

UV Spectra of *para*-Monosubstituted Azoxybenzenes in Sulfuric Acid*

by

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The reaction of 4-methylazoxybenzenes, 4-bromoazoxybenzenes and 4-nitroazoxybenzenes in concentrated sulfuric acid was traced by measuring UV spectra in order to estimate the rates of the Wallach rearrangement. The reaction rates of *para*-substituted azoxybenzenes in sulfuric acid were found to be in the following order : 4-methylazoxybenzenes, 4-bromoazoxybenzenes and 4-nitroazoxybenzenes : and those β -isomer are faster than α -isomer except 4-methylazoxybenzenes.**

1 Introduction

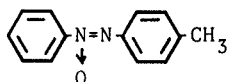
The studies on the rates in the Wallach rearrangement of 4-methyl-*O, N, N*-[1 α] and 4-methyl-*N, N, O*-azoxybenzene [1 β]¹⁾ and 4-bromo-*O, N, N*-[3 α] and 4-bromo-*N, N, O*-azoxybenzene [3 β]²⁾ have been carried out with kinetics. Gore³⁾ also stated that 4-nitro-*N, N, O*-azoxybenzene [2 β] reacts more rapidly than 4-nitro-*O, N, N*-azoxybenzene [2 α] in concentrated sulfuric acid.

Lately, occurrence of α, β -interconversion of 4-methylazoxybenzenes (between [1 α] and [1 β]) and 4-nitroazoxybenzenes (between [2 α] and [2 β]) was found under the Wallach rearrangement.⁴⁾ Therefore, α, β -interconversion needs to be taken into consideration

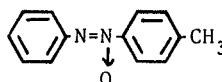
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** Although the IUPAC nomenclature on unsymmetrically substituted azoxybenzenes does not use the terms of α and β , we use here the signs α and β for convenience.



4-Methyl-*O, N, N*-azoxybenzene [1 α]
 α -Isomer



4-Methyl-*N, N, O*-azoxybenzene [1 β]
 β -Isomer

whenever the rate of unsymmetrically substituted azoxybenzenes in the Wallach rearrangement is discussed.

The present report deals with confirmation of the rates in the Wallach rearrangement by UV spectra measurement on six kinds of azoxybenzenes under consideration of α , β -interconversion. On the base of the results in UV spectra measurement of azoxybenzenes, we discuss here some step on the path of the Wallach rearrangement reaction investigated before.^{5),6)}

2 Experimental

2.1 Preparation of starting materials. A mixture of [1 α] and [1 β] was obtained from 4-methylazobenzene by oxidation with H₂O₂ in acetic acid, and then [1 α] ($\alpha/\beta=3.7$) and pure [1 α] were separated by fractional crystallization with ethanol.⁷⁾ [2 β] was also prepared by oxidation of 4-nitroazobenzene with H₂O₂,⁸⁾ and [2 β] was converted to [2 α] by warming with CrO₃ in acetic acid.⁸⁾ [3 α] was synthesized by bromination of azoxybenzene itself.⁹⁾ After 4-bromoazobenzene was oxidized with H₂O₂, [3 β] was obtained by repeated crystallization using a mixture of benzene-petroleum ether (1 : 1) until constant melting point was obtained.

2.2 UV Spectrum of 4-methyl-*O, N, N*-azoxybenzene [1 α] in sulfuric acid. A sulfuric acid solution of [1 α] (0.9mmol/l) was prepared and its UV spectrum was measured at intervals after 1 hr, 3 hr, 8 hr and 24 hr respectively. The same procedure was applied in other azoxybenzenes. In the case of [1 α] and [1 β], 85% sulfuric acid (H₂SO₄ : MeOH : H₂O=85.0 : 11.3 : 8.7) was used, and 90% sulfuric acid (H₂SO₄ : MeOH : H₂O=90.0 : 6.2 : 3.8) was used in other azoxybenzenes.

