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Formic Acid Reduction. XVIII.[1] Formic Acid Reaction of *p*-(Dialkylamino)azobenzenes

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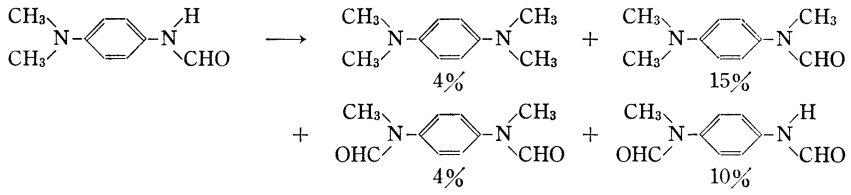
It has been found that *p*-(dialkylamino)azobenzenes undergo a novel reaction on heating with formic acid or the constant boiling liquid formate composed of formic acid and trialkylamine. The reaction involves a number of reaction stages such as reduction, bond fission and migration, giving a number of the products, N-alkyl and N-formyl derivatives of *p*-phenylenediamine and of aniline.

In an investigation related to chemical behavior of formic acid, there has been found a novel reaction of *p*-(dialkylamino)azobenzene induced by formic acid, which involves a number of reaction stages such as reduction, bond fission and migration, giving a number of the products, N-alkyl and N-formyl derivatives of *p*-phenylenediamine and of aniline.

The reaction was first realized, when *p*-(dimethylamino)azobenzene was heated at elevated temperature along with TMAF, which has been reported[3] as a distillable formate, bp 92° (18 mmHg), given by $5HCO_2H \cdot 2NMe_3$. Process of the reaction was indicated by disappearance of the color of the substrate in the reaction solution. In the reactions at 175—180° and 140—141°, the products formed are shown in runs 1 and 2 in Table I. As can be seen, these reactions are characterized by the formations of a number of the products, N-methyl and N-formyl derivatives of *p*-phenylenediamine and of aniline. Instead of *p*-(dimethylamino)azobenzene, *p*-(N-formyl-N-methylamino)azobenzene and *p*-(formylamino)-azobenzene were allowed to react with TMAF at 175—180°. As the results are shown in runs 4 and 5, in these reactions the reductive fission of the nitrogen-nitrogen double bond chiefly proceeded to give the corresponding N-formyl derivatives of *p*-phenylenediamine and of aniline. Although it is inferred that the above reaction of *p*-(dimethylamino)azobenzene involves such a reductive fission, the lower molar equivalent (0.30) of the formation of N-formyl-N′,N′-dimethyl-*p*-phenylenediamine in comparison with that (0.77) of formanilide and formations of the other products imply to involve some other reaction stages. The formations of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N-methyl-*p*-phenylenediamine, N,N-dimethylaniline and N-methylformanilide are not referred to as those formed through the simple reductive fission of the nitrogen-nitrogen double bond of the substrate and what stages these products are formed through comes into question.

In the preceding papers,[4,5] there has been reported the reaction of TMAF with N-methyl and N-formyl derivatives of *p*-phenylenediamine on heating at 175—180°, giving a number of the other analogous *p*-phenylenediamine derivatives, where both the N-methylation and the demethylation are effected by interaction of TMAF. For instance, the TMAF reaction of N-formyl-N,′N′-dimethyl-*p*-phenylenediamine at 175—180° for 30 hr has been reported

1) Part XVII: M. Sekiya, K. Mori, K. Ito, and K. Suzuki, *Tetrahedron*, **29**, 57 (1973).
2) Location: *2-2-1 Oshika, Shizuoka.*
3) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964).
4) M. Sekiya, S. Takayama, K. Ito, J. Suzuki, K. Suzuki, and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **20**, 2661 (1972).
5) M. Sekiya, S. Takayama, J. Suzuki, and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **20**, 2669 (1972).



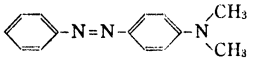
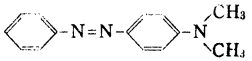
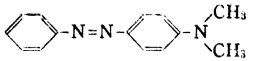
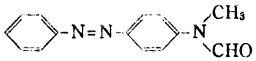
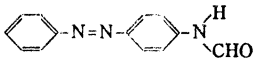
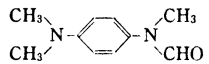
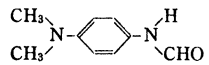
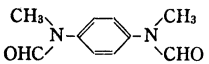
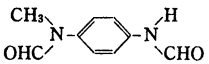
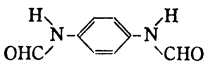
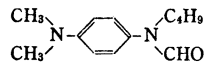
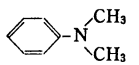
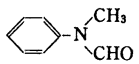
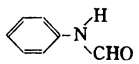
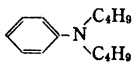
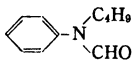
to give the above products in the given yields. That the product formation of *p*-phenylenediamine series in the reaction of *p*-(dimethylamino)azobenzene has resemblance to these formation appears to refer to this reaction as a final stage which is effected by the possible reductive fission intermediate, N-formyl-N′,N′-dimethyl-*p*-phenylenediamine. The TMAF reaction of *p*-(dimethylamino)azobenzene, however, proceeds with greater rapidity than the reported reaction of *p*-phenylenediamine derivatives, when compared the reaction periods of these reactions (0.5 hr against 30 hr of the reported reaction) and considered occurrence of the reaction (run 2) at the temperature of 140—141°, at which the *p*-phenylenediamine derivatives are inert. Taking account of these facts, the reported reaction is not almost involved in the reaction of *p*-(dimethylamino)azobenzene even in run 1.

