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Reaction of Aromatic Azo Compounds with Ozone

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SUMMARY

Ozonization of azobenzenes in chlorinated solvents gave 2-chloroazobenzene, 4-chloroazobenzene, azoxybenzene, glyoxal and hygroscopic compounds, whilst similar reaction of phenylazonaphthalenes and azonaphthalenes gave only limited formation of azoxy derivatives. The reaction of a series of azobenzenes with ozone to give azoxybenzenes was investigated with particular respect to substituent and solvent effects.

1 INTRODUCTION

In the reaction of multiple bonds with ozone, those of the azo group have received only limited attention.[1] Nevertheless, the reaction is of interest both from the viewpoint of ozone-fading of dyeings and from that of the reaction mechanisms involved. Ozone acts as a 1,3-dipole, electrophile, and electron acceptor[2] and since the nitrogen atoms of azo compounds have lone-pair electrons, the formation of the N—O bond is expected. We discuss here primarily the formation of azoxybenzenes by the reaction of azobenzenes with ozone (ozonization).

2 EXPERIMENTAL

2.1 General

Ozone was generated by a Nihon Ozon 0-1-2 type ozonizer, ultraviolet and mass spectra were measured with Hitachi EPS-3T, and Hitachi M-52

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TABLE 1
Materials

Run	*Compound*[a]	*Symbol*	*M.p. (°C)*	
			Observed	*Literature*
1	Azobenzene	**1a**	68·0–68·5	68[3]
2	2-Chloroazobenzene	**1b**	30·0–30·5	33[4]
3	3-Chloroazobenzene	**1c**	65·0–67·0	67·5[5]
4	4-Chloroazobenzene	**1d**	87·0–88·0	87·5[5]
5	4-Bromoazobenzene	**1e**	88·5–89·5	89[5]
6	4-Ethoxyazobenzene	**1f**	77·0–77·5	85[6]
7	4-Methoxyazobenzene	**1g**	51·5–54·0	54[6]
8	4-Methylazobenzene	**1h**	68·5–69·5	72[7]
9	4-Nitroazobenzene	**1i**	134·0–135·0	134–135[8]
10	4-Chloro-4′-methylazobenzene	**1j**	154·0–155·0	152[9]
11	4,4′-Dichloroazobenzene	**1k**	186·5–188·0	187·5–188·5[9]
12	4,4′-Dimethylazobenzene	**1l**	143·5–144·5	144–145[10]
13	Azoxybenzene	**2a**	35·0–35·5	36[11]
14	3-Chloro-*ONN*-azoxybenzene	**2c**	Oil	23·5–24·0[12]
15	4-Chloro-*ONN*-azoxybenzene	**2d**	79·5–80·0	82[13]
16	4-Bromo-*ONN*-azoxybenzene	**2e**	94·5–95·0	92–93[14]
17	4-Ethoxy-*ONN*-azoxybenzene	**2f**	74·0–75·0	76·0–76·5[14]
18	4-Methoxy-*ONN*-azoxybenzene	**2g**	51·0–52·0	53–54[12]
19	4-Methyl-*ONN*-azoxybenzene	**2h**	64·0–64·5	62·0–64·5[12]
20	4-Nitro-*ONN*-azoxybenzene	**2i**	150·0–152·0	150[15]
21	4-Chloro-4′-methyl-*ONN*-azoxybenzene	**2j**	108·0–109·5	109·5[13]
22	4,4′-Dichloroazoxybenzene	**2k**	155·0–155·5	154–156[12]
23	4,4′-Dimethylazoxybenzene	**2l**	68·0–68·5	68–69[12]
24	2-Chloro-*NNO*-azoxybenzene	**3b**	Oil	—
25	3-Chloro-*NNO*-azoxybenzene	**3c**	53·0–54·0	53·0–53·5[12]
26	4-Chloro-*NNO*-azoxybenzene	**3d**	67·0–67·5	68[13]
27	4-Bromo-*NNO*-azoxybenzene	**3e**	72·5–73·0	73·0–73·5[14]
28	4-Ethoxy-*NNO*-azoxybenzene	**3f**	72·0–73·5	73–74[14]
29	4-Methoxy-*NNO*-azoxybenzene	**3g**	71·0–72·0	72[13]
30	4-Methyl-*NNO*-azoxybenzene	**3h**	50·5–51·5	50[13]
31	4-Nitro-*NNO*-azoxybenzene	**3i**	152·0–154·0	156[15]
32	4-Chloro-4′-methyl-*NNO*-azoxybenzene	**3j**	107·0–108·0	107[13]
33	Glyoxal bis(phenylhydrazone)	**5**	166·0–168·0	169–170[16]
34	1-Phenylazonaphthalene	**6**	66·5–67·0	70[17]
35	1-(Phenyl-*ONN*-azoxy)naphthalene	**7**	83·5–84·0	82·5–84·0[12]
36	1-(Phenyl-*NNO*-azoxy)naphthalene	**8**	70·0–71·0	69·5–71·0[12]
37	2-Phenylazo-naphthalene	**9**	81·0–82·0	84[17]
38	2-(Phenyl-*ONN*-azoxy)naphthalene	**10**	123·0–125·5	125[17]
39	2-(Phenyl-*NNO*-azoxy)naphthalene	**11**	118·0–118·5	117[17]
40	1,1′-Azonaphthalene	**12**	188·5–190·5	190[17]
41	2,2′-Azonaphthalene	**13**	203·0–205·0	208[17]

