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Formic Acid Reduction. XIX.[1] Formic Acid Reduction of 4-Dialkylamino-substituted Nitro-, Nitroso-, Azoxy- and Azobenzenes

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4-Dimethylamino-substituted nitro- and nitrosobenzene and 4,4′-bis(dimethylamino)-substituted azoxy- and azobenzene have been shown to react with the distillable liquid formate, TMAF, composed of formic acid and trimethylamine to give a number of the products, N-methyl and N-formyl derivatives of *p*-phenylenediamine. Control experiments with several substrates, mostly nitrobenzene derivatives, and with the other formates and formic acid have been made, revealing source of the increasing N-methyl of the products and some features of the reaction.

In the previous paper[1] it has been reported that on heating 4-dialkylaminoazobenzene at elevated temperature (175—180°) along with formic acid or with distillable liquid formate composed of formic acid and trialkylamine reductive fission and transfer of N-alkyl are effected in several fashions to give a number of the products, N-alkyl and N-formyl derivatives of *p*-phenylenediamine and of aniline. In relation to this reaction we adopted 4-dimethylamino-substituted nitro- and nitrosobenzene and 4,4′-bis(dimethylamino)-substituted azoxy- and azobenzene as substrates to see how the formate reaction proceeds.

These compounds were allowed to react with the liquid formate (TMAF)[3] composed of formic acid and trimethylamine. The reactions were carried out in a flask with a long air condenser under the condition of heating at 175—180° until the color of the substrate in the solution disappeared. As the reaction proceeded, the refluxing temperature dropped because of the formation of water through the partial decomposition of formic acid. The temperature was controlled by topping the volatile liquid from the end of the condenser tube during the course of the reaction, where escape of a part of TMAF could not be avoided. Table I shows results of these experiments, where a variety of N-methyl and N-formyl derivatives of *p*-phenylenediamine, *i.e.*, N,N′-diformyl-N-methyl-*p*-phenylenediamine, N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, N-formyl-

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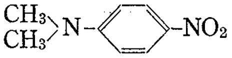
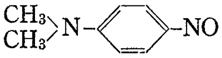
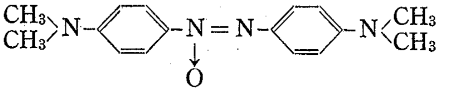
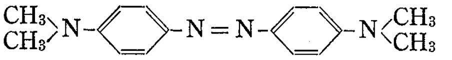
[1] Part XVIII: M. Sekiya, O. Matsuda, J. Suzuki and M. Tomie, *Chem. Pharm. Bull.* (Tokyo), 21, 372 (1973).

[2] Location: *2-2-1 Oshika, Shizuoka.*

[3] This material has been known as the constant-boiling liquid, bp 91—93° (18 mmHg), given by $5HCO_2H \cdot 2N(CH_3)_3$ [M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), 12, 677 (1964)].

N,N',N'-trimethyl-*p*-phenylenediamine and N,N,N',N'-tetramethyl-*p*-phenylenediamine, were obtained. Among these the last one was obtained mostly from the topping liquid because of its volatility.

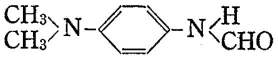
TABLE I. TMAF Reaction[a)] of 4-Dimethylamino-substituted Nitro-, Nitroso-, Azoxy- and Azobenzene

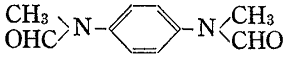
Run No.	Substrate	Reaction period (hr)	Product and yield[b)] (%)					
			A	B	C	D	E	Total
1		8	9	17	39	29	4	98
2		1.5	17	49	7	17	2	92
3		1.5	17	46	8	22	3	96
4		5	15	42	13	21	2	93

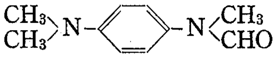
a) substrate to TMAF (based on HCO_2H) molar proportion, 1:25; reaction temperature, 175—180°

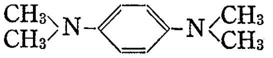
b) Yield is based on the product isolated. Theoretical yield of each product is estimated from one molar formation from one mole of the substrate for Runs 1 and 2 and from 1/2 mole of the substrate for Runs 3 and 4.

