Studies on the Reactivity of Azoxybenzenes. Part 12.[1] αβ-Interconversion of *para*-Monosubstituted Azoxybenzenes in the Wallach Rearrangement †

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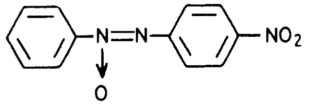
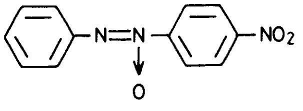
Under the reaction conditions for the Wallach rearrangement, 4-methyl-*ONN*- (1α), 4-methyl-*NNO*-(1β), 4-nitro-*ONN*- (2α), and 4-nitro-*NNO*-azoxybenzene (2β) were found to undergo αβ-interconversion, while 4-bromo-*ONN*- (3α) and 4-bromo-*NNO*-azoxybenzene (3β) do not. The αβ-interconversion occurs with both mono- and di-protonated forms of the azoxybenzenes.

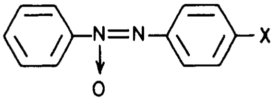
Despite the large number of studies on the Wallach rearrangement of azoxybenzenes,[2-4] little attention has been paid to the αβ-interconversion of unsymmetrically substituted azoxybenzenes during the rearrangement. Gore reported that 4-nitro-*NNO*-azoxybenzene (2β) was partly isomerized into 4-nitro-*ONN*-azoxybenzene (2α) in 98% sulphuric acid, while (2α) was not isomerized into (2β) under the same conditions.[5] This observation was confirmed by Duffy and Hendry.[6] We have found previously that βα-conversion of β-4-acetamido-azoxybenzene occurs in sulphuric acid.[7] This paper reports new findings on the αβ-interconversion of certain azoxybenzenes.



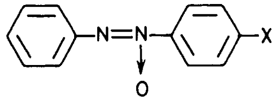
4-Nitro-*ONN*-azoxybenzene
α-Isomer



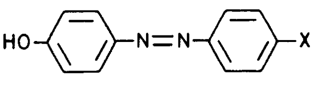
4-Nitro-*NNO*-azoxybenzene
β-Isomer



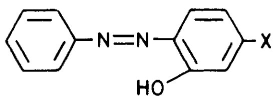
(1α) X = Me
(2α) X = NO$_2$
(3α) X = Br



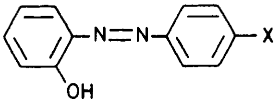
(1β) X = Me
(2β) X = NO$_2$
(3β) X = Br



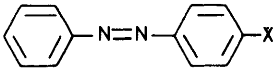
(4)



(5)



(6)



(7)

Results and Discussion

We took three sets of α- and β-isomers (1)—(3) for the present investigation. Each azoxybenzene underwent the Wallach rearrangement in 80—90% sulphuric acid to give the corresponding 4-hydroxyazobenzene (4) as the major product and two isomeric 2-hydroxyazobenzenes (5) and (6) and the corresponding azobenzene (7) as the minor products in different product ratios (Table 1). It should be noted that (1α) and (1β) gave (5) but not (6) while (2α), (2β), and (3β) gave only (6) but not (5). However, (3α) gave neither (5) and (6) under similar reaction conditions.

Next, the azoxybenzenes were analysed for the α : β isomer ratio at intervals in the course of the Wallach rearrangement. Starting from either (1α) and (1β), the α : β ratio became *ca.* 3 for the azoxybenzene recovered after 3 h reaction time [78% conversion with (1α) and 53% conversion with (1β)]. In the case of (2α) and (2β), the α : β ratio also became *ca.* 3 for the azoxybenzenes recovered after 2 h [nearly 50% conversion with both (2α) and (2β)]. However, αβ-interconversion was not observed for either (3α) or (3β) under similar reaction conditions, in accord with the previous report.[5]

The rearrangement product (4) and the reduction products (7) are known to be formed from the dication (A) (Scheme), which is produced *via* the mono- and di-protonated azoxybenzenes.[2-4,8,9] In order to establish whether αβ-interconversion occurs from both mono- and di-protonated azoxybenzenes, reaction of the azoxybenzenes in less acidic media was examined. When (2α) and (2β) were treated with 75% sulphuric acid at 50 °C, the reaction took place so slowly that the rearrangement products were detected only after 150 and 200 min, respectively, and the α : β ratio at these times was 12.0 and 0.15, respectively (Figure). Similarly, an α : β ratio of 0.12 was obtained after treating (1β) with 75% sulphuric acid at 35 °C for 60 min. Furthermore, the αβ-interconversion of (1α) was found to be accelerated in sulphuric acid of higher concentrations (Table 2). These results indicate that αβ-interconversion occurs from both mono- and di-protonated azoxybenzenes, and that the conversion rate from diprotonated form is much faster than that from the monoprotonated form.