The formation of a number of the N-methylated products prompted us to examine whether participation of methyl of trimethylamine of TMAF exists in the reaction. Then, in place of TMAF, TBAF, which has been reported[4] to be a liquid formate, bp 108—109° (20 mmHg), given by $7HCO_2H \cdot 3NBu_3$, was used as a reagent. The products obtained are presented in run 3 in Table I. As can be seen, there were obtained the N-butylated products, N-butyl-N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, N,N-dibutylaniline and N-butylformanilide, and small amount of some other products in addition to the simple reductive fission products. The observed nuclear magnetic resonance (NMR) spectrum of the product, N-butyl-N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, was interpreted to fit the structure by the following assignments: The triplet at τ 6.35 to the two hydrogens $>NC\underline{H}_2CH_2CH_2CH_3$, the triplet at τ 9.19 to the three hydrogens $>NCH_2CH_2CH_2C\underline{H}_3$, the multiplet at τ 8.30—8.95 to the four hydrogens $>NCH_2C\underline{H}_2C\underline{H}_2CH_3$, the singlet at τ 7.10 to the six hydrogens $-N(CH_3)_2$ and the singlet at τ 1.75 to the N-formyl hydrogen. The products, N,N-dibutylaniline and N-butylformanilide, were identified by gas chromatography with authentic specimens and quantitatively analyzed by internal standard method. The formation of these N-butylated products indicates incorporation of butyl of tributylamine in the TBAF reagent into the products. This fact forms characteristic of the reaction distinguishable from the reported formate reaction of *p*-phenylenediamine derivatives,[4,5] which shows no incorporation of alkyl of trialkylamine in the formate. It can therefore be presumed that incorporation of methyl of trimethylamine in TMAF into the products proceeds in some extent also in the TMAF reactions shown in runs 1 and 2 of Table I.

In order to avoid incorporation of methyl of trimethylamine of TMAF into the products, *p*-(dimethylamino)azobenzene was allowed to react with formic acid. Because of high reaction temperature, 175—180°, the reaction was carried out in a zirconium-lined autoclave. Result of this experiment is presented in run 6 of Table II. As can be seen, the same products as those obtained from the TMAF reaction were obtained in the given yields, disclosing characteristic of the reaction with formic acid.

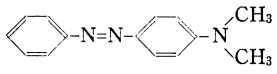
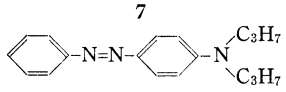
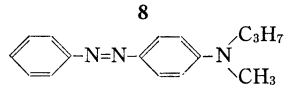
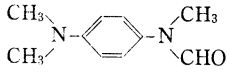
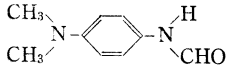
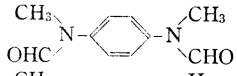
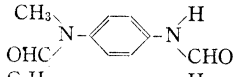
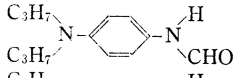
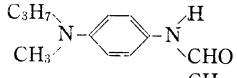
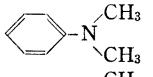
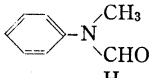
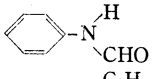
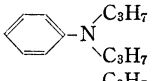
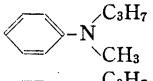
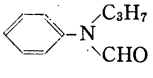
It is noticeable that in this reaction the formation of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, N,N-dimethylaniline and N-methylformanilide is observed. Since in this reaction there is no incorporation of alkyl of the trialkylamine such as that observed in the foregoing formate reaction, all the N-methyls of the products should be attributed to the N-methyls of the substrate, *p*-(dimethylamino)azobenzene. This indicates some novel reaction stages. In order to see effect of variation of N-alkyl, the reaction with *p*-(dipropylamino)azobenzene and *p*-(N-methyl-N-pro-

