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Preparations and Structures of 3-Chloro-ONN-4′-methylazoxybenzene and 4-Methoxy-ONN-4′-methylazoxybenzene†

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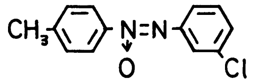
Synopsis. A treatment of 3-chloro-NNO-4′-methylazoxybenzene (**1β**) with CrO$_3$ in acetic acid gave 3-chloro-**ONN**-4′-methylazoxybenzene (**1α**) in good yield, whereas 4-methoxy-**ONN**-4′-methylazoxybenzene (**2α**) isomerized partially to 4-methoxy-**NNO**-4′-methylazoxybenzene (**2β**) under the same conditions. The structures of **1α** and **2α** have been determined by X-ray analysis.

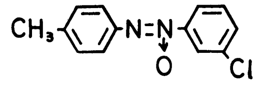
The transformations of azoxybenzene into 4-hydroxyazobenzene[1] and small amounts of 2-hydroxyazobenzene[2] were discovered by Wallach and Belli, respectivelly. A number of investigations on the Wallach rearrangement for various substituted azoxybenzenes have since followed. However, little has been studied regarding the Wallach rearrangement of unsymmetrically substituted azoxybenzenes or on the isomerization of the azoxybenzenes under the conditions of the Wallach rearrangement.[3–5] Recently, the α,β-isomerization††† based on a migration of an azoxy-oxygen atom was found in the reaction of some unsymmetrically substituted azoxybenzenes with sulfuric acid.[6–8] In order to reveal the mechanism of the Wallach rearrangement through the behavior of unsymmetrically substituted azoxybenzenes, it is necessary to determine their structure unambiguously, i.e. the relative position of the oxygen atom on the azoxy group. Here, we report on the preparation of 3-chloro-**ONN**-4′-methylazoxybenzene (**1α**) and 4-methoxy-**ONN**-4′-methylazoxybenzene (**2α**) and the structures of **1α** and **2α** determined by X-ray crystallographic analysis.

Results and Discussion

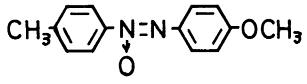
It was shown that some β-isomers converted into α-isomers upon treating with CrO$_3$ in acetic acid [4-(phenyl-**NNO**-azoxy)beozoic acid,[9] 4-nitro-**NNO**-azoxybenzene[10]]. When **1β** was warmed with CrO$_3$ in acetic acid, an oxygen atom of it transfered to a nitrogen atom, binding with 4-tolyl group (β,α-isomerization). In the reaction of a mixture of **2α** and **2β** with CrO$_3$ under some conditions (i.e. by using four different starting mixtures in molar ratio and changing the reaction time, adding amounts of CrO$_3$, and volume of AcOH), the preparation of pure **2α** was unsuccessful. However, an azoxy-oxygen atom partialy transfered to a remote nitrogen atom from the 4-tolyl group in a α,β-ratio (2α : 2β=0.5 : 1.0) in each case (Table 1).



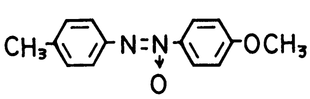
3-Chloro-**ONN**-4′-methylazoxybenzene
1α



3-Chloro-**NNO**-4′-methylazoxybenzene
1β



4-Methoxy-**ONN**-4′-methylazoxybenzene
2α



4-Methoxy-**NNO**-4′-methylazoxybenzene
2β

In order to separate the α and β-isomer of unsymmetrically substituted azoxybenzenes from each other, a fractional crystallization technique was spplied using ethanol [methyl 4-(phenylazoxy) benzoates,[9] 4-methylazoxybenzenes,[7] 4-phenylazoxybenzoic acid[9]]. When a hot equimolar ethanol solution of **2α** and **2β** was allowed to stand at room temperature, deposited first crystals had the same isomeric ratio as the starting mixture. In an effective separation of **2α** from a mixture of **2α** and **2β**, the deposited crystalline substance are filtered off from an ethanol solution at 50 °C. The structures of **1α** and **2α**, determined by the X-ray analyses, are shown in Fig.1. It could be guaranteed that both **1α** (δ 1.97) and **2α** (δ 1.98) had an azoxy-oxygen atom on the nitrogen atom, binding the 4-tolyl group, respectively.

Experimental

Preparation of 3-Chloro-4′-methylazoxybenzene (3). *p*-Nitrosotoluene (**4**) (6.3 g, 52.0 mmol) was dissolved in an equal volume solution of acetic acid and ethanol (40 ml in each) with warming; was added an acetic acid solution of *m*-chloroaniline (4.6 g, 45.6 mmol) to it. After the reaction, the mixture was kept at 50 °C for 30 min, and then allowed to stand overnight. A dark brown precipitate was filtered and washed throughly with water. The precipitate was dissolved in ether and the ether solution was washed with water: 3% NaOH aq soln, 5% HCl aq soln, and water. After the ether solution was dried, crude **3** was obtained by recrystallization with ethanol (150 ml). Mp 106.0—107.0 °C. Methyl signal δ=2.05. 4-Methyl-4′-methoxyazobenzene (**5**) (86.5%) was also

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† Reactivities of Azoxybenzenes. 17.

