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Facile Photorearrangement of Some Crowded Azoxyarenes via Two Concurrent Pathways

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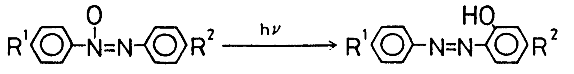
Synopsis. Naphthalene-1-*ONN*-azoxybenzenes and some unsymmetrically ortho-substituted *ONN*- and *NNO*-azoxybenzenes were prepared, and their photochemical behavior in ethanol was compared. The crowded azoxyarenes tend to undergo a facile Wallach rearrangement via the known *azoxy-ortho* oxygen mirgation and a concurrent pathway involving *ONN-NNO* isomerization. The relative contribution of the two pathways was affected by substituents.

The photo-Wallach rearrangement of azoxyarenes via azoxy-ortho migration of oxygen (Scheme 1) is established.[1] However, neither systematic study on the steric repulsion effect nor that on the electronic effect of unsymmetrical (*unsym-*) azoxyarenes has appeared because their *ONN* and *NNO* isomers have so far been difficultly accessible. The difficulty has recently been overcome by a convenient method for the independent preparation of *unsym*-azoxyarene isomers by the condensation of nitroarenes with aryliminodimagnesium reagent (ArN(MgBr)$_2$, aryl-IDMg, Scheme 2).[2]



Scheme 1.

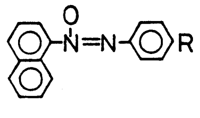
$$Ar^1NO_2 \quad + \quad Ar^2N(MgBr)_2 \longrightarrow$$

$$Ar^1N(O)=NAr^2 \quad + \quad Ar^1N=NAr^2 \quad + \quad Ar^2N=NAr^2$$

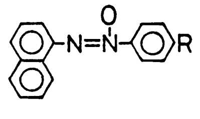
Scheme 2.

In this paper, the steric repulsion effect on the photoreactivity of crowded azoxyarenes and the directive effect of substituents on oxygen migration will be described. The azoxyarenes concerned are naphthalene-1-*NNO*-azoxybenzene ($\mathbf{1}^{H}_{NNO}$),[3] its more crowded *ONN*-isomer ($\mathbf{1}^{H}_{ONN}$), their *p*-Me and *p*-MeO derivatives ($\mathbf{1}^{Me}_{ONN}$ and $\mathbf{1}^{MeO}_{ONN}$), and some *o*-substituted *ONN*- and *NNO*-azoxybenzenes (**3** and **4**). The structure having an azoxy nitrogen combined to a bulky aryl group is indicated by *ONN*. Photochemical behavior was compared with one another and with that of non-crowded ones **2**. All the crowded and noncrowded azoxyarenes were prepared by the reaction of Scheme 2: $\mathbf{3}^{Et}_{NNO}$ was unavailable because of unsuccessful IDMg treatment (see Experimental).

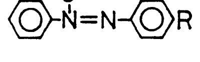
The azoxyarenes were dissolved in ethanol, introduced into quartz cells, and irradiated for 30 min by a high-pressure mercury lamp. In addition to the azoxy isomers, two photo-Wallach products were isolated. The normal product has an *o*-OH group on the benzene ring nearer to the original "azo" nitrogen, and the isomeric one has an *o*-OH group on the ring nearer to the original "azoxy" nitrogen (Scheme 1). Yields of isolated azoxy isomers, two Wallach products, and associated recoveries, based on amounts of azoxyarenes used, are given in Table 1 (Runs 1—11). When the azoxyarenes used in Runs 1—6 were irradiated in Pyrex glass cells of the same size, the yield of the normal Wallach product decreased by 4—11% and the recovery increased by 7—10%. By use of ordinary glass cells, additional decrease (1—5%) and increase (0—5%) were observed.



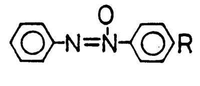
1^{H}_{ONN} : R = H
1^{Me}_{ONN} : R = Me
1^{MeO}_{ONN} : R = MeO



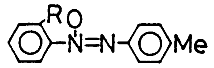
1^{H}_{NNO} : R = H
1^{Me}_{NNO} : R = Me



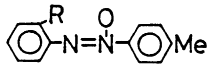
2^{Me}_{ONN} : R = Me
2^{MeO}_{ONN} : R = MeO



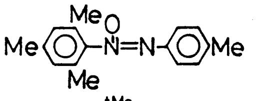
2^{Me}_{NNO} : R = Me
2^{MeO}_{NNO} : R = MeO



