

Synthesis and Characterization of *O,O'*-Alkylenedithiophosphato Complexes of Vanadium(V)

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Reactions of vanadiumoxytrichloride, VOCl_3 , with ammonium salts of *O,O'*-alkylenedithiophosphoric acid, $[\text{OGOPS}_2\text{NH}_4]$, in 1:3 molar ratio resulted in less common seven coordinated complexes of the type $[\text{VO}(\text{S}_2\text{POGO})_3]$ and the reactions of 2-chloro-2-oxo-1,3-dioxavanadacyclopentane and -vanadacyclohexane, $[\text{OG}'\text{OVOC}]$ (where $\text{G}' = -\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2\text{CH}_2-$), in equimolar ratio yielded compounds corresponding to $[\text{OG}'\text{OVOS}_2\text{POGO}]$ (where $\text{G} = -\text{CMe}_2\text{CMe}_2-$, $-\text{CH}_2\text{CMe}_2\text{CH}_2-$ or $-\text{CH}_2\text{C}(\text{Et})_2\text{CH}_2-$). These complexes have been characterized by elemental analyses, molecular weight determination and spectral studies like IR and NMR (^1H , ^{13}C and ^{31}P), which indicate bidentate linkages of dithiophosphate moieties leading to pentagonal bipyramidal and square bipyramidal geometry around the vanadium(V) atom.

Key words: alkylenedithiophosphoric acid, alkylenedithiophosphate, vanadacyclopentane, vanadacyclohexane, vanadiumoxytrichloride

**Studies on Mononuclear Chelates Derived from
Substituted Schiff Bases Ligands (Part 1):
Synthesis and Characterization of a New
Salicyliden-*p*-aminoacetophenoneoxime and
Its Complexes with Co(II), Ni(II), Cu(II) and Zn(II)**

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The new ligand salicyliden-*p*-aminoacetophenoneoxime (LH) was synthesized from *p*-aminoacetophenoneoxime and salicylaldehyde under reflux in absolute ethanol. Mononuclear complexes with a metal:ligand ratio of 1:2 have been prepared with Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ salts. Their structures have been elucidated on the basis of IR, ¹H- and ¹³C-NMR spectra, electronic spectra, elemental analyses, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses. According to the results, it is suggested that two ligands are coordinated to each metal atom by hydroxyl and the imino nitrogen to form high spin tetrahedral complexes with Co²⁺, Ni²⁺, Cu²⁺ and diamagnetic complex with Zn²⁺.

Key words: Schiff bases, imine compounds, oxime compounds, transition metal complexes

Tanacetamide C: One New Ceramide from *Tanacetum artemisioides*

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A reinvestigation with a modified extraction procedure of *Tanacetum artemisioides* resulted in the isolation and structure elucidation of one new ceramide named tanacetamide C and assigned structure 2*R*,3'*R*,3*R*,4'*S*,6*R*,4*E*-*N*-[3',4'-dihydroxydodecanoyl]-2-amino-4-nonacosene-1,3,6-triol (**1**). In addition 5,4'-dihydroxy-3,6,7-trimethoxyflavone (**2**), 5-hydroxy-3,6,7,4'-tetramethoxy flavone (**3**), leukodin (**4**) were also isolated for the first time from this species. The structure elucidation of the isolated new compound was based primarily on 1D and 2D NMR analysis, including COSY, HMQC, HMBC correlations.

Key words: *Tanacetum artemisioides*, Compositae, ceramide

Synthesis and Structure of Spirocyclic Tetrahydrothiophene Derivatives Bearing a ‘Cage’ Residue

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Trapping of the thiocarbonyl *S*-methanide **4** with tetracyanoethene and *N*-methylmaleimide led to the [3+2]-cycloadducts **11** and **12**, respectively. The structures of these cycloadducts were established by X-ray crystallography. The 1,3-dipole **4** has been generated by thermal decomposition of the corresponding 2,5-dihydro-1,3,4-thiadiazole **2**, which was prepared by the 1,3-dipolar cycloaddition of diazomethane with thioketone **1**.