A: 

B: 

C: 

D: 

E: 

Control experiments included examination to see how unsubstituted nitro-, nitroso-, azoxy- and azobenzene react with TMAF. When heated at 175—180° for much longer period (30—46 hr) these compounds were converted into formanilide and, except the first one, 4',4'''-biformanilide, accompanied with resinous products. In comparison with these facts the above results obtained from the reactions of the 4-dimethylamino-substituted compounds are noticeable.

In the course of the reactions such nitro, nitroso and azoxy compounds are expected to suffer, in advance, formic acid reduction to 4,4'-bis(dimethylamino)azobenzene, however, throughout the four runs in Table I nothing to suggest this in the data such as the reaction periods and the yields is shown, except resemblance in those only between Run 2 and Run 3. The formation of a number of the products obtained in each reaction indicates apparent demethylation, transfer of N-methyl and/or N-methylation. When reacting part of the substrate is roughly looked upon as that estimated from the total yield of the products, sum of the N-methyls of the products for Runs 1, 3 and 4 shows considerable increase over that of the N-methyls in the substrate used (28% for Run 1, 11% for Run 3, 10% for Run 4). Where the N-methyls of the products come from and how these are formed come into a problem. The previous papers have reported that the formate, TMAF, affects irreversibly the demethylation[4)] of aromatic amine possessing N-methyl and the N-methylation[5,6)] of aromatic amine by incorporation of formic acid. Besides, in the previously reported reaction[1)] with 4-dimethylaminoazobenzene TMAF affects not only the N-methylation by incorporation of methyl of its trimethylamine component but also the transfer of N-methyl to give N-methyl and N-formyl derivatives of *p*-phenylenediamine and of aniline. The transfer of N-methyl in the above reaction has been reported[1)] to occur in several complicated fashions.

[4)] M. Sekiya, M. Tomie and N.J. Leonard, *J. Org. Chem.*, 33, 318 (1968).

[5)] M. Sekiya, S. Takayama, K. Ito, J. Suzuki, K. Suzuki and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **20**, 2661 (1972).

[6)] M. Sekiya, S. Takayama, J. Suzuki and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **20**, 2669 (1972).

In view of these features involved in the previously reported reactions the foresaid TMAF reactions of 4-dimethylamino-substituted nitro-, nitroso-, azoxy- and azobenzene are supposed to include a number of the stages such as the transfer of N-methyl, the N-methylation and the demethylation, but how these stages take place would be a difficult problem to be solved. Occurrence of the N-methylation in the reactions is, however, rather clear, taking account of the total increase of the N-methyls in the products. In the light of the previously reported papers such N-methylation is suggested to be effected by incorporation of formic acid and/or methyl of trimethylamine component in the formate.

The N-methylation by incorporation of formic acid has been reported⁵⁾ in the TMAF reactions of N-methyl and N-formyl derivatives of *p*-phenylenediamine. For instance, the TMAF reaction of N-formyl-N',N'-dimethyl-*p*-phenylenediamine at 175—180° for 30 hr gives the following products in the given yields (Chart 1). In this run 61% recovery of the substrate is shown, therefore apparent increase of the N-methyls of the products over those of the substrate is calculated at 13%, which is contributed by incorporation of formic acid.

