The Wallach Rearrangement
The Behaviour of Monosubstituted Azoxybenzenes in Strongly Acidic Solution

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强酸溶液中에서의 Azoxybenzene 系化合物들의 轉移反應. Wallach 轉移反應

韓 治 善

(1962. 8. 30 受理)

Abstract

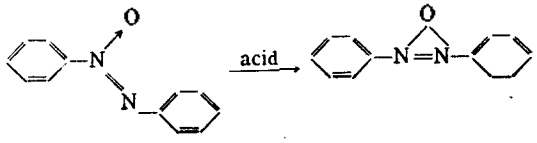
The rearrangement reaction of azoxybenzenes into hydroxyazobenzenes in strongly acidic solution has been studied by an U.V. spectrophotometric method and by isolation of the rearranged compound. In all cases under investigation, it appeared that the oxygen atom in the azoxy group migrated to the unsubstituted ring, depending neither on the substituent already present in the other ring, nor on the distance between the oxygen atom and the eligible position; whereas, the position in the open ring, *ortho* or *para*, to which the oxygen migrates depends on the substituent already present in the other ring. In all compounds besides α-and β-4-methyl azoxybenzene, the oxygen atom migrates to the *para* position. In the case of α and β-4-methylazoxybenzene, the oxygen atom migrates to the *ortho* position of the unsubstituted ring.

Introduction

While the author was measuring the basicities of substituted azobenzenes by an U.V. spectrophotometric method in order to study the characteristic nature of azoxy group, it was noted that azoxybenzenes show a very delicate and interesting behavior in the presence of strong acid. The measurements were made on azoxybenzene in solutions consisting of 20 vol. % EtOH and varying concentration of sulfuric acid. The absorbancy of each spectrum which could be duplicated below a certain concentration of sulfuric acid (ca. vol. 85%), could not be duplicated at higher concentration of sulfuric acid.

Such unusual behaviour of azoxybenzene in acidic solution was also found by Wallach[1]. It has been reported that azoxybenzene rearranges into 4-hydroxyazobenzene in acidic media and with heat. This rearrangement reaction is also brought about by the action of sunlight or ultraviolet light. Bandish[2] and Cumming[3] et al. have reported that the oxygen atom in the azoxy group of azoxynaphthalene or 2,2'-azoxynaphthalene migrates to the *ortho* position by the action of sunlight or ultraviolet light. Badger[4] has supported Cumming's work and proposed that the mechanism of the rearrangement is intramolecular in nature.

Shemyakin[5] et al. have recently reported their results of Wallach rearrangement carried out on azoxybenzene labeled with N^{15} isotope. Azoxybenzene recovered from the rearrangement reaction remained practically unchanged in isotope distribution. Based on the equalisation of isotope distribution during the rearrangement Shemyakin et al. considered that the initial step is probably formation of a 3-membered ring intermediate with two nitrogen and an oxygen atoms in the azoxy group.



and then the oxygen may finally migrate along the path including the cyclic ring symmetrically. On the other hand, at elevated temperature (90° C.), the recovered azoxybenzene was again shown to be unchanged, while the 4-hydroxyazobenzene rearranged gave an excess equilisation of distribution of N^{15} isotopes with higher N^{15} content at the N bound to the ring containing the hydroxyl group. In order to explain these results, they proposed an alternate mechanism in which the oxygen atom may migrate directly from azoxy group to the far ring, without involvement of the 3-membered cyclic oxide.

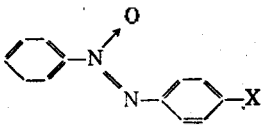
However, since no a priori reason exists why the latter alternate mechanism should contribute only at elevated temperatures, it is difficult at this point to state reasonable mechanism. And Badger's proposal did not have enough experimental data neither. To elucidate the mechanism of the Wallach rearrangement it is necessary to have sufficient experimental results on a series of substituted azoxybenzenes, not only on the azoxybenzene.

In this paper it was studied that the dependance of the migrating oxygen atom on (1) the substituent already present in benzene ring, and on (2) the distance between the oxygen atom and the eligible position. At the same time the orientation of the oxygen atom was discussed.

