Generation and Typical Reactions of Thiocarbonyl Ylides

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In recent years, thiocarbonyl ylides found new application as useful building blocks in syntheses of sulfur containing heterocycles. They were also shown to play an important role as key intermediates in two-step [3+2] cycloaddition reactions. Strategies explored for the generation of thiocarbonyl ylides and their typical reactions including [3+2] cycloadditions, 1,3- and 1,5-electrocyclizations, additions of OH, SH, and NH groups, and rearrangements are presented. Reactivities of isolable, push-pull stabilized thiocarbonyl ylides are compared with those proposed as transient species.
Quantitative Surface Analysis by X-ray Photoelectron Spectroscopy

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X-ray photoelectron spectroscopy (XPS) has become a powerful tool to study first few atomic layers at solid surfaces. This technique provides information on chemical state of atoms at the solid surface, and the composition of the analysed layer. Present work reviews the typical procedures of quantitative XPS analysis. The relatively accurate procedures are based on measurements involving standards, i.e. samples with known surface composition. However, these procedures may be applicable to perfect samples with similar surface structure as the standards. In general, such approach is impractical for use in routine analysis of samples consisting of large number of components. In experimental practice we frequently encounter the imperfect samples with rough surfaces, or in a form of a powder, for which the use of standards is not recommended. A convenient procedure to use in such a case is the relative sensitivity factor approach, which does not require the external standards. However, accuracy of this method is rather poor. A reasonable compromise for XPS analysis of complex samples is a variation of the relative sensitivity factor approach with sensitivity factors determined for a given instrument and the used XPS configuration. A good example of the modification of the relative sensitivity factor approach is the multiline approach. The surface composition is calculated then after statistical analysis of all intensities observed in the spectra. The details of such procedure are discussed in the present review.
Reaction of α- and β-Halogenostyrenes with Arenediazonium Tetrafluoroborates and Potassium Thiocyanate

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Reaction between α- and β-monohalogenostyrenes 1–4, arenediazonium tetrafluoroborates 5a–e and potassium thiocyanate under catalytic condition (Cu 2+) proceeds unusually. It was shown that direction of these reactions depends on the halogen position and the solvent: α-substituted (H, Cl or SCN) stilbenes or products of thiocyanatoarylation have been obtained. β-Chloro- 1 and β-bromostyrenes 2 react with 5a–e and KSCN to form substituted trans-stilbenes 6a–e and Z-α-thiocyanatostilbenes 7a–e. α-Chloro- 3 and α-bromostyrenes 4 react with 5a–e and KSCN in acetone or acetone-water medium to form products 6a–e and 7a–e. The 4-nitrobenzenediazonium tetrafluoroborate (5e) gives of Z-α-chloro-4-nitrostilbene (9e) besides 6e and 7e. In acetone-water medium α-chlorostyrene (3) gives also 1-chloro-1-thiocyanato-1-phenyl-2-arylethanes 8a–e and moreover products 6a–e and 7a–e. The radical cation mechanism for these reactions has been discussed. It is postulated that the reaction takes place through the formation of radical cations [PhCH=CHHal] + or [PhCHal=CH2]+ with further formation of phenylvinyl cations.
Hydride Reduction of 4-Nitro-1-phenylazoles

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Hydride reduction of 4-nitro-1-phenylimidazole and 2-methyl-4-nitro-1-phenylimidazole to the respective 1-aryl-4-oximinoimidazolidines by metal hydrides was studied under different conditions. 1-Aryl-4-oximinoimidazolidines were hydrolyzed to the respective imidazolidinones. For a comparison hydride reduction of 4-nitro-1-phenylpyrazole to the corresponding azoxy compound was carried out too.
Reduction of Epoxy Isophorone Oxime by Metal Hydrides

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Epoxy isophorone oxime (1) is reduced with LiAlH₄/CeCl₃/THF or NaBH₄/MoO₃/MeOH to a mixture of \( t-3 \)-amino-1,5,5-trimethyl-r-1-cyclohexanol (2) and \( c-3 \)-amino-1,5,5-trimethyl-r-1-cyclohexanol (3), 39:61 and 67:33, respectively. The reduction of 1 with NaBH₄ or LiAlH₄ affords a mixture of isomeric 3,5,5-trimethyl-3-hydroxycyclohexan-1-one oximes 4 and 5 (syn:anti 60:40 and 44:56, respectively). The reduction of 1 with NaBH₄/CeCl₃/7H₂O/ROH or CeCl₃/7H₂O/ROH (R = Me, Et, n-Pr) results in the nucleophilic opening of the epoxide ring to give 2-alkoxy-3-hydroxy derivatives \( 6a-c \), \( 7a-c \), and symmetric ethers \( 8 \) and \( 9 \). When 1 reacts with CeCl₃/7H₂O/t-BuOH only \( 8 \) and \( 9 \) are formed.
C(2)-(α-Mannosyl)indole: The Pivotal Intermediate Towards the Natural C-Glycopeptides