[a] All compounds except **2c**, **3b** and **5** were recrystallized from ethanol. The azoxybenzenes **2c** and **3b** were purified by column chromatography. The hydrazone **5** was recrystallized from toluene.

spectrometers respectively. Gas and liquid chromatography were performed on Shimadzu 8APF, and Jasco Familic-100N chromatographs respectively. Melting points were measured with a Yanagimoto MP-S2 micro-melting point apparatus and are uncorrected.

2.2 Materials

Materials used were prepared as described in the literature and their purity was confirmed by gas chromatography. Relevant data are shown in Table 1.

2.3 Ozonization reaction

The reaction was carried out with an ozone–nitrogen mixture (nitrogen: 100 ml min^{-1}) on 0·55 mmol of substrate in 50 ml of solvent. The reaction mixture was treated as outlined in Fig. 1. It was divided into two parts. Using

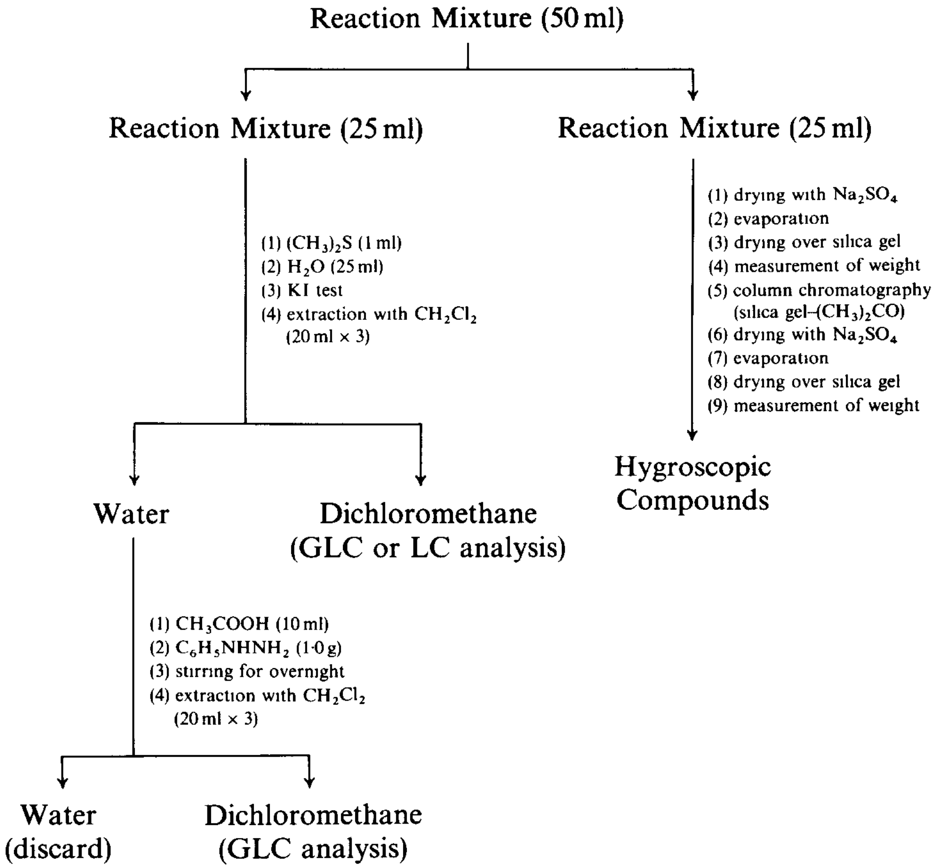


Fig. 1. Analytical procedure.

