# The Wallach Rearrangement of *p*-Nitroazoxybenzenes and the Reaction with Chlorosulfonic Acid

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**Summary**

The Wallach rearrangement of $\alpha$- and $\beta$-*p*-nitroazoxybenzenes using concentrated sulfuric acid was examined in detall in comparison with the previous reports. In addition to 4-hydroxy-4'-nitroazobenzene already known as a main product, 2-hydroxy-4'-nitroazobenzene and *p*-nitroazobenzene were isolated as by-products. The formation of 2-hydroxy-4'-nitroazobenzene from $\alpha$-*p*-nitroazoxybenzene is interpreted by an interconversion between $\alpha$- and $\beta$-*p*-nitroazoxybenzene which are formed from their monoprotonated form. The reaction of $\alpha$- and $\beta$-*p*-nitroazoxybenzene with chlorosulfonic acid was also brought about with the same results concerning the reaction products although high ortho-para ratio of hydroxyazo compounds was obtained in comparison with the Wallach rearrangement using sulfuric acid.

## 1 Introduction

Since Wallach et. al.[1] obtained *p*-hydroxyazobenzene by treatment of azoxybenzene with concentrated sulfuric acid and Bamberger[2] found that *o*-hydroxyazobenzene was formed simultaneously as a by-product in the same condition, the generality of the Wallach rearrangement was recognized for many azoxybenzene derivatives.[3] $\alpha$-(1) and $\beta$-*p*-nitroazoxybenzene (2) were synthesized by Angelli et. al.[4] and they reported the different behavior in the reaction with nitric acid (specific gravity ; 1.48) and irradiation of UV ray on both compounds. In addition, they obtained 4-hydroxy-4'-nitroazobenzene (3) by warming both compounds with sulfuric acid but its yield and material balance in this reaction are not clearly decided. Gore[5] indicated that the reaction rate of (2) was faster than that of (1) and $\beta \longrightarrow \alpha$ conversion occured in the reaction process with 98% sulfuric acid for 23 hrs. at 20°C. The recognization method for $\beta \longrightarrow \alpha$ conversion by Gore[6] was visual observation of the color change of recovered *p*-nitroazoxybenzene in concentrated sulfuric acid, but this method is not adaptable if $\alpha \longrightarrow \beta$ conversion occurs to a small extent. We authors

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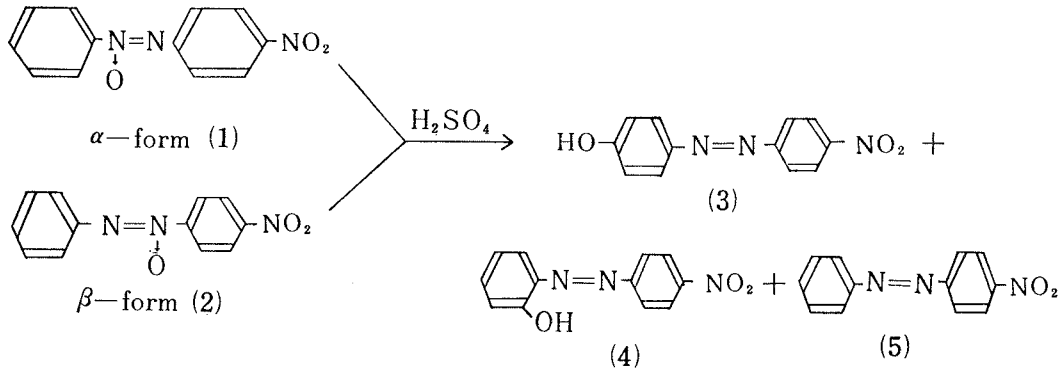
studied the Wallach rearrangement of (1) and (2) in order to know whether this reaction is the best synthetic method for obtaining (3) and also $\alpha,\beta$- interconversion occurs in the process, by bringing under notice material balance and by-products formation. We will report later in detail $\alpha,\beta$-interconversion on azoxybenzene derivatives. High yield of (3) was obtained as well as 2-hydroxy-4'-nitroazobenze (4) and *p*-nitroazobenzene (5) as the results of this examination.




