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THE MECHANISMS OF THE WALLACH TRANSFORMATION OF α- and β-2-PHENYLAZOXYNAPHTHALENES: TWO REACTION PATHWAYS LEADING TO A COMMON PRODUCT.

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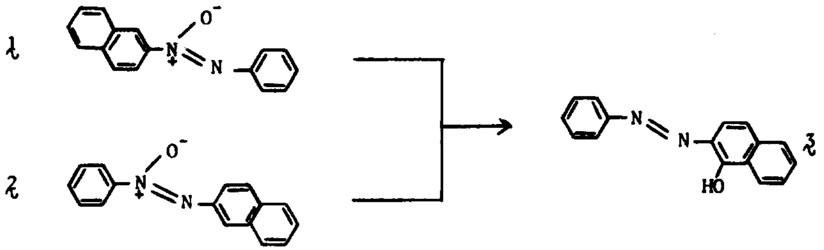
Whereas para orientation in the acid catalyzed Wallach rearrangement is the generally observed course of reaction (e.g. azoxybenzene → p-hydroxyazobenzene)[1,2], the literature contains conflicting reports concerning the importance of ortho orientation.[3-5] The mechanism of such ortho orientations has been uncertain, with evidence presented for both intra- and intermolecular mechanisms, whereas the para rearrangement is known to proceed only intermolecularly.[3-7] On the other hand, the photochemical Wallach rearrangement is known to yield only ortho hydroxyazo products, by an intramolecular process.[6-8] Recently the remarkable finding of acid catalysis in the photochemical Wallach rearrangement was reported, with o-hydroxyazobenzene as the sole product.[9]

We have shown[10] that the isomeric β- and α-2-phenylazoxynaphthalenes, 1 and 2, yield on rearrangement in moderately concentrated sulfuric acid a common product, the 2-phenylazo-1-naphthol 3 i.e. with ortho orientation (eq. 1). We now present evidence based on a kinetic investigation that these isomers react by different reaction pathways.



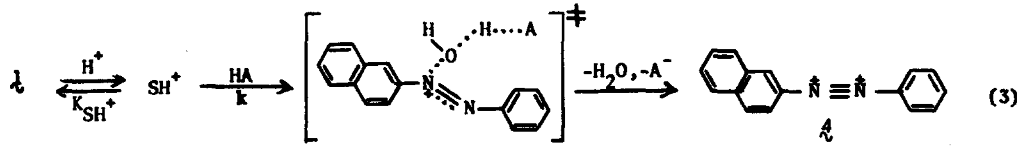
(1)

The rates of rearrangement of **1** and **2** were studied by uv-visible spectroscopy in aqueous H_2SO_4 containing 0.5% ethanol, at 44.4°. Reaction was followed[11] by monitoring the appearance with time of the protonated product absorption directly in the acid media, or by quenching with base and observing the azonaphtholate anion. Pseudo first order rate constants were calculated from linear plots of log $(A_\infty - A_t)$ vs. time. The data shown in Figs. 1 and 2 for the range 70-80% H_2SO_4 represent mean values of several determinations.[*] Since the pK_{SH^+} values of **1** and **2** are -5.00 and -5.03 respectively[12], it follows that both substrates are extensively monoprotonated in these acid media. The observation of an increasing reaction rate beyond complete monoprotonation is indicative of the requirement of a second proton transfer.

The significance of the plot $\log k_\psi - \log C_{SH^+}/(C_S + C_{SH^+})$ vs. $\log a_{H_2SO_4}$ (Fig. 1) is that a linear correlation in this relationship can be shown to be diagnostic of general acid catalysis by H_2SO_4 species rather than by H^+, according to eq. 2 (cf. also ref. 13).

$$\log k_\psi - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} = \log a_{HA} + \log k_o + \log \frac{f_s}{f_{\neq}} \qquad (2)$$

Thus reaction of **1** involves rate-limiting proton transfer to the oxygen of the protonated azoxy function with concerted loss of H_2O and formation of dicationic intermediate:



(3)

The dicationic species **4** will undergo nucleophilic attack by HSO_4^- at the 1-naphthyl position and the product is formed by proton loss with re-aromatization.

In the case of **2**, the plot of $\log k_\psi - \log C_{SH^+}/(C_S + C_{SH^+})$ vs. $\log a_{H_2SO_4}$ is curved, indicating that this substrate follows a different mechanism. A plot of $\log k_\psi - \log C_{SH^+}/(C_S + C_{SH^+})$ vs. H_o is also curved. The acidity dependence of compound **2** can however be accomodated on the basis of a mechanism involving quinoid intermediates as shown in eq. 4 (cf. ref. 13b for hexamethylazoxybenzene in 60-75% H_2SO_4).

