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M. S. T. Makk*, R. M. Abdel-Rahman and M. S. El-Shahawi

Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia

Abstract

The present investigation was aimed to synthesis a series of new 1-acyl/ benzoyl -1-anilido-4-methyl - aryl-1,3-butadiene derivatives (II-IV) for their uses as biocidal and analytical reagents. The compounds were prepared by warming 4-aminoantipyrine, 2-amino-5-chloropyridine, 2-amino-5-nitropyridine, 2-aminobenzthiazole, sulfanilamide and/ or sulfadiazine with pre heated ethyl acetoacetate and/ or ethyl benzoylacetate in dry conditions followed by condensation with crotonaldehyde and/or 4-dimethylaminocinnamaldehyde in boiling ethanol-piperidine. The compounds were fully characterized via their elemental analysis and spectroscopic measurements (UV Vis., IR, NMR). The biocidal effects of the prepared compounds (IIId, e, f, IV d, e, f) as antimicrobial agents and photochemical probe agents was investigated. The voltammetric behavior of the two compounds IIa and IVa in N,N-dimethylformamide was investigated. The compound IVa was successfully tested for the removal and / or separation of bismuth (III) employing polyurethane foam solid sorbent.

Keywords: Synthesis; 1-Acyl/ benzoyl -1-anilido-4-methyl - aryl-1,3-butadiene; Biocidal voltammetry; Wastewater

Introduction

Recent years have seen an upsurge of interest on the synthesis and spectroscopic characterization of β -diketones as potential ligands [1,2]. Complex formation in this class of compounds is conceived by replacement of the enolic proton by chelation with metal ions in a bidentate fashion [3,4]. β -diketone 3-salicylidene-2,4-pentanediones and related compounds have been used successfully as proper chelating agents with a series of many metal ions [5,6,7]. Knoevenagel condensate of substituted benzylidenes with active methylene compounds were performed efficiently employing ultra stable Zeolite as heterogeneous catalyst [8-11] have reported a series of benzoyl-acetanilides and their physico organic properties. The starting material was used by Abdel-Rahman [11] for building a series of novel bio-active pyrazoline derivatives. In addition, the thermodynamic characteristics and spectroscopic characterization of a series of compounds namely hydrazono-1,3-bi carbonyl derivatives and their lanthanide complexes have been investigated [9,10].

The chelation behavior of a series of dicarbonyl towards some metal ions has been reported [12-14]. Moreover, metal chelates of β -diones have interesting properties in particular in industrial applications [15-17]. The dimerized species of 2-diazo-3-methyl-1-phenyl-5-pyrazolone produced the compound 4-(5-hydroxy-4-pyrazolylimino-2-pyrazolin-5-one). Such investigations have indicated that, no work is known on the Knoevenagel condensate -ketoanilide and its metal chelates. Therefore, in continuation to our previous work [18-23], the present study is focused on the synthesis and characterization of a series of some β -diketone derivatives bearing anilido moieties and their unsaturated β -diketone derivatives. In view of the voltammetric behavior, one of the prepared compounds was successfully tested as a trapping agent for the pre-concentration of bismuth (III) from aqueous as a highly toxic metal ions the industrial waste water.

Experimental

Reagents and materials

Low density polyethylene (LDPE) bottles, Nalgene were carefully cleaned first with hot detergent, soaked in 50% HCl (Analar), HNO₃

and finally rinsed with distilled water. N,N-Dimethylformamide (DMF) and the supporting electrolyte tetraethyl ammonium chloride (TEACl) were purchased from BDH chemicals. The sample solution was

*Corresponding author: MST Makk, Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia, E-mail: mmakki@kaau.edu.sa

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of the compounds were preformed on Micro analytical center, Cairo University, Egypt. Microanalysis (Nitrogen %) was performed by microanalytical center Ain-Shams University-Cairo-Egypt. A Metrohm 797 VA trace analyzer and 797 VA stand were used for recording the cyclic voltammetric (CV) experiments. In the CV experiments, a three-compartment (Metrohm) voltammetric cell (10 mL) incorporating Pt wire as working, double-junction Ag/AgCl,(3M KCl), as reference and Pt wire (BAS model MW-1032) as counter electrodes, respectively. The surface area of the counter electrode was 100 times larger than the area of the working electrode.

Methodology

Preparation of acyl/benzoyl acetanilide Derivatives (I and III):
To preheated ethyl acetoacetate and/or ethylbenzylacetate (0.01mol) a selective hetero primary amines and/or sulfa drugs (0.01mol) were added in dry system then warmed for 10-15 min at 100-110°C, cooled and finally washed with diethyl ether. The resultant solid was dried and crystallized to give I and III respectively (Table 1).

Formation of 1-acyl/benzoyl-1-anilido-4-methyl/aryl-1,3-butadiene (II and IV): Equimolar mixture of compounds I and/or III and unsaturated aldehydes as crotonaldehyde and/or 4-dimethylaminocinnamaldehyde in absolute ethanol (100 mL), piperidine (0.5 mL) was heated under reflux for 8 h, cooled. The solvent was removed and the obtained solid was crystallized to give II and IV respectively (Table 1).

Preparation of the reagent IVa immobilized polyurethane foam packed column: Polyurethane foam (PUFs) cubes immobilized with the reagent IVa were prepared by mixing the dried foam cubes with the required weight of the reagent (0.05% w/v) in ethanol with efficient stirring for 10 min. The reagent immobilized PUF cubes were then dried to remove the excess reagent with filter papers as reported earlier [19-21]. The reagent immobilized PUFs were packed separately in the glass columns by applying the vacuum method of foams packing.

