

STUDY OF THE SYNTHESIS OF SOME ALKYL-AROMATIC DIOXIMES AND THEIR ANALYTICAL APPLICATIONS

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Received 20 March 2011
Accepted 120 September 2011

ABSTRACT

The synthesis of the alkyl-aromatic dioximes is of practical interest due to the complex potential determined by the presence in their structure of the oxymic groups, donor of electrons. Complexes formed by dioxime structures with transitional metals have a series of physical-chemical properties (colour, stability, solubility) important from the point of view of analytical applications. In this paper results relevant to the synthesis of some alkyl-aromatic dioximes as well as to the physical-chemical characterization of their complexes with some transitional metals are presented.

Keywords: alkyl-aromatic dioximes, metal complexes, spectral analysis.

INTRODUCTION

The dioxime structures are the object of several studies in respect to their structure and analytical applicability, a field which is interesting and in the same time meticulously investigated. The interest growing each day for this class of compounds is well understood, taking into account the various possibilities and the purposes in which these organic ligands and their metal complexes can be used. From the multiple and diverse applications of the asymmetric dioximes, the fact that dioxins are used on large scale as extraction agents in different sampling methods using conventional extraction and synergic processes must be mentioned [1]. Cobalt complexes of the dioximes, cobaltoximes $R-Co(Diox.H)_2L$, have a special importance in bio-analysis. They allow for the elucidation of many structural aspects and syntheses mechanisms of biological molecules, as well as mechanisms for evolution of the vital processes, being used as “models” of inorganic complexes similar in structure to the compounds of coordination in the biological systems. Presently, α -dioximes can be found in the composition of some sensors, used

for determination of Ni, Pd, Co traces in the water of the lakes, oceans and different biological materials [2].

Dioximates of the metals from the nickel triad, due to their crystallization properties, are used as electroluminescent substances in the production of LED. The key achievement realised in this field is the identification of the modalities in which substituents of the dioxime groups have influence on the liquid crystals properties of the dioximates of LEDs [3]. Another important aspect related to the applications of the dioximes is their use in a series of modern separation techniques like in chromatographic methods (GC, HPLC) where they are used to clear traces of transitional metals. Dioxime additions in the stationary phases used by chromatographic techniques contribute substantially to the separation resolution by increasing selectivity. Chemical bonding of α -dioxime structures to tridimensional polymeric nets leads to obtaining materials with changing properties of ions, characterised by proportionally increased selectivity [4]. It should be mentioned, also, that dioximes are used in biochemistry. An example is 1,1'-trimethylene-bis(4-formylpyridinium-bromide) dioxime (TMB-4) used for monitoring the inhibitor ef-

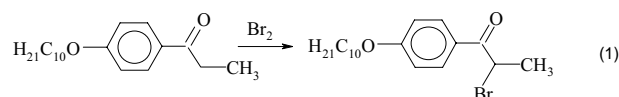
fect of paraoxon (diethyl-p-nitrophenylphosphate) on the acetylcholinesterase. A problem in these studies - the immobilization and reactivation of the enzyme has been solved by using the previously mentioned dioximes [5].

EXPERIMENTAL

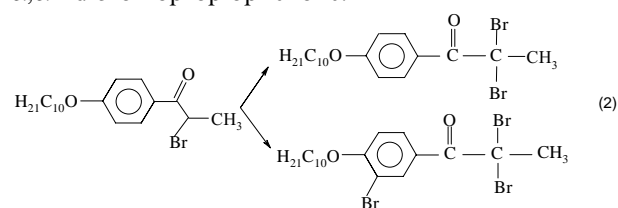
The synthesis of the α -dioximes might take place, generally, either by thermal decomposition of some heterocyclic compounds having in their molecule N and O, or by electrochemical oxidation or reduction of some amines, namely α - substituted nitrocompounds. For preparative purposes, the selective oxidation of monoketones containing active methylenic groups in proximal position to the carbonyl group, namely their isonitrosation, is preferred. Ketoximes formed in this way are treated with hydroxylamine, to obtain the correspondent dioximes [6].