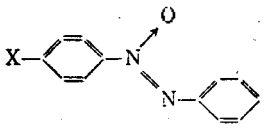
Experimental

A. Preparation of Compounds

(1) Unsymmetrical 4-Monosubstituted Azoxybenzenes....Preparation of both α-and β-forms of 4-monosubstituted azoxybenzenes can be divided into 3 steps, i.e; (a) the preparation of 4-substituted azobenzenes, (b) the oxidation of 4-substituted azobenzenes obtaind in the above step and (c) the separation of α-and β-forms of the unsymmetrical compound.

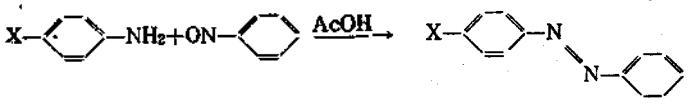


α-form



β-form

4-substituted azobenzenes were prepared according to the following general scheme.[6]



The 4-substituted azobenzenes prepared were oxidized[7] with 30% H_2O_2 and separated into each of α and β-form by liquid chromatography. All the azoxy compounds synthesized by this method are listed in Table I, along with their M. P.

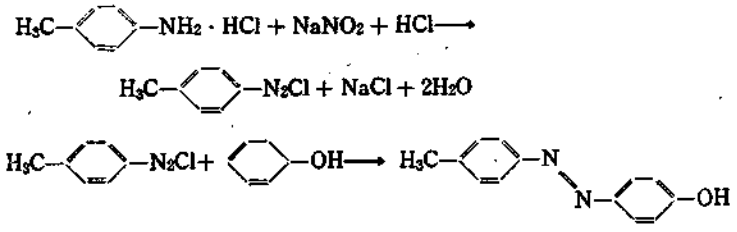
Table I

M.P. of 4-Substituted Azoxybenzenes

X	Y	Isomer	M.P.°C. (Obsd.)	M.P.°C. (Lit.)
H	CH_3	α	46–48	46
CH_3	H	β	65	65
H	Br	α	73–73.5	73
Br	H	β	92–92.5	92
H	OCH_3	α	66.5–67.5	(a)
OCH	H	β	42–43	(a)

(a) Not previously reported

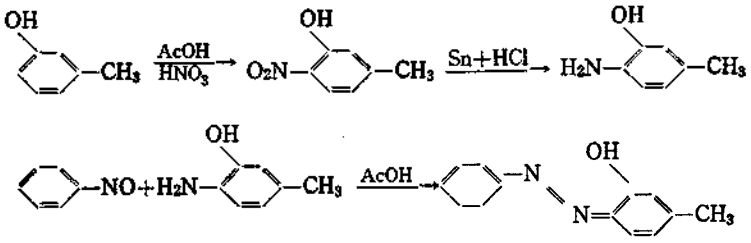
(2) 4-Hydroxy methylazobenzene...The compound was prepared by the coupling of the diazonium salt (chloride) of *p*-toluidine with phenol in alkaline solution.[8]



Recrystallized from 20% EtOH, M. P. 151°C.[9] The compounds of the same series, 4-hydroxy-4'-bromoazobenzene, 4-hydroxy-4'-methoxyazobenzene and 4-hydroxyazobenzene, were prepared by the same method.

(3) Preparation of 2-Hydroxy-4'-methylazobenzene.. This compound is obtained in a very small amount as a side product of *para* isomer, 4-hydroxy-4'-methylazobenzene. The *ortho* isomer was separated by forming copper salt with 50% alcoholic copper acetate, and was regenerated with HCl and ethyl ether. Recrystalized from boiling 95% EtOH; goldish yellow leaf-like crystal, M.P. 100-1°C (Lit.[10] 100-100.5°C.)

(4) 2-Hydroxy-4-methylazobenzene..This compound was synthesized by coupling of nitrosobenzene with 2-hydroxy-*p*-toluidine. The general scheme is as follows.



The separation of 6-nitro-*m*-cresol was followed by Kotinsky's method.[11] Recrytalized from benzene, M. P. 56°C. (Lit.[11b] 56°C.) The 6-nitro-*m*-cresol was reduced by Auwer's method.[12] White needle type crystal, M.P. 157-9°C. (Lit. [12] 195°C.) Analysis:

Found; C, 67.48, H, 7.04; N, 11.29. Calculated; C, 68.26; H, 7.38; N, 11.37. The final product, 2-hydroxy-4-methylazobenzene, was purified through chromatography column. The first fraction(from bottom) was eluted with ligroin. Bright reddish needle crystals, M. P. 122°C. (Lit. [13] 121-2°C.) Analysis:

Found; C, 72.93; H, 5.53; N, 13.44

Calculated; C, 73.56; H, 5.69; N, 13.21

(5) 3-Hydroxy-4'-methylazobenzene....This compound was prepared by coupling of *m*-aminophenol and 4-nitrosotoluene and purified from ligroin (60-90° fraction) by passing through an alumina chromatography column; orange needle, M.P. 70-1°C.

