



# Rearrangement of azoxybenzocrowns into chromophoric hydroxyazobenzocrowns and the use of hydroxyazobenzocrowns for the synthesis of ionophoric biscrown compounds



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## ABSTRACT

The Wallach rearrangement was used as a method for preparing *p*-hydroxyazobenzocrown ethers starting from different azoxybenzocrowns as substrates. Synthesis of a series of *p*-hydroxyazobenzocrowns under modified conditions and characterization of the obtained products are presented. *o*-Hydroxyazobenzocrowns were identified among the products of the photochemical rearrangement of azoxybenzocrowns. Novel biscrowns were synthesized from *p*-hydroxyazobenzocrown ethers. The synthesized host molecules, differing in the size of the macrocycles and in the substituents in the aromatic rings, have the same dioxymethylene linkers. They were used as potential sodium or potassium ionophores in classic and miniature (screen-printed) ion-selective electrodes. The properties (tautomerism, acid–base equilibrium) of newly prepared *o*-hydroxyazobenzocrown ethers and their *p*-substituted analogs were studied using spectroscopic methods and compared.

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## 1. Introduction

Azoxybenzene and its derivatives deserve special interest. Azoxybenzenes are characterized by high chemical and thermal stability; in addition, all compounds containing a nitrogen atom connected to the benzene ring may theoretically be transformed into azoxybenzenes by means of oxidation and reduction reactions.<sup>1</sup> Despite this fact, there are very few reactions of azoxybenzenes that find practical use. The most interesting one is the Wallach rearrangement.<sup>2</sup>

Wallach found that azoxybenzene in the presence of a strong acid undergoes rearrangement to *p*-hydroxyazobenzene (Fig. 1a). The rate of this rearrangement is largely dependent on the acidity of the reaction medium. Upon increasing the sulfuric acid concentration from 75% to 100%, the reaction rate is increased by five

orders of magnitude.<sup>3</sup> The range of acids used for the rearrangement is quite broad and includes Lewis acids and superacids. However, most systems demonstrate no real advantage over sulfuric acid.

The mechanism of the Wallach rearrangement turned out to be more complex than it was initially thought, and has not been unambiguously explained to date. It has been assumed, however that formation of *p*-hydroxyazobenzene in strongly acidic environment is an intermolecular reaction. The strongly acidic environment is required for the substrate—a weak base—to accept two protons, thus forming a dicationic, delocalized intermediate (Fig. 1b), as is assumed by one of dominant theories.<sup>4,5</sup> Such species are known to be formed in highly acidic systems. A quinoid intermediate has also been proposed as an alternative.<sup>6–8</sup> Quinoid intermediates (Fig. 1c) resulting from the attack of a nucleophile (Nu=HSO<sub>4</sub><sup>-</sup>) on the con-

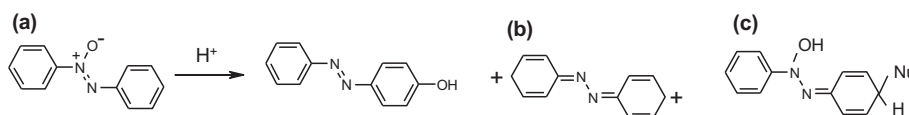


Fig. 1. a. Wallach rearrangement, b. dicationic intermediate, c. quinoid intermediate.

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jugate acid of the azoxyarene are believed to be formed in the lower acid concentration level.<sup>3</sup> The mechanism involving the quinoid intermediate is also probable in case of reactive azoxybenzene

derivatives and azoxynaphthalenes.<sup>5</sup> It is also proposed for the Wallach rearrangement of azoxybenzene conducted in the presence of acidic cation-exchange resin.<sup>8</sup>

The product of the rearrangement of azoxybenzene in concentrated sulfuric acid is azobenzene-4-hydrogen sulfate, while hydrolysis of which affords 4-hydroxyazobenzene.<sup>9</sup>

Byproducts may also be generated in Wallach rearrangement conditions; some of these byproducts are typical, but atypical byproducts are also formed. Typical byproducts of Wallach rearrangement conducted in sulfuric acid include: azobenzene, *o*-hydroxyazobenzene, sulfonic acid derivative of *p*-hydroxyazobenzene, aniline, and polymeric compounds.<sup>10,11</sup> The nature of these products depends largely on the reaction conditions. An increase in the amounts of azobenzene was observed with increasing acidity.<sup>10</sup> Formation of azobenzene was also promoted by high temperatures.<sup>12</sup>

Substituents on the benzene rings influence both the rate of the Wallach rearrangement and the nature of the product; therefore, the effect of the nature and position of substituents in the azoxybenzene molecule on the course of the rearrangement was studied particularly extensively. Typical models included halogenated derivatives. For example, when 4-haloazoxybenzenes were treated with sulfuric acid (92%, 50 °C, 30 min), the main rearrangement products were 4-halo-4'-hydroxyazobenzenes, i.e., the hydroxyl group was introduced to the non-substituted ring, and the composition of products was only weakly dependent on whether the substrate was the  $\alpha$ -isomer or the  $\beta$ -isomer.<sup>13</sup> Significant amounts of haloazobenzenes are also formed in the reaction (the heavier the halogen, the higher the amount of haloazobenzenes and the lower the amount of *p*-hydroxyazobenzenes), as well as small amounts of 2-OH and 2'-OH-derivatives. In the case of azoxybenzenes in which the halogen atoms were located at positions 2,2' or 3,3', the rearrangement afforded 4-hydroxydihaloazobenzenes and significant quantities of respective dihaloazobenzenes.