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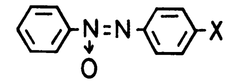
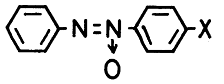
††† Although the IUPAC nomenclature on unsymmetrically substituted azoxybenzenes is not used the terms of α and β, we use these signs in this paper for convenience.

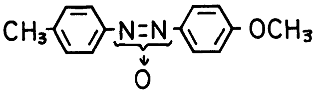
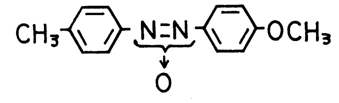


α-Isomer



β-Isomer

Table 1. The Reaction of the Mixture of 4-Methoxy-**ONN**- (**2α**) and 4-Methoxy-**NNO**-4′-methylazoxybenzene (**2β**) with CrO_3

Starting	Reaction condition[a]			Product[b]
	Time	CrO_3	AcOH	
g (mmol)	h	g (mmol)	ml	g (%)
2.51 (10.36) (α : β=0.98 : 1.00)	3.0	2.0 (20.0)	100	2.00 (80.0) (α : β=0.50 : 1.00)
3.29 (13.58) (α : β=0.40 : 1.00)	4.0	3.5 (35.0)	100	2.60 (79.1) (α : β=0.50 : 1.00)
3.90 (16.10) (α : β=0.66 : 1.00)	4.5	2.5 (25.0)	100	3.29 (84.4) (α : β=0.50 : 1.00)
2.60 (10.73) (α : β=0.50 : 1.00)	6.0	6.0 (60.0)	150	0.90 (34.6) (α : β=0.50 : 1.00)

a) Reaction temperature: 60 °C. b) In high reaction temperature, benzene insolubles were found.

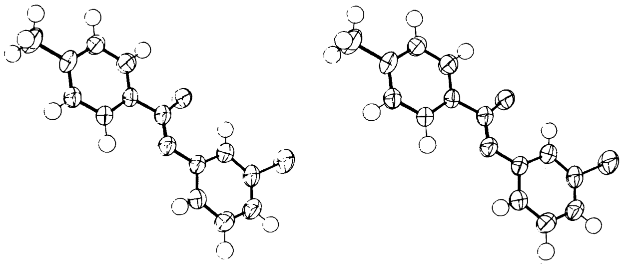


Fig. 1(a).

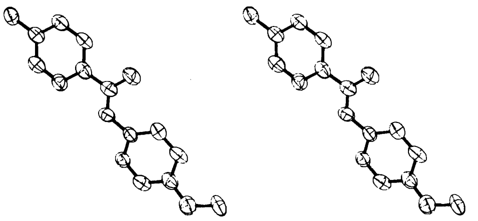


Fig. 1(b).

Fig. 1. Stereoscopic views of (a) **1α** and (b) **2α**.

prepared in a reaction of **4** with *p*-anisidine: mp 111.0 °C (lit,[11] 110.0—111.0 °C) δ=2.07.

Preparation of 3-Chloro-ONN-4′-methylazoxybenzene (1α). An acetic acid solution (500 ml) of **3** (5.0 g, 24.2 mmol) was kept at around 65 °C with 30% H_2O_2 (50 ml). When the orange-reddish solution changed to yellow, the reaction mixture was poured into water. The precipitate was filtered and washed with water until the smell of acetic acid disappeared. An equimolar mixture of **1α** (δ=1.97) and 4-methyl-**ONN**-3′-chloroazoxybenzene (**1β**) (δ=2.09) was obtained (5.3 g, 97.1%) mp 76.5—77.0 °C. The mixture (5.0 g, 22.3 mmol) was kept in the range 30—40 °C in acetic acid and CrO_3 (5.1 g, 51.0 mmol) was added in three portions during 30 minutes. After the reaction mixture was warmed in the range 55—60 °C for 3 h and allowed to stand over night, it was poured into cold water and filtered. **1α** was thoroughly washed with water and dried (4.25 g, 85.0%). The oxidation of **5** with H_2O_2 was carried out by the same procedure and an equimolar mixture (85.0%) of **2α** (δ=1.98) and **2β** (δ=2.08) was obtained. An ethanol solution (80 ml) of the mixture was kept in the range 60—70 °C. When the temperature of the solution dropped to 50 °C, the deposited crystals were filtered and dried (5.1 g, 81.0%), (**2α** : **2β**=5.67 : 1.00). The same procedure was applied for a mixture (5.1 g, 24.6 mmol) using ethanol (100 ml) again. After being worked up, pure **2α** (2.86 g, 55.0%) was obtained mp 110.5—111.0 °C (δ=1.98).