B. **Preparation of Solutions.**

Since preliminary tests have shown that a solution 1.0×10^{-4} M with respect to azoxy-compounds was suitable for measurements with Cary Mode 11 recording spectrophotometer, this solution was prepared from the stock solution (1.0×10^{-2} M) by the 1:10 dilution procedure.

In order to rearrange the azoxy-compounds, this solution was diluted 5 times with 100% H_2SO_4 to give a 1.0×10^{-4} M solution. The hot solution was not cooled, so that the azoxy-compound in the solution might be rearranged as far as possible. The rearranged solution was then further diluted to 10 times its volume with 20% EtOH, so that the solvent consist of 10 vol. % H_2SO_4 and 20% EtOH, and its concentration becomes 10^{-5} M. The solutions of hydroxyazobenzenes were also prepared in the same manner. The spectra measurements under investigation were made using a Cary Model 11 automatic recording spectrophotometer. One and ten cm. cells were used for the 10^{-4} M and 10^{-5} M solution respectively.

C. Isolation of the Rearranged Azoxybenzenes. The rearranged compounds were isolated by neutralizing the solution with conc. NaOH solution, which was stopped approximately at pH 9. The compound was then extracted from ethyl ether and recrystallized from toluene. The other rearranged hydroxyazobenzenes were also extracted by the same method.

Results and Discussion

A. Azoxybenzene

To date there is no report on spectrophotometric study of the Wallach rearrangement in the literature. In connection with the study of the basicities

of azoxybenzenes, the author has investigated the behaviour of azoxybenzene in H_2SO_4 solution. The U.V. spectra of azoxybenzene solutions in which solvent was 20 vol. % EtOH—9, 90 and 100% H_2SO_4 are shown in Fig. 1.

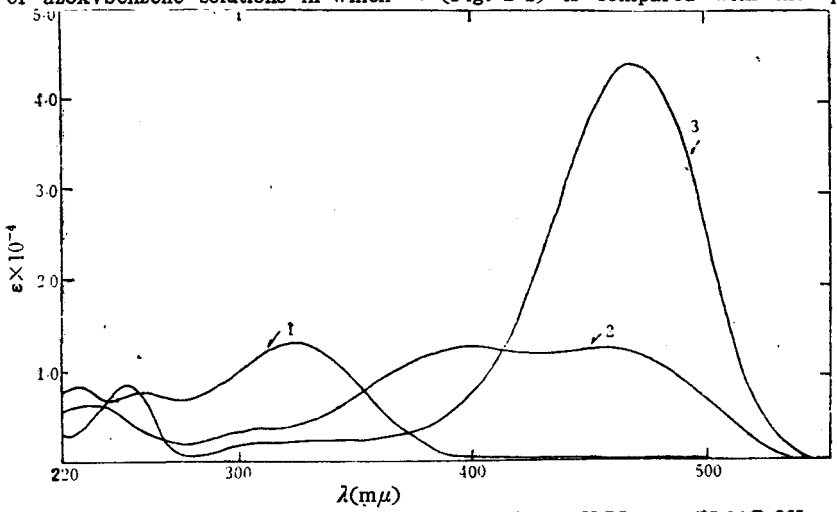


Fig. 1-U.V. Spectra of Azoxybenzene. 1. in 9% H_2SO_4-20%(Vol.)EtOH
2. in 90% H_2SO_4-20%(Vol.)EtOH 3. in 100% H_2SO_4-20%(Vol.)EtOH

A solution originally diluted with 90 vol. % H_2SO_4 was further diluted to 10 times its volume with 20% EtOH. In order to find out the reversibility of the conjugate acid of azoxybenzene in strong acidic solution, the spectrum of the resulting 9.0% solution solution in which the original solvent was 9.5 vol. % H_2SO_4-20% EtOH (Fig. 2-3, same one as Fig. 1-1) (Fig. 2-1) is compared with the spectrum of a

