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The Structure of 4-Methoxy-*ONN*-azoxybezene and Oxygen Transfer Reaction of 4-Methoxyazoxybenzenes in Sulfuric Acid

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Synopsis. The structure of 4-methoxy-*ONN*-azoxybenzene (**1α**)[†] has been determined by X-ray analysis. In sulfuric acid **1α** gave a rearrangement product 4-hydroxy-4′-methoxyazobenzene, together with 4-methoxyazobenzene and 4-methoxy-*NNO*-azoxybenzene.

Since the transformation of azoxybenzene into 4-[1] and 2-hydroxyazobenzene[2] with concentrated sulfuric acid was found, investigations of the Wallach rearrangement on many symmetrically substituted azoxybenzenes has followed.[3–5] Studies of unsymmetrically substituted azoxybenzenes has, however, been insufficient.

Recently, the reactions of 4-methyl-*ONN*- and 4-methyl-*NNO*-azoxybenzene with sulfuric acid[6,7] and some metallic halides[8],[9] were investigated. Furthermore, it was found that some para-substituted azoxybenzenes having a proton acceptable group (-COOH, -$COOH_3$, and -$OCOCH_3$) underwent α,β-interconversion or β,α-conversion under Wallach rearrangement conditions.[10] The Wallach rearrangements of 4-methoxy-*ONN*- (**1α**) and 4-methoxy-*NNO*-azoxybenzene (**1β**) have been shown to give 4-hydroxy-4′-methoxyazobenzene (**4**) as a rearrangement product.[11] Little attention, however, has been paid on the mechanism of this rearrangement. Although the stereo-chemistry of **1α** and **1β** was reported by Szegö,[12] the results are ambiguous. We had to determined the structure of **1α** or **1β** before an investigation of the Wallach rearrangement of 4-methoxyazoxybenzenes was started. Since the separation of pure **1β** was unsuccessful, the structure of **1α** was determined by X-ray analysis.

Results and Discussion

The molecular structure of **1α** with its atomic numbering is given in Fig. 1. All of the non-hydrogen atoms of the molecules lie in a plane with mean deviation of 0.04 Å. C(13) deviates by 0.07 Å from the plane.

The Wallach rearrangement of **1α** in 65% sulfulic acid at 55 °C gave 4-hydroxy-4′-methoxyazobenzene (**4**) as a rearrangement product together with 4-methoxyazobenzene (**3**). The yields of **3** and **4** increased with reaction time. Compound **1α** isomerized to **1β** and the ratio of **1α** to **1β** in recovered 4-methoxyazoxybenzenes increased to 1.6 after 1 h (Entries 1—4 in Table 1). Under the same reaction conditions, the reaction of a mixture of **1α** and **1β** ($\alpha:\beta=0.5:1.0$) was slow and the ratio of **1α** to **1β** changed from 0.50 to 0.33 (Entry 6 in Table 1). When **1α** was treated with 60% sulfuric acid, no change of the β/α ratio was found in the recovered 4-methoxyazoxybenzenes (Entry 5 in Table 1).

Since azobenzenes are produced through the diprotonated species under Wallach rearrangement conditions,[13] it is unlikely that $[\mathbf{1\alpha}\mathrm{H}_2]^{2+}$ is formed in the reaction of **1α** with 60% sulfuric acid, $[\mathbf{1\beta}\mathrm{H}_2]^{2+}$ is also detected in 65% sulfuric acid (Entries 5 and 6 in Table 1). In general, para-hydroxyazobenzenes are given by a nucleophillic displacement with a hydrogensulfate anion on the dication in a Wallach rearrangement of azoxybenzenes.[3–5] In comparison with the reaction of **1α** using 60 and 65% sulfuric acid, it was shown that a nucleophillic attack with a hydrogensulfate anion occurs even in monocation $[\mathbf{1\alpha}\mathrm{H}]^+$ to afford **4** (Entries 3 and 5 in Table 1).

Some reaction intermediates in the Wallach rearrangement of azoxybenzenes have already been reported: monocation, diprotonated species and dication.[14,15] Scheme 1 summarizes the pathway for the oxygen transfer reaction of **1α** and **1β** including an α,β–isomeric conversion. Compound **1α**, and **1β** first change to $[\mathbf{1\alpha}\mathrm{H}]^+$ and $[\mathbf{1\beta}\mathrm{H}]^+$, respectively, in sulfuric acid, which are then further transformed into $[\mathbf{1\alpha}\mathrm{H}_2]^{2+}$ and $[\mathbf{1\beta}\mathrm{H}_2]^{2+}$. The transformation process from $[\mathbf{1\beta}\mathrm{H}]^+$ to $[\mathbf{1\beta}\mathrm{H}_2]^{2+}$ seems to be much slower than the proton-adding process on $[\mathbf{1\alpha}\mathrm{H}]^+$, since a β,α-isomeric conversion from **1β** to **1α** was observed only in a small amount and a lower yield of **4** was found. The α,β-isomeric conversion proceeds via diprotonated species (Entries 3,5, and 6 in Table 1). The α,β-isomeric