In the case of photochemical rearrangement of azoxybenzene, the main product is *o*-hydroxyazobenzene, formed from the singlet state of azoxybenzene in an intramolecular reaction. The presence of oxygen does not affect the product distribution in the absence of sensitizer.<sup>1,14–16</sup>

The Wallach rearrangement and its mechanism were studied for azoxybenzene and its simple derivatives. Azoxy compounds of the naphthalene series also undergo the Wallach rearrangement.<sup>17</sup> Similar reaction was also conducted using phenylazopyridines<sup>18</sup> and azoxyquinoxaline.<sup>19</sup> According to our best knowledge, studies on Wallach rearrangement have not been conducted outside our group on more complex compounds, including macrocyclic compounds.

As we have already shown,<sup>20,21</sup> the Wallach rearrangement can also be used as a method for preparing hydroxyazobenzocrown ethers starting from azoxybenzocrown substrates. Preliminary results were promising and encouraged more detailed research. The first reaction series was carried out in a mixture of ethanol and concentrated sulfuric acid at ca. 90 °C, over ca. 30–40 min. The 10-, 13- and 16-membered azoxybenzocrowns and their differently substituted derivatives yielded respective hydroxyazobenzocrowns as reported in a preliminary communication.<sup>20</sup> Azobenzocrowns with hydroxyl groups in the *para* position to the azo group were mainly obtained from parent azoxybenzocrowns.<sup>21</sup> However, the problem was the formation of significant quantities of ethoxyazobenzocrowns as byproducts, not observed when azoxybenzene was submitted to the rearrangement in analogous conditions, in line with the expected azobenzocrowns as byproducts. The resulting difficulties with obtaining higher yields (>50%) of hydroxyazobenzocrowns required the reaction conditions to be modified. We present the synthesis of a series of hydroxyazobenzocrowns under modified conditions and the characterization of the obtained products. We compare the course

of the rearrangement in azoxybenzocrowns with that of the reaction conducted under analogous conditions using azoxybenzene and 2,2'-dimethoxyazoxybenzene.

Hydroxyazobenzocrowns are compounds with chromoionic properties. These properties are one of the reasons for which these compounds are synthesized,<sup>22,23</sup> although they may also act as universal substrates for a series of derivatives: azobenzocrowns with side chains increasing the compounds' lipophilicity or containing additional functional groups, as well as bisazobenzocrowns.<sup>21,22,24</sup> We present the synthesis of a novel group of bisazobenzocrowns characterized by short, dioxymethylene linkers and the presence of several substituents—different hydrocarbon groups in different positions of the benzene rings. Bisazobenzocrowns may be used as ionophores in ion-selective membrane electrodes that are selective to sodium or potassium ions, depending on the size of the macrocyclic ring.<sup>21</sup> The novel biscrowns were used as membrane components in both classical and miniature (screen-printed) electrodes. In preliminary work, we examined the properties of the obtained potentiometric sensors.

It is well known that azo compounds with electron-donor substituents, such as –OH, –NH<sub>2</sub> in *ortho* or *para* positions to the azo group can exist in two tautomeric forms. Tautomeric equilibrium depends among the others on such factors as solvent, pH, ionic environment, etc. Tautomeric equilibrium and pH influence on it was studied, with the use of spectroscopic methods, both for newly prepared *o*-hydroxyazobenzocrowns and their *p*-substituted analogs.

## 2. Results and discussion

### 2.1. Synthesis

**2.1.1. Rearrangement of azoxybenzocrowns.** Azoxybenzocrowns **1**, **2**, **4**, **6–9**—macrocyclic compounds with 13- or 16-membered rings—were prepared by the previously reported method.<sup>21,25–28</sup> New compounds **3** and **5** were prepared analogously to compound **2**.<sup>21</sup> Azoxy derivatives **1** and **2** were transformed into hydroxyazobenzocrowns **10** and **11** (Fig. 2) in a reaction analogous to Wallach rearrangement by heating to 90–95 °C for 30–40 min in the mixture of concentrated sulfuric acid and ethanol (ca. 5:7 v/v).<sup>21</sup> Exploratory reactions with several azoxybenzocrowns substituted at the benzene rings were also performed under similar conditions.<sup>20</sup> Continuation of research regarding the applicability of Wallach rearrangement in macrocyclic compounds, i.e., azoxybenzocrowns, focused mainly on the attempts to: 1. modify the reaction conditions, mainly so as to reduce the quantities of organic solvents used to obtain hydroxyazobenzocrowns, as well as to increase the yields, particularly in reactions involving larger macrocycles (e.g., 16-membered); and; 2. change the organic solvent so as to replace ethanol, which generates significant amounts of ethoxyazobenzocrowns as reaction byproducts in this class of compounds. No information on identification of an analogous byproduct in the reactions of azoxybenzene derivatives conducted in ethanol/concentrated sulfuric acid mixtures was found in the literature. While maintaining the overall conditions of the previously described procedure,<sup>21</sup> the concentration of the sulfuric acid was reduced to 92%. The yields of the three main products of the reaction conducted in these conditions were assessed. The 16-membered *p*-hydroxyazobenzocrown **11** was obtained in 30% yield. Azobenzocrown **11a** obtained in 13% yield and *p*-ethoxyazobenzocrown **11b** obtained in 17% yield were also isolated from the reaction mixture (Fig. 2). A series of experiments was conducted with increasing substrate concentrations. A six-fold increase in substrate concentration led to a slight decrease in the reaction yield (to 24%), while analogous reactions conducted in

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