Synthesis of Polyfunctional Organic Systems Containing 1- Acyl / Aroyl - anilido-butadienes and their uses as Photochemical Probes and Chelating Agents for Removal of Bismuth (III) from Industrial Wastewater

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Abstract

The present article reports the synthesis of a series of some new 1-acyl/ benzoyl -1-anilido-4-methyl /aryl-1, 3-butadiene derivatives (II - IV) by warming primary heteroamines and / or sulfa drugs with pre heated ethyl acetoacetate and / or ethyl benzoyleacetate in dry conditions followed by condensation with unsaturated aromatic aldehydes in boiling ethanol-piperidine. The chemical structures of the compounds were characterized via their elemental analysis and spectroscopic measurements (UV Vis., IR, 1H NMR). Some of the compounds (III, e, f, IV d, e,f) were tested as antimicrobial and photochemical probe agents. Compound IVa was physically loaded onto polyurethane solid sorbent and successfully used for the removal and / or pre concentration of bismuth (III) from industrial wastewater. The voltammetric behavior of the two compounds Ila and IVa in N, N-dimethylformamide was investigated.

Keywords: Synthesis; 1, 3-butadiene derivatives; Photochemical probes; Chelating agent; Bismuth (III); Wastewater; Voltammetry

Introduction

Polyfunctionally substituted oxo anilides e.g. azoloazines have received considerable interest in recent years (Hussein et al., 2009). Such class of compounds has diverse physiological activities e.g. acting as central nervous systems depressants and calcium sensitizing agents and possess hypnotic, diuretic, antiinflammatory, antimicrobial and hypoglycemic activities (Fathalla et al., 2001). The synthesis and spectroscopic characterization of \( \beta \)-diketones as potential ligands have been reported by Funk et al., 1993; Zheng and Swager, 1994. In this class of compounds, complex formation is conceived by replacement of the enolic proton by \( \beta \)-ketoanilide and its metal chelates. Therefore, in continuation to our previous work (Bashammakh et al., 2008; Farag et al., 2007; Zaki et al.1995), the present study is focused on the synthesis and characterization of a series of some \( \beta \)-diketone derivatives bearing anilido moieties and their unsaturated \( \beta \)-diketone derivatives. In view of their properties, some of the compounds were tested as antimicrobial and photochemical agents. Moreover, one of the prepared compounds for the pre-concentration/separation of bismuth (III) from aqueous as a highly toxic metal ions the industrial waste water. The cyclic voltammetry of two selected compounds were also investigated.

Experimental

Apparatus & measurements

A Perkin Elmer (Lambda EZ-210) double beam spectrophotometer (190-1100 nm) with 1cm (path width) was used for recording the electronic spectra of the prepared solutions. A Perkin-Elmer (Analyst TM 800, USA) atomic absorption spectrometer (AAS) was used for measuring the concentration of bismuth (III) ions before and after extraction at the optimum operational parameters of the instrument. A Perkins Elmer model RXI-FT-IR system 55529 was used for recording the IR spectra of the prepared compounds. A Brucker advance

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Cl-) were purchased from BDH chemicals. The sample solution was 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

selective hetero primary amines and/or sulfa drugs (0.01mol) were

acid was used. A series of standard bismuth (III) solutions in the range

weights and elemental analysis of the compounds were preformed on Micro analytical center, Cairo University, Egypt. Microanalysis of nitrogen and sulfur (%) was performed in Microanalytical Center, Ain-Shams University, Cairo, Egypt.

Reagents & materials

Low density polyethylene (LDPE) bottles, Nalgene were carefully cleaned first with hot detergent, soaked in 50% HCI (Analar), HNO3 (2.0 mol L-1), subsequently washed with dilute HCl (0.5 mol L-1) and finally rinsed with distilled water. N, N-Dimethylformamide (DMF) and the supporting electrolyte tetraethyl ammonium chloride (TMA+ Cl-) were purchased from BDH chemicals. The sample solution was stored in LDPE bottles and stored at -20°C. Britton – Robinson (B –R) buffers of pH 2-10 were prepared from the acid mixture of phosphoric acid, boric acid, acetic acid (0.04 mol L-1) and adjusting the pH to the required value with sodium hydroxide (0.2molL-1). A stock BDH stock solution of bismuth (1000 µg mL-1) in dilute nitric acid was used. A series of standard bismuth (III) solutions in the range 1-100 µg mL-1 was then prepared in doubly distilled water in the presence of few drops of nitric acid (5% m/v). Stock solutions (1x 10-5 mol L-1) of the compounds –acyl-1-anilido-4- methyl-1,3- butadiene, Ila and 1-benzoyl-1-anilido-4- methyl-1,3- butadiene, IVa in DMF were prepared.