one part, the hygroscopic compounds produced during the reaction were determined by measuring the weight before and after column chromatography treatment (silica gel–acetone). To the other half of the reaction mixture, dimethyl sulfide was added. The disappearance of peroxide activity was checked by a KI test. The reaction products were then extracted with dichloromethane. The analysis of this solution gave 2- and 4-chloroazobenzenes (**1b** and **1d**, respectively) and azoxybenzene (**2a**). The water layer was further treated with phenylhydrazine and extracted with dichloromethane. The analysis of this solution gave glyoxal bis(phenylhydrazone) (**5**). The product was identified by comparing the mass spectrum with that of an authentic sample.

Product determination was also carried out by gas or liquid chromatography. The conditions in the analysis were as follows: (a) GLC 1, 1 m × 3 mm, 2% Silicone OV-1 on Gas Chrom Q (60–80 mesh), programmed from 80°C to 240°C at 10°C min^{-1}, FID; (b) GLC 2, 1 m × 3 mm, 5% FFAP on Gas Chrom Q (80–100 mesh), programmed from 80°C to 210°C at 10°C min^{-1}, FID; (c) GLC 3, 50 m × 0·24 mm, SS-10, 210°C, FID; (d) GLC 4 25 m × 0·24 mm, Silicone OV-1, 220°C, FID; (e) LC (1), 0·15 m × 0·5 mm, SS-10, dichloromethane, 10 μl min^{-1}, 254 nm; and (f) LC (2), 0·15 m × 0·5 mm, SS-10, carbon tetrachloride, 10 μl min^{-1}, 254 nm.

3 RESULTS AND DISCUSSION

The ozonization reactions of aromatic azo compounds are summarized in Table 2. The reactions were complicated and the reactivity of azobenzene (**1a**) with ozone was small. When **1a** was treated with four equimolar amounts of ozone in dichloromethane at 0°C, 25% of **1a** reacted to give 2-chloroazobenzene (**1b**), 4-chloroazobenzene (**1d**), azoxybenzene (**2a**), and glyoxal (**4**) (run 1). Yellow hygroscopic compounds which showed the presence of a chlorine atom by a Beilstein test were also produced during the reaction (run 1). These hygroscopic compounds were not identified.

Azoxybenzene (**2a**) was a main product in the ozonization of **1a** (runs 1–7). The yields of **1b** and **1d** in dichloromethane and chloroform were greater than those in carbon tetrachloride (runs 1, 6 and 7). As the reaction proceeded, the yield of **2a** decreased, while that of the hygroscopic compounds increased (runs 1–3). Likewise, the ozonization of **2a** gave **4** and hygroscopic compounds (run 8). The higher the reaction temperature, the greater was the yield of the hygroscopic compounds (runs 1, 4 and 5). Phenylazonaphthalenes reacted readily with ozone but gave only low yields of the phenylazoxynaphthalene isomers (runs 9 and 10). Azonaphthalenes reacted more readily with ozone than phenylazonaphthalenes but in this

TABLE 2

Ozonization of Aromatic–Aromatic Azo Compounds[a]

Run	*Sub-strate*	*Solvent*	*Temp. (°C)*	*Ozone introduced (mmol)*	*Conversion (%)*	*Yield*[b] (%)							*Hygroscopic compounds (mg)*
						1b	***1d***	***2a***	***4***	***7***	***8***	***10, 11***	
1	**1a**	CH_2Cl_2	0	2·10	25	10	2	12	2	—	—	—	33
2	**1a**	CH_2Cl_2	0	3·26	49	5	2	9	2	—	—	—	45
3	**1a**	CH_2Cl_2	0	5·55	70	3	1	6	2	—	—	—	83
4	**1a**	CH_2Cl_2	−20	3·57	32	1	1	10	2	—	—	—	28
5	**1a**	CH_2Cl_2	−78	3·38	34	Trace	Trace	10	1	—	—	—	2
6	**1a**	$CHCl_3$	0	1·05	24	9	3	23	2	—	—	—	18
7	**1a**	CCl_4	0	3·42	24	Trace	Trace	13	1	—	—	—	22
8	**2a**	CH_2Cl_2	0	3·62	38	—	—	—	2	—	—	—	40
9	**6**	CH_2Cl_2	0	0·09	22	—	—	—	1	1	Trace	—	7
10	**9**	CH_2Cl_2	0	0·10	27	—	—	—	—	—	—	3[c]	9
11	**12**	CH_2Cl_2	0	0·11	34	—	—	—	—	—	—	—	6
12	**13**	CH_2Cl_2	0	0·12	48	—	—	—	—	—	—	—	10