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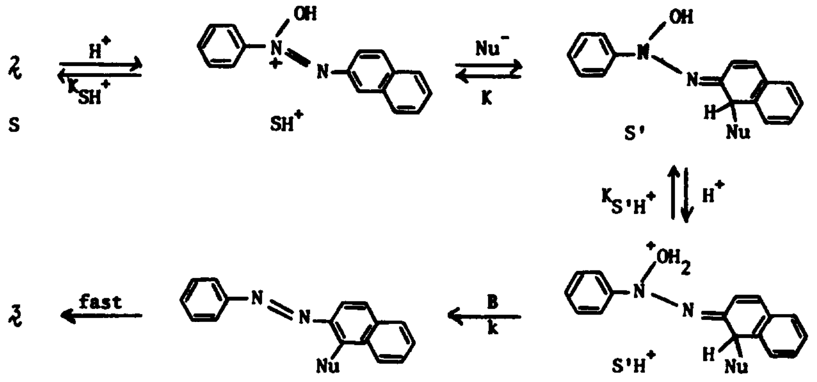
[*] For compound **1**, k_ψ increases from $1.96 \times 10^{-6}\ s^{-1}$ to $1.75 \times 10^{-4}\ s^{-1}$ over the range 69.65 - 80.59% H_2SO_4 (H_o = -5.74 to -7.43), while for compound **2**, over the same range of acidity, k_ψ increases from $6.35 \times 10^{-6}\ s^{-1}$ to $2.78 \times 10^{-4}\ s^{-1}$.



(4)

A kinetic scheme for the system can be derived as previously[13b] and leads to eq. 5.

$$\log k_\psi - \log \frac{C_{SH^+}}{C_S + C_{SH^+}} - \log \frac{C_{S'H^+}}{C_{S'} + C_{S'H^+}} = \log a_{Nu}a_B + \log k_o{}'K + \log \frac{f_{SH^+}f_{S'H^+}}{f_{\neq}f_{S'}} \quad (5)$$

This will be applicable in the general case that the species S, S', SH^+ and $S'H^+$, are all present in significant concentrations. The value of $pK_{S'H^+}$ can be derived as -7.12 on analysis of the data, so that $C_{S'H^+}/(C_{S'} + C_{S'H^+})$ can be calculated. In accord with eq. 5, a linear plot with slope 1.05 is obtained when $\log k_\psi$ is plotted against $2 \log a_{HSO_4^-} + \log C_{SH^+}/(C_S + C_{SH^+}) + \log C_{S'H^+}/(C_{S'} + C_{S'H^+})$, as shown in Fig. 2.

There are several reasons for the occurrence of specific reaction pathways in the case of isomers **1** and **2**. For compound **2**, eq. 4 provides a relatively low energy pathway in media of moderate acidity, (a) since HSO_4^- (which serves the function of B and Nu^-) is the most abundant species in such media[14], and (b) since it avoids formation of structures with two positive charges. However, **1** cannot react by the quinoid intermediate pathway, since the ^+NOH function is not correctly oriented with respect to the naphthyl ring, while the phenyl moiety is insufficiently activated to form quinoid intermediates. Hence **1** must react by another mode, namely the dicationic intermediate mechanism, as followed by azoxybenzene itself.[11,13a]

The dichotomy of mechanistic pathways - dicationic vs. quinoid intermediates - has been advanced previously;[16,17] however the present study has allowed delineation of the determining structural factors as well as providing kinetic criteria for the two mechanisms. Results of an extended study, involving all the known members of the series of phenyl-naphthyl and naphthyl-naphthyl azoxy compounds,[12] are in full accord with the conclusions described in the present communication and will be published in due course.

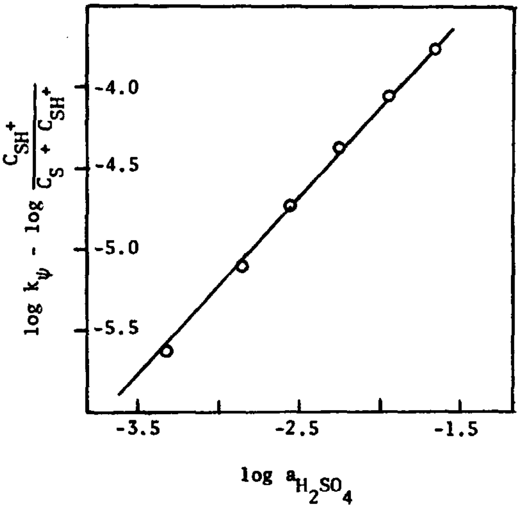


Fig. 1. Test of dicationic intermediate mechanism for compound **1**(eqs. 2,3).

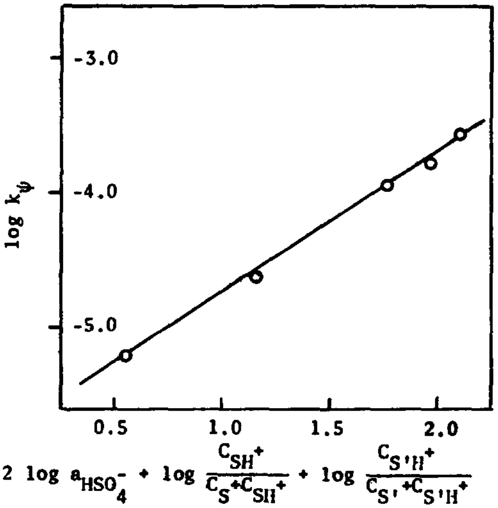


Fig. 2. Test of quinoid intermediate mechanism for compound **2**(eqs. 4,5).

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