Selective oxidation of the asymmetric monoketone

With this method bromine water oxidation of p-(n-decanol)-propiophenone at the α -carbon in respect to the carbonyl group is realised. This reaction takes place in dichloromethane, at room temperature and leads to p-(n-decanol)- α -bromopropiophenone:

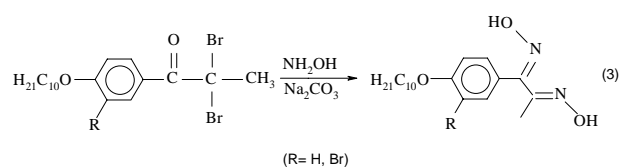


The dibromide of the monoketone is obtained in more active conditions. Using a double quantity of bromine and a very high temperature is not sufficient to obtain the dibromide derivative. The hydrobromic acid formed as secondary product, acts like a reducing agent, transforming the dibromide derivative in monobromide derivate. That is why p-(n-decanol)- α -bromopropiophenone is isolated from the reaction mixture and is treated with another mole of bromine. The product formed in these conditions is p-(n-decanol)- α,α' -dibromopropiophenone:



Synthesis of the bromide in thionyl chloride of p-(n-decanol)- α -bromopropiophenone

As thionyl chloride does not dissolve hydracids, the dibromide reaction can be realised also in this solvent, but in these conditions the bromination of the aromatic nucleus takes place. The main products of the reaction are 3-bromo-p-(n-decanol)- α,α' -dibromopropiophenone. Dioximes are formed by treating the α,α' -dibromoketone with hydroxylamine. The formed hydrobromic acid is neutralized with sodium carbonate.



Synthesis p-(n-decanol)-propiophenone-1,2-dioxime can be realised in the following stages:

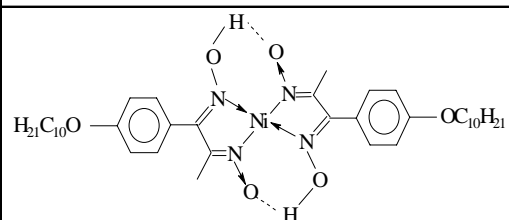
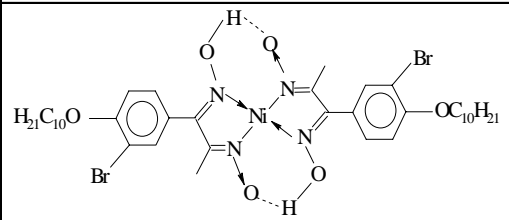
- synthesis of p-(n-decanol)- α -bromopropiophenone: 10 g of p-(n-decanol)-propiophenone is dissolved in 200 ml of dichloromethane and to the obtained solution are added 5,6 g bromide in dichloromethane. After about 5 minutes, the solvent is separated by distillation.

- synthesis of p-(n-decanol)- α,α' -dibromopropiophenone: 3,1 g of p-(1-decanol)- α - bromopropiophenone in 100 ml chloroform are treated at boiling with 1,6 g bromide in chloroform. The mixture is heated at reflux by an water bath for 1 hour. After cooling the solvent is removed by vacuum distillation. The residues are purified by column chromatography (eluent dichloromethane/hexane 1:1).

For bromide in thionyl chloride of p-(n-decanol)- α -bromopropiophenone, about 5,3 g are diluted in 100 ml of thionyl chloride. Then 5 g of bromide are added and boiled for about three hours in reflux. Collign takes place at room temperature and the solvent is separated by vacuum distillation. The remaining residual after distillation is purified by column chromatography (eluent dichloromethane /hexane 1:3).

- synthesis of p-(n-decanol)-propiophenone-1,2-dioxime: 1 g of p-(n-decanol)- α,α' -dibromopropiophenone is treated with 1 g of hydroxylamine and 6 g of sodium carbonate in 100 ml ethanol. The mixture is heated in reflux for 1 hour. After cooling, the formed dioxime is filtered and washed with water. The product is recrystallised from methanol.

Table 1. The nickel (II) chelates with p-R-propioiphenon-1,2-dioxime.

Synthesized complex structure	Yield, %	Colour	Melting point
	77	red	109,3
	82	red	155,6

To obtain 3-bromo-p-(n-decanol)-propioiphenone-1,2-dioxime we act in a similar manner, namely: 2,5 g of 3-bromo-p-(n-decanol)- α,α' -dibromopropioiphenone is treated in aqueous solution of 2 g hydroxylamine and 11 g sodium carbonate. The mixture is heated for 1 hour at reflux. The product is filtered and washed with water, then recrystallised from methanol. The yield is 82 %.

Physical – chemical characterization of nickel chelates with asymmetric alkyl –aromatic dioximes. Alkyl-aromatic asymmetric dioximes form with some transitional metals (Ni, Pd) complexes with square planar structure (Table 1). The nickel compositions with p-R- substituted alkyl-aromatic dioxime have been obtained in alcoholic solution, treating the ligand with mineral salt corresponding in percentage of 2:1. The compounds of Ni (II) in alcoholic solution have yellow colour, while as solids are red-purple. These are hardly water soluble compounds, but are soluble in organic solvents: chloroform, dichloromethane, acetone, benzene.