TABLE I. Formate Reaction[a] of *p*-Aminoazobenzene Derivatives

Run No.	1	2	3	4	5
Substrate					
Reagent	TMAF	TMAF	TBAF	TMAF	TMAF
React. temp. (°C)	175—180	140—141	175—180	175—180	175—180
React. time (hr)	0.5	3.0	0.75	4.0	1.0
Products and yields[b]					
	0.27	0.22	0.02	—	—
	0.30	0.29	0.64	—	—
	0.09	0.14	—	—	—
	0.25	0.24	0.01	0.82	—
	—	—	—	—	0.91
	—	—	0.20	—	—
	0.02	trace[c]	—	—	—
	0.04	0.09[c]	0.003[c]	0.04	—
	0.77	0.76	0.75	0.81	0.87
	—	—	0.02[c]	—	—
	—	—	0.06[c]	—	—

a) molar ratio: substrate/TMAF or TBAF (based on HCO_2H)=1/25
b) Yield is based on the product isolated except those marked by footnote c) and is written as molar amount derived from one mole of the substrate in calculation.
c) This yield is based on quantitative gas chromatographic analysis of the product.

TABLE II. Formic Acid Reaction[a] of *p*-(Dialkylamino)azobenzene

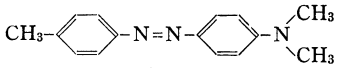
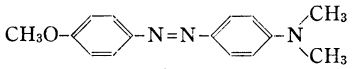
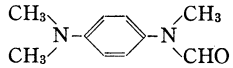
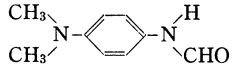
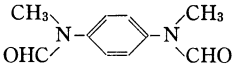
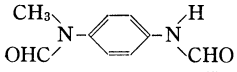
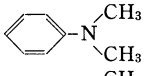
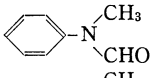
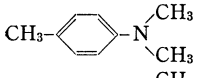
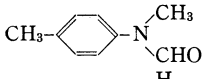
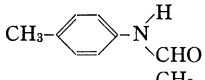
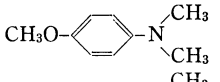
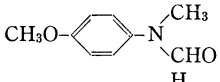
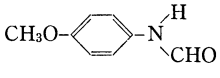
Run No.	6	7	8
substrate			
Products and yields[b]			
	0.14	—	—
	0.27	—	—
	0.09	—	—
	0.36	—	—
	—	0.81	—
	—	—	0.81
	0.04	—	—
	0.18	—	0.15
	0.59	0.57	0.56
	—	0.10	—
	—	—	0.09
	—	0.17	0.08

a) reagent: HCO_2H; molar ratio: substrate/HCO_2H=1/40; reaction temperature: 175—180°; reaction time: 1.5 hr
b) Yield is based on the product isolated and is written as molar amount derived from one mole of the substrate in calculation.

pylamino)azobenzene were examined under the same conditions and resulted in the formation of the products shown in runs 7 and 8 of Table II. Although the product formations in these reactions are more simple than that of the reaction of *p*-(dimethylamino)azobenzene, the considerable formations of N,N-dialkylaniline and N-alkylformanilide are noticeable. However, in these reactions it is unable to distinguish whether the benzene rings of these products are derived from either of the two benzene rings of the substrates. In order to make it possible to distinguish two aromatic rings of the substrates distributed in the products, we then selected *p*-dimethylamino-*p'*-methylazobenzene and *p*-dimethylamino-*p'*-methoxyazobenzene as substrates for the reaction. These compounds were subjected to heating with formic acid at 175—180° in the zirconium-lined autoclave. Products formed and their yields in these reactions are described in Table III.

A number of stages leading to the formations of a variety of the products are too complicated to be clarified, however, from these and the accumulated facts occurrence of the following reductive stages (refer to Table IV) is inferred, although details of these stages are not clear.

TABLE III. Formic Acid Reaction[a] of *p'*-Substituted *p*-(Dimethylamino)azobenzene

Run No.	9	10
substrate		
React. time (hr)	1.5	1.0
	Products and yields[b]	
	0.06	0.02
	0.28	0.32
	0.10	0.12
	0.36	0.45
	0.02	0.02
	0.01	trace[c]
	0.10	—
	0.13	—
	0.59	—
	—	0.15
	—	0.16
	—	0.56

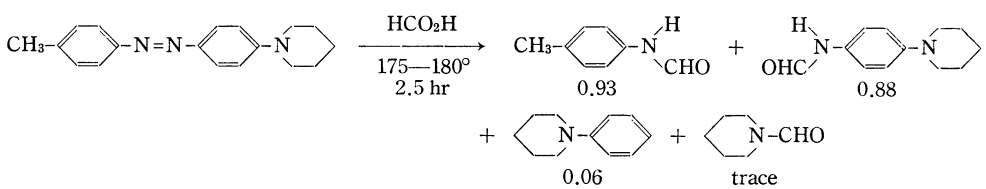
a) reagent: HCO_2H; molar ratio: substrate/HCO_2H=1/40; reaction temperature: 175—180°
b) Yield is based on the product isolated except that marked by footnote c) and is written as molar amount derived from one mole of the substrate in calculation.
c) This is based on gas chromatographic analysis.

