

Homologation of Protected Monosaccharides at the Terminal Position with Grignard C₁ Reagents

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The survey presents details of the recently introduced general method of homologation of monosaccharides. This method is based on chain-elongation of a protected monosaccharide from the terminal carbon atom. The terminal CH₂OH group is oxidized to the aldehyde grouping and next reacted with an alkoxymethylmagnesium chloride (C₁ Grignard) to form directly stereoisomeric homologues. The yields of the homologation products are high. Experiments aiming at improvement of the stereoselectivity of the reactions are described. The application of another C₁ Grignard reagent, (phenyldimethylsilyl)methylmagnesium chloride, is presented. The advantages and disadvantages of the method are discussed. All syntheses connected with the important bacterial heptose, *L-glycero-D-manno*-heptose and its oligosaccharides are described.

Solution Properties of Cu(II) Complex of a Moderately Hydrophobic Water-Soluble Porphyrin and Investigation of Its Interaction with Human Serum Albumin

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The association behavior of Cu(II) complex of 5,10,15,20-tetrakis(4-N-benzyl-pyridyl)porphyrin (Cu(II)TBzPyP) in aqueous solution at various ionic strength was studied by optical absorption and resonance light scattering (RLS) spectroscopies. The results show that Cu(II)TBzPyP exists as a monomer at low ionic strength and ill-defined aggregates at high ionic strength. The binding of the Cu(II)TBzPyP to human serum albumin (HSA) at 0.005 M phosphate buffer, pH 7.0 and 27°C has been also studied by optical absorption and RLS spectroscopies. The optical absorption spectral patterns of Cu(II)TBzPyP at various concentration of HSA represent two distinct stages in the process of interaction. The existence of an isosbestic point in first titration stage can be related to the equilibrium of free Cu(II)TBzPyP with that of Cu(II)TBzPyP:HSA complex. The aggregation of HSA molecules around porphyrin has occurred in the second titration stage. The analysis of binding process by calculation on absorption data led us to estimate binding constant for formation of HSA:Cu(II)TBzPyP complex. The RLS spectra of Cu(II)TBzPyP at various concentration of HSA do not show any aggregation of Cu(II)TBzPyP in the presence of HSA, which certified the results of UV-Vis studies. The fluorescence emission of HSA chromophore was quenched due to the porphyrin binding. The process of quenching has been analyzed by Stern-Volmer equation. Hence the binding constant of Cu(II)TBzPyP to HSA has also been estimated as the Stern-Volmer quenching constant, which is in good agreement with the result of UV-Vis studies.

Phase Equilibria in the Ternary System MgO–Na₂O–P₂O₅. The Partial System MgO–Na₃PO₄–Na₄P₂O₇

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A partial system of MgO–Na₃PO₄–Na₄P₂O₇ in the ternary system MgO–Na₂O–P₂O₅ was investigated and its phase diagram was obtained. Thermal analysis (heating and cooling), powder X-ray diffraction, and optical microscopy using reflected light were applied. In the composition range of interest two ternary compounds occur, which melt congruently and have the formulae MgNa₄(PO₄)₂ (m.p. 1655°C) and MgNa₆P₂O₉ (m.p. 1665°C). The phosphates compose a quasi-binary section with continuous solid solutions and exhibit a temperature minimum about 1520°C.

DNA Effect on the Photoisomerization of Naphthalenevinylpyridinium Derivatives

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The binding study, photoisomerization and spectral behavior of novel DNA interacting dyes, 1-[2-(N-methylpyridinium-4-yl)vinyl]naphthalene iodide (**1**) and 2-[2-(N-methylpyridinium-4-yl)vinyl]naphthalene iodide (**2**), are reported. Ligand-DNA interactions were investigated by UV-Vis absorption and circular dichroism measurements. The ligands have different binding characteristics, depending on the structure of the isomers. The nonplanar *cis* isomers have lower affinity to DNA. Photoisomerization experiments in the absence and the presence of DNA showed significant differences in the composition of resulting photostationary states (pss). The lower values of pss in the presence of DNA indicate that *trans* → *cis* isomerization of DNA-bound ligands is suppressed, which leads finally to *trans* isomer-rich pss. Moreover, the quantum yield of *trans* → *cis* photoisomerization (ϕ_{TC}) decreased dramatically.

Simple Approach to 1-Alkyl-2-isopropylhydrazines

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Ditosylates of 1-alkyl-2-isopropylhydrazines were prepared by *N*-alkylation of *t*-butyl isopropylidene-carbazate (**2**) followed by reduction of *N*-alkyl-*t*-butyl isopropylidene-carbazate (**3**) with lithium aluminum hydride in boiling tetrahydrofuran. The removal of *N*-Boc protecting group was quantitatively achieved by refluxing *N*-alkyl-*t*-butyl isopropylcarbazate (**4**) with *p*-toluenesulfonic acid monohydrate in dichloromethane.