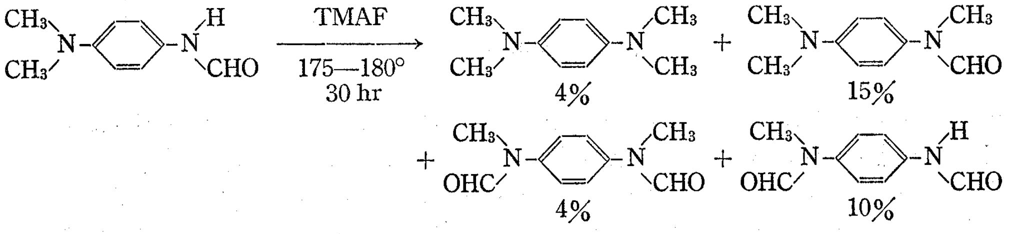


Chart 1

The formation of the same compound, N-formyl-N',N'-dimethyl-*p*-phenylenediamine, can be seen as one of the products in the four runs in Table I. Therefore, it is likely that the formation of the other *p*-phenylenediamine derivatives are brought about by the reaction through N-formyl-N',N'-dimethyl-*p*-phenylenediamine, because the product composition bears resemblance to that of the above reaction (Chart 1). However, when compared the reaction periods (1.5—8 hr against 30 hr), the reaction shown in Chart 1 is not considered to occur in a considerable extent. Considerable increases of N-methyl in the three runs represent that the observed N-methylation exceeds the N-methylation by incorporation of formic acid. Next, how much participation of methyl of trimethylamine component in TMAF exists in the reactions comes into a problem. An attempt was made to carry out a reaction of 4-nitro-N,N-dimethylaniline by the use of formic acid in place of TMAF. When heated with formic acid at 175—180° in a zirconium-lined autoclave, the reaction proceeded to give the following products (Chart 2). Except absence of N,N,N',N'-tetramethyl-*p*-phenylenediamine the products identical with those from the reaction with TMAF were obtained, but there was no increase of N-methyl in the products. From this result the increase of N-methyl in the reaction with TMAF is very likely to be attributed to incorporation of methyl of trimethylamine component in TMAF.

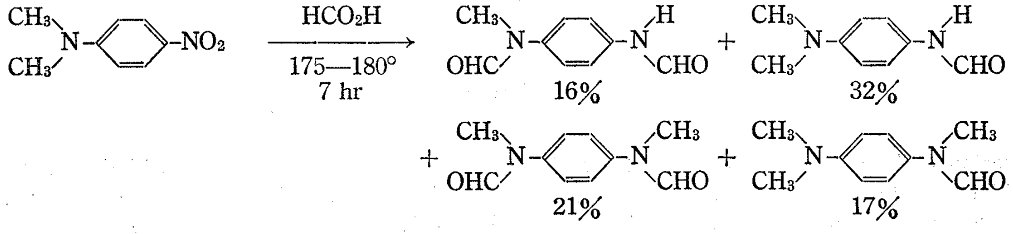


Chart 2

Further experiment included examination to see whether alkyl of trialkylamine component in the formate is incorporated into the products as their N-alkyl. Using the formate reagent, TEAF, which has been known[7] as the distillable liquid formate, bp 95° (15 mmHg), given by $5HCO_2H \cdot 2N(C_2H_5)_3$, a reaction of 4-nitro-N,N-dimethylaniline was carried out on heating at 175—180°. Incorporation of ethyl of triethylamine component in TEAF into the product was clarified by isolation of a considerable amount of N-ethyl-N,N'-diformyl-N'-methyl-*p*-phenylenediamine (16% yield) in this reaction (Chart 3).

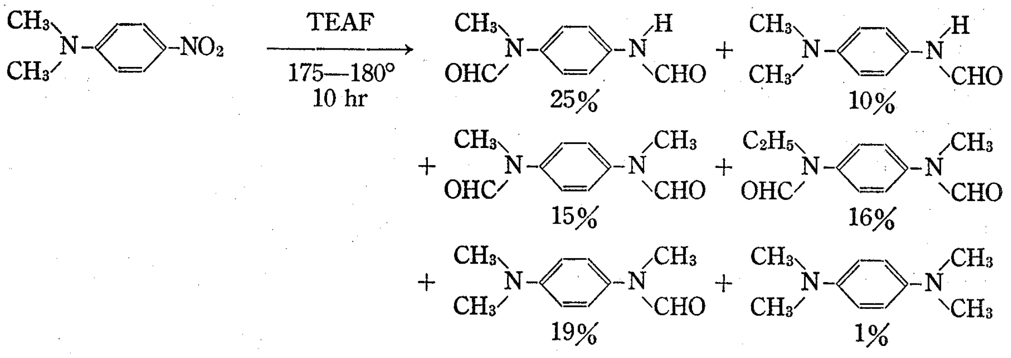


Chart 3

Comparative effect of variation of N-alkyl of the substrate was next examined with 4-diethylamino- and 4-dipropylamino-substituted nitrobenzene by carrying out the reactions with the formate containing trialkylamine possessing the same alkyl as that of the 4-dialkylamino substituent. In an experiment with the latter substrate a formate containing tripropylamine was newly prepared, which was shown to be a liquid of bp 98° (17 mmHg) analyzed as $5HCO_2H \cdot 2N(C_3H_7)_3$. Results of these experiments are described in Chart 4, where it is indicated that the product composition becomes simpler in the case of the substrate possessing such bulkier N-alkyl groups.