Key words: thiocarbonyl ylides, 1,3-dipolar cycloaddition, tetrahydrothiophenes, 2,5-dihydro-1,3,4-thiadiazoles, polycyclic compounds, crystal structure

Lactones 17. Synthesis of Bicyclic Lactones with the Methyl- or *gem*-Dimethylcyclopropane System

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A new method of synthesis of bicyclic γ -lactones with the methyl- or *gem*-dimethylcyclopropane system from γ,δ -unsaturated esters is described. The reaction of γ -halo- δ -lactones with DBU is the key step of this synthesis. The mechanism of the dehydrohalogenation–cyclization process of γ -halo- δ -lactones is proposed. The structures of products were confirmed by both spectroscopic and crystallographic methods.

Key words: γ -halo- δ -lactones, δ -halo- γ -lactones, cyclization, DBU, elimination, bicyclic lactones

Catalytic Ketonisation over Oxide Catalysts. Part XI. Cross-Ketonisation of Esters of Aliphatic and Aromatic Acids

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The cross-ketonisation of a mixture of ethyl acetate and ethyl benzoate under flow conditions has been studied over 20wt%MO₂/Al₂O₃ (M = Mn, Ce or Zr) catalysts, at 673–723 K. High conversions of aromatic ester up to 98% and moderate yields of acetophenone (< 45%) have been observed. The main product was accompanied by numerous side-products, among which ethylbenzene, styrene and benzoic acid were identified. CeO₂/Al₂O₃ catalyst was the least selective. In its presence, the yield of styrene (34%) exceeded that of acetophenone (31%). Unexpectedly, pure Al₂O₃ support exhibited the highest selectivity and moderate activity, at 723 K the yield as high as 51% of acetophenone was noted. The transformations of mixtures of various ethyl alkanoates with ethyl benzoate over alumina have been studied. In the case of straight-chain aliphatic esters, the yields of the corresponding 1-phenyl-1-alkanones were in the range of 41–51%. The presence of a methyl group in the α position of the ester (isobutyrate) reduced the yield of ketone strongly (11%); two methyl groups (pivalate) completely inhibited the reaction. The reactivity of a series of alkyl acetates was also studied in the cross-ketonisation reaction with ethyl benzoate over alumina. It has been found that secondary and tertiary alkyl acetates were slightly more selective than their primary counterparts due to the absence of products of transesterification. For these esters at 723 K the yields of acetophenone were in the range of 64–67%. The cross-ketonisation of a mixture of ethyl acetate with substituted ethyl benzoates led to the corresponding derivatives of acetophenone. It has been found that the position of the substituent in the benzene ring plays a crucial role in the reactivity of the ester and determines the extent of yield of the product. The highest yield of ketone (62%) was observed at 723 K for 3-methylacetophenone. 2-Methylacetophenone was formed with low yields (<10%) in the whole range of reaction temperatures, probably due to steric effect in the ortho position. At 698 K the maximum yield of 4-methylacetophenone (27%) was attained. The ketonisation of ethyl acetate with ethyl esters of 4-t-butyl- and 4-chlorobenzoic acids led to moderate yields (24–27%) of 4-t-butyl- and 4-chloroacetophenone, respectively.

Key words: cross-ketonisation, aliphatic and aromatic esters, phenylalkanones, alumina

On n - π Electron Distribution in Simple Acyclic Tetrad and Pentad Tautomeric Systems

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Variations of the n - π electron distribution during the tautomeric interconversion were analysed for simple acyclic tetrad and pentad tautomeric systems using the geometry-based HOMA index. Internal effects such as γ -conjugation, push-pull effect and intramolecular H-bonding were discussed.

Key words: tautomerism, tetrad and pentad systems, n - π electron distribution, HOMA indices

Free Radical Addition and Cyclization Reactions of [2-(4-(*S*)-Isopropyl-2-oxazoline)-5-phenyl]dialkyltin Hydrides

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Radical addition reactions of [2-(4-(*S*)-isopropyl-2-oxazoline)-5-phenyl]dibutyl and dimethyl hydrides to activated double/triple bonds took place in good yields. Triethylborane in presence of oxygen can serve as a radical initiator. Addition of stannyl radicals to *N,N*-(2-methoxycarbonyl-allyl)benzyl glycinate results in formation of the corresponding piperidine derivatives. The intramolecular tandem radical addition/cyclization process can be performed in high yields and good diastereoselectivity.