1. Fission at Nitrogen-nitrogen Double Bond of Diazo Group

As stated above occurrence of this reductive fission leading to two molar equivalent of N-formylamino compounds is already clarified by the results of the above experiments.

2. Fission at the Bond between Diazo-nitrogen and *p*-Dialkylaminophenyl Carbon

This fission is deduced from the formation of N,N-dimethylaniline in runs 9 and 10. Occurrence of this fission is also supported by the formation of N-phenylpiperidine in the formic



acid reduction of *p*-methyl-*p'*-piperidinoazobenzene as shown above. In this scheme numerical values of the products represent molar amount of the products derived from one mole of the substrate in calculation.

3. Transfer of Dialkylamino Group to the Other Benzene Carbon with Removal of Diazo-nitrogen

This is deduced from the facts, the considerable formations of N,N-dimethyl-*p*-toluidine and N,N-dimethyl-*p*-anisidine in runs 9 and 10, respectively.

Fission of piperidino-nitrogen bond attached to phenyl carbon involving in this stage is substantiated by the formation of N-formylpiperidine in the reaction of *p*-methyl-*p'*-piperidinoazobenzene described in 2.

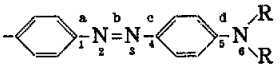
The formation of N,N-dimethylaniline, N,N-dipropylaniline and N-methyl-N-propylaniline in runs 6, 7 and 8, respectively, are caused by both the course of 2 and this course.

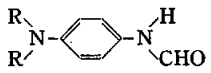
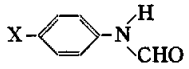
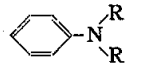
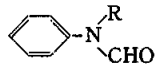
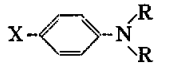
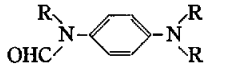
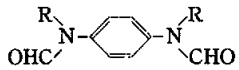
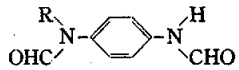
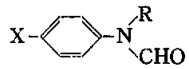
4. Transfer of N-Methyl of the Substrate to Diazo-nitrogen bound to *p*-Dimethylamino-phenyl Carbon

Intermolecular type of this transfer may be deduced from the formations of N-formyl-N,N',N'-trimethyl-*p*-phenylenediamine and N,N'-diformyl-N-methyl-*p*-phenylenediamine in runs 6, 9 and 10. This transfer is effected only in the cases of *p*-(dimethylamino)azobenzenes. The formation of N,N'-diformyl-N-methyl-*p*-phenylenediamine is also likely through the following Stage 5.

Course of the formation of N,N'-diformyl-N,N'-dimethyl-*p*-phenylenediamine in runs 6, 9 and 10 is not clear and if discussed, this type of transfer in intramolecular or simultaneous transfer of N-methyl of each between two molecules may cause this formation.

TABLE IV. Possible Reductive Fissions and Transfers deduced from the Product Formations

Substrate: 

Product	Possible reductive fission and transfer deduced from the formation	Stage No.
	fission of bond b	1
	fission of bond b	1
	fission of bond c	2
	fission of bond c with transfer of N-methyl (see Stage 4 and 5)	2
	fission of bond d with replacement of N_2 by N_6	3
	intermolecular transfer of N_6-methyl to N_3 with fission of bond b	4
	intramolecular or bimolecular transfer of N_6-methyl to N_3 with fission of bond b	4
	intermolecular transfer of N_6-methyl to N_2 and/or transfer of N_6-alkyl to N_2, with fission of bond b	4 and/or 5
	transfer of N_6-alkyl to N_2 with fission of bond b	5

5. Transfer of N-Alkyl of the Substrate to Diazo-nitrogen bound to the Other Benzene Ring

This is deduced from the formation of N-methyl-*p*-formotoluidide and N-methyl-*p*-formanisidide in runs 9 and 10, respectively. The formation of N-propylformanilide in run 7 and the formations of N-methyl and N-propyl-formanilide in run 8 are also suggested this stage.

Experimental[6]

Reaction of *p*-(Dimethylamino)azobenzene with TMAF——a) Run 1 in Table I: In a flask provided with a thermometer and an air condenser were placed 22.5 g (0.1 mole) of *p*-(dimethylamino)azobenzene and 174.0 g (2.5 mole based on HCO_2H) of TMAF. The mixture was heated at 175—180° with stirring, while considerable evolution of carbon dioxide was observed, and after 0.5 hr the orange color of the substrate in the solution disappeared. Because of partial decomposition of formic acid a volatile liquid containing water and some other materials was topped from the end of the air condenser tube. By usual treatment of this topping liquid, 0.3 g of N,N-dimethylaniline was isolated.