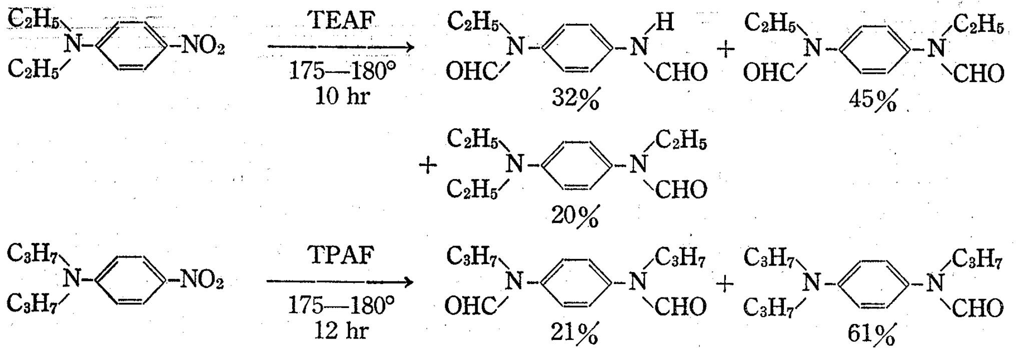


Chart 4

Experimental[8]

Preparation of TPAF——To 50 g of 98% HCO_2H 50 g of tripropylamine was added in a small portion on cool. The resultant solution was subjected to distillation under reduced pressure, giving a constant-boiling fraction after removal of H_2O and of excess HCO_2H. Redistillation gave a liquid of bp 98° (17 mmHg) and of n_D^{26} 1.4300, weighing 84 g (93%), which was analyzed as $5HCO_2H \cdot 2N(C_3H_7)_3$. *Anal.* Calcd. for $C_{23}H_{52}O_{10}N_2$: C, 53.45; H, 10.14; N, 5.42. Found: C, 53.09; H, 10.17; N, 5.37.

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[7] K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966).

[8] All melting points are uncorrected. Infrared (IR) and ultraviolet (UV) spectra were recorded with a Hitachi EPI-G2 spectrophotometer and a Hitachi EPS-2U spectrophotometer, respectively. Nuclear magnetic resonance (NMR) spectra were taken with a JEOL-C-60-H spectrometer (at 60 MHz) in $CDCl_3$ solution using tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

General Procedure for TMAF Reactions of 4-Dimethylamino-substituted Nitro-, Nitroso-, Azoxy- and Azobenzene——The following four compounds shown with their melting points were used as substrates: 4-nitro-N,N-dimethylaniline,[9] mp 163—164°; 4-nitroso-N,N-dimethylaniline,[10] mp 85°; 4,4′-bis(dimethylamino)azoxybenzene,[11] mp 107—108°; 4,4′-bis(dimethylamino)azobenzene,[12] mp 264—265°.

In a flask provided with a long air condenser and a thermometer, a mixture of the substrate and TMAF in molar proportion of 1: 25 (as HCO_2H) was heated at 175—180° with constant stirring until the color of the substrate in the solution disappeared. In the case of using 4-nitroso-N,N-dimethylaniline, explosive reaction could be controlled by adding the substrate in a small portion into the preheated TMAF at 165—170° with vigorous stirring and then heating and stirring at 175—180° until the color of the refluxing liquid disappeared. During the course of each reaction escape of a part of TMAF could not be avoided. Reaction period required for each run is recorded in Table I.

Each of the products was isolated by the following general procedure. The deposited crystals in the reaction mixture on cool, if any, were collected by filtration and were identified as N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, mp 201—202°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 254 mμ. In the run with 4-nitro-N,N-dimethylaniline, crystals of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, mp 102—103°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 266 mμ, were deposited along with N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine. The former was isolated from the mixture by extraction with dry ether. The filtrate of the reaction mixture was concentrated under reduced pressure. To the distillate combined with the topping liquid obtained during the course of the reaction KOH was added in the presence of H_2O and a liberated oil was extracted with ether. From the ether extract N,N,N′,N′-tetramethyl-*p*-phenylenediamine, mp 50°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ, was isolated.

The residue obtained in the foregoing was thoroughly extracted several times with petr. ether on refluxing. Removal of petr. ether from the combined extracts gave N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine. The extraction residue was subjected to distillation under reduced pressure to give a solid distillate of N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, mp 108°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 278 mμ. The distillation residue was subjected to fractional recrystallization from EtOH to give N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine and N,N′-diformyl-N-methyl-*p*-phenylenediamine, mp 138—141°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ 268 mμ, the former being less soluble than the latter.