Organic preparation

Preparation 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-dimethylaminomandaldehyde 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 I and III respectively (Table 1).

Preparation of 1-acetylbenzoyl-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-dimethylaminomandaldehyde 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 I and IV respectively (Table 1).

Preparation of the reagent IVa immobilized PUFs packed column

Polurethane 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 (Abou-Mesalam et al., 2003; El-Shahawi and El-Sonbati, 2005; El-Shahawi et al., 2008). 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±0.01g) of the reagent IVa treated foam cubes was equilibrated with 50 mL of an aqueous solution containing bismuth (III) ions at concentration of 10 µg mL-1. The solutions were then adjusted to the required pH with B-R buffer (pH 2-10). The test solutions were then shaken for 2 h on a mechanical shaker. The aqueous phase was then separated out by decantation and the amount of bismuth (III) remained in the aqueous phase was determined with atomic absorption spectrometry at the optimum wavelength. The amount of bismuth (III) retained on the PUFs cubes was determined from the difference between the concentration of bismuth (III) solution before (C0) and after (Cf) shaking with the foam cubes.

Results and Discussion

Spectroscopic characterization

Synthesis of 1,3-dicarboxyl anilido and their unsaturated derivatives is very simple and of general applicability. It gives pure compounds with improved yields. Thus, warming some hetero primary amines such as 4-aminooantipyrine, 2-amino-5-chloropyridine, 2-amino-5-nitropyridine, 2-amibenzothiazole and

| Compd No. | M.P. (°C) | Yield (%) | Solvent | M. Formula | M. Weight | Nitrogen, % | Sulfur, % |
|----------|-----------|-----------|---------|------------|-----------|------------|-----------|
| Ia | 130 | 80 | Pet. ether 60-80 | C11H10N2O2 | 205 | 207 | 210 | 212 | 217 | 219 |
| Ib | 165 | 70 | Pet. ether 60-80 | C11H10N2O4 | 231 | 234 | 235 | 237 | 241 | 244 |
| Ic | 158 | 75 | Pet. ether 60-80 | C11H10N2O6 | 254 | 256 | 258 | 260 | 264 | 266 |
| Id | 225 | 75 | Pet. ether 60-80 | C11H10N2O7 | 333 | 334 | 336 | 337 | 339 | 341 |
| Ie | 135 | 80 | Pet. ether 60-80 | C11H10N2O8 | 377 | 380 | 382 | 384 | 386 | 388 |
| If | 210 | 85 | Pet. ether 60-80 | C11H10N2O9 | 284 | 286 | 288 | 290 | 292 | 294 |
| Ig | 150 | 72 | THF | C11H10N2O10 | 345 | 348 | 350 | 352 | 354 | 356 |
| Ih | 170 | 75 | THF | C11H10N2O11 | 273 | 275 | 277 | 279 | 281 | 283 |
| Ii | 140 | 73 | Pet. Ether 100-140 | C11H10N2O12 | 283 | 285 | 287 | 289 | 291 | 293 |
| Ij | 170 | 78 | Pet. Ether 100-140 | C11H10N2O13 | 296 | 298 | 300 | 302 | 304 | 306 |
| Ik | 162 | 80 | Pet. Ether 100-140 | C11H10N2O14 | 296 | 298 | 300 | 302 | 304 | 306 |
| Il | 300 | 90 | Pet. Ether 100-140 | C11H10N2O15 | 314 | 316 | 318 | 320 | 322 | 324 |
| Im | 240 | 85 | Pet. Ether 100-140 | C11H10N2O16 | 396 | 398 | 400 | 402 | 404 | 406 |
| In | 335 | 82 | Pet. Ether 100-140 | C11H10N2O17 | 441 | 443 | 445 | 447 | 449 | 451 |
| Ia | 125 | 70 | Diethyl ether | C11H10N2O18 | 346 | 348 | 350 | 352 | 354 | 356 |
| Ib | 280 | 72 | Diethyl ether | C11H10N2O19 | 451 | 453 | 455 | 457 | 459 | 461 |
| Ic | 140 | 60 | Diethyl ether | C11H10N2O20 | 451 | 453 | 455 | 457 | 459 | 461 |

*Analytical data of C and H for the compounds are within the range ± 0.4-0.7% of the theoretical values.