The monocationic state of (2) seemed to exist as a common intermediate because (4) was formed as the ortho isomer in the Wallach rearrangement of (1) and (2). Peal et. al.[7] indicated that *p*-hydroxyazobenzene was produced by treatment with ammonium hydroxide solution after the reaction of azoxybenzene and chlorosulfonic acid (6). There is little investigation on the reaction of azoxybenzene derivatives and (6) except $\alpha$-*p*-methylazoxybenzene[8]. The same results were also obtained in the reaction of (1) and (2) with (6), as the case with the Wallach rearrangement.

## 2 Experimental

### 2.1 Synthesis of $\alpha$-(1) and $\beta$-*p*-nitroazoxybenzene (2)

Crude (4) was synthesized by nitration using glacial acetic acid-nitric acid[9]. After it was extracted with acetone, red crystal was obtained by recrystalization using ethanol, m.p. 136.0~137.0°C (Literature,[10] 139.0°C). (2) was led by oxidation of (5)with hydrogen peroxide in glacial acetic acid, m.p. 146.5~147.0°C (Literature,[10] 152.0°C) and (1) was led from (2) by treatment with chromium trioxide in glacial acetic acid, m.p., 153.5°C, (Literature[10], 152.0°C).

### 2.2 The Wallach rearrangement of $\alpha$-(1) and $\beta$-*p*-nitroazoxybenzene (2)

1.0g ($4.1\times10^{-4}$ Mol.) of *p*-nitroazoxybenzene and 15ml sulfuric acid were poured into 100 ml round bottomed flask. After 1hr. at 80°C, the reaction products were separated by the method as indicated in Fig. 1.