The two solutions compared have equal acid concentrations. The two spectra seem to be nearly, but not completely, superimposable. It is, therefore,

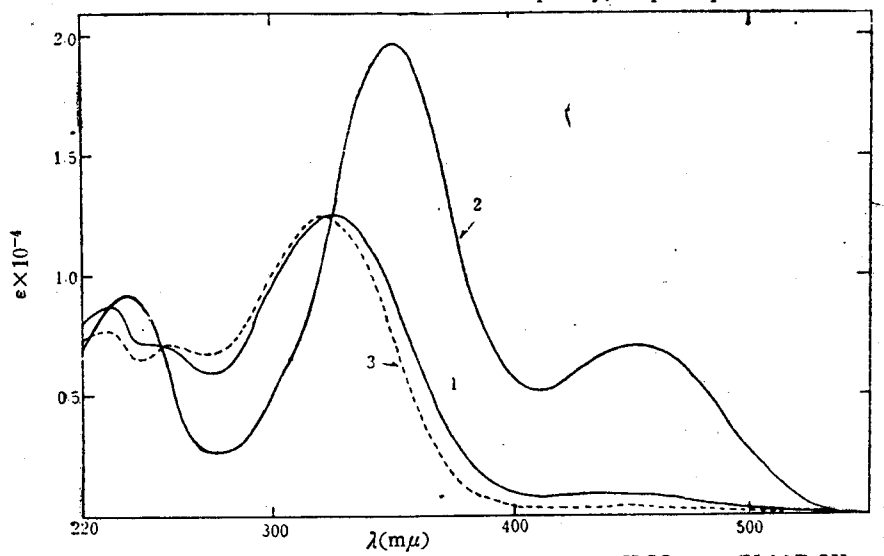


Fig. 2-U.V. Spectra of Azoxybenzene. 1. dil. in 9% H_2SO_4-20%(Vol.)EtOH
2. in dil. 10% H_2SO-20%(Vol.)EtOH 3. in original 9% H_2SO_4-20%(Vol.)EtOH

obvious that only a few percent of the compound have been modified by the treatment with 90% H_2SO_4. The same 1:10 dilution procedure was applied to a solution of azoxybenzene originally diluted with 100% H_2SO_4. The spectrum of the resulting solution

is also shown in Fig. 2-2, and is seen to be drastically different from the others.

Accordingly it seems reasonable to conclude that although reversible formation of the conjugate acid of azoxybenzene is substantially completed at a H_2SO_4 concentration of 70 vol. %, an irreversible reaction occurs only to a relatively minor extent when the concentration of acid is up to 90 vol. %. However, an irreversible reaction goes virtually to completion when the solvent is 100% H_2SO_4.

The resulting product of this irreversible reaction was ascertained from the comparison of spectra of azoxybenzene treated with 100% H_2SO_4, both before and after further dilution, and of a solution of *p*-hydroxyazobenzene diluted in the same manner. These spectra are shown in Fig. 3. The spectra of azoxybenzene in 100% H_2SO_4 (Fig 3-1). and in 10% H_2SO_4 diluted (Fig. 3-2) can be perfectly superimposed with those of *p*-hydroxyazobenzene in the corresponding media (Fig. 3-3 and 3-4).

Thus, there can not be any doubt that azoxybenzene under these conditions clearly rearranges to *p*-hydroxyazobenzene.

B. α-and β-Mono-*para*-substituted Azoxybenzenes.

In the cases of azoxybenzene and symmetrical 4,4' di-substituted azoxybenzenes, it is impossible to investigate to which of the two rings, distinguished by their relation to the oxygen atom of the azoxy group, the oxygen atom migrates, since these rings are indistinguishable in the final product. When both *para* positions are blocked, the Wallach rearrangement leads to *ortho*-hydroxy compounds;[2,3] little is known, however, about the rearrangement in monosubstituted azoxy-compounds, in which it is possible to determine to which ring migration occurs. To investigate these problems α- and β-*p*-bromo, methyl- and methoxyazoxybenzenes were investigated by U. V. spectrophotometry in the same way as the cases of azoxybenzene, and the rearranged compounds were isolated and identified.