2.3 The Wallach rearrangement of 4-methyl-*O, N, N*-azoxybenzene [1 α]. After 0.5g (0.4mmol) of [1 α] was dissolved in 30ml of 85% sulfuric acid (H₂SO₄ : MeOH : H₂O=85.0 : 11.3 : 3.7), the solution was kept at 30-32°C. Five ml of the reaction mixture was pipeted out at intervals and poured into ice-water in order to stop the reaction. After the precipitates were dissolved with benzene, the benzene solution was extracted with 3% sodium hydroxide aqueous solution again, and alkali solution was acidified with dil. HCl. The precipitate of rearrangement products was obtained by extraction with benzene, followed by washing with water, dryness and evaporation of benzene. 2- and 4-Hydroxyazobenzenes were not separated because the amount of *o*-isomer was not small compared with that of *p*-isomer. Alkali insoluble layer was washed with water, dil. HCl and water again, and then 4-methylazobenzene and the starting material were separated from each other by column chromatography (benzene-silica gel). The same procedure was also applied to [1 β]. Hydroxyazobenzenes were identified by comparison with authentic samples (mp and IR), which were synthesized by the coupling reaction of phenols with benzenediazonium salts.¹⁰⁾

2.4 α/β Ratio determination of the recovered starting materials. NMR signals at δ

2.05 and 1.95 for methyl group of [1 α] and [1 β] were used for determination of the α/β ratio respectively.¹¹⁾ The α/β ratio of the recovered 4-nitroazoxybenzenes was estimated by UV spectrophotometry using a calibration curve obtained by plotting the spectrum of a few kinds of mixture of [2 α] and [2 β]. [2 α] : $\lambda_{\max}^{\text{EtOH}}$ 337nm (ϵ :19200) and [2 β] : $\lambda_{\max}^{\text{EtOH}}$ 337nm (ϵ : 19200), $\lambda_{\max}^{\text{EtOH}}$ 263nm (ϵ :9500). In the case of [3 α] and [3 β], melting point determination was used for analysis because they are undistinguishable by their UV and NMR spectra. The melting point of the starting and recovered 4-bromoazoxybenzenes was simultaneously measured in the same bath at several times and the melting point of the recovered 4-bromoazoxybenzenes were compared with those of the mixture of [3 α] and [3 β] at various ratio. The melting point determination was carefully done with the capillary tubes of the same diameter and the temperature elevation was carried out in the rate of two degrees per minute.

3 Results and Discussion

Sulfuric acid solutions (85%) of both [1 α] ($\alpha/\beta=3.7$) and [1 β] ($\alpha/\beta=0$) were measured four times at intervals during 24 hr. The same pattern in their UV spectra was drawn and each λ_{\max} in ethanol solution (395nm) shifted toward 441nm, which is identical to λ_{\max} of 4-hydroxy-4'-methylazobenzene itself in 85% sulfuric acid. In this case, two isosbestic points were found at 259nm and 415nm (Fig. 1). The α/β in 85% sulfuric acid solution of [1 α] and [1 β] at 30-32°C was known to be 3 after 3 hr.⁴⁾ This is the reason why they give the same spectra in both cases. In the next place, a consumption of starting materials and yield of the