Table 1: Physical properties of prepared compounds I-Iv.
some sulfa drugs as sulfanilamide and sulfadiazine with preheated ethyl acetoacetate and/or ethyl/benzoyl acetate at 100-110°C for 10-15 min in dry condition led to the formation of acyl/bezoyl acetanilide derivatives I and III (Scheme I, II). Knoevenagel condensation of compounds I and III with unsaturated aldehydes such as crotonaldehyde and/or 4-dimethylcinnamaldehyde in boiling ethanol with few drops of piperidine as catalyst afforded 1-acyl/bezoyl -1-anilido-4-methyl-1,3-butadiene (II) and 1-acyl/benzoyl -1-anilido-4-(4`-dimethylaminophenyl)-1,3-butadiene (IV), respectively. The compounds prepared are summarized in schemes 1-III. Both carbonyl compounds I-IV having a second carbonyl at \( \beta \)-position, are termed as \( \beta \) diketones. In general hydrogen bonding is possible only in syn form and not in anti form, where the orientation of enolization is towards the aryl or phenyl groups (Mishra et al., 1991) indicating the high enolic content of 4-aryl-1,3-diketones and not in 4-methyl-1,3-diketones.

**UV – Visible spectra of compounds II and IV have two strong bands around 360 and 260 nm which characteristics bands of carbonyl chromophore and the conjugated C=O of butadiene (n→\( \pi^* \) and \( \pi \to \pi^* \) transitions) while that of compounds I and III recorded a low bands at 330 and 240 nm due to a bathochromic shift, indicating the involvement of the two carbonyl groups isolated by methylene group, assigned to the intramolecular charge transfer interaction involving the whole molecule (Sawyer et al., 1984).

**IR spectra of compounds I and III show no characteristic C=O absorption band at \( \nu \) 1725-1710 cm\(^{-1} \) which is present in the spectrum of acetylacetone \( \sim 1680 \) cm\(^{-1} \) while that of II and IV recorded of strong absorption bands at \( \nu \) 1650 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 δ~15 ppm confirming the presence of strong intramolecular hydrogen bonded enol proton, in addition, a signal appeared at δ 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 δ 6.7-7.7 ppm. The tautomer forms of compounds I and III were confirmed via 1HMNR where, one in addition of aromatic protons at δ 4.66 ppm was noticed. The structures of the compounds II and III were deduced from 13C NMR. The spectrum of compound IId showed δ at 29.9 (CH3), 202.8 (C=O), 51.7 (CH3), 164 (b C=O), 174.5 (C=N), 153, 130 (C, & C of thiazole) and 118 -121.8 ppm (benzocarbons); while compound IVd revealed δ at 194.2 (C=O), 117 (HO-C=C), 66 (CH=CH–OH), 174.5 (C–C=N), 153, 130.8 (C, & C of thiazole) and 118.3 -122.8, 136 -128 ppm (benzo and phenyl protons). Based on 1H and 13C NMR data, the acy/benzyol anilide derivatives are mainly present in enolic structure with intra molecular hydrogen bonding in solution state. The acy/ benzoyl anilides existed predominantly in the cis- form via some type of interaction.

Mass spectra of compounds I-IV confirmed the degree of stability as indicated from the equilibrium between ketonic and enolic forms. Fragmentation also revealed the loss of Me-CO and Ar-CO from their chemical 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-NHICO derivatives in aqueous NaOH which confirm that the enolization forms take place towards aryl and or phenyl groups (Mishra et al., 1991).

Applications of the prepared compounds

Biocidal activity: Some of the synthesized compounds were tested in-vitro against microorganisms such as bacteria Escherichia. coli and the fungi Aspergillus fumigates in DMF using the agar diffusion disk method (Barry et al., 1981; Winker et al., 1962). The results are compared with piperclillin and mycostatine as standard antibiotic. The antimicrobial potentialities of the tested compounds were evaluated by placing pre sterilized filter paper disks (11 mm diameter) impregnated with 50 mg/disk using DMSO as solvent which revealed no zone (IZ) after 5 days incubation at 28°C for fungi (Table 2). Photochemical probe effects of these compounds were determined before and after using UV light at 366 nm as a second test (Table 2). The compounds IId,e,d,f and IV,c,d,f showed a highly biocidal effect and only compounds IId,d,f were found characterized by photo chemical probe action lower than other prepared compounds. This behavior is most likely attributed to the rich oxygen atoms in their structures with multi excitation states.