A TMAF distillate obtained by distillation of the reaction solution under reduced pressure was shown to contain N-methylformanilide. This was liberated by basification of the distillate with KOH followed by usual treatment, weighing 0.6 g.

To the residue obtained by the foregoing distillation of the reaction solution, benzene was added where small amount of an insoluble resinous material was removed. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing. Removal of petr. ether followed by recrystallization from ether gave 4.8 g of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine.

The insoluble residue on the foregoing extraction with petr. ether was subjected to distillation under reduced pressure to give two solid fractions of formanilide, bp 164—168° (15 mmHg), and N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, bp 165—169° (0.2 mmHg), after purification, weighing 9.3 g and 4.9 g respectively.

The residue obtained by the above distillation was extracted with benzene where small amount of a resinous material remained undissolved. After removal of benzene, the solid residue was fractionally recrystallized from EtOH to give 1.7 g of N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine and 4.5 g of N,N′-diformyl-N-methyl-*p*-phenylenediamine.

The products obtained by the foregoing procedures are listed in the following with their physical data. These products were indentified by noting well correspondence of their infrared (IR) spectra with those of authentic specimens and in the cases of crystals, no depression of their melting points on admixture.

N-Formyl-N,N′,N′-trimethyl-*p*-phenylenediamine: Needles (from ether), mp 102—103° (lit.[4] mp 102—103°). IR ν_{CO}^{KBr} cm^{-1}: 1665. NMR (10% solution in $CDCl_3$) τ: 1.73 (1H, s, -CHO), 2.80—3.43 (4H, m, aromatic protons), 6.80 (3H, s, $C\underline{H}_3$-N-CHO), 7.08 (6H, s, $-N(CH_3)_2$).

N-Formyl-N′,N′-dimethyl-*p*-phenylenediamine: Plates (from benzene), mp 107—108° (lit.[7] mp 108°). IR ν_{CO}^{KBr} cm^{-1}: 1675. NMR (10% solution in $CDCl_3$) τ: 1.52 (1H, b, >NH), 1.77 (1H, d, J=2.3 Hz, -CHO), 2.55—3.42 (4H, m, aromatic protons), 7.06 (6H, $-N(CH_3)_2$).

N,N′-Diformyl-N,N′-dimethyl-*p*-phenylenediamine: Needles (from EtOH), mp 201—202° (lit.[4] mp 201—202°). IR ν_{CO}^{KBr} cm^{-1}: 1670. NMR (5% solution in $CDCl_3$) τ: 1.52 (2H, s, -CHO), 2.76 (4H, s, aromatic protons), 6.66 (6H, s, >N-$C\underline{H}_3$).

N,N′-Diformyl-N-methyl-*p*-phenylenediamine: Prisms (from EtOH), mp 136—138° (lit.[8] mp 138—141°). IR ν_{CO}^{KBr} cm^{-1}: 1650, 1700. NMR (10% solution in DMSO-d_6) τ: −0.34 (1H, b, >NH), 1.53 (1H, s, CH_3-N-C$\underline{H}$O), 1.71 (1H, d, J=2.0 Hz, -NHC$\underline{H}$O), 2.26—2.78 (4H, m, aromatic protons), 6.80 (3H, s, >N-CH_3).

N-Methylformanilide: Colorless oil, bp 132—133° (23 mmHg). n_D^{20} 1.5538. *Anal.* Calcd. for C_8H_9ON: C, 71.09; H, 6.71; N, 10.37. Found: C, 70.79; H, 6.71; N, 10.44. IR $\nu_{CO}^{liq.}$ cm^{-1}: 1672.

Formanilide: Needles (from ether–petr. ether), mp 48°.

b) Run 2 in Table I: The same mixture of *p*-(dimethylamino)azobenzene and TMAF as in a) was allowed to react at 140—141° for 3 hr and worked up by the same procedures as in a). In this run the formation

6) All melting points and boiling points are uncorrected. NMR spectra were taken with a JEOL JNM-C-60-H high resolution spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, b=broad. IR spectra were recorded with a Hitachi EPI-G2 spectrophotometer. All the gas chromatographic analyses in this work were carried out using Parkin-Elmer F-11 gas chromatography (detector: FID) equipped with 2 m column (1/8 inch diameter, packed with Carbowax 20M on Chromosorb W-AW) using nitrogen as carrier gas (inlet pressure: 2.5 kg/cm²). Column temperature was 180°.

7) J. Pinnow and G. Pistor, *Ber.*, **26**, 1314 (1893).

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

of N,N-dimethylaniline was detected in the N-methylformanilide distillate as trace by vapor phase chromatography (VPC). Product composition in this run is shown as run 2 in Table I.

Reaction of *p*-(Dimethylamino)azobenzene with TBAF (Run 3 in Table I)——A mixture of 22.5 g (0.1 mole) of *p*-(dimethylamino)azobenzene and 313.0 g (2.5 mole based on HCO_2H) of TBAF was heated at 175—180° for 0.75 hr as in the same manner described in run 1.

