

Regioselective Synthesis of New Chelating Bistetrazole Ligands and Study of Their Copper(II) Complexes

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Synthesis of some new N-substituted bistetrazoles is described. 1,5-Bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane (btop) is obtained by regioselective alkylation of 1,5-bis(5-tetrazolyl)-3-oxopentane with *tert*-butyl alcohol in 96% sulphuric acid media. 1,5-Bis(1-methyl-5-tetrazolyl)-3-oxopentane (mtop) is synthesized by exhaustive methylation of 1,5-bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane followed by the removal of *tert*-butyl group from the formed tetrazolium methyl sulphate in acidic conditions. Isomeric tetrazolium perchlorate is converted in analogous conditions to perchlorate of 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane. Synthesized bistetrazoles are found to react with copper(II) chloride in ethyl alcohol or acetone solutions giving solid [Cu(mtop)Cl₂] and [Cu(btop)Cl₂] complexes. Perchlorate of 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane reacts with copper(II) chloride in ethyl alcohol leading to formation of complex [Cu(mtop)Cl₂], whereas in aqueous solution complex [Cu(mtop)₂](ClO₄)₂ is formed. According to X-ray study of chloride complexes, Cu(II) is surrounded by a tridentate chelating ligand and two halide anions resulting in distorted square pyramidal geometry.

Synthesis, Nuclear Magnetic Resonance and Infrared Studies of Zinc(II) and Cadmium(II) Complexes of Thiosemicarbazones Derived from Fluorenone and *p*-Anisaldehyde

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Fluorenone (FTSCH) and *p*-anisaldehyde (ATSCH) thiosemicarbazones react with zinc(II) and cadmium(II) acetates forming M:L 1:2 complexes, characterized by IR, ¹H and ¹³C NMR spectra and elemental analyses. The coordination mode of the ligands is discussed and four-coordinate, pseudo-tetrahedral structures are suggested.

Bis(dialkylaminomethyl)phosphinic Acids and Their Addition Compounds with Tetrahedral $[\text{MCl}_4]^{2-}$ Ions ($\text{M} = \text{Cu}^{\text{II}}, \text{Co}^{\text{II}}$)

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Monohydrate monohydrochloride of bis(dialkylaminomethyl)phosphinic acids of the composition, $[(\text{R}_1\text{HCH}_2)_2\text{PO}_2]\text{Cl}\cdot\text{H}_2\text{O}$ $\{\text{R}_1 = \text{Me}_2\text{N}, \text{Et}_2\text{N}, (\text{n-Bu})_2\text{N}, \text{C}_5\text{H}_{10}\text{N}, \text{OC}_4\text{H}_8\text{N}\}$, dihydrate dihydrochloride of bis(dialkylaminomethyl)phosphinic acids, $[(\text{R}_2\text{HCH}_2)_2\text{P}(\text{O})\text{OH}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ $\{\text{R}_2 = \text{Me}_2\text{N}, \text{C}_4\text{H}_8\text{N}, \text{C}_5\text{H}_{10}\text{N}, \text{OC}_4\text{H}_8\text{N}\}$, and their copper(II) and cobalt(II) addition compounds with tetrahedral $[\text{MCl}_4]^{2-}$ ions $\{\text{M} = \text{Cu}^{\text{II}}, \text{Co}^{\text{II}}\}$ have been prepared and characterized by elemental analyses, effective magnetic moments, IR, VIS, and ^1H and ^{31}P -NMR spectra. Crystal and molecular structures of $[(\text{OC}_4\text{H}_8\text{NHCH}_2)_2\text{PO}_2]\text{Cl}\cdot\text{H}_2\text{O}$ and $[(\text{OC}_4\text{H}_8\text{NHCH}_2)_2\text{PO}_2]_2\text{CuCl}_4$ have also been determined.