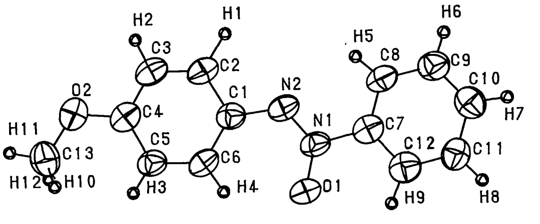
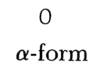
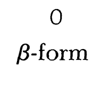


Fig. 1. Molecular structure of 4-methoxy-*ONN*-azoxybenzene with atomic labelling scheme. The harmonic parts of the displacement ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

[†] Although the terms of α and β are not used in the IUPAC nomenclature in unsymmetrically substituted azoxybenzenes, we use these terms for convenience here.



α-form

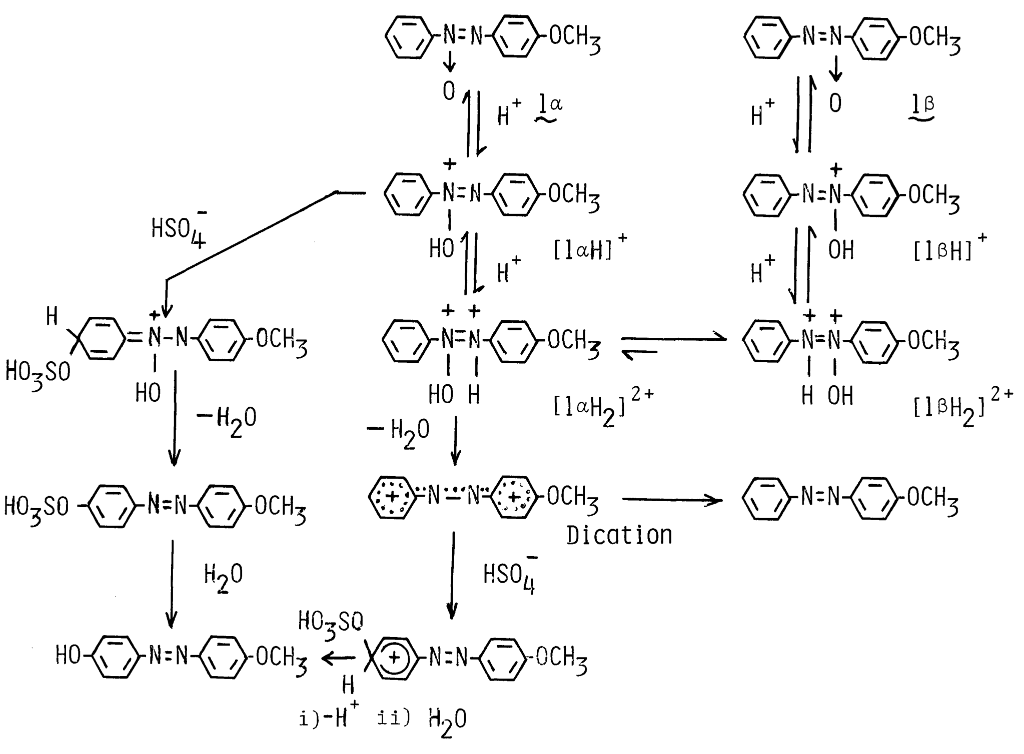


β-form

Table 1. The Reaction of 4-Methoxy-*ONN*-azoxybenzene **1α** and 4-Methoxy-*NNO*-azoxybenzene **1β** with Sulfuric Acid

Entry	Starting materials	Reaction conditions[a,b]		Products/%		Recovered azoxybenzenes			
		H_2SO_4 %	Time min	4	3	%	α	:	β
1	1α (α:β=1.0:0.0)	65	5	15	18	23	4.8	:	1.0
2			20	20	21	16	4.6	:	1.0
3			40	24	26	10	3.9	:	1.0
4			60	26	31	9	1.6	:	1.0
5		60	40	8	c)	91	1.0	:	0.0
6	1β (α:β=0.5:1.0)	65	60	10	c)	28	0.3	:	1.0

a) Each sulfuric acid solution contains some methanol to increase solubility of starting materials. b) Each run is carried out at 55 °C. c) Not detected.



Scheme 1.

conversion in the reaction of **1α** and **1β** with sulfuric acid is also considered to proceed intramolecularly.[16] Compound **4** is given by a nucleophilic attack with the hydrogensulfate anion on $[\mathbf{1\alpha}H_2]^{2+}$ followed by deprotonated and hydrolysis. Compound **3** is given as a result of an interaction with $[\mathbf{1\alpha}H_2]^{2+}$.

Experimental

Synthesis of Starting Materials. Compound **3** was synthesized by the reaction of 4-hydroxyazobenzene with dimethyl sulfate in an aqueous sodium hydroxide solution: Mp 52.5—53.5 °C (lit,[17] 53.5—54.5 °C). A mixture of **1α** and **1β** was obtained by the oxidation of **3** with hydrogen peroxide in acetic acid.[17] Compound **1α** and **1β** were separated by fractional crystallization with ethanol. The ^1H NMR data (in C_6H_6) and mp of these compounds are as follows: **1α** δ=3.25 (s, MeO), mp 67.0—68.0 °C (lit,[11] 66.5—67.5 °C). **1β** (as a 2:1 mixture with **1α**) δ=3.15 (s, MeO), mp 39.0—40.0 °C (lit,[11] 42.0—43.0 °C).