By distillation of the reaction solution under reduced pressure, TBAF was completely distilled off and this distillate was diluted with water and excess of KOH was added on cool. A liberated tributylamine layer was separated and an aqueous layer was extracted with benzene. The tributylamine layer combined with the benzene extract was dried over anhydrous potassium carbonate. After benzene and tributylamine were distilled off, further distillation under reduced pressure gave a liquid boiling at 134—158° (23 mmHg) which by VPC was shown to be a mixture of N,N-dibutylaniline, N-butylformanilide and N-methylformanilide. Their retention times were the same as those of the authentic samples prepared by the another route.[9] Quantitative analyses of these were made by internal standard method using N-benzylmorpholine (for N,N-dibutylaniline and N-methylformanilide) and N-methyldibenzylamine (for N-butylformanilide) as internal standards to give the following results: N,N-dibutylaniline, 0.37 g; N-butylformanilide, 1.15 g; N-methylformanilide, 0.04 g.

To the residue obtained by the foregoing distillation of the reaction solution, benzene was added so as to remove small amount of an insoluble resinous material. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing. Concentration of the petr. ether solution gave a solid residue which was triturated with petr. ether on cool giving 2.0 g of N-butyl-N-formyl-N′,N′-dimethyl-*p*-phenylenediamine. The mother liquid was concentrated and the residue was subjected to silica gel column chromatography using benzene as an eluent. Concentration of the first eluent gave further 2.3 g of N-butyl-N-formyl-N′,N′-dimethyl-*p*-phenylenediamine. Total yield, 4.3 g. Concentration of the second eluent gave 0.4 g of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine.

The insoluble residue on the foregoing extraction with petr. ether was subjected to distillation under reduced pressure to give two solid fractions of formanilide, bp 123—130° (2 mmHg), and N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, bp 175—180° (2 mmHg), after purification, weighing 9.1 g and 10.5 g, respectively. The residue obtained by the above distillation was triturated with benzene and the resulting powder was dissolved in EtOH. Decolorization with charcoal and evaporation of EtOH gave 0.1 g of N,N′-diformyl-N-methyl-*p*-phenylenediamine.

The products obtained in this run, N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N-methyl-*p*-phenylenediamine and formanilide, were the same as those obtained in run 1. Their identities were made by noting well correspondence of their IR spectra with those of the authentic samples and no depression of their melting points on admixture.

Identity of N-butyl-N-formyl-N′,N′-dimethyl-*p*-phenylenediamine is in the following: Needles (from petr. ether), mp 70°. *Anal.* Calcd. for $C_{13}H_{20}ON_2$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.99; H, 9.13; N, 12.82. IR ν_{CO}^{KBr} cm^{-1}: 1670. NMR (12% solution in $CDCl_3$) τ: 1.75 (1H, s, -CHO), 2.90—3.48 (4H, m, aromatic protons), 6.35 (2H, t, J=7.5 Hz, $>NC\underline{H}_2CH_2CH_2CH_3$), 7.10 (6H, s, $-N(CH_3)_2$), 8.30—8.95 (4H, m, $>NCH_2C\underline{H}_2C\underline{H}_2CH_3$), 9.19 (3H, t, J=6.0 Hz, $>NCH_2CH_2CH_2C\underline{H}_3$).

Reaction of *p*-(N-Formyl-N-methylamino)azobenzene with TMAF (Run 4 in Table I)——A mixture of 23.9 g (0.1 mole) of *p*-(N-formyl-N-methylamino)azobenzene and 174.0 g (2.5 mole based on HCO_2H) of TMAF was heated at 175—180° for 1 hr with stirring.

A TMAF distillate obtained by distillation of the reaction solution under reduced pressure was shown to contain N-methylformanilide. This was liberated by basification of the distillate with KOH followed by usual treatment, weighing 0.6 g.

To the residue obtained by the foregoing distillation of the reaction solution, benzene was added where small amount of an resinous material remained undissolved. Concentration of the benzene solution and distillation of the resulting residue under reduced pressure gave 9.8 g of formanilide. The above distillation residue was extracted with benzene. Removal of benzene followed by recrystallization of the residue from EtOH gave 14.7 g of N,N′-diformyl-N-methyl-*p*-phenylenediamine.

The products obtained in the above were identified by noting well correspondence of their IR spectra with those of the authentic samples obtained in the foregoing, and in the cases of formanilide and N,N′-diformyl-N-methyl-*p*-phenylendiamine, no depression of their melting points on admixture.