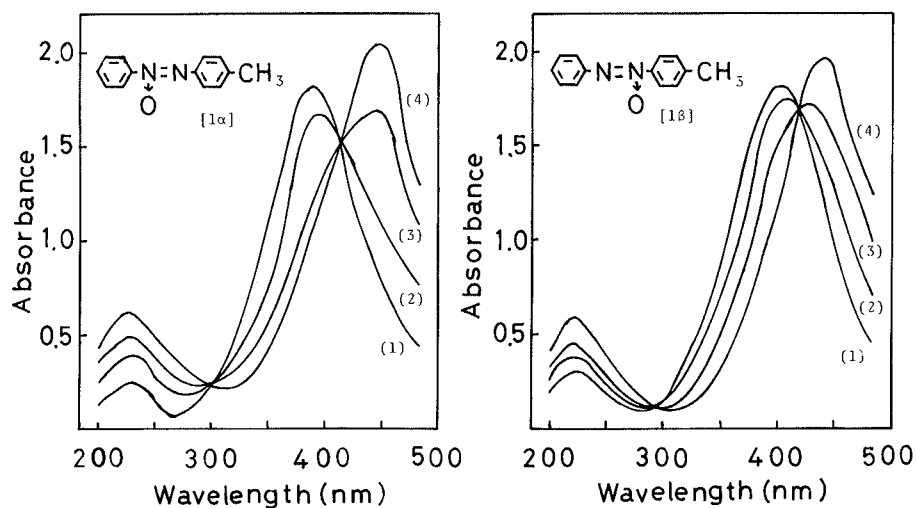


Fig. 1 UV Spectra of 4-methy-*O,N,N*- [1 α] ($\alpha/\beta=3.7$) and 4-rethyl-*N,N,O*- azoxybenzene [1 β] in 85% sulfuric acid
 Reaction conditions- Reaction medium ; H_2SO_4 : MeOH : H_2O (85.0 : 11.3 : 8.3)
 Reaction temperature ; 18-20°C
 Measurement intervals/hr ; (1) 1 (2) 3 (3) 8 (4) 24

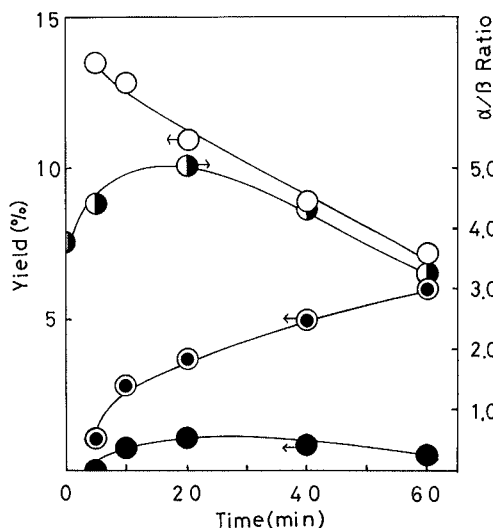


Fig. 2 The Wallach rearrangement of 4-methyl-*O,N,N*-azoxybenzene [1 α]

Reaction conditions-

Starting material ; 0.5g (2.4mmol), mp 42-43°C ($\alpha/\beta=3.7/1$)

Reaction medium ; H₂SO₄ : MeOH : H₂O (85.0 : 11.3 : 8.7), 30ml

Reaction temperature ; 30-32°C

⊙ : 2- and 4- Hydroxy - 4'-methylazobenzene

○ : 4-Methylazobenzene

● : Recovered starting material

⊙ : The α/β ratio of recovered starting material

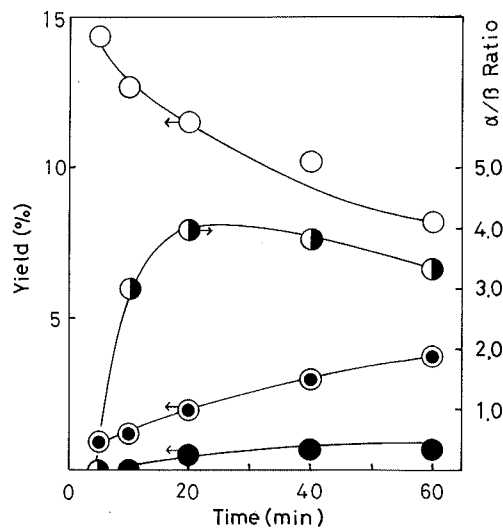


Fig. 3 The Wallach rearrangement of 4-methyl-*N,N,O*-azoxybenzene [1 β]

Reaction conditions-

Starting material ; 0.5g (2.4mmol), mp 62-63°C ($\alpha/\beta=0/1$)

Reaction medium ; H₂SO₄ : ReOH : H₂O (85.0 : 11.3 : 8.3), 30ml

Reaction temperature ; 30-32°C

⊙ : 2- and 4- Hydroxy - 4'-methylazobenzene

● : 4-Methylazobenzene

○ : Recovered starting material

⊙ : The α/β ratio of recovered starting material

products in the Wallach rearrangement of [1 α] ($\alpha/\beta=3.7$) and [1 β] ($\alpha/\beta=0$) were shown in Fig. 2 and Fig. 3. 2-Hydroxy-4'-methylazobenzene [4] was not separated from 4-hydroxy-4'-methylazobenzene [5] because the yield of [4] was too low in comparison with that of [5]. The change of α/β ratios first increased to maximum in 20 min. and then gradually reached 3. As [1 α] transferred to products very soon throughout the change of the α/β ratio, [1 β] was converted into [1 α] to keep 3. Thus, it is concluded that the rate of the Wallach rearrangement of [1 α] is greater than that of [1 β] in agreement with results of the previous kinetic study.¹⁾