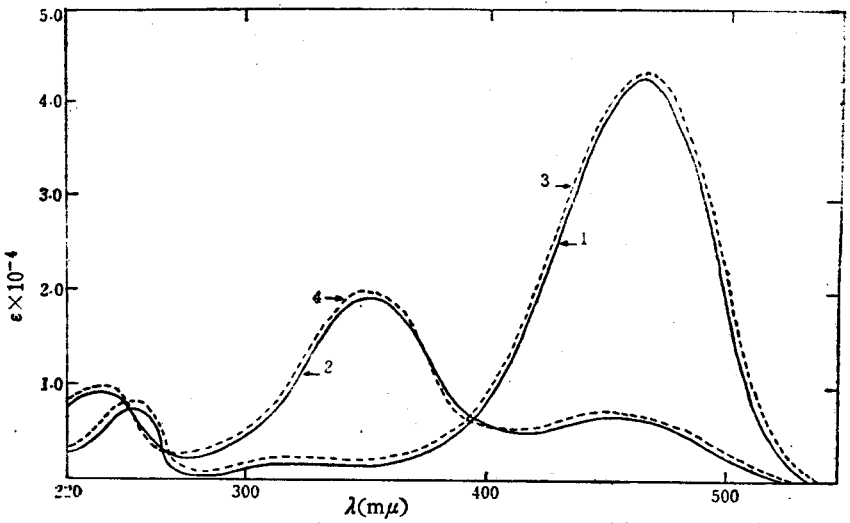


Fig. 3-Absorption spectra of 1. Azoxybenzene in 100% H_2SO_4 2. Azoxybenzene in 10% H_2SO_4, diluted from 100% H_2SO_4 3. 4-Hydroxyazobenzene in 100% H_2SO_4 4. 4-Hydroxyazobenzene in 10% H_2SO_4, diluted from 100% H_2SO_4

The spectra of α-and β-isomers of 4-bromo-azoxybenezene solution in 20% EtOH-10% H_2SO_4 which were obtained by dilution of solutions treated originally with 100% H_2SO_4 are shown in Fig. 4. The spectrum of 4-hydroxy-4'-bromoazobenzene in EtOH diluted with 10% H_2SO_4 is also shown in Fig. 4-3 for comparison. These spectra can be superimposed perfectly. This fact indicates that both α- and β-4-bromoazoxybenzene in 100% H_2SO_4 solution rearrange to 4-hydroxy-4'-bromoazobenzene, independent of the position of the bromine already present in the starting material. In other words, the oxygen atom

of the azoxy group of the compounds migrates to the *para* position of unsubstituted ring.

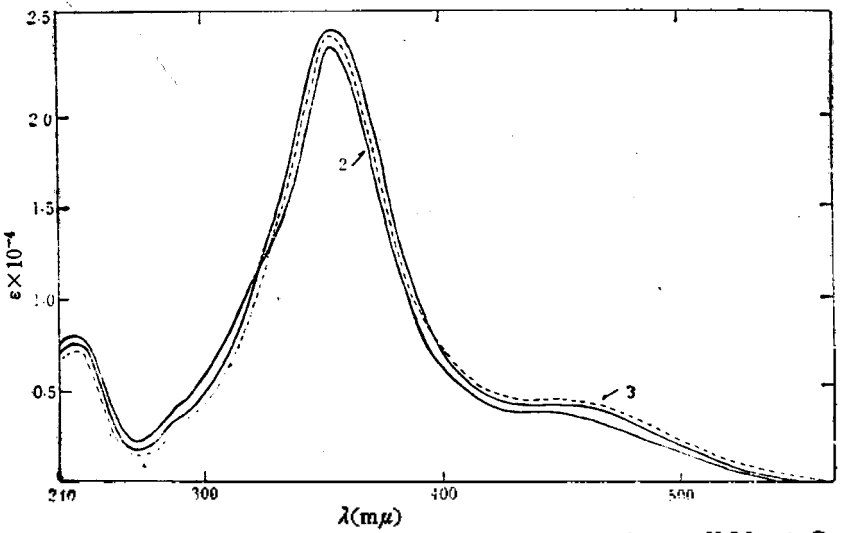
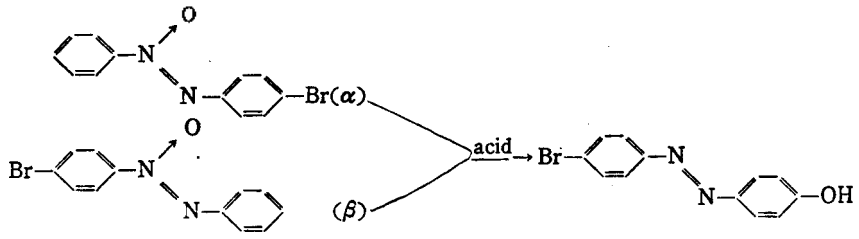