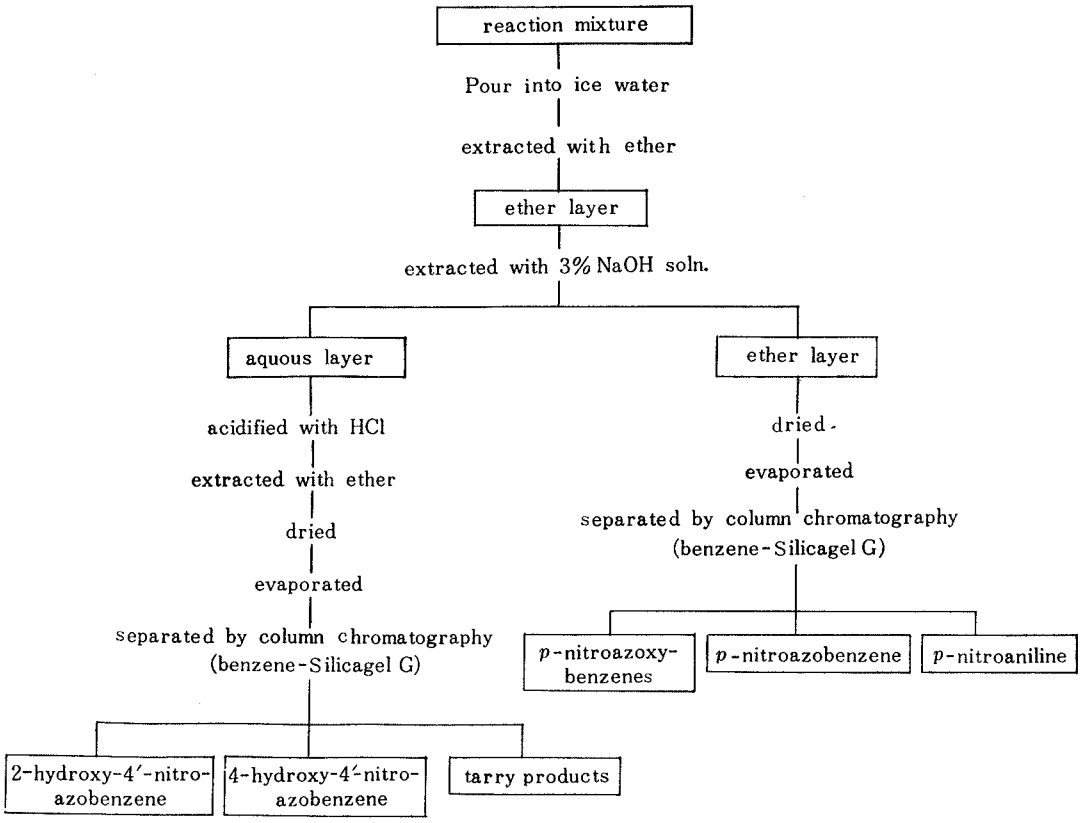



**Fig.1 Separation of products in the Wallach rearrangement of $\alpha$-and $\beta$-*p*-nitroazoxybenzene**

2.3 The reaction of $\alpha$-(1) and $\beta$-*p*-nitroazoxybenzene (2) with chlorosulfonic acid (6)

2.0g ($8.2\times10^{-4}$ Mol.) of *p*-nitroazoxybenzene was put into 100 ml four-necked flask and the mixture was stirred for 40 min. at 40°C. The reaction mixture was gradually poured into ice-water to form the precipitate. The precipitate was allowed to stand over-night in concentrated ammonium hydroxide solution and the resultant red crystal was dissolved in benzene. The separation of the products was carried out by the method indicated in Fig. 1.

Identification of the products ; (3) agreed with authentic sample synthesized by standard method, m.p. 214.0~215.0°C (Literature,[4] 213.0°C), Rf value in TLC (Wakogel G-benzene) and IR spectra. (4) also agreed with authentic sample by the synthetic method above, Rf value in TLC (WakogelG-benzene) and IR spectra, and in addition, IR spectra of complex of (4) with cuprous acetate agreed with that of the complex of authentic sample. *p*-Nitroaniline (7) has the same IR spectra with authentic sample too[14].

## 3 Results and Discussion

Tracing on the products yield in treatment of (1) and (2) with sulfuric acid in various concentration, the material balances over 90% were obtained in all cases. In the case of (2) with 92% sulfuric acid, 83% of (3), 5.2% of (4) and 8.4% of (5) were respectively obtained without recovered (2). Almost the same results were also obtained in the case of (2). The Wallach rearrangement of both *p*-nitroazoxybenzenes seemed to be the best method for preparation of (3) because of easiness on separation of (3) from other products. Noticing the disappearance of *p*-nitroazoxybenzene and the formation of (3) as indicated in Fig. 2 and Fig. 3, the rearrangement rate of (1) seems to be later than that of (2) as Gore[5] has once reported.

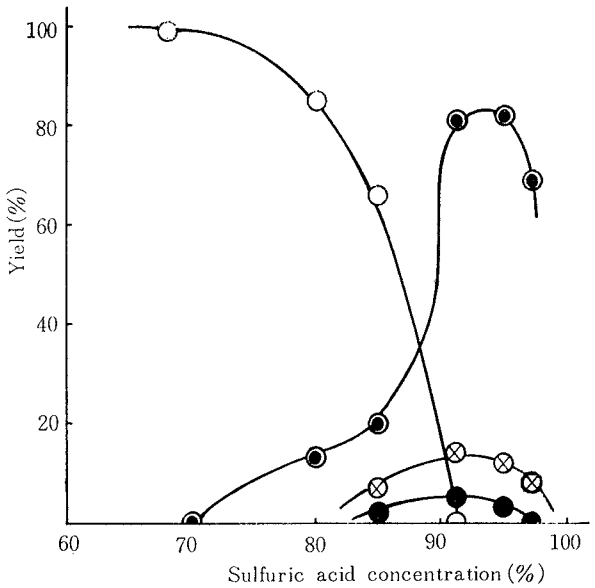



**Fig. 2 The sulfuric acid concentration dependance on the product ratio in the Wallach rearrangement of *α*-*p*-nitroazoxybenzene (1)**

**Reaction condition**

Reaction temperature; 80°C, Reaction time ; 1hr.,
Amounts of starting material ; 1.0g ($4.1\times10^{-3}$ Mol.)
Sulfuric acid ; 15ml.
—⊙— ; 4-Hydroxy-4'-nitroazobenzene(3)
—●— ; 2-Hydroxy-4'nitroazobenzene(4)
—⊗— ; *p*-Nitroazobenzene(5)
—○— ; Recovered *α*-*p*-nitroazoxybenzene(1)

The reaction rate became larger remarkably as concentration of sulfuric acid approaches nearly to 90%. The result is in accordance with the kinetic study reported by Buncel et. al.[15] that a lot of dications are formed with increasing sulfuric acid concentration and the reaction rate becomes large rapidly so as to effect smoothly nucleophilic attack on the dications by water molecule. The dication was pointed