The α/β ratio in the cases of [2 α] and [2 β] was known to come near in 90% sulfuric acid after 2 hr at 33-34°C.⁴⁾ When [2 α] and [2 β] were treated in 90% sulfuric acid during 24 hr at around 18°C, [2 α] was not converted into [2 β] but [2 β] did slightly. The UV spectra of [2 α] and [2 β] in the same conditions as indicated above were found to be quite different from each other (Fig. 4). In the UV spectrum of [2 α] in 90% sulfuric acid, λ_{\max} (377nm) was not changed but its absorbance decreased with time, and two isosbestic points were observed

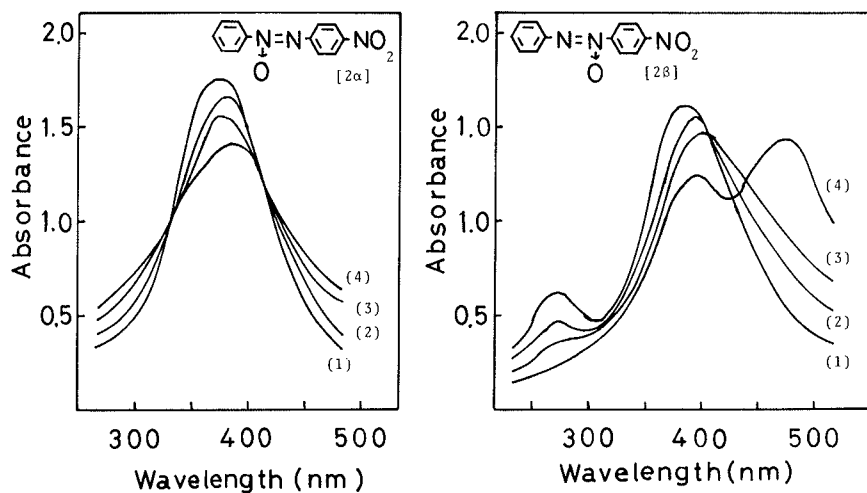


Fig. 4 UV Spectra of 4-nitro-*O,N,N*- [2 α] and 4-nitro-*N,N,O*-azoxybenzene [2 β] in 90% sulfuric acid
 Reaction conditions- Reaction medium ; H₂SO₄ : MeOH : H₂O (90.0 : 6.2 : 3. 8)
 Reaction temperature ; 18-20°C
 Measurement intervals/hr ; (1) 1 (2) 3 (3) 8 (4) 24