Fig. 4-Absorption spectra of 1. Rearranged α-4-bromoazoxybenzene in 10% H_2SO_4 2. Rearranged β-4-bromoazoxybenzen in 10% H_2SO 3. 4-Hydroxy-4-bromoazoben in 10% H_2SO_4



It seems that the migration of the oxygen atom does not depend on the distance between the oxygen atom and the eligible position. The oxygen atom does not migrate to the *ortho* position of either of the rings, whether substituted or not. This finding was confirmed by isolation of 4-hydroxy-4'-bromoaz-

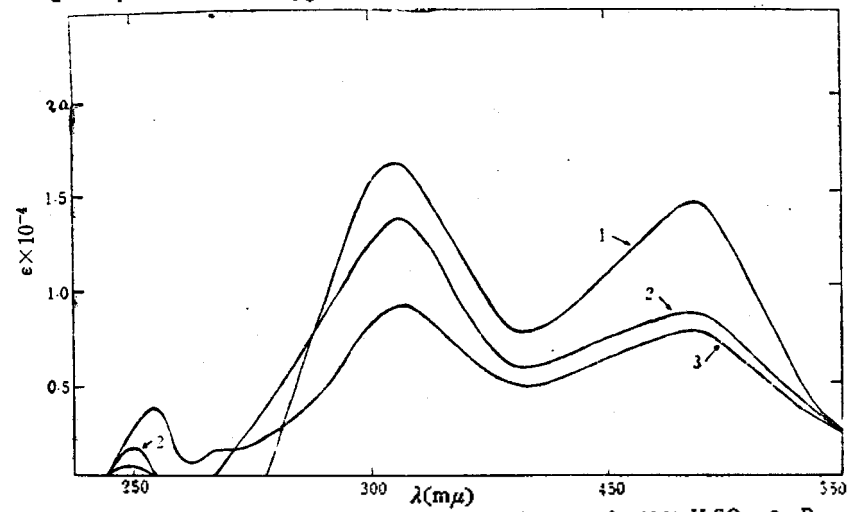
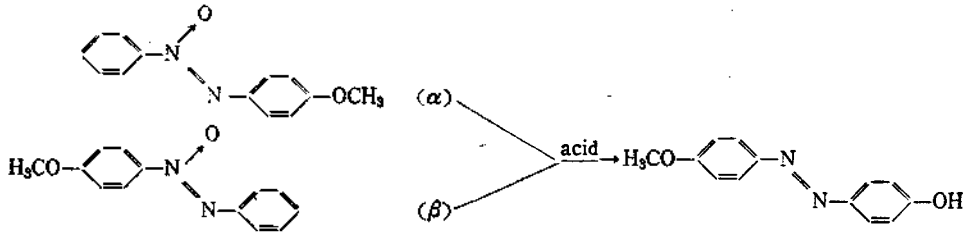


Fig. 5-Absorption spectra of 1. 4-Hydroxy-4-methoxyazobenzene in 10% H_2SO_4 2. Rearranged-4-methoxyazobenzen in 10%H_2SO_4 3. Rearranged-4-methoxyazoxybenzene in 10% H_2SO_4

obenzene from the solution of α-4-bromoazoxybenzene treated with 100% H_2SO_4.

The spectra of α- and β-4-methoxyazoxybenzene in 20%, EtOH-10%-H_2SO_4 solution, diluted from the original 100% H_2SO_4 solution, are shown in Fig. 5, and the spectrum of 4-hydroxy-4,-methoxyazobenzene in the same medium is also shown in Fig. 5. It can be seen from the comparison of the spectra that most of α- and β-isomers of 4-methoxyazobenzene rearranged to 4-hydroxy-4′-methoxyazobenzene in strongly acidic solution, but it appears that the rearrangements of the methoxy compounds do not proceed as completely as in the cases of azoxybenzene and α-, β-isomer of 4-bromoazoxybenzene. Furthermore, we can see that a larger amount of α-4-methoxyazoxy benzene was rearran ged than of the β-isomer under the same condition, and hence one may conclude that the α-isomer rearranges more readily than the β-isomer. However, no comparison of rates of th erearrangements has been made so far. The lack of superimposability of the spectra might be due to a mixture of product of 4-hydroxy-4,-methoxyazobenzene and some other compound(s).