Dimeric Silver(I) Complexes with Trimethylphosphine and Aliphatic Perfluorinated Carboxylates

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Silver(I) complexes with trimethylphosphine and perfluorinated carboxylates of general formula $[\{Ag(PMe_3)_2\}_2(\mu-OOCR)_2]$, where $R = CF_3, C_2F_5, C_3F_7, C_4F_9, C_7F_{15}$, have been prepared and characterized with IR, 1H , ^{13}C , ^{19}F , ^{31}P NMR. Spectral analysis suggests four coordinated Ag(I) with two monodentate trimethylphosphine and bidentate carboxylates forming bridges between silver(I) ions. Thermal decomposition process was studied between 293–973 K in nitrogen. Decomposition proceeds in one exothermic stage corresponding to the elimination of perfluorinated carboxylate and trimethylphosphine. The final product was a mixture of metallic silver and carbon, formed between 473–633 K.

The Reactions of Selected Terpene Alcohols with Acetonitrile in the Presence of Boron Trifluoride Etherate

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A series of thirteen terpene alcohols **1–13** of bornane, fenchane and isotricyclene systems was subjected to the reaction with acetonitrile in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst to give respective acetamides and/or alkenes. The use of boron trifluoride etherate instead of the usually applied protonic donors let us establish beyond any doubt the carbonium ion stage participation. The assumed reaction course was corroborated by cationic Wagner-Meerwein, Namietkin and homoallylic rearrangements observed during studies under investigation. Simultaneously no evidence for the imidate formation was found. Such a mode of the reaction mechanism was alternatively suggested earlier by Sjöberg [9] for the reaction of *sec*- and *tert*-butanol with acetonitrile in the presence of boron trifluoride etherate.

New Version of the TEMPO-based Catalytic System for the Oxidation of Alcohols to Aldehydes

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A new chemoselective catalytic system for the title oxidation was developed using methyltrioxorhenium (3 mol%), KBr (10 mol%) and TEMPO (3 mol%) as co-catalysts and Oxone[®] as a terminal oxidant.

**Synthesis of Heterocycles on the Basis of Arylation
Products of Unsaturated Compounds. Part 9.
Dialkyl 2,6-Diamino-4-arylfuro[2',3':4,5]benzo[b]furan-
3,7-dicarboxylates from 2-Aryl-1,4-benzoquinones
and Cyanoacetic Esters**

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2-Aryl-1,4-benzoquinones **1a–h** (aryl = RC₆H₄, R = H, 4-Me, 3-CF₃, 4-COOH, 3-Cl, 4-Cl, 4-F, 4-NO₂) react with methyl **2a** and ethyl **2b** cyanoacetates in the presence of some bases to form dialkyl 2,6-diamino-4-arylfuro[2',3':4,5]benzo[b]furan-3,7-dicarboxylates **3a–l**. Regardless of the reagents ratio benzodifuran derivatives are formed selectively. Only in reaction of 2-(4-nitrophenyl)-1,4-benzoquinone **1h** with **2b** ethyl 2-amino-5-hydroxy-4-(4-nitrophenyl)benzo[b]furan-3-carboxylate **4** is formed as minor component besides of **3l**. Starting compounds **1a–h** are prepared by arylation of the 1,4-benzoquinone with arenediazonium chlorides (Meerwein reaction).

New Proctolin Analogues Modified in Position 2 or 3 of the Peptide Chain and Their Myotropic Effects in Insects

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New analogues of insect neuromodulator proctolin (H-Arg-Tyr-Leu-Pro-Thr-OH) modified in position 2 and 3 of the peptide chain by natural or non-natural amino acid residues were synthesized. For modification of proctolin at position 2 a series of novel L-homophenylalanine derivatives H-Hpa(4-NO₂)-OH (**1**), Boc-Hpa(4-NO₂)-OH (**2**), Boc-Hpa(4-NH₂)-OH (**3**), Boc-Hpa(4-NH-Z)-OH (**4**), Boc-Phg(4-Me₂N)-OH (**5**) were obtained. The following two groups of proctolin analogues modified at positions 2 and 3 such as: 1/ H-Arg-X²-Leu-Pro-Thr-OH, where X² = Hpa (**6**), Hpa(4-NO₂) (**7**), Hpa(4-NH₂) (**8**), and Hpa(4-N-Me₂) (**9**), and 2/ H-Arg-Tyr-X³-Pro-Thr-OH, where X³ = Ile (**10**), Phe (**11**), Arg (**12**), Sar (**13**), Nva (**14**), Nle (**15**), Asn (**16**), Asp (**17**), Gln (**18**), Glu (**19**), Lys (**20**), and γ -Abu (**21**), were synthesized. Myotropic activity of proctolin analogues (**6–21**) was assayed *in vitro* on the semi-isolated heart of the yellow mealworm *Tenebrio molitor*. Analogues **10–12** and **20** retained more than 60% of proctolin activity. Other analogues showed a weak or none activity.