The Scheme summarizes the steps in the αβ-interconversion of *para*-substituted azoxybenzenes together with the pathways of their Wallach rearrangement. The α- and β-azoxybenzenes accept a proton to form the monoprotonated species $(\alpha H)^+$ and $(\beta H)^+$, respectively, which undergo αβ-interconversion, possibly *via* the protonated intermediate (B).[9] At this monoprotonation stage, the intramolecular migration of the hydroxy-group occurs from both $[\alpha H]^+$ and $[\beta H]^+$ to give *o*-hydroxyazobenzenes (5) and (6) depending upon the sub-

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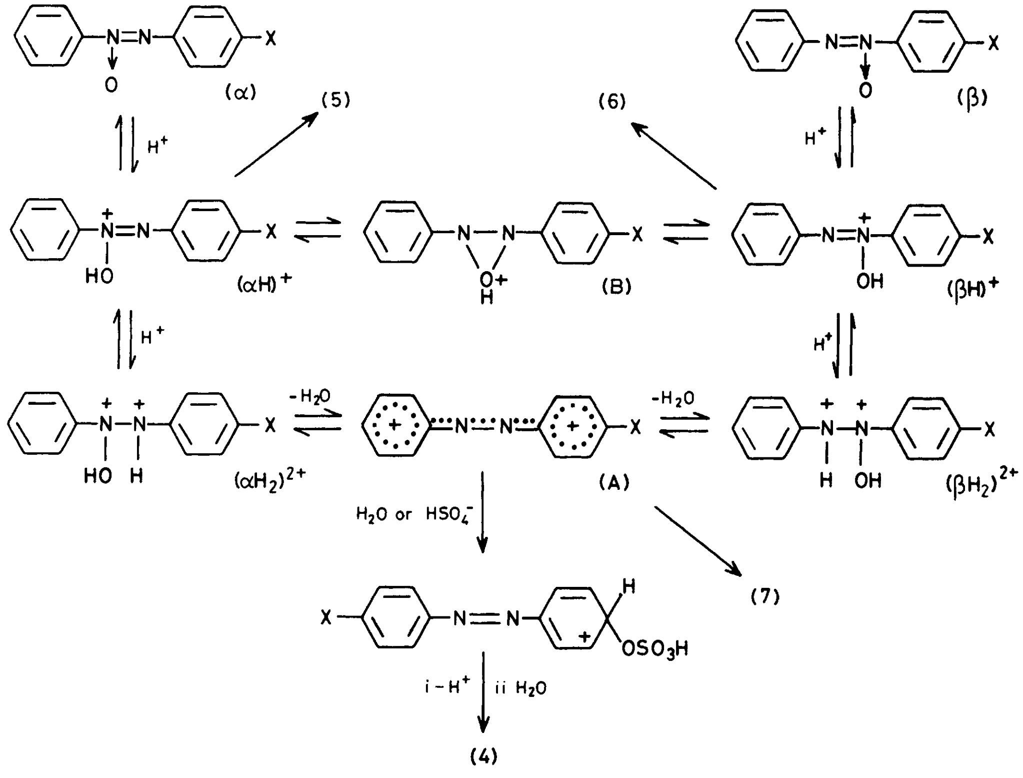
† Although the αβ-nomenclature for azoxybenzenes is not approved by IUPAC, we use it here.



Scheme

Table 1. Wallach rearrangement products of *p*-substituted azoxybenzenes

	Reaction conditions			Yield of products (%)				
Azoxybenzene	H_2SO_4 : MeOH : H_2O (wt %)	Temperature (°C)	Reaction time (min)	Recovered azoxybenzenes	(4)	(5)	(6)	(7)
(1α) *	85.0 : 11.5 : 5.3	30—32	180	22	71	3		2
(1β)	85.0 : 11.5 : 5.3	30—32	180	47	31	2		13
(2α)	90.0 : 6.2 : 3.8	33—34	120	51	30		2	8
(2β)	90.0 : 6.2 : 3.8	33—34	120	49	33		4	6
(3α)	80.0 : 8.5 : 12.5	80	40	26	22.5			26
(3β)	80.0 : 8.5 : 12.5	70	30	12.5	33		2.5	12.5

* A mixture of (1α) and (1β) (3.7 : 1) was used, since the isolation of pure (1α) was unsuccessful.

Table 2. αβ-Conversion of 4-methyl-*ONN*-azoxybenzene (1α) in sulphuric acid at different concentrations

		Yield (%)		
H_2SO_4 : MeOH : H_2O (wt %)	Reaction time (min)	Recovered 4-methyl-azoxybenzenes	Products (4)—(6)	α : β Ratio
75.0 : 22.7 : 2.3	60	43.5	54.2	5.07
80.0 : 17.5 : 2.5	20	75.1	24.9	4.07
85.0 : 12.4 : 2.6	10	87.3	12.7	2.78