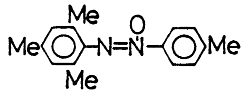
3^{Et}_{ONN} : R = Et
3^{MeO}_{ONN} : R = MeO



3^{Et}_{NNO} : R = Et
3^{MeO}_{NNO} : R = MeO



4^{tMe}_{ONN}



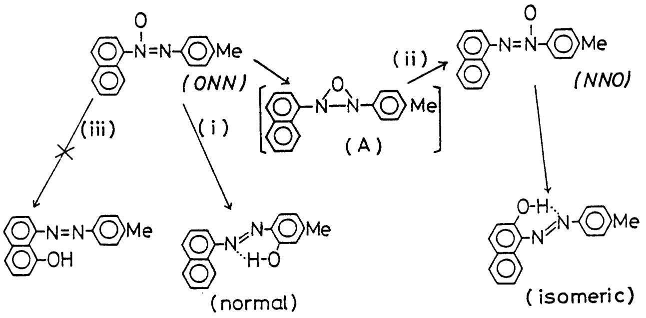
4^{tMe}_{NNO}

The higher reactivity of the crowded 1-naphthyl-*ONN* derivatives ($\mathbf{1}_{ONN}$), ascribable to the steric repulsion of *peri*-hydrogen, is shown by their recoveries (18 and 40%, Runs 1 and 2) lower than those of the noncrowded phenyl derivatives ($\mathbf{2}_{ONN}$ and $\mathbf{2}_{NNO}$, Runs 3—6). The latter are converted via the known pathway of Scheme 1. According to the "normal" pathway i) of Scheme 3, $\mathbf{1}^{Me}_{ONN}$ gave the normal Wallach product in higher yield (35%, Run 1) than $\mathbf{2}^{Me}_{ONN}$ (30%, Run 3). Participation of the other pathway ii) involving the *ONN-NNO* isomerization, probably via the oxadiaziridine intermediate **A**,[4,5] is shown by the isolation of an inseparable red oily mixture in 24% yield. The oil was composed of the less crowded $\mathbf{1}^{Me}_{NNO}$ and the "isomeric"

Table 1. Photochemical Rearrangement of Some Sterically Crowded Azoxyarenes

Run No.	Azoxyarenes $Ar^1N(O)=NAr^2$			Yield/%		Recovery/%
	No.	Ar^1	Ar^2	Wallach product	*NNO*-Isomer and/or isomeric Wallach product	
1	$\mathbf{1}^{\mathrm{Me}}_{\mathrm{ONN}}$	1-NaPh	*p*-MePh	35	24[a)]	18
2	$\mathbf{1}^{\mathrm{MeO}}_{\mathrm{ONN}}$	1-NaPh	*p*-MeOPh	33	low[b)]	40
3	$\mathbf{2}^{\mathrm{Me}}_{\mathrm{ONN}}$	Ph	*p*-MePh	30	0	54
4	$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{ONN}}$	Ph	*p*-MeOPh	25	0	60
5	$\mathbf{2}^{\mathrm{Me}}_{\mathrm{NNO}}$	*p*-MePh	Ph	27	0	51
6	$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{NNO}}$	*p*-Meph	Ph	17	0	77
7	$\mathbf{3}^{\mathrm{Et}}_{\mathrm{ONN}}$	*o*-EtPh	*p*-MePh	44	0	35
8	$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{ONN}}$	*o*-MeOPh	*p*-MePh	37	15	37
9	$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{NNO}}$	*p*-MePh	*o*-MeOPh	7[c)]	5[c)]	61[e)]
10	$\mathbf{4}^{\mathrm{tMe}}_{\mathrm{ONN}}$	2,4,6-Me_3Ph	*p*-MePh	22	42	9
11	$\mathbf{4}^{\mathrm{tMe}}_{\mathrm{ONN}}$	*p*-MePh	2,4,6-Me_3Ph	0	29[d)]	29[e)]

a) An oily mixture composed of the *NNO*-isomer and the corresponding Wallach product (see text). b) No *NNO*-isomer was isolated, but the formation was suggested (see text). c) Two isomeric Wallach products were obtained as an inseparable mixture. The minor one (5%) is the same as that obtained in Run 8. d) The product is the same as the Wallach product obtained in Run 10. e) Smaller overall amount due to unidentified decomposition products.



Scheme 3.