[a] Ozonization was carried out with an ozone–nitrogen mixture on 0·55 mmol of substrate in 50 ml of solvent.

[b] Yield was based on the substrate reacted.

[c] Mixture.

case the reaction was more complicated and the azoxynaphthalenes were not produced (runs 11 and 12).

Oxidation of unsymmetrical azobenzenes gives azoxy isomers. The selectivity of the reaction is defined by the relationship (1).

$$\text{Selectivity} = ONN/NNO \qquad (1)$$

where *ONN* and *NNO* are the yields of *ONN*- and *NNO*-azoxybenzenes, respectively. In order to determine the selectivity, the azoxybenzene isomers **2c**–**2j** and **3b**–**3j** were synthesized. 2-Chloro-*ONN*-azoxybenzene (**2b**) was not synthesized. However, since the most prominent fragmentation process of azoxybenzenes occurs by cleaving the C—N bond α to the N—O group with the charge mainly retained in the aromatic system, the azoxybenzene **2b** formed in the ozonization of **1b** was identified by comparing the mass spectrum with that of **3b**.[18] The result was as follows: **2b** (20 eV) m/z (relative intensity) 232 (M^+; 28), 111 ($C_6H_4Cl^+$; 100), and 77 ($C_6H_5^+$; 49). **3b** (20 eV) m/z (relative intensity) 232 (M^+; 6), 197 ($M^+ - Cl$; 100), 111 ($C_6H_4Cl^+$; 10), and 77 ($C_6H_5^+$; 99).

The solvent effect on the selectivity was examined and the results are shown in Table 3. The parameters of the selectivity were calculated to be 0·8–0·9, suggesting that there was no solvent effect on the selectivity (runs 1–7).

The substituent effect on the selectivity was then examined and the results are shown in Table 4. Ozonization of 4,4′-dimethyl-, and 4,4′-dichloroazobenzenes gave the corresponding azoxybenzenes in 9 and 32% yield respectively (runs 1 and 2). The yields increased in the order of substituent,

TABLE 3
Solvent Effect on the Formation of Isomeric 4-Chloroazoxybenzenes[a]

Run	*Solvent*	*Ozone introduced (mmol)*	*Conversion (%)*	*Yield[b] (%)*		*Selectivity (ONN/NNO)*
				ONN	*NNO*	
1	CCl_4	2·93	27	10	12	0·8
2	$CHCl_3$	0·92	25	12	13	0·9
3	CH_2Cl_2	0·81	26	8	9	0·9
4	MeOH	2·04	24	14	15	0·9
5	AcOEt	1·55	24	14	16	0·9
6	C_6H_{14}	4·34	19	21	23	0·9
7	AcOH	2·14	17	3	4	0·8

[a] Ozonization was carried out with an ozone–nitrogen mixture on 0·2 mmol of 4-chloroazobenzene (**1d**) in 50 ml of solvent at 0°C.

[b] Yield was based on the substrate reacted with ozone.

[c] At 20°C.