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Two different approaches were investigated to prepare the unusual modified peptide C(2)-mannosylated indole residue. Direct glycosylation of 2-metallated indoles or 2-trimethylsilylindole derivative by reaction with perbenzylated α-D-mannopyranosyl bromide was incompatible due to the intermediate generation of a nucleophilic anomeric carbon atom followed by elimination of the functional group at C-2. Palladium-catalyzed coupling/cyclization approach was examined as a novel route towards indole-(C)-glycosides. Coupling of the mannopyranosyl donors with o-ethynylaniline derivative in the presence of Pd(0) followed by cyclization of the newly formed alditols were also described.


$^1$H and $^{13}$C NMR Studies of 5,6,11-Trimethyl-6H-indolo[2,3-b]quinolinium Methylsulfate and Some of Its Derivatives

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$^1$H and $^{13}$C NMR spectra of the parent 5,6,11-trimethyl-6H-indolo[2,3-b]quinolinium methylsulfate and of its nine 2- and 9-methyl-, methoxy- and fluoro-substituted derivatives were measured and assigned from COSY $^1$H-$^1$H, HETCOR $^1$H-$^{13}$C and SPT INEPT experiments. Proton and carbon-13 chemical shifts and long range spin-spin coupling constants ($^n$J$_{HH}$, n = 3, 4) were considered in terms of the electron density distribution in the indoloquinolinium moiety and compared with the corresponding data obtained earlier for 5,11-dimethyl-5H-and 6,11-dimethyl-6H-indolo[2,3-b]quinoline derivatives. The sensitivity of the proton chemical shifts to the changes in concentration was found for all the compounds studied.
Novel Oxidative, Liquid-Phase Chlorination Procedures for the Preparation of (Dichloroiodo)arenes from Iodoarenes

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One improved and eight novel oxidative, liquid-phase chlorination procedures for the preparation of (dichloroiodo)arenes, ArICl₂, from iodoarenes, ArI, are presented in this paper. KMnO₄, activated MnO₂, KClO₃, NaIO₄, NaIO₃·H₂O, concentrated nitric acid, sodium perborate monohydrate, sodium percarbonate, and a stable urea·H₂O₂ complex are used as oxidants, which oxidize hydrochloric acid to produce in situ a very active chlorine. The crude yields for the PhICl₂ obtained are good or excellent (63.5–99%).
Aggregation of the Silica Suspension by Al-Coagulants

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“SiO₂-Al” aggregates, obtained with Al-coagulants, were studied. An advanced photographic method for measuring the size and velocity of aggregates was applied. The study on “fresh” and “old” sludge obtained in the pH range of 5–9 with the optimal or doubled Al-dose was carried out. Fractal dimension (D) values from 1.67 to 2.00 at the mean coefficient of determination $r^2 = 0.916$ were measured. An effect of the type of coagulant, pH, Al-dosage and age of the aggregates on D was examined and explained. Fluctuations of “solid mass” contribution, reaching 1:20, to the total mass of the average sludge were ascertained. Fractal dimension has appeared a powerful tool in the research on the structure and composition of sludge aggregates. This tool was sensitive enough to indicate even such subtle changes as sludge ageing or coagulant overdosing.
Multi-Periodic and Chaotic Cyclic Voltammograms at Anodic Dissolution of Copper

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Periodic (up to period 8) and chaotic voltammograms are obtained during multicycle scanning of applied potential during copper dissolution in a copper sulphate-sulphuric acid solution. Dynamic character of voltammograms is analysed by the reconstruction of attractors, Poincaré sections and return maps. Obtained results show that changes of bifurcation parameters (a sweep rate or an upper potential limit) cause that voltammograms change according to period doubling sequence.
Structures of Diguanidinium Sulfate and Guanidinium Hydrogen Sulfate

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Novel Norbornene to Norcarene Rearrangement: An Exceptionally Facile 1,3-Carbon Sigmatropic Shift

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Synthesis, Spectroscopic Characterization and Magnetic Properties of Nickel(II), Cobalt(II) and Manganese(II) Complexes Containing 4-Amino-3,5-dimethyl-1,2,4-triazole and N-Bridging Thiocyanate

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