Identities of the products obtained above were made by noting good correspondence of their IR spectra with those of authentic samples obtained in the previously reported papers[1,5] and by mixed melting point test. Yields of the products for each run are recorded in Table I.

Reaction of 4-Nitro-N,N-dimethylaniline with Formic Acid——In a zirconium-lined autoclave were placed 16.6 g (0.1 mole) of 4-nitro-N,N-dimethylaniline and 200 ml (5.2 mole) of 99% HCO_2H. The mixture was heated at 175—180° for 7 hr. Decomposing gas was occasionally released through the valve in case of danger. After removal of excess of HCO_2H by concentration, product isolation from the resultant residue was carried out in the same manner as described for the foregoing TMAF reaction. The products obtained are shown below. Their identities were made by noting good correspondence of their IR spectra with those of authentic samples[1,5] and by mixed melting point test.

N-Formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, mp 102—103°, yield 3.1 g (17%); N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, mp 107—108°, yield 4.9 g (32%); N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, mp 201—202°, yield 3.7 g (21%); N,N′-diformyl-N-methyl-*p*-phenylenediamine, mp 137—139°, yield 2.7 g (16%).

Reaction of 4-Nitro-N,N-dimethylaniline with TEAF——A mixture of 20.0 g (0.12 mole) of 4-nitro-N,N-dimethylaniline and 260 g (3 mole as HCO_2H) of TEAF was allowed to react on heating at 175—180° for 10 hr in the same manner as described for the TMAF reaction. The reaction mixture was thoroughly concentrated under reduced pressure, where excess of TEAF was removed. From this distillate combined with the topping liquid obtained during the course of the reaction, 0.2 g (1%) of N,N,N′,N′-tetramethyl-*p*-phenylenediamine, mp 49—50°, was isolated by usual treatment.

The residue was extracted several times with petr. ether on refluxing. Removal of petr. ether from the combined extracts followed by distillation under reduced pressure gave 4.1 g (19%) of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, bp 145—150° (2 mmHg), mp 102—103°. The residue insoluble in petr. ether was subjected to distillation under high reduced pressure to give a distillate, bp 150—170° (0.1 mmHg), and a solid residue, which were separately treated as follows.

N-Formyl-N′,N′-dimethyl-*p*-phenylenediamine, mp 105—106°, was obtained by extraction of this distillate with dry ether on cool, weighing 2.0 g (10%). The residual oil insoluble in ether solidified on standing, which was identified as N-ethyl-N,N′-diformyl-N′-methyl-*p*-phenylenediamine. Recrystallization from EtOH gave prisms, mp 101—102°. *Anal.* Calcd. for $C_{11}H_{14}O_2N_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 63.89; H, 6.69; N, 13.73. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1650, 1670 (CON<). NMR τ: 1.46 (1H, s, CHO), 1.60 (1H, s,

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9) A.E. Senear, M.M. Rapport, J.F. Mead, J.T. Maynard and J.B. Koepfli, *J. Org. Chem.*, **11**, 378 (1946).
10) Organic Syntheses, Coll. Vol. 2, p. 223 (1943).
11) M. Sekiya and S. Takayama, *Chem. Pharm. Bull.* (Tokyo), **18**, 2146 (1970).
12) D. Vorländer and E. Wolferts, *Ber.*, **56**, 1229 (1923).

CHO), 2.70 (4H, s, aromatic protons), 6.13 (2H, q, $J=7$ Hz, CH_2), 6.66 (3H, s, N–CH_3), 8.81 (3H, t, $J=7$ Hz, C–CH_3). Yield, 3.9 g (16%).

The foregoing residue was fractionally recrystallized from EtOH to give 3.4 g (15%) of N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, mp 201—202°, and 5.3 g (25%) of N,N′-diformyl-N-methyl-*p*-phenylenediamine, mp 136—138°.

Except N-ethyl-N,N′-diformyl-N′-methyl-*p*-phenylenediamine, identities of the products obtained in this run were made by noting good correspondence of their IR spectra with those of authentic samples[1,5] and by mixed melting point test.