RESULTS AND DISCUSSION

The melting point of the bromide-substituted complex is higher than the one of the un-substituted complex. In most cases, the melting point decreases for groups containing aromatic center substituted with halogen, the reason being the decrease of the molecular symmetry. Regarding the present group, the symmetry of the molecule does not modify in rapport with the un-substituted group. The melting point increases by a Van

der Waals effect and with supplementary introduced dipoles. In a solid status, the molecules of the Ni dioximate are arranged in a parallel manner and positioned in layers. These stratified arrangement can be explained by an association of the group, caused by some intermolecular Me-Me interactions.

The structural characteristics of the Ni complex dioximates have been studied by spectroscopic UV-VIS analysis.

Spectroscopic characterization of the alkyl –aromatic groups - p-R-substituted

The spectra of the Ni(II) complex with asymmetric alkyl – aromatic dioxime-p-R-substituted have been registered in a crystalline status as well as in dif-

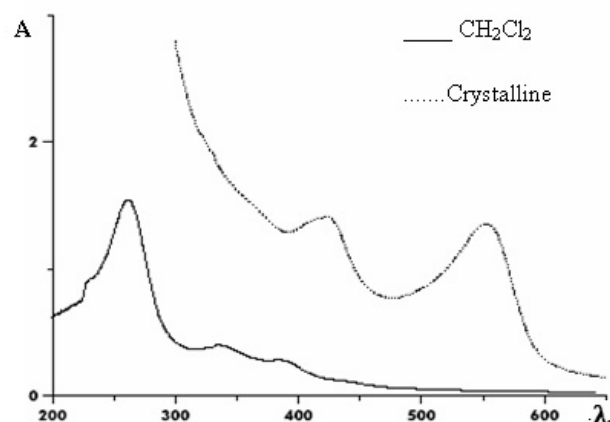


Fig. 1. UV-VIS spectra of bis[p-(n-decanol)-propioiphenone-1,2-dioximate] of Ni(II).

Table 2. Spectrometric data UV-VIS in CH₂Cl₂.

λ max /nm ($\epsilon/l \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$)	
Complex (I)	Complex (II)
432,5 (900)	435,5 (1000)
383,5 (2050)	373,5 (2900)
333,5 (2950)	326,5 (3800)
261,5 (11200)	259,5 (16300)

ferent solvents. Groups' solutions in alcohol, as shown before, are of yellow color, while the crystals have red color. In Fig. 1 are presented for comparison, the UV-VIS spectra of bis- [p-(n-decanol)-propiophenone-1,2-dioximate] of Ni(II) in crystalline status and in solution.

For the solid substance a powerful absorption at $\lambda = 552$ nm (green colour) which is responsible for the colour of the complex (complementary colour) red purple can be observed. This absorption peak is absent in the spectrum of the complex solution. Here the band of the blue violet field of the spectrum, indicating the yellow complementary colour for dioxime solutions appears. The spectrum of the complex in methanol is almost identical with the one in dichloride methanol. The visible difference between the spectrum of the complex in solid state and the ones in liquid state is due to an association of the molecules of the groups in crystalline state, by a reciprocal action metal-metal. In Table 2 are presented the absorption maximum limits and the values of the molar coefficients of extinction of the groups: *bis*[p-(n-decanol)-propiophenone-1,2-dioximate] of Ni(II) marked with (I) and *bis*[3-bromo-p-(n-decanol)-propiophenone-1,2-dioximate] of Ni(II) marked with (II) in solution of dichloromethane. In the spectrum of the solution, the absorption strip of the solid the solution appearing at $\lambda = 552$ nm. The green absorption band from the spectrum of the solid substance cannot be observed in the spectrum of the solution, having as a result the change of the colour from red to yellow. In solution the groups are not any longer associated, so that the reciprocal metal-metal effect is cancelled. A diminution of the association can be observed also at the of the groups. The red colour of

the solid substance becomes lighter with the increase of the temperature. The change of colour is reversible. The explanation of this thermochrome effect might be the loss of intermolecular connection metal-metal with the increase of the temperature.

CONCLUSIONS

A restricted number of the alkyl-aromatic dioximes is known presently in the special literature. The syntheses of such compounds, generally, encounter experimental difficulties because of their formation in several stages with sometimes inconvenient yields. This paper presents the groups of nickel alkyl-aromatic dioximes which have been studied from the structural point of view by UV-VIS spectral analysis. The alkyl-aromatic dioximes can be successfully used in the chemical analyses, in a series of analytical determinations, namely:

- in gravimetric analysis, the groups of transitional metals with dioximes from this class have generally favourable gravimetric factors;
- in the elaboration of some volumetric, namely spectrometric methods for determination of transitional metals. Their application in spectral analysis is due to favourable properties (colour, solubility) and a characteristic spectrum in UV-VIS, allowing the quantitative analysis of metals, like nickel or palladium.

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