¹⁹F NMR Measurements – A Potential Tool for the Determination of Amino Acids in Body Fluids

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N-substituted 2,4-dinitro-6-trifluoromethylphenyl and 2-fluoro-4-nitrophenyl derivatives of several amino acids were prepared and characterized by ¹H, ¹³C and ¹⁹F NMR and IR spectroscopy. Fluorine chemical shift values of these compounds were found to be a good parameter for the identification of amino acids in urine and blood.

**Synthesis of [3-[2-(Dimethylamino)ethyl]-2-
[[3-(dimethylamino)ethyl]-1*H*-indol-5-yl]methyl]-1*H*-
indol-5-yl]-*N*-methylmethanesulfonamide – the Main
Sumatriptane Impurity**

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Alkylation of sumatriptane in position 2 by 3-[2-(dimethylamino)ethyl]-5-indolemethanol has been described. Alternative multistep synthesis of 3-[2-(dimethylamino)ethyl]-5-indolemethanol has been presented.

1:3 Complex between β -Cyclodextrin and Dendrimer with Three Branches Involving Four Glycine and One Adamantyl Group

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The first-generation dendrimer, benzene-*sym*-tris-*N,N,N*-carbonyltriglycylglycine *N'*-1-adamantylamide, was synthesized by a modification of a described procedure. Its complexation with α -, β - and γ -cyclodextrins was studied by NMR. The complexation induced fit and NOESY studies indicate that, in agreement with molecular mechanics calculations, the complex with β -cyclodextrin is considerably stronger than those with α - and γ -cyclodextrins.

Hydroxyethylation of Tiron with Ethylene Oxide

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An efficient method for the preparation of disodium 4,5-bis(2-hydroxyethoxy)-1,3-benzenedisulfonate in reaction between Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate) and ethylene oxide under mild conditions is described. The influence on the reaction of the molar ratio of reagents used, temperature and different divalent metal salts as catalysts, is discussed.

Conductance Study of Complexation of Ammonium and Alkylammonium Ions with Some Aza-Substituted Crown Ethers in Binary Acetonitrile-Dimethylsulfoxide Mixtures

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A conductance study of the interaction between ammonium and four different alkylammonium ions and dibenzodiazia-15-crown-4 (DBDA15C4), diaza-18-crown-6 (DA18C6), aza-18-crown-6 (A18C6) and dibenzyl diaza-18-crown-6 (DBzDA18C6) in acetonitrile-dimethylsulfoxide mixtures was carried out at 25°C. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and, in the case of all cations used, found to vary in the order DBDA15C4 > DA18C6 > A18C6 > DBzDA18C6. In all cases, the substitution of alkyl groups on the ammonium ion is found to decrease the stability of the resulting macrocycles' complexes, the sequence of which being $\text{NH}_4^+ > \text{MeNH}_3^+ > \text{EtH}_3^+ > \text{Et}_2\text{NH}_2^+ > \text{Et}_3\text{NH}^+$. The stability of all complexes in the binary mixtures used was found to decrease with increasing mole fraction of dimethylsulfoxide.

Oxidation of 3-Hydroxy-6-methyl-2-pyridinemethanol by Chromium(VI) in Acidic Aqueous Media; Kinetic and EPR Studies

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Kinetics of oxidation of 3-hydroxy-6-methyl-2-pyridinemethanol (hmpol) by Cr^{VI} at HClO_4 was studied under the pseudo-first-order conditions. The hmpol oxidation products were the appropriate aldehyde (hmpal) and acid (hmpac) coordinated to the chromium(III). The linear dependence of the pseudo-first-order rate constant (k_{obs}) on [hmpol] at 1.0 and 2.0 M HClO_4 and a parabolic dependence of k_{obs} on $[\text{H}^+]$ were established. The apparent activation parameters were determined from the second-order rate constants at 1.0 M HClO_4 . The presence of the Cr^{II} and Cr^{IV} intermediates was deduced, based on rate retardation effect caused by O_2 and Mn^{II} respectively, whereas the presence of Cr^{V} was established by EPR. Some correlations between the structure and stability of intermediate chromium(V) complexes have been discussed from EPR spectra, recorded during the redox process.

**Equilibrium in Water Ternary Systems:
MgH₂Y–CaH₂Y, CaH₂Y–BaH₂Y, CaH₂Y–SrH₂Y**

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Synthesis of 1-(2,5-Dimethoxy-2,5-dihydrofuran-2-yl)ethanol from 2-Acetylfuran

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