Reaction of 4-Nitro-N,N-diethylaniline with TEAF——A mixture of 19.4 g (0.1 mole) of 4-nitro-N,N-diethylaniline,[13] mp 75—76°, and 216 g (2.5 mole as HCO_2H) of TEAF was allowed to react on heating at 175—180° for 10 hr in the same manner as described above. The reaction mixture was concentrated under reduced pressure, whereupon deposited crystals were collected by filtration, washed with a small amount of EtOH and dried. This crystals, weighing 5.2 g, were identified as N,N′-diethyl-N,N′-diformyl-*p*-phenylenediamine. Recrystallization from 95% EtOH gave prisms, mp 126—127° (lit.[14] mp 126—129°). *Anal.* Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$: C, 65.43; H, 7.40; N, 12.72. Found: C, 65.69; H, 7.40; N, 12.72. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1665 (CON<). NMR τ: 1.60 (2H, s, CHO), 2.72 (4H, s, aromatic protons), 6.10 (4H, q, $J=7$ Hz, CH_2), 8.80 (6H, t, $J=7$ Hz, CH_3).

The above filtrate combined with the washings was further concentrated under reduced pressure. The resulting residue was subjected to extraction with petr. ether several times on refluxing. Additional 0.5 g of N,N′-diethyl-N,N′-diformyl-*p*-phenylenediamine was obtained, which was deposited in the extracts on cooling. After removal of petr. ether from the filtrate the residue was subjected to distillation under reduced pressure to give a liquid of bp 148—149° (0.1 mmHg), n_D^{18} 1.5594, which was identified as N,N,N′-triethyl-N′-formyl-*p*-phenylenediamine. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{20}\text{ON}_2$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.46; H, 9.53; N, 12.44. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1650 (CON<). NMR τ: 1.80 (1H, s, CHO), 3.33 (4H, q, aromatic protons), 6.26 (2H, q, $J=7$ Hz, $\text{CHO}\overset{|}{\text{N}}\text{–CH}_2$), 6.64 (4H, q, $J=7$ Hz, $\text{–CH}_2\overset{|}{\text{N}}\text{CH}_2\text{–}$), 8.83 (6H, t, $J=7$ Hz, $\text{C}\underline{\text{H}}_3\text{CH}_2\overset{|}{\text{N}}\text{CH}_2\text{C}\underline{\text{H}}_3$), 8.87 (3H, t, $J=7$ Hz, $\text{CHO}\overset{|}{\text{N}}\text{CH}_2\text{C}\underline{\text{H}}_3$). Yield, 4.3 g (20%). Hydrolysis by heating with 10% HCl gave N,N,N′-triethyl-*p*-phenylenediamine dihydrochloride, needles from EtOH, mp 221—222° (decomp.). *Anal.* Calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_2\text{Cl}_2$: C, 54.34; H, 8.36; N, 10.56; Cl, 26.74. Found: C, 54.36; H, 8.40; N, 10.42; Cl, 26.05.

The residue obtained by the foregoing petr. ether extraction was subjected to fractional distillation under reduced pressure to give two fractions. As the first solid distillate, bp 175—179° (0.03 mmHg), additional 4.1 g of N,N′-diethyl-N,N′-diformyl-*p*-phenylenediamine was obtained. Total yield, 9.8 g (45%). The second distillate, bp 196—205° (0.02 mmHg), which gradually solidified on standing, was identified as N-ethyl-N,N′-diformyl-*p*-phenylenediamine. Recrystallization from benzene gave needles, mp 79—81° (lit.[14] mp 79—81°). *Anal.* Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.35; H, 6.38; N, 14.58. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3300 (NH), 1700, 1650 (CON<). NMR τ: *ca.* 0.80 (1H, broad s, NH), 1.65 (1H, s, CHO), 1.70 (1H, s, CHO), 2.21—2.92 (4H, m, aromatic protons), 6.14 (2H, q, $J=7$ Hz, CH_2), 8.84 (3H, t, $J=7$ Hz, CH_3). Yield, 6.1 g (32%).

