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Formic Acid Reduction. VIII.[1] Reduction of Nitrosobenzenes to Azoxybenzenes

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TMAF, $5HCO_2H \cdot 2N(CH_3)_3$ was found to be efficient reagent for reduction of nitrosobenzenes to azoxybenzenes. Reductions of a variety of nitrosobenzenes revealed the usefulness of the method for the preparation of azoxybenzenes. Comments on the course of the reduction are given.

With the recent development[1,3-8] of the trialkylammonium formates, constant boiling liquids, which are generally represented by $5HCO_2H \cdot 2NR_3$, as reducing agents, it became of interest to investigate other potential uses of these reagents. It has now been found that reduction of aromatic nitroso compounds to azoxybenzenes can be effected with the reagent, $5HCO_2H \cdot 2N(CH_3)_3$, bp 92° (18 mmHg), abbreviated by TMAF.

A number of benzenoid nitroso compounds with varying substituents on the aromatic rings were submitted to the reduction. Yields and reactivities were compared by carrying out the processes under standard conditions as follow: a mixture of nitroso compound and a large excess of TMAF was heated on a boiling water bath, while the reaction set in as evidenced by the emission of carbon dioxide. The results are summarized in Table I. In most cases, excellent yields of azoxybenzenes were obtained, revealing the efficiency of the method for their preparation. As it can be seen from the reductions of *o*-, *m*- and *p*-nitronitrosobenzene in Table I, the reduction was selective at the nitroso groups, the nitro groups of the substrate not being concerned in the process. The case of the substrate possessing *o*-NO_2, *p*-$N(CH_3)_2$ or *p*-$C_5H_{10}N$ as a substituent made an exception to the above, being distinguishable from the others by more exothermic reactions and formation of the by-products, blackish amorphous materials, which were not investigated further, and formylamino reduction product, in one case, accompanied with free amine reduction product.

As it can be deduced from the observation of the carbon dioxide emission during the course of the reactions, formic acid as a component of TMAF participates in the reducing courses leading to azoxybenzenes. Nevertheless, if in place of TMAF 99% formic acid was used under the same conditions, in an experiment with nitrosobenzene, no azoxybenzene was obtained resulting only in formation of resinous materials.

In the course of the reduction giving azoxybenzene, the following two-step process, involving phenylhydroxylamine as an intermediate, may be adopted on the basis of the facts described below.

$$ArN{=}O + HCO_2H \longrightarrow ArNHOH + CO_2 \qquad (1)$$

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[1] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 810 (1969).
[2] Location: *2-2-1, Oshika, Shizuoka.*
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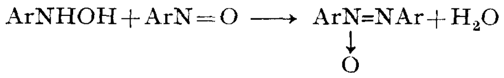
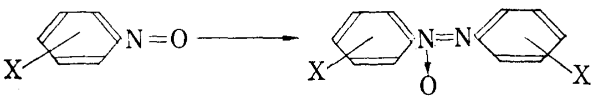
[7] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 747 (1969).
[8] M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 752 (1969).



$$ArNHOH+ArN{=}O \longrightarrow \underset{\substack{\downarrow\\ O}}{ArN{=}NAr}+H_2O \qquad (2)$$

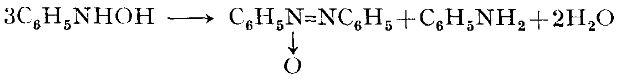
The step (2) has been described in several papers[9] and is known to proceed generally in the presence of base. In TMAF medium this step was also substantiated with phenylhydroxylamine and nitrosobenzene to proceed easily and quantitatively even at low temperature. Phenylhydroxylamine is known[10] to be very sensitive to acids, giving *p*-aminophenol and a number of by-products. Phenylhydroxylamine in 99% formic acid gave a blackish resinous material, also in the presence of nitrosobenzene, as it has been observed in the above mentioned experiment when heating nitrosobenzene in 99% formic acid. On heating at 98—100° in TMAF phenylhydroxylamine gave azoxybenzene and formanilide in 15% and 49% yield, respectively. This reaction implies an occurrence of the disproportionation reaction, which has already been known[11] to take place in neutral or basic medium. However, this reaction cannot be considered as main intermediate course of the reaction of nitrosobenzene with TMAF, because in the several runs almost no formation of formanilide was observed as shown in Table I.