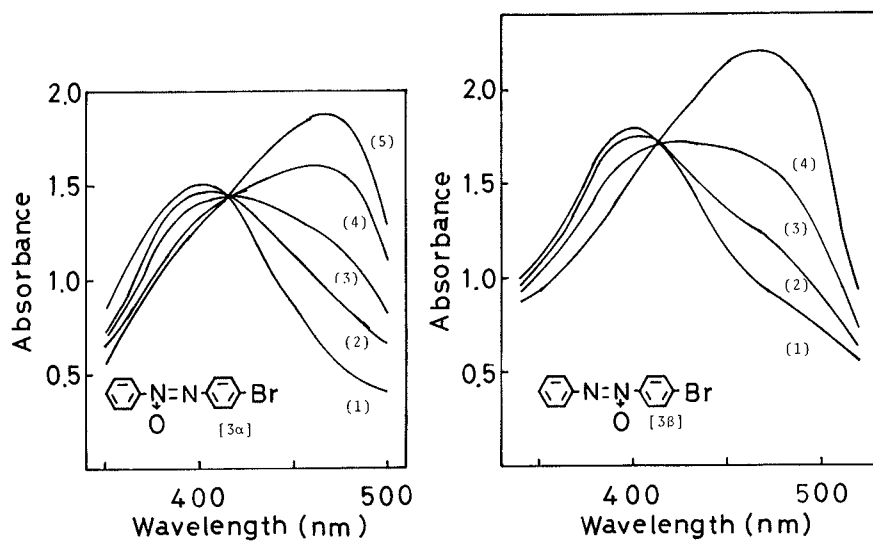


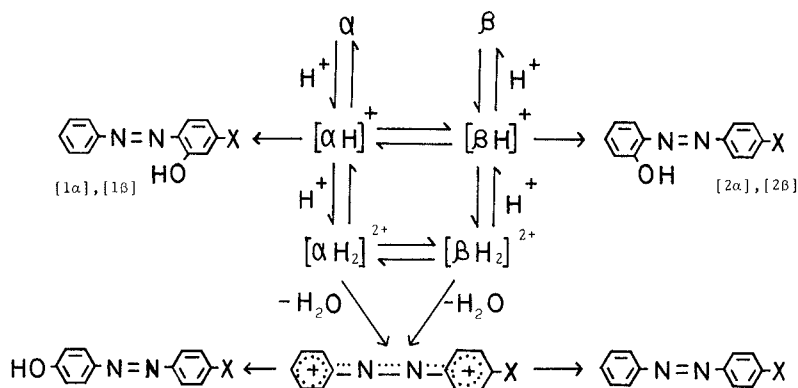
Fig. 5 UV Spectra of 4-bromo-*O,N,N*- [3 α] and 4-bromo-*N,N,O*-azoxybenzen [3 β] in 90% sulfuric acid
 Reaction conditions- Reaction medium ; H₂SO₄ : MeOH : H₂O (90.0 : 6.2 : 3. 8)
 Reaction temperature ; 18-20°C
 Measurement intervals/hr ; [3 α] : (1)3 (2)20 (3)40 (4)60 (5)175
 [3 β] : (1)3 (2) 10 (3)20 (4)40

at 370nm and 420nm respectively. On the other hand, λ_{\max} of $[2\beta]$ shifted to longer wavelength with decrease in absorbance and finally λ_{\max} was observed at 475nm, which is just the λ_{\max} of 4-hydroxy-4'-nitroazobenzene in 90% sulfuric acid, and characteristic λ_{\max} (274nm) of $[2\beta]$ in 90% sulfuric acid disappeared with time. Those results indicate that the rapid Wallach rearrangement of $[2\beta]$ occurs with slow β , α -conversion.

The α , β -interconversion between $[3\alpha]$ and $[3\beta]$ has been known not to take place under the usual Wallach rearrangement conditions.^{4,12)} Both $[3\alpha]$ and $[3\beta]$ had an isosbestic point (410nm) and λ_{\max} (400nm) shifted to 470nm with time in each case (**Fig. 5**). As $[3\beta]$ came near λ_{\max} of 4-hydroxy-4'-bromoazobenzene faster than $[3\alpha]$, it is concluded that $[3\beta]$ reacts faster than $[3\alpha]$.

Next, the path in the Wallach rearrangement of $[1\alpha]$, $[1\beta]$, $[2\alpha]$ and $[2\beta]$ is shown below (**Scheme 1**). After $[\alpha\text{H}]^+$ and $[\beta\text{H}]^+$ are formed in monoprotection process^{5,6)} from sulfuric acid to each azoxybenzene, they convert into each other between α and β forms. Furthermore, both $[\alpha\text{H}]^+$ and $[\beta\text{H}]^+$ are transferred into $[\alpha\text{H}_2]^{2+}$ and $[\beta\text{H}_2]^{2+}$ by acceptance of another proton^{5,6)} and they interconvert faster than monoprotated species ($[\alpha\text{H}]^+$ and $[\beta\text{H}]^+$).⁴⁾ 2-Hydroxyazobenzenes are formed by intramolecular migration *via* monocation of azoxybenzenes,⁵⁾ but the structure of 2-hydroxyazobenzenes seems to depend on the kinds of their substituents.⁴⁾ A dication which is formed by dehydration of $[\alpha\text{H}_2]^{2+}$ and $[\beta\text{H}_2]^{2+}$ is attacked by either HSO_4^- or H_2O to form 4-hydroxy-4'-substituted azoxybenzenes⁴⁾ (**Scheme 1**).

