obtained for the rate-determining step of FeSsal + Sn²⁺ → Fe²⁺ + Sn³⁺ + Ssal³⁻ with rate constant \( k_2 = 1.4 \times 10^{-4} \) M⁻¹ s⁻¹ at 60°C. Effect of fluoride consists in the decrease of FeSsal concentration, due to the formation of extra Fe(III)–fluoride complexes, resulting in the decrease of the reaction rate.

Interaction between water and ethers in dilute aqueous solutions was investigated by water-heptane partition of twelve linear aliphatic ethers containing various number of carbon atoms (from 2 to 8), and one branched homologue. Standard free energy (Gibbs) and enthalpy of partition were calculated from partition constants and from their temperature dependence. The differences in the free energy and entropy result from different hydrophobic hydration of these amphiphilic solutes in the aqueous phase. The position of the oxygen atom in an ether molecule affects the hydrophilic-hydrophobic properties of the molecule. The methylene groups in the \( \alpha \) and \( \beta \) positions in respect to the oxygen atom are distinctly less hydrophobic than those more distant, therefore, different are their hydrophobic contributions into standard thermodynamic functions of hydration. The commonly accepted group contribution models, which assume equal contributions from the same fragments irrespectively of their position (additivity principle), should be revised.
Kinetic Isotope Effect in Hydrogen Isotope Exchange Between Hydrogen Sulphide or Thiol and Alcohol in Gas and Solution

by A. Wawer and J. Szydłowski

Department of Chemistry, Warsaw University, Żwirki i Wigury 101, 02-089 Warszawa, Poland
E-mail: jszydlow@chem.uw.edu.pl

(Received July 11th, 2001; revised manuscript August 22nd, 2001)

The kinetic parameters of the tritium exchange between H2(S,D)S or MeSH(MeSD) and MeOH(MeOD) vapours on PTFE and glass surface were measured. The *HH/*DD kinetic isotope effects are significantly lower than those for the reaction of phosphines with methanol. The kinetics of deuterium exchange between BuSH and EtOD in solutions of C6D12 and CD3CN had been studied and HH/DD isotope effect was evaluated. It appeared to be smaller than that in the vapours. These results suggest that contrary to the exchange reactions in phosphine, the elementary reaction of HH-transfer in four center transition state is not the rate limiting step and H-bond formation as well as diffusion controlled processes should be taken into account.

Density Functional Theory Calculations of Adsorption of Hydrogen on the (100) Titanium Hydride Surface

by M. Gryciuk and J. Górecki

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
(Received April 4th, 2001; revised manuscript October 9th, 2001)

Electronic structure calculations based on the density functional theory (DFT) have been applied to the adsorption of hydrogen on the (100) plane of TiH₂. Calculations are performed for a single hydrogen atom placed over a supercell of TiH₂ and the periodic boundary conditions are used, so effectively such system describes a submonolayer coverage. The total energy have been calculated for three different positions of hydrogen over the TiH₂ supercell. The results based on the local density approximation (LDA) and the generalized gradient approximation (GGA) are compared.
An Empirical Estimation of the Interactions H\(^{5+}\)…Cl\(^-\).
The Crystal and Molecular Structure of the
1-Methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride

by T.M. Krygowski\(^1\), S.J. Grabowski\(^2\), R. Anulewicz-Ostrowska\(^1\),
J. Izdebski\(^1\) and D. Fiertek\(^1\)

\(^1\)Department of Chemistry, University of Warsaw, L. Pasteura 1, 02-093 Warsaw, Poland
\(^2\)Institute of Chemistry, University in Białystok, Al. J. Piłsudskiego 11/4, 15-443 Białystok, Poland

(Received April 30th, 2001; revised manuscript October 3rd, 2001)
Crystal and Molecular Structure of Lithium Iodide Complex of 13-Membered Azoxycrown Ether

by E. Luboch\textsuperscript{1}, V.Ch. Kravtsov\textsuperscript{1} and V. Kessler\textsuperscript{2}

\textsuperscript{1}Department of Chemical Technology, Technical University, 80-952 Gda\'nsk, Poland
\textsuperscript{2}Swedish University for Agricultural Sciences, Chemistry Department, Uppsala, Sweden

(Received July 2nd, 2001; revised manuscript October 11th, 2001)
An Account of the Regioselectivity of β-Substituted Nitroalkenes in Nitrone [2+3] Cycloaddition by FMO Theory

by A. Barański, R. Jasiński and M. Bujak

Department of Chemical Engineering and Technology, Cracow University of Technology, 31-216 Kraków, ul. Warszawska 24, Poland

(Received September 6th, 2001; revised manuscript October 25th, 2001)
COMMUNICATION

On Surface Phosphorus Activity in VPO Catalysts

by J. Stoch¹, A. Stoch², M. Mikołajczyk¹ and A. Brożek²

¹Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek 1, 30-239 Kraków, Poland
²University of Mining and Metallurgy, Faculty of Materials Science and Ceramics,
Department of Crystallochemistry and Chemistry of Silicates,
al. Mickiewicza 30, Kraków 30-059 Poland

(Received January 25th, 2001; revised manuscript October 29th, 2001)