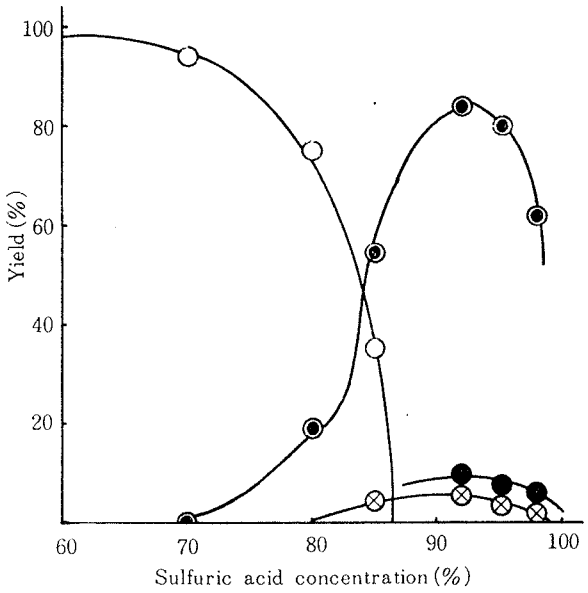



**Fig. 3 The sulfuric acid concentration dependance on the product ratio in the Wallach rearrangement of *β*-*p*-nitroazoxybenzene(2)**

**Reaction condition**

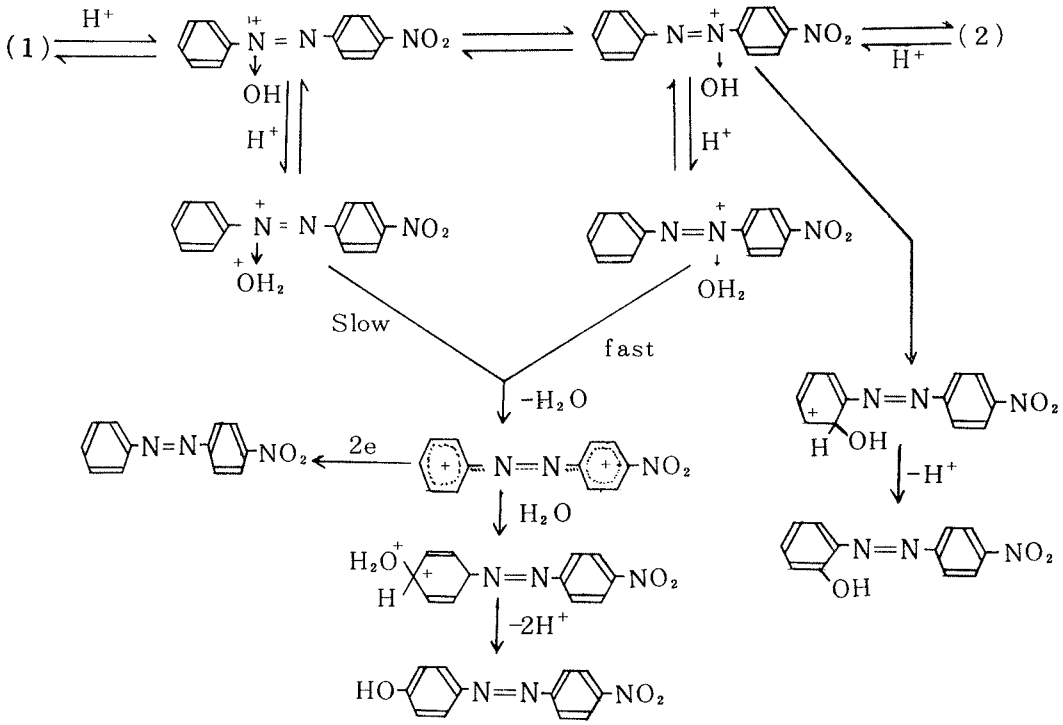
Reaction temperature ; 80°C, Reaction time ; 1hr,
Amounts of starting materal ; 1.0g ($4.1\times10^{-3}$ Mol.)
Sulfuric acid ; 15ml.
—⊙— ; 4-Hydroxy-4′-nitroazobenzene(3)
—●— ; 2-Hydroxy-4′-nitroazobenzene(4)
—⊗— ; *p*-Nitroazobenzene(5)
—○— ; Recovered *α*-*p*-nitroazoxybensene(1)

out to be an intermediate in the process of the Wallach rearrangement by Oae et. al.[16] and recently has been detected by Olah et. al.[17] using NMR in $SbF_5$—HF-$SO_2$ system at -78°C. The Wallach rearrangement to ortho position seemed to proceed via intramolecular rearrangement toward remote phenyl ring from monocationic state[16] of azoxyoxygen as shown by Oae et. al.[16]