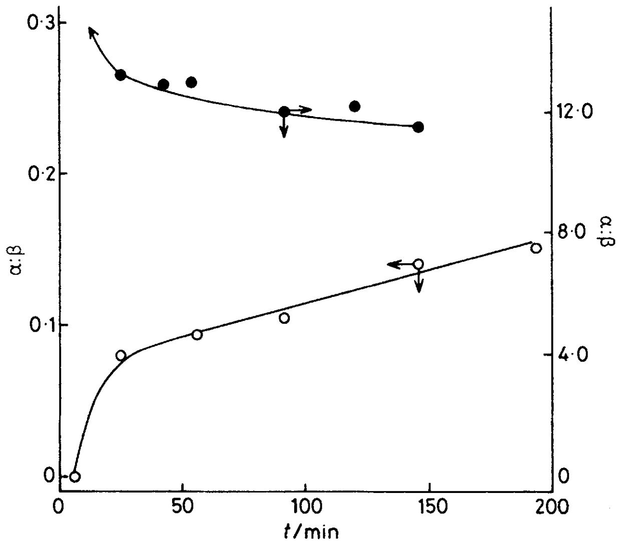
Reaction conditions: starting material (0.1 g, 0.48 mmol; α : β 5.25); solvent, 10 ml; temperature, 31—34 °C.

stituent at the *para*-position. At higher sulphuric acid concentrations, the diprotonated species $(\alpha H_2)^{2+}$ and $(\beta H_2)^{2+}$ undergo αβ-interconversion directly or *via* the dication intermediate[2] which is further converted into the corresponding *p*-hydroxyazobenzene (4) and reduced to the corresponding azobenzene (7).

Experimental

Preparation of Starting Materials.—Oxidation of 4-methylazobenzene with hydrogen peroxide in acetic acid gave a mixture of 4-methyl-*ONN*- (1α) and 4-methyl-*NNO*-azoxybenzene (1β),[10] which was separated by fractional crystallization from ethanol to give pure (1α) and a mixture of (1α) and (1β) (3.7 : 1). 4-Nitroazobenzene was oxidized with hydrogen peroxide to give 4-nitro-*NNO*-azoxybenzene (2β),[11] which was converted into 4-nitro-*ONN*-azoxybenzene (2α) by treating with chromium trioxide in acetic acid.[11] 4-Bromo-*ONN*-azoxy- (3α) was prepared by the bromination of azoxybenzene.[12] 4-Bromo-*NNO*-azoxybenzene (3β) was obtained by repeated crystallization from benzene–light petroleum of the oxidation product of 4-bromoazobenzene with hydrogen peroxide.[12]

The Wallach Rearrangement of para-*Substituted Azoxybenzenes.*—In a typical run, (1α) (0.5 g, 0.4 mmol) (α : β 3.7) was dissolved in 85% sulphuric acid (H_2SO_4 : MeOH : H_2O 85.0 : 11.5 : 3.5) (30 ml) and the solution was warmed at 30—32 °C. 5 ml of the mixture were pipetted out at intervals



αβ-Interconversion of 4-nitro-*ONN*-azoxybenzene (2α) and 4-nitro-*NNO*-azoxybenzene (2β) (each 0.5 g, 2.1 mmol) in 75% sulphuric acid at 50 °C in H_2SO_4-MeOH-H_2O (75.0 : 8.3 : 16.7): ●, α; ○, β

and poured onto ice-water to stop the reaction. After work-up, the rearrangement products, 2- and 4-hydroxyazobenzene, were identified by comparison with authentic samples (m.p. and i.r.) synthesized by the coupling of phenols with benzenediazonium salts.[13] The 2-hydroxyazobenzenes were also characterized by the formation of a brown complex by the reaction with copper(II) acetate.[14,15]

α : β *Ratio Determination of the Recovered Azoxybenzenes*.—^{1}H N.m.r. signals at δ 2.05 and 1.94 for the methyl group of (1α) and (1β), respectively,[16] were used for determining the α : β ratio. The α : β ratio of the 4-nitroazoxybenzenes (2α) and (2β) was estimated by u.v. spectroscopy using a calibration curve: (2α), $\lambda_{max.}$ (EtOH) 337 nm (ε 19 200); (2β), $\lambda_{max.}$ (EtOH) 337 (ε 19 200) and 263 nm (9 500). For the 4-bromoazoxybenzenes (3α) and (3β), a m.p. determination was used for analysis, as they are indistinguishable by u.v. and n.m.r. spectra. The m.p.s of the recovered 4-bromoazoxybenzenes were compared with those of mixtures of (3α) and (3β) at various ratios. There was no evidence that αβ conversion took place.

αβ-*Conversion of* 4-*Methyl*-ONN-*azoxybenzene* (1α).—A mixture of (1α) and (1β) (α/β 5.25) (10.5 g, 2.4 mmol) dissolved in 75% sulphuric acid (H_2SO_4 : MeOH : H_2O 75.0 : 8.3 : 16.3) (10 ml) was allowed to stand for 1 h at 33—35 °C. After the products were separated, the α : β ratio of the recovered 4-methylazoxybenzenes was determined. The same procedure was also applied to the reactions in 80 and 85% sulphuric acid. The results are shown in Table 2.

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