Pre concentration and / or separation of bismuth (III) onto reagent IVa immobilized PUFs

In preliminary experiments the use of the reagent IVa immobilized PUFs for the pre concentration of bismuth (III) from aqueous solution was examined by batch mode of separation. Reasonable amount of bismuth (III) ions are retained onto the reagent immobilized PUFs from the test aqueous solutions. The amount of bismuth (III) retained on the reagent treated PUFs depends on the solution pH. Thus, the sorption profile of bismuth (III) (10.0 µg mL−1) from aqueous solutions (50.0 mL) containing excess of KCl, KBr or KI at different pH (pH 2 -10) 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 by. The amount of bismuth (III) retained, the extraction percentage, % and the distribution ratio, D was then calculated as reported earlier (Abou-Mesalam et al., 2003; El-Shahawi et al., 2005; El-Shahawi et al., 2008). Maximum retention of bismuth (III) by the immobilized reagent PUFs was achieved from the aqueous media of pH 2-3 containing excess iodide ions and the sequence of bismuth (III) uptake followed the order: iodide> bromide > chloride.

On the other hand, the retention 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 [BiI4 ]− and the species formed between BiI3− and the reagent immobilized polyurethane foams. Similar trends were also reported earlier (Abou-Mesalam et al., 2003; El-Shahawi et al., 2005; El-Shahawi et al., 2008). Thus, a “weak base anion exchanger” and a “solvent extraction” mechanism of the [BiI4 ]− may be proposed for the uptake onto the protonated ether (–CH2–HO–CH2–) or urethane (–NH–COO−) 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 (II) uptake was fast and reached maximum within ~ 10-15 min contact time. The half-life time (t½) of the equilibrium sorption of bismuth (III) as calculated from the plot of -log(Cb/Ca) versus time onto the reagent immobilized PUFs from the aqueous media to reach 50% saturation of the sorption capacity was in the range 1-1.5 min (Figure 1). The uptake of bismuth (III) ions was fast within the first 10 min and increased up to a constant value in less than 60 min shaking time. Thus, a shaking time of 60 min was adopted in subsequent experiments.

The analytical utility of the reagent IVa treated PUFs solid sorbent was successful assessed using the reagent IVa immobilized PUFs in packed column for complete retention of different concentrations (100 mL, 5-1000 µg L−1) of bismuth (III) in de ionized water. The sample solutions were percolated through the PUFs packed column

Table 2: The Biocidal and photochemical Effects of Some Compounds

| Compound | 50 mg/mL | Before UV irradiation | After UV irradiation | Bacteria Escherichia coli | Fungi Aspergillus fumigates | Bacteria Escherichia coli | Fungi Aspergillus fumigates |
|----------|----------|-----------------------|----------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|
| IId      | 15       | 17                    | 16                   | 17                       | 22                          | 17                       | 22                          |
| e        | 15       | 22                    | 16                   | 17                       | 22                          | 17                       | 22                          |
| IVd      | 13       | 12                    | 13                   | 14                       | 14                          | 14                       | 14                          |
| e        | 12       | 10                    | 12                   | 13                       | 12                          | 13                       | 12                          |

*Highly active >20 mm; moderate (15 ~ 20 mm) and weak < 15 mm.

Figure 1: Rate of sorption of bismuth (III) onto the reagent AMP-loaded foams at 35°C onto the reagent AMP immobilized foams.
at flow rate of 10 ml min⁻¹. Quantitative retention of bismuth (III) was achieved onto PUFs packed column as noticed from the analysis of bismuth in the effluent solutions by FAAS.

The removal of bismuth (III) from industrial wastewater was also carried out following the same procedures. The water samples of industrial wastewater (0.1 L) of electroplating industry after acidified with phosphoric acid was spiked with various concentrations (1 and 5 µg mL⁻¹) of bismuth (III), acidified with phosphoric acid and filtered through a 0.45 µm cellulose membrane filter. The test water samples were percolated through the reagent packed column at 5 ml min⁻¹ flow rate. The analysis of bismuth in the effluent solution by FAAS revealed complete retention of cadmium from the test solution. The results are summarized in Table 3. Bismuth was quantitatively recovered with acidified solution of nitric acid (10 mL, 3.0 M) and analyzed by FAAS. A satisfactory recovery percentage of total cadmium was achieved in the range 94 – 96.0±2.7.