New Analogues of Bradykinin Substituted in the C-Terminal Part of the Molecule with Naphthylalanine

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This paper describes the synthesis and some pharmacological properties of eight new analogues of a previously synthesized bradykinin antagonist, D-Arg-Arg-Pro-Hyp-Gly-Thi-Ser-D-Phe-Thi-Arg. Two peptides were designed by substitution of Thi⁸ with L-1- and L-2-naphthylalanine. In two further analogues this modification was combined with placement in position 7 of D-2-naphthylalanine residue. Finally, we obtained four analogues by acylation of N-terminus of the peptides mentioned above with 1-adamantaneacetic acid. The activity of analogues was assessed by their ability to inhibit vasodepressor response to exogenous bradykinin (rat blood pressure test). Our results indicate that the modification proposed decreased the B₂ antagonistic activity, however, the range of this effect was different. We also observed that even minor changes in the structure of the C-terminal part of the B₂ antagonists may significantly influence their activity.

Analogues of *Ecballium elaterium* Trypsin Inhibitor II (EETI-II) with L-Cysteine Residues Substituted by L-Penicillamine (Pen) and L-Homocysteine (Hcy) in Positions 19, 21 and 27

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Two analogues of peptidic trypsin inhibitor isolated from seeds of *Ecballium elaterium* (EETI-II): [Pen^{19,21,27}] EETI-II (1) and [Hcy^{19,21,27}] EETI-II (2) were synthesized by the solid-phase method using the Fmoc/Bu^t procedure. Their inhibitory activity was determined by the calculation of association equilibrium constants (K_a) with bovine β -trypsin. In comparison with the parent compound, both analogues showed reduced trypsin inhibitory activity more than 7 and 18 times, respectively. We postulate that the observed differences may reflect the role of disulfide bridges in the interaction of inhibitors with trypsin or the introduced modifications change the conformational equilibrium of the analogues synthesized towards conformation(s) less favorable for the interaction with the enzyme.

**Theoretical Description of the Calorimetric Effects
Accompanying Mixed-Gas Adsorption Equilibria:
Non-Symmetrical Dubinin-Astakhov
Energy Distribution Function**

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Possibilities of Integral Equation (IE) Approach to study the mixed-gas adsorption equilibria are considered. Generalization of Dubinin-Astakhov equation for the case of mixed-gas adsorption is presented and the corresponding expressions for isosteric heats of adsorption are obtained, taking into account the interactions between adsorbed molecules. To predict phase diagrams and isosteric heats of mixture components only the knowledge of single-gas isotherm adsorption and accompanying calorimetric effects are required. A special attention is given to possibilities of arriving at relatively simple analytical or combined analytical/numerical solutions.

Hydrodechlorination of Dichlorodifluoromethane (CFC-12) on Silica-Supported Palladium and Palladium-Gold Catalysts