Wallach product (1-(4-methylphenylazo)-2-naphthol) in a molar ratio of 8 : 2 (see Experimental). Similarly, $\mathbf{1}^{\mathrm{MeO}}_{\mathrm{ONN}}$ gave the normal Wallach product in higher yield (33%, Run 2) than $\mathbf{2}^{\mathrm{MeO}}_{\mathrm{ONN}}$ (25%, Run 4). Neither the less crowded $\mathbf{1}^{\mathrm{MeO}}_{\mathrm{NNO}}$ nor the isomeric product was isolated from a small amount of complex mixture, but the second lowest amount of recovery among Runs 1—6 suggests a more or less participation of pathway ii). The conversion of *p*-MeO derivatives lower than that of the corresponding *p*-Me derivatives (Runs 1—6) is in accord with the electronic substituent effect of symmetrical azoxybenzenes.[6)]

Also in solid state, $\mathbf{1}_{\mathrm{ONN}}$'s are highly photosensitive as shown by color change of pure crystals from pale yellow into red even in an ordinary glass bottle placed under a fluorescent ceiling light. In the dark, their crystals or benzene solutions (even under refluxing) suffer no color change. All the other azoxyarenes used in this study were handled in the usual manner. Some effect of naphthalene ring sensitive to different wavelengths may also be responsible for the unique behavior of $\mathbf{1}_{\mathrm{ONN}}$'s. No existence of the alternative pathway iii) (Scheme 3) via the *azoxy-peri* oxygen migration[7)] was confirmed (see Experimental).

In the case of the *o*-substituted *ONN*-azoxybenzenes having a *p*′-Me group (Runs 7, 8, and 10) and their *NNO* isomers (Runs 9 and 11), the former are more reactive than the latter but the directive effects are somewhat complicated. Whereas $\mathbf{3}^{\mathrm{Et}}_{\mathrm{ONN}}$ reacts via the single pathway i), $\mathbf{3}^{\mathrm{MeO}}_{\mathrm{ONN}}$ reacts via the two pathways i) and ii). The highly crowded $\mathbf{4}^{\mathrm{tMe}}_{\mathrm{ONN}}$ was most easily converted, as shown by the lowest amount of recovery, to give the normal Wallach product and *NNO*-isomer via the two pathways. The lowest conversion of $\mathbf{1}^{\mathrm{MeO}}_{\mathrm{NNO}}$ is understandable because it may be electronically stabilized by the less hindered *o*′-MeO group[4)] (vide infra), but the reaction proceeds via the two pathways. Since $\mathbf{4}^{\mathrm{tMe}}_{\mathrm{NNO}}$ has no ortho-hydrogen essential to the "normal" rearrangement, the exclusive formation of the "isomeric" product in lower yield is explicable. The lower combined yields and recovery in Runs 9 and 11 arise from the partial decomposition leading to some unidentified materials.

The primary conclusion is that the crowded azoxyarenes undergo the facile rearrangement via the two pathways, whereas the less crowded ones react sluggishly via the single and normal pathway. The conclusion is reasonable because the oxadiaziridine intermediate[4,5)] is effective for the release of steric repulsion. With regard to the directive effect, the results of Runs 7 and 9 are exceptional to the conclusion, as seen from their contrast with those of Run 8. The comparably bulky *o*-Et and *o*-MeO groups exhibit the comparable reactivities but different directive effects. In conflict with no detection of the isomeric Wallach product from $\mathbf{2}^{\mathrm{MeO}}_{\mathrm{NNO}}$ (Run 6, vide supra), the normal and isomeric ones were previously isolated[4)] probably due to different conditions of irradiation. The quite low reactivity of $\mathbf{2}^{\mathrm{MeO}}_{\mathrm{NNO}}$ suggests that the previous result arises from the electronic stabilization of oxadiaziridine by the *p*′-MeO group. The conversion of $\mathbf{1}^{\mathrm{MeO}}_{\mathrm{ONN}}$ lower than that of $\mathbf{1}^{\mathrm{Me}}_{\mathrm{ONN}}$ is similarly explaina-

Table 2. Melting Points and ^{1}H NMR Data of "Normal" Wallach Products (*o*-Hydroxyazoarenes)