TABLE I. Formation[a] of Azoxybenzenes from Nitrosobenzenes



No.	X	Yield (%) Azoxy compound	Yield (%) Formamido compound
1	p-NO_2	89	
2	m-NO_2	97	
3[b]	o-NO_2	21	19.5[c]
4	p-CO_2Et	97	
5	m-CO_2Et	93	
6	p-Cl	93	
7	m-Cl	93	
8	o-Cl	94	
9	p-H	92	
10	p-CH_3	95	
11	m-CH_3	92	
12	o-CH_3	93	
13[b]	p-OEt	85	
14[b]	p-NMe_2	7	30
15[b]	p-$C_5H_{10}N$	9	40

a) General procedures are given in Experimental.
b) In these runs side-reactions occured and gave blackish amorphous materials.
c) This yield is given by summing up both the products, *o*-nitroformanilide (6.5 %) and *o*-nitroaniline (13 %).



$$3C_6H_5NHOH \longrightarrow \underset{\substack{\downarrow\\ O}}{C_6H_5N{=}NC_6H_5}+C_6H_5NH_2+2H_2O$$

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[9] S. Oae, T. Fukumoto and M. Yamagami, *Bull. Chem. Soc. Japan*, **36**, 728 (1963); M.M. Shemyakin, V.A. Maimind and B.K. Vaichunaite, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1957**, 1260 [*C.A.*, **52**, 6231*h* (1958)]; S. Jozkiewicz, *Trav. Soc. Sci. lettres Wroclaw*, Ser. B, No. **73**, 48 (1956) [*C.A.*, **52**, 3711*f* (1958)].

[10] S. Okazaki and M. Okumura, quated by S. Oae, T. Fukumoto and M. Yamagami, *Bull. Chem. Soc. Japan*, **36**, 601 (1963); E.T. Hughes and C.K. Ingold, *Quarterly Revs.*, **6**, 45 (1952).

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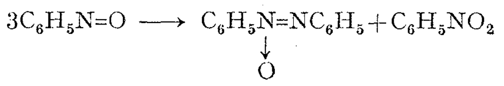
In a previously published paper, it has been reported,[12] with several examples, that azoxybenzenes are also formed when heating nitrosobenzenes with formamide. A further investigation of this reaction was made in relation to the TMAF reduction. We began with an experiment with nitrosobenzene using acetamide in place of formamide and found that a reaction proceeds to give nearly equimolar amounts of azoxybenzene and nitrobenzene. Evidently this reaction is recognized as the disproportionation, comprehended previously.[13]



$$3C_6H_5N{=}O \longrightarrow C_6H_5\underset{\underset{O}{\downarrow}}{N}{=}NC_6H_5 + C_6H_5NO_2$$

Table II. Reaction[a] of Nitrosobenzene with Amide

Amide	Yield[b]	
	$PhNO_2$	$Ph\underset{\underset{O}{\downarrow}}{N}{=}NPh$
CH_3CONH_2	0.25	0.303
$HCONH_2$	0.09	0.34

a) molar ratio of amide to nitrosobenzene: 10/1 (0.1 mole); reaction temperature: 95—100°

b) Yields are described as molar equivalent estimated from one mole of the starting nitrosobenzene. In both runs unknown resinous materials are also obtained as by-products.

Taking account of this fact, reexamination of the formamide reaction was made with an expectation to obtain nitrobenzene other than azoxybenzene. The result is shown in Table II together with that of the acetamide reaction for comparison. As the amount of the nitrobenzene was much smaller than that of the acetamide reaction, the above mentioned disproportionation reaction was shown also to occur in some extent. Formamide itself is known to be inert to reduction reaction. Greater formation of azoxybenzene is presumed to be induced by the action of small amount of ammonium formate which is unavoidably contaminated in formamide and can recycle from formamide and water formed in the reaction.

Experimental

General Procedure for the Reduction of Nitrosobenzenes with TMAF——The following aromatic nitroso compounds, which were purified as it can be seen from the following melting points, were used as substrates: *p*-nitronitrosobenzene[14] (mp 117—118°), *m*-nitronitrosobenzene[15] (mp 89—90°), *o*-nitronitrosobenzene[15] (mp 125—126°), *p*-ethoxycarbonylnitrosobenzene[16] (mp 79—80°), *m*-ethoxycarbonylnitrosobenzene[15] (mp 52—53°), *p*-chloronitrosobenzene[17] (mp 87—88°), *m*-chloronitrosobenzene[15] (mp 71—72°), *o*-chloronitrosobenzene[15] (mp 54—55°), nitrosobenzene[18] (mp 67—68°), *p*-methylnitrosobenzene[17] (mp 47—48°), *m*-methylnitrosobenzene[15] (mp 52—53°), *o*-methylnitrosobenzene[15] (mp 72°), *p*-ethoxynitrosobenzene[19] (mp 33—34°), *p*-nitrosodimethylaniline[20] (mp 85°), N-(*p*-nitrosophenyl)piperidine[21] (mp 52—53°).