Reaction of *p*-(Formylamino)azobenzene with TMAF (Run 5 in Table I)——A mixture of 22.5 g (0.1 mole) of *p*-(formylamino)azobenzene and 174.0 g (2.5 mole based on HCO_2H) of TMAF was heated at 175—180° for 4 hr with stirring. The reaction solution was concentrated under reduced pressure and excess of TMAF was removed. The resulting residue was pre-extracted with EtOH at room temperature. After

9) Butylation of aniline was carried out with butyl bromide in the benzene solution in the presence of $NaNH_2$, giving N-butyl and N,N-dibutylaniline. N-Formylation of the former with formic acid gave N-butylformanilide.

evaporation of EtOH, the residue was extracted with benzene. Removal of benzene followed by distillation of the residue under reduced pressure gave 10.5 g of formanilide.

Most part of both the extraction residues with EtOH and with benzene was shown to be N,N′-diformyl-*p*-phenylenediamine. Recrystallization from water gave needles, mp 212—214° (lit.[4] mp 204—205°), weighing 15.0 g. NMR (10% solution in HMPA) τ: −1.14 (2H, b, >NH), 1.73 (2H, d, J=1.8 Hz, -CHO), 2.34 (4H, s, aromatic protons).

IR spectra of the above two products were consistent with those of authentic specimens and their melting points were not depressed on admixture.

Reaction of *p*-(Dimethylamino)azobenzene with Formic Acid (Run 6 in Table II)——In a zirconium-lined autoclave were placed 22.5 g (0.1 mole) of *p*-(dimethylamino)azobenzene and 151 ml (4.0 mole) of 99% formic acid. The mixture was heated at 175—180° for 1.5 hr. The reaction solution was concentrated under reduced pressure. To the resulting residue benzene was added where small amount of an insoluble resinous material was removed. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing. Evaporation of petr. ether and fractional distillation of the residue under reduced pressure gave 0.5 g of N,N-dimethylaniline, bp 90—92° (17 mmHg), 2.4 g of N-methylformanilide, bp 125—128° (17 mmHg), and 2.5 g of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, bp 183—186° (0.2 mmHg).

The insoluble residue on the foregoing petr. ether extraction was subjected to distillation under reduced pressure to give two distillates, formanilide, bp 124—127° (0.3 mmHg), and N-formyl-N,N′-dimethyl-*p*-phenylenediamine, bp 173—176° (0.3 mmHg), after purification, weighing 7.2 g and 4.5 g, respectively. The residue obtained by the above distillation was extracted with benzene where small amount of a resinous material remained undissolved. After removal of benzene, the resulting solid residue was subjected to fractional recrystallization from EtOH to give 1.7 g of N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine and 6.4 g of N,N′-diformyl-N-methyl-*p*-phenylendiamine.

The products obtained in this run were identified by noting well correspondence of their IR spectra with those of the authentic samples obtained in the foregoing and, in the cases of crystals, no depression of their melting points on admixture.

Reaction of *p*-(Dipropylamino)azobenzene[10] with Formic Acid (Run 7 in Table II)——In a zirconium-lined autoclave were placed 28.1 g (0.1 mole) of *p*-(dipropylamino)azobenzene and 151 ml (4.0 mole) of 99% formic acid and the mixture was heated at 175—180° for 1.5 hr. The reaction solution was concentrated under reduced pressure. To the resulting residue benzene was added so as to remove small amount of an insoluble resinous material. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing. Removal of petr. ether and fractional distillation of the resulting residue under reduced pressure gave 1.8 g of N,N-dipropylaniline and 2.8 g of N-propylformanilide.

The insoluble residue on the foregoing petr. ether extraction was subjected to distillation under reduced pressure to give formanilide, bp 153—157° (12 mmHg), and N-formyl-N′,N′-dipropyl-*p*-phenylenediamine, bp 165—168° (0.05 mmHg), after purification, weighing 6.9 g and 17.8 g, respectively.

The following is physical and analytical data of the products obtained.

N,N-Dipropylaniline: Colorless oil, bp 123—128° (15 mmHg). n_D^{21} 1.5433 (lit.[11] n_D^{20} 1.5422). *Anal.* Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.22; H, 10.78; N, 8.18. NMR (12% solution in $CDCl_3$) τ: 2.80—3.50 (5H, m, aromatic protons), 6.78 (4H, t, J=7.5 Hz, >N$\underline{CH_2}CH_2CH_3$), 8.05—8.75 (4H, m, >N$CH_2\underline{CH_2}CH_3$), 9.10 (6H, t, J=6.9 Hz, >N$CH_2CH_2\underline{CH_3}$).

N-Propylformanilide: Colorless oil, bp 136—140° (15 mmHg). n_D^{23} 1.5342 (lit.[11] n_D^{25} 1.5332). *Anal.* Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.79; H, 8.10; N, 8.66. IR ν_{CO}^{KBr} cm^{-1}: 1664. NMR (10% solution in $CDCl_3$) τ: 1.55 (1H, s, -CHO), 2.35—2.95 (5H, m, aromatic protons), 6.18 (2H, t, J=7.5 Hz, >N$\underline{CH_2}CH_2CH_3$), 8.10—8.80 (2H, m, >N$CH_2\underline{CH_2}CH_3$), 9.11 (3H, t, J=6.9 Hz, >N$CH_2CH_2\underline{CH_3}$).