Product formed from (Run No.)	Mp θ_m/°C	^{1}H NMR Data/δ
$\mathbf{1}^{\mathrm{Me}}_{\mathrm{ONN}}$(1)	112—113	12.88 (1H, s), 8.44—8.56 (1H, m), 7.45-8.04 (7H, m), 6.80—6.94 (2H, m), 2.40 (3H, s).
$\mathbf{2}^{\mathrm{MeO}}_{\mathrm{ONN}}$(2)	134—136	14.38 (1H, s), 8.50—8.62 (1H, m), 7.56—8.10 (7H, m), 6.56—6.78 (2H, m), 3.92 (3H, s).
$\mathbf{3}^{\mathrm{Et}}_{\mathrm{ONN}}$(7)	80.5—82	12.63 (1H, s), 7.80—7.66 (2H, m), 7.33—7.00 (3H, m), 6.80—6.56 (2H, m), 2.96 (2H, q), 2.33 (3H, s), 1.33 (3H, s).
$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{ONN}}$(8)	128—128.5	13.13 (1H, s), 7.93—7.73 (2H, m), 7.63—6.60 (5H, m), 4.00 (3H, s), 2.36 (3H, s).
$\mathbf{3}^{\mathrm{MeO}}_{\mathrm{NNO}}$(9)[a)]	—	Pairs of singlets at 13.53 and 13.13, 4.00 and 3.90, and 2.36 and 2.28 were observed.
$\mathbf{4}^{\mathrm{tMe}}_{\mathrm{ONN}}$(10)	104.5—105	12.30 (1H, s), 7.50 (2H, d), 6.70—6.43 (3H, m), 2.36 (6H, s), 2.33 (3H, s), 2.23 (3H, s).

a) The mixture gave three pairs of OH, OCH_3, and CH_3 singlets. Relative intensities are recognized as the composition of the mixture.

ble. The exceptions and conflict ascribable to the electronic directive effect on oxygen migration possibly involving the mutual conversion of *unsym*-azoxy isomers via oxadiaziridine[5)] (see Scheme 3) remain to be studied.

Experimental

Azoxyarenes. The reactions of Scheme 2 were carried out as previously reported.[2)] The azoxyarenes were separated from the reaction mixture by column chromatography, and purified by recrystallization. Attempts to prepare $\mathbf{3}^{\mathrm{Et}}_{\mathrm{NNO}}$ were unsuccessful because the treatment of *p*-$MeC_6H_4NO_2$ with *o*-EtC_6H_4-IDMg gave only a trace amount and the treatment of *o*-$EtC_6H_4NO_2$ with *p*-MeC_6H_4-IDMg afforded only $\mathbf{3}^{\mathrm{Et}}_{\mathrm{ONN}}$ (vide infra). The *NNO*-derivative, $\mathbf{1}^{\mathrm{tMe}}_{\mathrm{NNO}}$ (Run 11), was obtained by the photoreaction of Run 10; it was also obtained by a lucky *ONN-NNO* isomerization in the reaction of *p*-MeC_6H_4-IDMg with 2,4,6-$Me_3C_6H_2NO_2$.[8)] The assignment of structures of *o*-substituted azoxyarenes and the product distributions in the reactions of Scheme 2 will be reported elsewhere.[8)]

Procedures. The photoreactions were carried out using 0.002 M (1 M=1 mol dm^{-3}) solution in spectro-grade ethanol.[6)] The quite low conversion in benzene and no effect of atmosphere were reported.[6)] The solutions in quartz cells were placed at a distance of 4.5 cm from a water-jacketted mercury lamp of a merrygo-round UV-irradiation apparatus, and were irradiated for 30 min at room temperature (15—20 °C). The amounts of Wallach products and recovered and/or isomeric azoxyarenes were determined by chromatographic separation and/or by comparison of intensities of ^{1}H NMR signals with those of authentic samples.

Products. The authentic samples for photo-Wallach products, *o*-hydroxyazoarenes, were obtained as the minor products of coupling reactions of appropriate aryldiazonium salts with phenolates (except 2-naphthol derivatives, which were obtained as major products). They were isolated from the filtrates of crystallization of the major *p*-hydroxyazoarenes by column chromatography (Wako Gel C-200 and C-300), and were purified by recrystallization. The melting points (uncorrected) and ^{1}H NMR data of the "normal" products in Runs 1, 2, and 7—10 are summarized in Table 2. The elemental analyses gave satisfactory results. The minor isomeric product in Run 9 is the same as the normal one obtained in Run 8, and the product in Run 11 is the same as the normal one obtained in Run 10. The products obtained in Runs 3—6 are known.[4,9)]

The composition of the inseparable mixture of $\mathbf{1}^{\mathrm{Me}}_{\mathrm{NNO}}$ and "isomeric" product (Run 1) was estimated from the relative intensities of two Me-proton ^{1}H NMR signals. The authentic sample of alternative *azoxy-peri* oxygen migration (cf. Run 1) was prepared in low yield by treating 8-nitro-1-naphthol[10)] with a large excess of *p*-MeC_6H_4-IDMg.

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