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15) This was prepared by the same procedure as that of the *p*-substituted compound.

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19) A. Rising, *Chem. Ber.*, 37, 46 (1904).

20) G.M. Bennett and E.V. Bell, "Organic Syntheses," Coll. Vol. II, ed. by A.H. Blatt, John Wiley and Sons, Inc., New York, N.Y., 1943, p. 223.

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In a flask provided with an air condenser tube and a thermometer, a mixture of 0.05 mole of a nitroso compound and 69.6 g (1.0 mole as HCO_2H) of TMAF was heated on a boiling water bath with stirring; a constant stream of air free from CO_2 was passed in order to check the transfer of the CO_2 emitted by barium hydroxide solution. The reactions were exothermic and ended (2—4 hr in most cases) when the emission was almost ceased. In most cases azoxy compound formed was almost completely crystallized in the reaction mixture on cooling. After allowing the flask to stand overnight in a refrigerator, the crystals were collected by filtration, washed with water, dried and weighed. The resulting product was almost pure without any recrystallization. In the case of *m*-methylnitrosobenzene, the product was separated by distillation of the reaction mixture, as it was released in an oily state. The runs with *p*-nitrosodimethylaniline, *N*-(*p*-nitrosophenyl)piperidine and *o*-nitronitrosobenzene made exceptions to the above procedures. In these cases, formamido compounds (the presense of free amino compound was seen in case of *o*-nitronitrosobenzene) and blackish amorphous materials were obtained in addition to the azoxy compound. In addition, the reaction of *p*-nitrosophenol under the above described condition, resulted in no formation of azoxy compound but that of a blackish amorphous product which was not investigated further.

Yields of the products obtained in the above experiments are listed in Table I and physical data and identities of the products are described in the following.

4,4′-Dinitroazoxybenzene: Yellow needles from EtOH, mp 188—190° (lit.[22] mp 192°). *Anal.* Calcd. for $C_{12}H_8O_5N_4$: C, 50.00; H, 2.80; N, 19.44. Found: C, 50.09; H, 2.67; N, 19.38. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 270 (4.07), 345 (4.29) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 227, 267, 281, 342).

3,3′-Dinitroazoxybenzene: Yellow needles from EtOH, mp 146—147° (lit.[22] mp 143°). *Anal.* Calcd. for $C_{12}H_8O_5N_4$: C, 50.00; H, 2.80; N, 19.44. Found: C, 50.02; H, 2.89; N, 19.70. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 257 (4.36), 318 (4.16) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 251, 257, 314, 324).

2,2′-Dinitroazoxybenzene: The reaction was exothermic. Filtration of the reaction mixture gave azoxy compound, yellow plates from $CHCl_3$; mp 174—175° (lit.[23] mp 175.5°). *Anal.* Calcd. for $C_{12}H_8O_5N_4$: C, 50.00; H, 2.80; N, 19.44. Found: C, 49.96; H, 2.88; N, 19.56. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 240s (3.43), 304 (3.69). The filtrate was concentrated under reduced pressure to remove excess of TMAF. The blackish tarry residue was extracted with $CHCl_3$ and after evaporation of the solvent, the residue was fractionally distilled under reduced pressure to give two substances: (A) bp 96—103° (0.14 mmHg); red brown needles, mp 68—69° (lit.[24] mp 69.7°), which was identified as *o*-nitroaniline. (B) bp 103—105° (0.14 mmHg); yellow needles from EtOH, mp 122—123° (lit.[25] mp 122°), which was identified as *o*-nitroformanilide.

4,4′-Diethoxycarbonylazoxybenzene: Yellow needles from EtOH, mp 115—123° (lit.[26] mp 114.5—121.5°). *Anal.* Calcd. for $C_{18}H_{18}O_5N_2$: C, 63.15; H, 5.30; N, 8.18. Found: C, 63.05; H, 5.36; N, 8.04. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 268 (4.09), 337 (4.30).