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Silica-supported palladium and palladium-gold catalysts were screened in the reaction of dichlorodifluoromethane with dihydrogen at 180°C. The Au-containing sample appeared superior as far as the selectivity towards difluoromethane (desired reaction product) is concerned (95% vs. ~30% for Pd/SiO₂). A comparative X-ray diffraction study of the catalysts, before and after reaction, confirmed our earlier findings that during the hydrodechlorination massive amounts of carbon originated from CCl₂F₂ dissolve in palladium. However, a similar conclusion cannot be drawn from XRD studies of the Pd-Au/SiO₂ catalyst, because upon entering Pd bulk both gold and carbon may produce analogous shifts of the XRD reflections. For that reason, temperature programmed hydrogenation of carbon deposited in the Pd and a Pd-Au catalyst was used. In contrast to the behaviour of monometallic Pd/SiO₂, only insignificant quantity of carbon was found in the bimetallic Pd-Au/SiO₂ sample subjected to hydrodechlorination. This result supports the idea that a complete hydrodehalogenation of CCl₂F₂ to methane would occur *via* bare carbon adspecies. Thus, one can associate a superior catalytic behaviour of Pd-Au alloy catalysts (selectivity to CH₂F₂ ~95%) with a low abundance of C₁ adspecies.

Equilibrium Isotope Effects on the Crotonase Reaction

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Equilibrium isotope effects on the enoyl-CoA hydratase (crotonase, ECH) – catalyzed reaction were modeled by a mixed QM/MM method. The classical region (27 aminoacids essential for the catalysis) was treated at the MM level using universal force field UFF. The quantum atoms of 4-(*N,N*-dimethylamino)cinnamoyl-CoA (DAC-CoA), one water molecule, and two glutamate residues (Glu164 and Glu144) in the active site were treated at the PM3 level.

Spectroscopic Studies and VFF Model Calculations on Dynamic and Electrooptic Characteristics of N–H Bonds in Amides

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IR spectroscopic studies of propionamide, n-butyramide, benzamide and 2-(F, Cl, Br)-benzamides within the $\nu(\text{NH})$ and $\delta(\text{HNH})$ absorption range of $-\text{NH}_2$ group for the “free” (in CCl_4 solutions) molecules and forming complexes with proton acceptor solvents (benzene, toluene, acetonitrile, dimethylformamide, dimethylsulphoxide and hexamethylphosphoramide) have been performed. Modifying the strength of the intermolecular interactions one can achieve the canceling of the primary non-equivalency of the N–H bonds in the $-\text{NH}_2$ group of amides. It allows establishing, for the first time, quantitative measures of dynamic ($K(\text{NH})$) and electrooptic ($\partial\mu/\partial q$) characteristics of N–H bonds in amides in framework of the R- NH_2 valence force field model. Dynamic and electrooptic non-equivalencies enhance with the increase of the hydrogen bonding strength. For the hydrogen-bonded complexes with acetonitrile, dimethylformamide, dimethylsulfoxide and hexamethylphosphoramide, the dynamic non-equivalency of NH bonds is increased 10–20%, while the electrooptic parameters $\partial\mu_1/\partial q_1$ and $\partial\mu_2/\partial q_2$ grow two or even three times. The electrooptic coupling of the N–H bonds (the parameter $\partial\mu_i/\partial q_j$, where $i, j = 1, 2; i \neq j$) increases with the strength of the hydrogen bonding.

Chromophoric Carbazole Methacrylates as Intermediates for Photorefractive Applications

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Methacrylate monomers containing a carbazole fragment and a chromophoric azophenyl sulfonyl group were synthesized, being characterized as definite chemical species and as potential intermediates for photorefractive applications. Quantum chemical calculations were carried out to get values of dipole moments, polarizabilities and hyperpolarizabilities. These values were used to calculate figure of merit (FOM) of the monomers, which indicated a contribution of linear and nonlinear optical effects to photorefractive phenomena. It was found that in the monomers in question the linear optical effect contribution prevailed over nonlinear one.

**Hydrogen and Oxygen Adsorption
on Re/ γ -Al₂O₃ Catalyst of Low Metal Content**

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**Synthesis, Magnetic and Spectroscopic Study of
(Ph₄As)₂[Re(NCS)₆]·2H₂O**

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**Water-Gas Shift Reaction over the Carbon-Based
Magnetite Catalyst Doped with Chromium Oxide**

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**Comments on the Isotopic and Chemical Studies of the
Thermal Decomposition of Ammonium Nitrate**

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