Since (1) and (2) form (4) as an ortho isomer, these *p*-nitroazoxybenzenes are interchanged to each other in monocationic state, and on the other hand, (4) seems to be produced from monocationic state of (2) via intermolecular rearrangement.

The presence of monocation was also recognized by Olah et. al.[17] using NMR in F$SO_3$H-$SO_2$ system at -78°C. The monocation[16)17)] of (1) and (2) are interchanged to one another, and on the other hand, they are transformed into dication[15)16)17)] followed by nucleophilic attack by water molecule. The reason why rearrangement rate of (2) was faster than that of (1) seems to be due to the more rapid formation rate of dication, since diprotonated (2) is dehydrated more easily than the same form of (1) because of the stronger effect of nitro group. The reason for the formation of (5) as by-product seems to be due to two-electron reduction of dication[15)16)17)]

although it was not clear where electrons were produced. The possible reaction mechanism is as follows.




(7) was formed as an other by-product as much as 4.7% in 95% sulfuric acid only with (2). The results of the reaction of (1) and (2) with (6) were indicated in Table 1.

**Table 1 The Reaction of α-(1) and β-p-Nitroazoxybenzene (2) with Chlorosulfonic acid (6)**

| *P*-Nitro-azoxybenzenes | Reaction temperature (℃) | Medium | (3) (%) | (4) (%) | (5) (%) | Recovered starting material (%) | ortho-para ratio (4)/(3) | Tarry products | Note |
|---|---|---|---|---|---|---|---|---|---|
| (2) | −10 | $HSO_3Cl$ (6)[a] | 51.9 | 5.4 | 5.8 | 23.0 | 0.104 | 3.3 | |
| | 20 | $HSO_3Cl$ (6)[a] | 59.7 | 5.9 | 10.5 | 0 | 0.100 | 8.3 | |
| | 40 | $HSO_3Cl$ (6)[a] | 62.4 | 6.2 | 14.8 | 0 | 0.100 | 8.6 | |
| | 60 | $HSO_3Cl$ (6)[a] | 47.4 | 5.2 | 10.3 | 0 | 0.110 | 21.7 | |
| | 80 | 80 % $H_2SO_4$[b] | 19.0 | 0 | 0 | 75.2 | 0 | 1.5 | |
| | 80 | 95 % $H_2SO_4$[b] | 80.3 | 2.4 | 4.6 | 0 | 0.030 | 6.0 | *p*-Nitroaniline formed 4.2% |
| (1) | 40 | $HSO_3Cl$ (6)[a] | 76.4 | 2.0 | 9.7 | 0 | 0.026 | Trace | |
| | 80 | 80 % $H_2SO_4$[b] | 12.0 | 0 | 0 | 85.0 | 0 | 3.0 | |
| | 80 | 95 % $H_2SO_4$[b] | 80.6 | 2.0 | 11.9 | 0 | 0.023 | 1.1 | |

Reaction condition,

a) Reaction time ; 40min., Starting material ; 2.0g ($8.2\times10^{-3}$Mol.), (6) ; 10g ($8.7\times10^{-2}$Mol.)

b) Reaction time ; 1 hr., Starting material ; 1.0g ($4.1\times10^{-3}$Mol.), $H_2SO_4$ ; 15ml

After the optimum reaction condition on temperature was investigated for the reaction of (2) and (6), this reaction condition was also applied to the case of (1). The data of the Wallach rearrangement were added in comparison with the reaction (1) and (2) with (6) in Table 1. The higher ortho-para ratio were fenerally obtained in the case (6) than that of the Wallach rearrangement, the reason being the weaker nucleophilic character of chlorosulfonic anion in comparison with sulfonic anion. 4-nitro-4'-chlorosulfonyl azobenzene formed in the reaction of (1) and (2) with (6) was detected by the method indicated in the literature[8].

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