3,3′-Diethoxycarbonylazoxybenzene: Orange prisms from EtOH, mp 75—77° (lit.[27] mp 78°). *Anal.* Calcd. for $C_{18}H_{18}O_5N_2$: C, 63.15; H, 5.30; N, 8.18. Found: C, 63.12; H, 5.37; N, 8.12. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 224.5 (4.49), 243s (4.26), 324 (4.19).

4,4′-Dichloroazoxybenzene: Yellow needles from EtOH, mp 154—155° (lit.[22] mp 155—156°). *Anal.* Calcd. for $C_{12}H_8ON_2Cl_2$: C, 53.95; H, 3.02; N, 10.48; Cl, 26.55. Found: C, 53.98; H, 3.08; N, 10.55; Cl, 26.86. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 226s (3.96), 238 (4.01), 245s (3.97), 273s (3.92), 334 (4.27) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 223, 236, 330).

3,3′-Dichloroazoxybenzene: Yellow needles from EtOH, mp 96—97° (lit.[22] mp 96°). *Anal.* Calcd. for $C_{12}H_8ON_2Cl_2$: C, 53.95; H, 3.02; N, 10.48; Cl, 26.55. Found: C, 53.97; H, 3.25; N, 10.82; Cl, 26.60. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 232s (4.10), 243s (4.40), 258s (3.94), 324 (4.19) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 227, 236, 251, 324).

2,2′-Dichloroazoxybenzene: Yellow needles from EtOH, mp 53—54° (lit.[22] mp 55—56°). *Anal.* Calcd. for $C_{12}H_8ON_2Cl_2$: C, 53.95; H, 3.02; N, 10.48; Cl, 26.55. Found: C, 54.18; H, 3.26; N, 10.52; Cl, 26.85. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 236 (4.03), 308 (3.89) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 223, 304).

Azoxybenzene: Yellow needles from EtOH, mp 36° (lit.[12] mp 34—35°). UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 228s (3.90), 232 (3.96), 238s (3.91), 262 (3.88), 323 (4.20) (lit.[28] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 231, 261, 323).

4,4′-Dimethylazoxybenzene: Yellow needles from EtOH, mp 66—68° (lit.[29] mp 71°). *Anal.* Calcd. for $C_{14}H_{14}ON_2$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.81; H, 6.23; N, 12.69. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 225s (3.88), 234s (3.97), 238 (3.98), 244s (3.92), 270s (3.84), 334 (4.29) (lit.[22] UV $\lambda_{\max}^{\text{EtOH}}$ mμ: 227, 236, 330).

3,3′-Dimethylazoxybenzene: After the reaction the mixture was concentrated under reduced pressure to remove excess of TMAF. The resulting residue was distilled under reduced pressure to give azoxy com-

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pound, bp 150—153° (0.15 mmHg); yellow needles from MeOH, mp 34° (lit.[30] mp 37°). *Anal.* Calcd. for $C_{14}H_{14}ON_2$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.37; H, 6.17; N, 12.44. UV λ_{max}^{EtOH} mμ (log ε): 234 (3.96), 242s (3.89), 265 (3.84), 327 (4.16).

2,2′-Dimethylazoxybenzene: Yellow needles from EtOH, mp 58—59° (lit.[22] mp 60°). *Anal.* Calcd. for $C_{14}H_{14}ON_2$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.34; H, 6.20; N, 12.27. UV λ_{max}^{EtOH} mμ (log ε): 235 (3.96), 250s (3.81), 312 (3.95) (lit.[22] UV λ_{max}^{EtOH} mμ: 228, 238, 312).

4,4′-Diethoxyazoxybenzene: Orange yellow needles from EtOH, mp 136—163° (lit.[12] mp 138—166°). *Anal.* Calcd. for $C_{16}H_{18}O_3N_2$: C, 67.11; H, 6.34; N, 9.78. Found: C, 67.42; H, 6.44; N, 9.60. UV λ_{max}^{EtOH} mμ (log ε): 224 (3.698), 360 (4.14).