The products of the rearrangements of α- and β-4-methylazoxybenzene differs markedly from the others described above. The spectra of α-and β-methylazoxybenzene, 4-hydroxy-4′-methylazobenzene and 2-hydroxy-4′-methylazobenzene, treated in the same manner as the other compounds, are shown in Fig. 6. It appears obvious that both α- and β-isomer of 4-methylazoxybenzene rearrange to the same compound, and that this product is 2-hydroxy-4′-methylazobenzene, not 4-hydroxy-4′-methylazobenzene. Thus, the oxygen atom of the azoxy group of both α- and β-4-methylazoxybenzene migrates to *ortho* position of the unsubstituted ring under the same conditions, not to the *para* position like in the compounds discussed above.



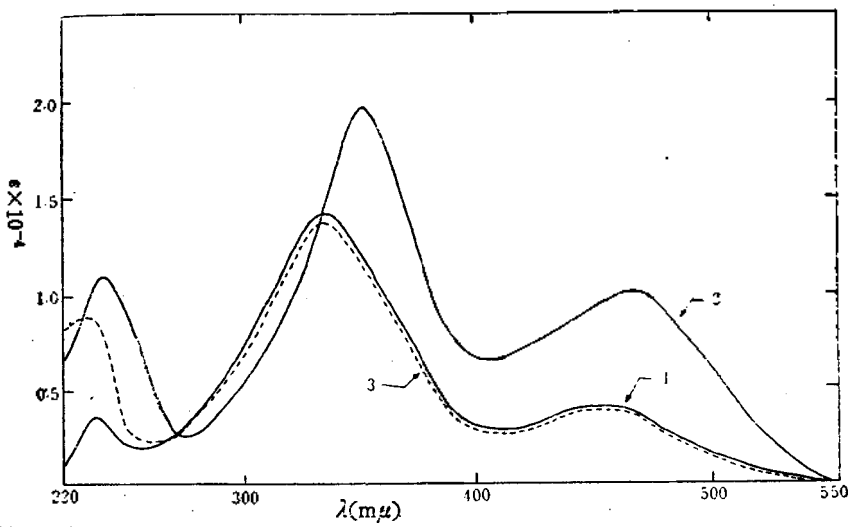
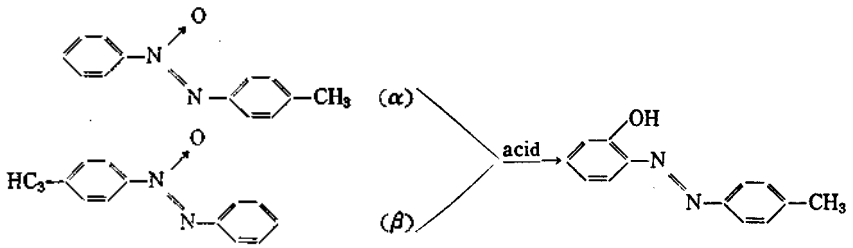


Fig. 6-Absorption spectra of 1. Rearranged α- and β-methylazobenzene in 10% H_2SO_4 2. 4-Hydroxy-4-methylazobenzene in 10% H_2SO_4 3. 2-Hydroxy-4-methylazobenzene in 10% H_2SO_4

Although the intensities of the 243 mμ band of



authentic 2-hydroxy-4-methylazobenzene and rearranged α- and β-4-methylazoxybenzene differ slightly, the 336 mμ and 450 mμ bands are clearly superimposable. The discrepency of the intensity at 243 mμ cannot be explained at the present time.

In order to confirm that the rearrangement of 4-methylazoxybenzenes leads to the *ortho* substituted products, the rearranged product was isolated from the solution in which β-4-methylazoxybenzene was diluted with 100% H_2SO_4. The spectrum of the isolated compound in the same medium is compared with the spectra of the authentic compound and the rearranged one in Fig. 7. The main bands of all spectra are clearly superimposable. There can, thus, be no doubt that α- and β-4-methylazoxybenzene in strongly acid solution completely rearranges to 2-hydroxy-2-methylazobenzene.