Reaction of 4-Nitro-N,N-dipropylaniline with TPAF——A mixture of 15.0 g (0.067 mole) of 4-nitro-N,N-dipropylaniline,[15] mp 59°, and 173 g (1.68 mole as HCO_2H) of TPAF was allowed to react on heating at 175—180° for 12 hr in the same manner as described above. The reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to extraction with petr. ether several times on refluxing. After removal of petr. ether from the combined extracts the residue was distilled under reduced pressure to give a liquid of bp 148—150° (0.3 mmHg), n_D^{23} 1.5380, weighing 8.5 g, which was identified as N-formyl-N,N′,N′-tripropyl-*p*-phenylenediamine. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{26}\text{ON}_2$: C, 73.24; H, 9.99; N, 10.68. Found: C, 73.10; H, 10.25; N, 10.55. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1670 (CON<). NMR τ: 1.72 (1H, s, CHO), 3.17 (4H, q, aromatic protons), 6.32 (2H, t, $J=7$ Hz, $\text{CHO}\overset{|}{\text{N}}\text{–CH}_2$), 6.73 (4H, t, $J=7$ Hz, $\text{–CH}_2\overset{|}{\text{N}}\text{CH}_2\text{–}$), 8.06—8.73 (6H, m, $\text{C–CH}_2\text{–C}$), 9.07 (6H, t, $J=7$ Hz, CH_3), 9.12 (3H, t, $J=7$ Hz, CH_3). Hydrolysis with 10% HCl gave N,N,N′-tripropyl-*p*-phenylenediamine dihydrochloride, needles from EtOH, mp 219—220° (decomp.). *Anal.* Calcd. for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{Cl}_2$: C, 58.62; H, 9.18; N, 9.12. Found: C, 58.23; H, 9.08; N, 9.06.

The residue obtained by the foregoing petr. ether extraction was subjected to silica gel column chromatography using chloroform as an eluent. Concentration of the first eluate gave additional 2.2 g of N-formyl-N,N′,N′-tripropyl-*p*-phenylenediamine. Total yield, 10.7 g (61%). Concentration of the second eluate gave 3.5 g (21%) of crystals, which were identified as N,N′-diformyl-N,N′-dipropyl-*p*-phenylenediamine. Needles from 30% EtOH, mp 89—90°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.49; H, 8.10; N, 11.56. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1660 (CON<). NMR τ: 1.54 (2H, s, CHO), 2.71 (4H, s, aromatic protons), 6.17 (4H, t, $J=7$ Hz, CH_2N), 8.38 (6H, sextet, $J=7$ Hz, $\text{C–CH}_2\text{–C}$), 9.09 (6H, t, $J=7$ Hz, CH_3).

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13) A. Groll, *Ber.*, **19**, 198 (1886).

14) S.R. Buc and S.A. Glickman, U.S. Patent, 2647815 (1953) [*C. A.*, **48**, 1017 (1954)].

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Hydrolysis with 10% HCl gave N,N′-dipropyl-*p*-phenylenediamine dihydrochloride, leaves from EtOH, mp 240—241° (decomp.). *Anal.* Calcd. for $C_{12}H_{22}N_2Cl_2$: C, 54.34; H, 8.36; N, 10.56. Found: C, 54.12; H, 8.33; N, 10.35.

General Procedure for TMAF Reactions of Nitrobenzene, Nitrosobenzene, Azoxybenzene and Azobenzene——To 175 g (2.5 mole as HCO_2H) of TMAF 0.1 mole each of nitrobenzene, nitrosobenzene, azoxybenzene and azobenzene was added and the mixture was allowed to react on heating at 175—180° in the same manner as described for the foregoing TMAF reaction. Reaction periods are as follows: 30 hr for nitrobenzene, 45 hr for nitrosobenzene, 46 hr for azoxybenzene, 36 hr for azobenzene.

Crystals deposited in the reaction mixture on cool were collected by filtration. Recrystallization from TMAF gave leaves, mp 251—258° (decomp.), which were identified as 4′,4‴-biformanilide.[16] *Anal.* Calcd. for $C_{14}H_{12}O_2N_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.19; H, 5.17; N, 11.98. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$: 292 mμ(log ε 4.54). IR $\nu_{\max}^{\mathrm{KBr}}$ $\mathrm{cm^{-1}}$: 1705, 1695 (CONH). Formation of this material was recognized by heating benzidine with TMAF at 175—180°. No depression of the melting point was observed on admixture. Yields of this product are as follows: 0% for nitrobenzene, 18% for nitrosobenzene, 21% for azoxybenzene, 6% for azobenzene.

The filtrate obtained above was subjected to distillation under reduced pressure, and the resulting residue was extracted with benzene. Removal of benzene followed by distillation under reduced pressure gave a solid distillate of formanilide, bp 145—147° (12 mmHg), mp 47—48°. Yields of formanilide are as follows: 57% for nitrobenzene, 32% for nitrosobenzene, 48% for azoxybenzene, 63% for azobenzene. Benzene insoluble resine was not further investigated.

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