4,4′-Di(dimethylamino)azoxybenzene: The reaction was considerable exothermic. Azoxy compound was obtained by filtration of the reaction mixture. Orange prisms from benzene, mp 239—240° (lit.[12] mp 237—240°). *Anal.* Calcd. for $C_{16}H_{20}ON_4$: C, 67.58; H, 7.09; N, 19.71. Found: C, 67.51; H, 7.00; N, 19.65. UV λ_{max}^{EtOH} mμ (log ε): 242 (4.09), 324 (3.75), 427 (4.58). The filtrate was concentrated under reduced pressure to remove excess of TMAF. The blackish tarry residue was extracted with 5% AcOH. After decolorization with charcoal and concentration, the solution was strongly basified with K_2CO_3 and the liberated oily material was extracted with benzene. After drying over K_2CO_3, evaporation of the solvent gave 30% of N,N-dimethyl-N′-formyl-*p*-phenylenediamine; mp 107—108° (lit.[31] mp 108°), undepressed on admixture with an authentic sample.

4,4′-Dipiperidinoazoxybenzene: The reaction was exothermic. Azoxy compound was obtained by filtration of the reaction mixture. Orange yellow needles from benzene, mp 209—213°. *Anal.* Calcd. for $C_{22}H_{28}ON_4$: C, 72.49; H, 7.74; N, 15.37. Found: C, 72.79; H, 7.90; N, 15.58. UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 330s(3.76), 422(4.58). The filtrate was concentrated under reduced pressure to remove excess of TMAF. The resulting blackish residue was exrtacted with benzene. After drying over K_2CO_3, evaporation of the solvent gave 40% of N-(*p*-formylaminophenyl)piperidine; mp 137—139°. *Anal.* Calcd. for $C_{12}H_{16}ON_2$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.63; H, 7.91; N, 13.72. IR ν_{max}^{KBr} cm^{-1}: 1680 (C=O).

Reaction of Phenylhydroxylamine with TMAF——A mixture of 15.0 g (0.137 mole) of phenylhydroxylamine, 191 g (2.74 mole based on formic acid) of TMAF was heated with stirring at 98—100° for 1 hr. After the reaction, the mixture was allowed to stand overnight in refrigerator. The resulting precipitates were collected, washed with a small amount of water, and dried: weighing 2.1 g (15%), yellow needles, mp 36°, and were identified as azoxybenzene. TMAF of the filtrate was removed under reduced pressure affording a blackish tar. Distillation under reduced pressure gave colorless syrup, bp 145—147° (12 mmHg), which was identified as formanilide by comparison of the infrared spectra. Recrystallization from ether–petr. ether gave colorless needles, mp 47°, yield 8.2 g (49%).

Condensation Reaction of Nitrosobenzene and Phenylhydroxylamine in TMAF——A mixture of 2.0 g (0.0183 mole) of phenylhydroxylamine, 1.96 g (0.0183 mole) of nitrosobenzene and 50.0 g (0.0723 mole based on formic acid) of TMAF was heated with stirring at 50—53° for 2 hr. After the reaction, the mixture was cooled in an ice water bath. The resulting precipitates were collected, washed with a small amount of water and dried, weighing 3.4 g (94%), which was identified as azoxybenzene.

Reaction of Nitrosobenzene with Acetamide——A mixture of 10.7 g (0.1 mole) of nitrosobenzene, 59.1 g (1.0 mole) of acetamide was heated with stirring at 95—100° for 3.5 hr. After the reaction, the mixture was dissolved in 30 ml of water and extracted with benzene. The extract was washed with 60% H_2SO_4 and dried over $MgSO_4$. After removal of benzene distillation of the residue under reduced pressure gave two substances: (A) bp 88 —90° (15 mmHg); yield 3.1 g (76%); yellow liquid, which was identified as nitrobenzene by comparison of the infrared spectra. (B) bp 134—136° (0.2 mmHg); yield 6.0 g (91%); needles from EtOH, mp 36°, which was identified as azoxybenzene.

Reaction of Nitrosobenzene with Formamide——A mixture of 10.7 g (0.1 mole) of nitrosobenzene, 45.0 g (1.0 mole) of formamide was heated with stirring at 95—100° for 2.75 hr. After the reaction, the mixture was extracted with benzene, washed with 60% H_2SO_4 and dried over $MgSO_4$. After removal of benzene distillation of the residue under reduced pressure gave two substances: (A) bp 88—90° (15 mmHg); yield 1.1 g (27%); yellow liquid, which was identified as nitrobenzene. (B) bp 127—128° (0.15 mmHg); yield 6.8 g (103%); needles from EtOH, mp 36°, which was identified as azoxybenzene.

Acknowledgement The authors are indebted to the members of the Analysis Center of this College for elemental analyses and for measurement of UV spectra.

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