λ_{\max} of six kinds of azoxybenzenes at the beginning were compared in ethanol, 75% and 85% ($[1\alpha]$ and $[1\beta]$) or 90% sulfuric acid ($[2\alpha]$, $[2\beta]$, $[3\alpha]$ and $[3\beta]$) (**Table 1**). Their λ_{\max} were approximately the same when they were measured under the rearrangement conditions (85% and 90% sulfuric acid). According to UV spectra of azoxybenzenes in 75% sulfuric acid, complete monoprotection for substrates did not occur because the absorbance was slightly lower in comparison with those under rearrangement conditions. Unlike in 85-



Scheme 1

90% sulfuric acid, λ_{\max} . of the absorbance in 75% sulfuric acid did not shift with time at all, but their absorbances increased slightly. The UV spectra in 75% sulfuric acid should indicate monoprotonated state ($[\alpha\text{H}]^+$ and $[\beta\text{H}]^+$) of azoxybenzenes.⁴⁾ As almost the same λ_{\max} . in UV spectra at the beginning were observed under the rearrangement conditions in comparison with those in 75% sulfuric acid, it may be concluded that azoxybenzenes accept a proton from sulfuric acid immediately and exist fairly stably in monoprotonated state (Table 1). Although pka of various azoxybenzenes was measured,¹³⁾ the rates in concentrated sulfuric acid were regardless of their pka values. The rates of the Wallach rearrangement are different with the kinds of substituents and with relative position of oxygen for substituents (α -isomer and β -isomer), because the pka in another stage of other protonation for each monocation (pka') seems remarkably different in individual cases. In the case of $[2\alpha\text{H}]^+$, pka' is too low to protonate furthermore in 90% sulfuric acid. On the other hand, $[1\alpha\text{H}]^+$ has a enough high pka' value to be capable for additive protonation.

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Table 1 Absorption spectra of *para*-monosubstituted azoxybenzenes in EtOH and sulfuric acid

Azoxybenzenes		$\lambda_{\max}, (\epsilon)(\text{nm})$ in $\text{H}_2\text{SO}_4 : \text{MeOH} : \text{H}_2\text{O}^{\text{b),c)}$		
mp (°C)	(Lit. mp)	$\lambda_{\max}, (\epsilon)(\text{nm})$ in EtOH ^{b)}	Under the Wallach Rearrangement condition	In the monoprotonated state ^{f)}
[1 α] ^{a)}	42-43 (46) ⁷⁾	329(13900), 239(9300)	405(12000), 237(2900) ^{d)}	396 (10300)
[1 β]	62-64 (65) ⁷⁾	323(16400), 231(10200)	400(13800), 235(3200) ^{d)}	393 (14800)
[2 α]	153.5 (152) ⁸⁾	337(19200)	377(17900) ^{e)}	373(15200)
[2 β]	147.5 (148) ⁸⁾	337(19290), 263 (9500)	378(16500), 274(6500) ^{e)}	373(13900), 273(4900)
[3 α]	73-74 (73-74) ⁹⁾	323(16400), 228 (9600)	400(15100), 225(7200) ^{e)}	389.5(17100)
[3 β]	93-94 (92-93) ⁹⁾	323(16800), 233(10400)	400(17800), 237(7500) ^{e)}	393.5(17900)

a) A mixture of α - and β -isomers with $\alpha/\beta=3.7$ (The ratio was obtained by NMR analysis). b) Concentration : 0.1 mmol/l. c) The spectra in sulfuric acid medium were measured within 3 minute after mixing azoxybenzenes with sulfuric acid. d) $\text{H}_2\text{SO}_4 : \text{MeOH} : \text{H}_2\text{O}$; (85.0 : 11.4 : 3.6). e) $\text{H}_2\text{SO}_4 : \text{MeOH} : \text{H}_2\text{O}$; (90.0 : 5.4 : 3.6). f) $\text{H}_2\text{SO}_4 : \text{MeOH} : \text{H}_2\text{O}$; (75.0 : 8.3 : 16.7).

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