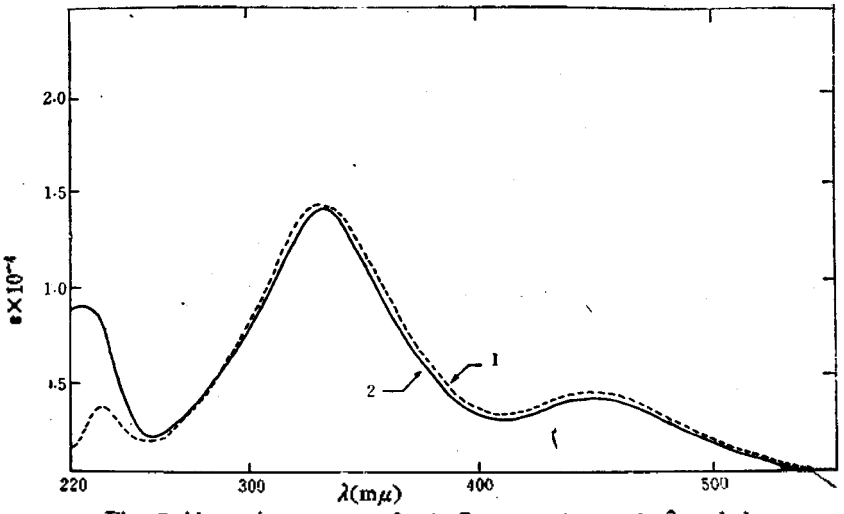


Fig. 7-Absorption spectra of 1. Rearranged α-and β-methylazoxybenzene in 10%EtOH 2. Isolated and Authentic α-Hydroxy-4-methylazobenzene in 10% H_2SO_4

According to the Badger's paper[4] the rearranged product was 2-hydroxy-4-bromoazobenzene in the case of α-4-bromoazoxybenzene; was not 4-hydroxy-4'-bromoazobenzene This is contrast with author's result. Badger explained that the oxygen atom is closer to the *ortho*-position in the substituted ring than to that in the adjacent ring due to the -N- valency angle is 120°. If we assume the oxygen atom migrates to closer position, the β-4-bromoazoxybenzene would ber earranged under the same conditions into bromo-6-hydroxyazobenzene rather than any other possible one. However, Badger did not mentioned about the β-isomer, and the author's experiments proved that the oxygen atom in the both case of the α- and β-bromoazoxybenzene migrated into the *para*-position of unsubstituted ring clearly. Not only the bromine substituted compound, but all the unsymmetrically substituted azoxybenzenes under investigation shown the same result, that is, the oxygen atom of azoxy group migrated to the unsubstituted ring; depending neither on the substituent already present in benzene ring nor steric effect such as Badger's.

However, the migrating position in the unsubstituted ring seems to depends on the nature of the

substituent as the result has shown. It is hardly to state what effect(s) due to at the present time. Further investigation such as the reaction conditions and the mechanism by a kinetic method would be necessary for the elucidation of the problem.

Acknowledgement

This study has been done at the University of Cincinnati, U. S. A. The author is grateful to Dr. H.H. Jaffé for his untiring advise throughout the course of investigation.

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The Absorption Spectra of Substituted Azoxybenzenes and the Additivity of their Absorption Maxima

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Azoxybenzene 系化合物들의 分光學的硏究 및 그 最大吸收波長의 加成性

韓 治 善

(1962. 8.30 受理)

Abstract

The ultraviolet and visible absorption spectra of *trans*, *cis*-azoxybenzene, substituted azoxybenzenes and their conjugate acids have been studied. The 320-350mμ main bands of free-base of azoxybenzenes are due to $\pi \rightarrow \pi^*$ transition. These bands of their conjugate acids shown bathochromic shift into visible range. The following empirical relationship between absorption maxima of the main bands was found. $\lambda_{max} = \lambda^{\circ}_{max} + \Delta\lambda_x + \Delta\lambda_y$ This relationship in terms of wave number is also hold in good agreement. $\nu = \nu_{\circ} - (\Delta\nu_x + \Delta\nu_y)$

The ultraviolet and visible absorption spectra of *trans*-azoxybenzene and substituted trans-azoxybenzenes have been studied by many workers. Auwers and Heimke[12] seem to have been the first group to have measured the spectra of azoxybenzene and of some of its substitution products. A number of