### Voltammetric study

The cyclic voltamograms (CVs) of the compounds 1-acyl-1-anilido-4-methyl-1,3-buta diene, Ila and 1-benzoyl-1-anilido-4-methyl-1,3-buta diene, IVA in DMF -TMA+Cl- at Pt working electrode versus Ag/AgCl reference electrode at various scan rate were investigated. The results are shown in Figure 2 and Figure 3. The CV of compound Ila (Figure 2) at 100 mVs⁻¹ revealed two well-defined cathodic peaks at 0.1 and -0.75 V versus Ag/AgCl electrode. One well defined anodic peak at -0.15 V was observed on the reverse scan suggesting the irreversible nature of the observed electrochemical process in the employed potential range (-2.0 - 2.0 V). On raising the scan rate (>100 mV s⁻¹), the potential of the two cathodic peaks were shifted cathodically, while the anodic peak shifted anodically confirming the irreversible nature of the observed electrochemical processes (Bashammakh et al., 2009; Bard and Fulkner, 1980). The observed cathodic peaks are most likely assigned to the reduction of the carbonyl group via 2H⁺/2e in two successive one electron / one proton reduction steps (Bard and Fulkner, 1980). Continuous scan of the CV significantly decreased the peak current height indicating passivity of the surface of the Pt electrode via formation of polymeric oxidation product or fouling of the Pt electrode by the produced reduction products suggesting prior adsorption on the surface of the electrode in the potential range (Bard and Fulkner, 1980).

In DMF- TMA+Cl- the CVs of the compound IVA (Figure 3) at the Pt working electrode showed two reduction peaks at 0.1 -0.15 and -0.65 -0.8 V coupled with one broad anodic peak in the potential range 0.3-0.4 V at scan rates of 50-1000 mVs⁻¹ versus Ag/AgCl electrode. The cathodic peaks are safely assigned to the reduction of the carbonyl group in two successive H⁺/e redox steps (Bashammakh et al., 2009). The peak –peak potential difference (ΔE = (Ep,a – Ep,c)) between the cathodic (Ep,c) and anodic peaks (Ep,a) indicated that, the observed redox processes are irreversible. On raising the scan rate both cathodic and anodic peaks are shifted to more negative and positive potential, respectively confirming the irreversible nature of the observed redox process (Bard and Fulkner, 1980). The plot of the the cathodic peak current (i p,c) versus the square root of the scan rate was linear indicating that the electrochemical processes is diffusion controlled processes (Bard and Fulkner, 1980). The plot of E p,a versus log scan rate was found linear at Ag/AgCl. Thus, it can be concluded that, the first reduction processes of the compound precede according to the well known electrode- coupled (EC) chemical reaction mechanism (Bard and Fulkner, 1980). The overall results suggest the possible use of the two compounds as complexing agent in cathodic stripping voltammetry for determination of bismuth (III) ions in water.

### Conclusion

The redox behavior of the tested compounds suggest the possible application of the compounds as chelating agent for the determination of ultra trace concentration of heavy metal ions employing differential pulse – adsorptive stripping voltammetry. Moreover, immobilization of one of the prepared compounds on polyurethane foam solid sorbent as trapping agent for minimization and / or separation of bismuth (III) from industrial wastewater was achieved. Work is still continuing for application of the compound in cathodic stripping voltammetric procedures for trace metal analysis in different matrices.

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**Table 3: Retention and recovery of bismuth (III) in wastewater samples by the reagent IVA treated PUFs packed column.**

| Added, µg/mL | Found, µg/L |
|-------------|-------------|
| 1.0         | 0.38        |
| 5.0         | 4.7         |

*Average ± relative standard deviation

**Figure 2: Cyclic voltammograms of the compound 1-acyl-1-anilido-4- methyl-1,3-buta diene, IId in DMF-TMA+Cl- at Pt working electrode vs. Ag/AgCl electrode at various scan rates.**

**Figure 3: Cyclic voltammograms of 1-benzoyl-1-anilido-4- methyl-1,3-buta diene, IId in DMF-TMA+Cl- at Pt working electrode vs. Ag/AgCl electrode at various scan rates.**
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