Crystallographic Measurements. The diffraction data of the crystals of **1α** and **2α** were measured at room temperature on a microcomputer-controlled four-circle diffractometer.[12] The crystal data are as follows: **1α**; $C_{13}H_{11}N_2OCl$, M=246.7, monoclinic, space group $P2_1/n$, a=12.133(5), b=12.805(5), c=7.738(4) Å, β=93.69(5)°, V=1199.7 Å^3, Z=4, D_c=1.37 g cm^3. **2α**: $C_{14}H_{14}N_2O_2$, M=242.3 monoclinic, space group $C2$, a=25.485(7), b=3.986(3), c=13.428(5) Å, β=116.42(5)°, V=1221.6 Å^3 Z=4, D_c=1.32 g cm^3. The intensities were measured up to 2θ=120° by a θ—2θ scan technique using Ni-filtered Cu$K\alpha$ radiation. The reflections with $F>2\sigma_F$ were used for subsequent caluculations. The numbers of measured and significant reflections were 1784 and 1368, respectivelvely,for **1α**, and 1019 and 778, respectively for **2α**. Periodically monitored reflections showed no significant change in intensity. The intensities were corrected for the Lorenz and polarization factors.

Structure Determination. The structure of **1α** was solved by the direct method.[13] Since an attempt to solve the structure of **2α** by a direct method was unsuccessful, the vector search method[14] was applied; the parameters of the orientation and the translation of azoxybenzene were deter-

Table 2. Final Atomic Coordinates of **1α** with Their Estimated Standard Deviations in Parentheses

	x	y	z
C(1)	0.0376(3)	0.6938(3)	0.7470(5)
C(2)	0.0106(4)	0.7969(4)	0.7311(6)
C(3)	−0.0328(4)	0.8482(4)	0.8703(6)
C(4)	−0.0480(4)	0.7939(4)	1.0231(5)
C(5)	−0.0205(4)	0.6892(4)	1.0340(5)
C(6)	0.0232(4)	0.6379(3)	0.8960(6)
C(7)	0.1671(3)	0.4937(3)	0.4906(5)
C(8)	0.1934(4)	0.3940(4)	0.5428(6)
C(9)	0.2456(4)	0.3247(4)	0.4367(6)
C(10)	0.2734(4)	0.3586(4)	0.2743(6)
C(11)	0.2482(4)	0.4576(4)	0.2242(6)
C(12)	0.1939(4)	0.5281(3)	0.3249(6)
C(13)	−0.0951(5)	0.8497(4)	1.1767(7)
N(1)	0.0846(3)	0.6421(3)	0.5970(4)
N(2)	0.1162(3)	0.5496(3)	0.6216(4)
O(1)	0.0878(3)	0.6949(3)	0.4598(4)
Cl	0.2845(1)	0.4998(1)	0.0214(2)

Table 3. Final Atomic Coordinates of **2α** with Their Estimated Standard Deviations in Parentheses

	x	y	z
C(1)	0.1655(4)	0.0104(31)	0.2794(7)
C(2)	0.1083(4)	0.1102(29)	0.2273(6)
C(3)	0.0709(4)	0.0563(30)	0.2778(7)
C(4)	0.0924(4)	−0.0963(29)	0.3816(7)
C(5)	0.1511(4)	−0.1950(29)	0.4326(7)
C(6)	0.1879(4)	−0.1408(31)	0.3826(7)
C(7)	0.2948(4)	0.0000(29)	0.2299(6)
C(8)	0.3480(4)	−0.1419(31)	0.2984(7)
C(9)	0.3949(4)	−0.1292(32)	0.2718(7)
C(10)	0.3876(4)	0.0319(29)	0.1742(7)
C(11)	0.3339(4)	0.1754(29)	0.1051(7)
C(12)	0.2873(4)	0.1552(27)	0.1320(7)
C(13)	0.0512(4)	−0.1609(34)	0.4356(8)
C(14)	0.4310(4)	0.2096(40)	0.0564(7)
N(1)	0.2024(3)	0.0607(24)	0.2242(5)
N(2)	0.2548(3)	−0.0402(25)	0.2756(5)
O(1)	0.1790(3)	0.2105(26)	0.1308(5)
O(2)	0.4354(3)	0.0413(22)	0.1549(5)

mincd by the program RICS.[15] The renaining non-hydrogen atoms were located in a successive Fourier synthesis. Positional and anistropic temperature factors for **1α** and **2α** were refined by a block diogonal least-squares method.[16] All hydrogen atoms of **1α** were located in the difference Fourier synthesis and included in the subsequent refinement. The positions of the hydrogen atoms of **2α**, except those of the methyl group, were caluculated geometrically and included in the refinement. The isotopic temperature factors of these hydrogen atoms of **2α** were fixed to those of the atoms to which they were bonded. The weighting scheme used in the final cycle of the refinement for **1α** was w=1.0 for $F_o \leqq 18$ and w=$[1.0+0.25\,(F_o-18)]^{-1}$, for $F_o>18$ and that for **2α** was w=1.0 for $F_o \leqq 30$ and w=$[1.0+0.2(F_o-30)]^{-1}$ for $F_o>30$. The final R values are 0.071 and 0.083 for **1α** and **2α**, respectivelly. The final atomic parameters are given in Tables 2 and 3.[17] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[18]

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