Key words: addition and cyclization reactions, hydrostannations, radicals, tin hydrides

Homoconjugation of Some Organic Bases in Acetonitrile

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The largest value of the homoconjugation constant in acetonitrile has been found for tribenzylamine $K_{\text{HOMO}} = 7.73$ and the lower for N-methylpiperidine $K_{\text{HOMO}} = 3.44$. For triethylamine, tri-n-propylamine, tributylamine, 1,3-diphenylguanidine, 2-tert-butyl-1,1',3,3'-tetramethylguanidine, 1,1',2,2',3-pentamethylguanidine, 1,8-bis(dimethylamino)naphthalene, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene bases no homoconjugated complexes BH^+B were formed. Additionally the basicity of tribenzylamine $\text{p}K_{\text{a}} = 16.13$, 1,3-diphenylguanidine $\text{p}K_{\text{a}} = 18.79$, 1,1',2,2',3-pentamethylguanidine $\text{p}K_{\text{a}} = 23.12$, and 2-tert-butyl-1,1',3,3'-tetramethylguanidine $\text{p}K_{\text{a}} = 23.56$ in acetonitrile are given.

Key words: organic bases, basicity, $\text{p}K_{\text{a}}$, homoconjugation constant, acetonitrile solvent

**Phase Equilibria in the Ternary System MgO–Na₂O–P₂O₅.
The Partial System
Mg₂P₂O₇–Mg₆Na₈(P₂O₇)₅–NaPO₃–Mg(PO₃)₂**

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The partial system Mg₂P₂O₇–Mg₆Na₈(P₂O₇)₅–NaPO₃–Mg(PO₃)₂ in the ternary system MgO–Na₂O–P₂O₅, have been investigated and its phase diagram has been proposed. Investigation was carried out by the differential thermal analysis (heating and cooling), X-ray diffraction methods, and microscopy in reflected light. In the composition range under investigation, five ternary phosphates: Mg₆Na₈(P₂O₇)₅, Mg₂Na₃P₅O₁₆, MgNa(PO₃)₃, MgNa₂(PO₃)₄ and MgNa₄(PO₃)₆ appear. Two of them, Mg₆Na₈(P₂O₇)₅ and MgNa₄(PO₃)₆, congruently melt at 808 and 915°C, respectively, the remaining three melt incongruently. Phosphate Mg₂Na₃P₅O₁₆ melts incongruently at 675°C during heating and decomposes in a few stages. Peritectic melting point of MgNa(PO₃)₃ phosphate is 942°C, and that of MgNa₄(PO₃)₆ is 785°C. For the composition range of Mg₂P₂O₇–Mg₆Na₈(P₂O₇)₅–NaPO₃–Mg(PO₃)₂, it has been found that six quasi-binary sections, four ternary peritectics ($t_{p_1} = 660^\circ\text{C}$, $t_{p_2} = 876^\circ\text{C}$, $t_{p_3} = 578^\circ\text{C}$, $t_{p_4} = 555^\circ\text{C}$) and three ternary eutectics ($t_{E_1} = 560^\circ\text{C}$, $t_{E_2} = 845^\circ\text{C}$, $t_{E_3} = 540^\circ\text{C}$) occur.

Key words: phase equilibria, magnesium-sodium phosphates, DTA, X-ray powder diffraction

Experimental Studies on Isonicotinato Zinc(II) Complex $[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]$ and Density Functional Calculations

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Isonicotinato zinc(II) complex $[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]$ has been synthesized by hydrothermal method and characterized by elemental analysis, electronic-spectra and thermogravimetric analysis. Density functional theory (DFT) method calculations of the structure, atomic charges distribution, electronic spectra, natural population analysis and the thermodynamic properties at different temperatures have been performed. The calculated results show the electronic transitions are mainly derived from the contribution of $\pi \rightarrow \pi^*$ bands and the decomposition of the title compound should firstly occur at the bond of Zn–O, then at the bond of Zn–N, which agrees very well with the experimental data.