X-Ray Experiment. The title compound **1α** was crystallized from a methanol solution. A yellow crystal (0.10×0.10×0.01 mm³) was mounted on a Rikagaku AFC-5 automatic four-circle diffractometer (graphite-monochromated Cu*Kα*, λ=1.5418 Å). Unit cell dimensions were obtained by a least-squares fit using 18 reflections over the range $40 < 2\theta < 60°$. Intensity data were collected using a θ–2θ scan mode within the range from 3 to 63° in θ: $0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 4$, $-12 \leqslant l \leqslant 11$. The fluctuations of three standard reflections monitored after every 100 reflections were within ±1.2% in F. The Lorentz and polarization effects were corrected, but not for absorption. Out of the 1121 observed reflections, 947 reflections with $F_o > 3\sigma(F_o)$ were used for the analysis. The structure was solved by MULTAN 78.[18] The

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters/Å^2 with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}[a)]
O(1)	0.23490(3)	0.4773(1)	0.64882(3)	6.1(1)
O(2)	−0.10777(3)	0.3746(1)	0.09786(3)	5.3(1)
N(1)	0.29225(3)	0.3174(1)	0.59670(3)	4.3(1)
N(2)	0.26664(3)	0.2204(1)	0.48256(4)	4.4(1)
C(1)	0.16775(3)	0.2806(1)	0.39710(4)	4.1(1)
C(2)	0.15712(4)	0.1590(1)	0.27510(4)	4.5(1)
C(3)	0.06586(4)	0.1957(1)	0.17959(4)	4.7(1)
C(4)	−0.01977(3)	0.3474(1)	0.19982(4)	4.4(1)
C(5)	−0.01144(4)	0.4724(1)	0.32080(4)	4.4(1)
C(6)	0.07991(4)	0.4380(1)	0.41790(4)	4.4(1)
C(7)	0.39868(3)	0.2456(1)	0.67251(4)	4.4(1)
C(8)	0.46674(4)	0.0866(2)	0.62136(4)	4.8(1)
C(9)	0.56945(4)	0.0367(2)	0.69544(5)	5.1(1)
C(10)	0.60239(4)	0.1326(2)	0.81835(5)	5.2(1)
C(11)	0.53245(4)	0.2860(2)	0.87163(4)	5.1(1)
C(12)	0.43138(4)	0.3458(2)	0.79859(4)	5.0(1)
C(13)	−0.19390(4)	0.5440(2)	0.11268(5)	5.6(1)

a) $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$.

positional and themal parameters for non-hydrogen atoms were refined anisotropically by a blockdiagonal least-squares method.[19)] with the function minimizing $\sum w(F_o-F_c)^2$. All of the hydrogen atoms were located on a difference Fourier map refined isotropically. Final values of $R=0.066$, $wR=0.076$ and $S=0.769$ were obtained. The weighting scheme was $w=1.0$ for $0<F_o\leqslant 15$ and $w=[1.0+0.852\ (F_o-15)]^{-1}$ for $F_o>15$. The maximum Δ/σ was 0.35. The maximum and minimum $\Delta\sigma$ in the final difference Fourier synthesis were 0.37 and −0.35 eÅ^{-3}. The final atomic parameters for non-hydrogen atoms are listed in Table 2.[20)] The atomic scattering factors were taken from International Tables for X-ray Crystallography.[21)] All of the computations were carried out a HITAC 280D at the Information Center of Tottori University.

Crystal data: $C_{13}H_{12}N_2O_2$, F.W.=228.25, monoclinic, $P2_1$, $a=13.305(5)$, $b=3.693(2)$, $c=11.148(4)$ Å, $\beta=108.30(2)°$, $V=566.4(5)$ Å^3, $Z=2$, $D_x=1.339$, $\mu=0.71$ mm^{-1}, $F(000)=240$.

The Wallach Rearrangement of 4-Methoxy-*ONN*-azoxybenzene (1*α*). A mixture of **1*α*** (0.50 g, 2.19 mmol) in 65% sulfuric acid (40 ml) was kept at 55 °C. Each aliquot (5 ml) of the reaction mixture was poured into water at intervals and extracted with ether. The ether solutions were extracted with a 5% sodium hydroxide solution. The alkaline solutions were acidified with hydrochloric acid. The acidic solutions were extracted with ether. The ethereal layers were evaporated to give **4**. After an ether solution containing the alkali-insoluble part was washed with water and dried, 4-methoxyazoxybenzenes (**1*α*** and **1*β***) and **3** were separated by chromatography [(benzene–hexane=2:1)–silica gel]. The α/β ratio in a mixture of **1*α*** and **1*β*** was estimated by ^{1}H NMR spectroscopy.

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