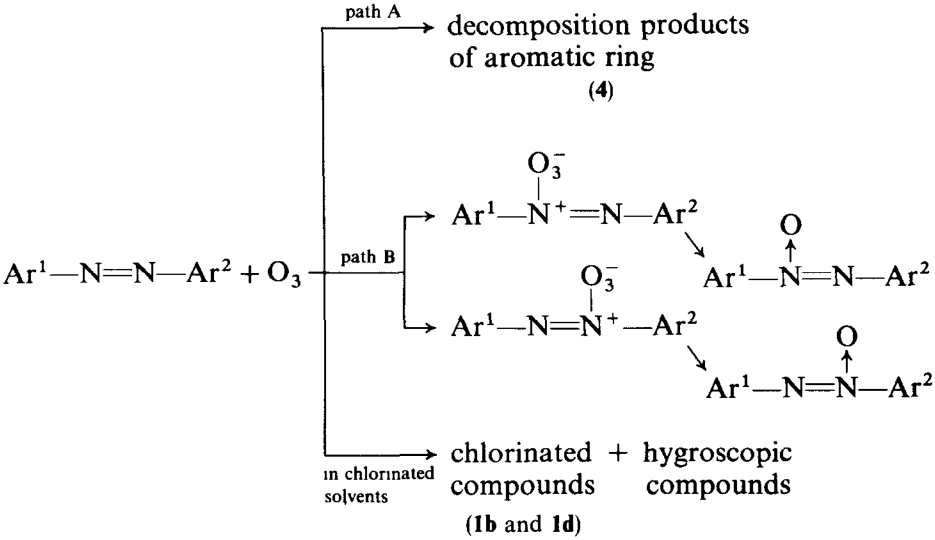
TABLE 4
Substituent Effect on the Formation of Isomeric Azoxybenzenes[a]

Run	*Substrate*	*Conversion* (%)	*Yield*[b] (%)		*Selectivity* (*ONN*/*NNO*)
			ONN	*NNO*	
1	**1k**	24	32		—
2	**1l**	63	9		—
3	**1d**	27	10	12	0·8
4	**1h**	38	11	9	1·2, 1·22[c]
5	**1e**	34	8	10	0·8
6	**1f**	56	4	3	1·3
7	**1g**	53	3	2	1·5, 1·78[c]
8	**1i**	28	12	29	0·4
9	**1j**	40	6	7	0·4
10	**1b**	40	7	27	0·4
11	**1c**	37	10	15	0·7

[a] Ozonization was carried out with an ozone–nitrogen mixture (ozone: 2·9 mmol, nitrogen: 150 ml min^{-1}) on 0·2 mmol of substrate in 50 ml of carbon tetrachloride at 0°C.
[b] Yield was based on the substrate reacted with ozone.
[c] Reference 19.

4,4′-dimethyl < 4-methyl < 4-chloro < 4,4′-dichloro, suggesting that the lower the reactivity of the aromatic ring with ozone, the greater was the yield of the azoxybenzenes (runs 1–4). Ozonization of 4-chloro-, 4-bromo, 4-ethoxy- and 4-methyl-azobenzenes showed no significant selectivity (runs 3–6) but those of 4-methoxy-, 4-nitro-, and 4-chloro-4′-methyl-azobenzenes showed a marked selectivity (runs 7–9). The selectivity by ozonization is less than that by perbenzoic acid (runs 4 and 7). These results suggest that the electronic effect of the substituent plays an important role in the selectivity. When 2-, 3- and 4-chloroazobenzenes were ozonized, the selectivity increased in the substitution order $4 < 3 < 2$, suggesting that steric hindrance is also an important factor in the selectivity (runs 3, 10 and 11).

A probable ozonization mechanism of aromatic azo compounds is shown in Scheme 1. Ozone electrophilically attacks not only the aromatic rings (path A), but also the nitrogen atoms (path B). When an electron-donor substituent is present in the azobenzenes, the ozone attack to the aromatic ring is enhanced. Since the oxidation potential of azobenzene is too high ($E^{\text{ox}}_{1/2} = 1{\cdot}82\,\text{V}$ versus SCE in acetonitrile) to induce an electron-transfer reaction, ozone does not therefore act as an electron acceptor in this reaction.[20] In the case of path B, ozone preferentially attacks the more electron-rich nitrogen atom and the azoxy isomers are produced via the corresponding ozone adducts. The azoxy compounds are then further



Scheme 1. Ozonization mechanism.

ozonized to give glyoxal and hygroscopic compounds. Since the ozonization of azobenzene (**1a**) gave 2-chloroazobenzene (**1b**) and 4-chloroazobenzene (**1d**), the yields of which were greater in dichloromethane and chloroform than those in carbon tetrachloride, a chlorine atom must be produced during the reaction. The formation of a chlorine ion during the ozonization reaction has been previously reported.[21] The chlorine atom and/or ion reacts with nitrogen-containing compounds formed during the reaction to give the unidentified yellow hygroscopic compounds observed during the course of this present work.

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