Key words: isonicotinato zinc(II) complex, density functional theory, electronic spectra, thermal property analysis

Comparative Studies of Film-Forming Properties of Partially Fluorinated Tetracosanes

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Contrary to simple n-alkanes of moderate molecular weight, which are not capable of Langmuir monolayer formation, partially fluorinated hydrocarbons of the general formula: $F(CF_2)_m(CH_2)_nH$ (abbreviated as FmHn) were found to form monomolecular layers at the air/water interface. The aim of this study was to characterize several semifluorinated alkanes (SFA) containing 24 carbon atoms in total (tetracosanes) differing in the m/n ratio, as Langmuir monolayers at the free water surface. The following compounds have been investigated: F4H20, F6H18, F8H16, F10H14 and F12H12. Surface pressure (π) and electric surface potential (ΔV) isotherms were recorded in addition to quantitative Brewster angle microscopy results. The negative sign of ΔV evidenced for the orientation of all the semifluorinated tetracosanes investigated here, regardless the length of the hydrogenated segment, with their perfluorinated parts directed towards the air. As inferred from apparent dipole moment values and relative reflectivity results, tetracosanes with shorter perfluorinated fragment (F4H20 and F6H18) were found to take vertical orientation at the air/water interface, while those with longer perfluorinated moiety (F8H16, F10H14 and F12H12) remain tilted even in the vicinity of the film collapse. The observed differences may result from a different conformation of the perfluorinated chain, *i.e.* more fluorinated tetracosanes (F10H14 and F12H12) have their perfluorinated parts sufficiently long to form a helix, while less fluorinated derivatives (F4H20 and F6H18) may possibly exist in all-trans configuration. In particular, the perfluorinated fragment in F8H16 is considered to have an intermediate character between these two structures.

Key words: Langmuir monolayers, air/water interface, semifluorinated alkanes, surface potentials, effective dipole moments, Brewster angle microscopy

Electrode Open Circuit Potentials and Oxidation Process at Au and Pt Electrodes/Solid Oxide Electrolyte Interfaces in Common Methane+Air Gas Mixture

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Difference of potentials between two diversified electrodes, Au and Pt at a solid ionic conductor in a common gas mixture of fuel and oxidant, $x\text{CH}_4+(1-x)(0.2\text{O}_2+0.8\text{Ar})$ has been studied on the example of electrodes at $\text{ZrO}_2+8\%\text{Y}_2\text{O}_3$ electrolyte. The open circuit potentials of both electrodes have been determined as dependent on concentration of O_2 in the gas mixture. Within some domain of gas composition the difference of open circuit potential (OCP) values achieves a stable value of *ca.* 700 mV. Experimental OCP values are compared to calculated ones and discussed as the results of chemical and/or electrochemical equilibria and steady states which may occur at the electrodes.

Key words: fuel cells, solid ionic conductors, single chamber fuel cell

**Geometry of Lidocaine-like Molecules:
3. Structure of a Potent Antiarrhythmic Agent:
2-Methyl-2-(1-morpholinyl)-N-(2,6-dimethylphenyl)
acetamide**

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Crystal structure of an alanylyl analog of lidocaine with its amine function incorporated into morpholine ring and showing promising type I antiarrhythmic activity was studied in form of free base and hydrochloride. Crystal data: free base $a = 9.498(2)$, $b = 11.716(2)$, $c = 13.497(2)$; hydrochloride $a = 10.820(1)$, $b = 11.971(3)$, $c = 12.564(1)$; both $P2_12_12_1$ ($Z = 4$); $R_1 = 0.039$ and 0.037 , respectively. Substitution at C_α and incorporation of N amine atom into the aliphatic morpholinic ring significantly change conformational preference around $C_\alpha-C(O)$ and $C_\alpha-N(\text{ring})$ bonds, as compared with parent lidocaine. The most interesting conformational change observed was that the title molecule in the protonated form (being probably the biologically active) has gauche orientation of $^{\oplus}N-H(\text{amine})$ bond in relation to $C=O$ group, while all other structures have different orientations, either antiperiplanar or synperiplanar (unprotonated lidocaine only). And the two groups are crucial for hydrogen bonds formation with a perspective receptor of type I antiarrhythmics.

Key words: type I antiarrhythmics, acyl-2,6-xylidines, lidocaine chiral analogs, crystal structure

Thermal Decomposition of Chemical Hydrides

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**Tautomeric Equilibria (1,5-Proton Shift)
in Simple Heteroconjugated Systems
 $\text{HX-A=B-C=Y} \rightleftharpoons \text{X=A-B=C-YH}$ in Relation
to π Electron Delocalization**

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