Pre concentration and/ or separation of bismuth (III) by reagent IVa treated PUFs: An accurate weight (0.1 ± 0.01 g) of the reagent IVa treated foam cubes was equilibrated with 50 mL of an aqueous

I and III show no characteristic C=O absorption band (at 1725-1716 cm⁻¹) which is present in the spectrum of acetylacetone ~ 1680 cm⁻¹ of true C=O group. Also, intramolecular as well as intermolecular hydrogen bonding are observed in the regions 2700-2500 and 3000-2900 cm⁻¹ respectively. The presence of absorption bands at 1610-1480 cm⁻¹ (C=C) and 960-900 cm⁻¹ confirm the presence of trans -CH=CH- moiety of compounds II and IV respectively. These vibrations indicate that the transformation of the electronic effect is quite apparent through the part comprising the NH, OH and CO groups.

¹H NMR spectra of compounds I and III showed a one proton signal at ~15 ppm which confirms the presence of strong intramolecular hydrogen bonded enol proton, in addition, a signal appeared at 6.5-6.8 (methine) 6.9-7.9 ppm (aryl) protons. In such systems, the maximum enolization is two especially if containing aryl moieties. On the other hand, ¹H NMR spectra of compounds II and IV, showed a resonance signals at 8.0-8.5 ppm (olefinic), 2.5 ppm (methyl protons due to an allylic coupling between HC=CH and methyl group), in addition of aromatic protons at 6.7-7.7 ppm. Also, the tautomeric forms of compounds I and III is evidenced by PMR which showed one resonated singlet for proton linked to sp² carbon at 4.66 ppm. Moreover, structures of the compound II and III were deduced from ¹³C NMR, II recorded at 29.9 (CH₃), 202.8 (C=O), 51.7 (CH₂), 164 (b C=O), 174.5 (S-C=N), 153, 130 (C₄ & C₅ of thiazole) and 118 -121.8 ppm (benzocarbons); while compound III recorded at 194.2 (C=O), 117 (HO-C=C), 66 (CH=C-OH), 174.5 (S-C=N), 153, 130.8 (C₄ & C₅ of thiazole) and 118.3 -122.8, 136 -128 ppm (benzo and phenyl protons). According to the ¹H and ¹³C NMR data, the acyl/benzoyl anilide derivatives have mainly an enolic structure with intramolecular hydrogen bonding in solution state, while the styryl of acyl/benzoyl anilides exist predominantly in the cis-form established by some type of interaction.

Mass spectroscopy of compounds I-IV give another indication of their stability which shows the degree between ketonic and enolic equilibrium. Also, fragmentation results give us a different way between Me-CO and Ar-CO structures. A good physico-chemical evidence for the presence of enolic and/or ketonic tautomers of compounds I and III was deduced from free solubility of their Ar-NHCO derivatives in aqueous NaOH which confirms that the enolization forms take place towards aryl and/or phenyl groups [5].

Biocidal effect

Some synthesized compounds were tested *in vitro* using the agar diffusion disk method [20,21]. The antimicrobial potentialities of the test compounds were estimated by placing pre-sterilized filter paper disks (11 mm diameter) impregnated with 50 mg/disk using DMSO as solvent, which showed no inhibition zone (IZ) of tested compounds (mm) were measured after 24h incubation at 37°C for bacteria and after 5-days incubation at 28°C for fungi (Table 2). Photochemical probe effects of these compounds can be determined using UV – 360 as

was then calculated as reported earlier [19-21]. Maximum retention of bismuth (III) by the immobilized reagent PUFs was achieved from the aqueous media at pH 2-3 containing iodide ions and the sequence of the uptake followed the order: iodide>bromide>chloride. The uptake of bismuth (III) from the aqueous iodide media decreases on increasing the solution pH.

The observed decrease on the bismuth (III) retention at pH>3.5 is most likely attributed to the instability of bismuth-iodide or the ternary complex involving $[BiI_4]^{-IVa^+}$ due to the hydrolysis of the species formed between $[BiI_4]^{-IVa^+}$ and the reagent immobilized polyurethane foams. Similar trends were also reported earlier [19-21]. Thus, a "weak base anion ion exchanger" and a "solvent extraction" mechanism of the $[BiI_4]^{-IVa^+}$ may be proposed for the uptake onto the protonated ether ($-CH_2-HO^+-CH_2-$) or urethane ($-NH_2COO-$) linkages of the immobilized PUFs.

The effect of contact time and shaking time on the retention of bismuth by the treated AMP-PUFs of bismuth (III) from the aqueous solution containing high excess of KI (5-7% w/v) by AMP-loaded foam was carried out at pH 2.0. The bismuth (III) uptake was fast and reached maximum within ~ 10-15 min contact time. The half-life time ($t_{1/2}$) of the equilibrium sorption of bismuth (III) as calculated from the plot of $-\log(C_b)$

examined by batch mode of separation. Reasonable amount of bismuth (III) ions are retained onto the reagent immobilized PUFs from the test aqueous solutions and the amount of bismuth (III) retained on the PUFs depends on the solution pH. Thus, the sorption profile of bismuth (III) at selected concentration ($10.0 \mu\text{g ml}^{-1}$) from the test aqueous solution (50.0 mL) containing excess of KCl, KBr or KI at different pH (pH 2 -8) onto the reagent loaded foams was examined. After shaking the solutions for 2 h, the amount of bismuth (III) remained in the aqueous solution was determined. The amount of bismuth (III) retained, the extraction percentage, %E and the distribution ratio, D

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