N-Formyl-N′,N′-dipropyl-*p*-phenylenediamine: Colorless oil, bp 165—168° (0.05 mmHg). n_D^{18} 1.5715. *Anal.* Calcd. for $C_{13}H_{20}ON_2$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.79; H, 9.27; N, 12.32. IR ν_{CO}^{liq} cm^{-1}: 1668. NMR (13% solution in $CDCl_3$) τ: 1.65 (1H, s, -CHO), 1.84 (1H, s, >NH), 3.02—3.55 (4H, m, aromatic protons), 6.25 (4H, t, J=7.5 Hz, >N$\underline{CH_2}CH_2CH_3$), 8.25—8.75 (4H, m, >N$CH_2\underline{CH_2}CH_3$), 9.15 (6H, t, J=6.9 Hz, >N$CH_2CH_2\underline{CH_3}$).

Reaction of *p*-(N-Methyl-N-propylamino)azobenzene[12] with Formic Acid (Run 8 in Table II)——In a zirconium-lined autoclave, a mixture of 25.3 g (0.1 mole) of *p*-(N-methyl-N-propylamino)azobenzene and

10) This material was prepared by azo coupling reaction of dipropylaniline with benzenediazonium chloride. A reddish orange liquid, bp 168—172° (0.005 mmHg). n_D^{16} 1.6781. *Anal.* Calcd. for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24; N, 14.93. Found: C, 77.96; H, 8.14; N, 13.81. UV λ_{max}^{EtOH} mμ (log ε): 416 (4.46), 259 (3.96).

11) R.M. Robert and F.A. Hussein, *J. Am. Chem. Soc.*, **82**, 1950 (1960).

12) This material was prepared by azo coupling reaction of N-methyl-N-propylaniline with benzenediazonium chloride. A reddish orange plates (from MeOH), mp 33—35°. *Anal.* Calcd. for $C_{16}H_{19}N_3$: C, 75.85; H, 7.56; N, 16.59. Found: C, 76.19; H, 7.53; N, 16.34. UV λ_{max}^{EtOH} mμ (log ε): 415 (4.47), 257 (3.96).

151 ml (4.0 mole) of 99% formic acid was heated at 175—180° for 1.5 hr. After concentration of the reaction solution under reduced pressure, benzene was added to the resulting residue so as to remove small amount of an insoluble resinous material. The benzene solution was concentrated and the resulting residue was subjected to extraction with petr. ether several times on refluxing.

Removal of petr. ether and distillation of the residue under reduced pressure gave three oily fractions, 1.4 g of N-methyl-N-propylaniline, bp 109—113° (15 mmHg), 2.0 g of N-methylformanilide, bp 122—124° (15 mmHg), and 1.3 g of N-propylformanilide, bp 135—139° (15 mmHg).

The insoluble residue on the foregoing petr. ether extraction was subjected to distillation under reduced pressure to give formanilide, bp 155—160° (15 mmHg), and N-formyl-N′-methyl-N′-propyl-*p*-phenylenediamine, bp 163—165° (1.5 mmHg), after purification, weighing 6.8 g and 15.6 g, respectively.

Identities of the products obtained above were made by the following data.

N-Propylformanilide and N-methylformanilide exhibited the IR spectra and retention times on VPC consistent with those of the authentic specimens obtained in the foregoing.

N-Methyl-N-propylaniline: Colorless oil, bp 109—113° (15 mmHg). n_D^{20} 1.5415 (lit.[13]) $n_D^{19.5}$ 1.5403). *Anal.* Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.22; H, 10.02; N, 9.53. NMR (12% solution in $CDCl_3$) τ: 2.70—3.45 (5H, m, aromatic protons), 6.75 (2H, t, J=7.5 Hz, $>NC\underline{H}_2CH_2CH_3$), 7.12 (3H, s, $>N\text{-}CH_3$), 8.10—8.75 (2H, m, $>NCH_2C\underline{H}_2CH_3$), 9.11 (3H, t, J=6.9 Hz, $>NCH_2CH_2C\underline{H}_3$).

N-Formyl-N′-methyl-N′-propyl-*p*-phenylenediamine: Colorless oil, bp 163—165° (1.5 mmHg). n_D^{19} 1.5785. *Anal.* Calcd. for $C_{11}H_{16}ON_2$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.21; H, 7.75; N, 14.86. IR ν_{CO}^{KBr} cm^{-1}: 1642. NMR (11% solution in $CDCl_3$) τ: 1.80 (1H, s, -CHO), 1.90 (1H, s, >NH), 2.92—3.42 (4H, m, aromatic protons), 6.37 (2H, t, J=7.5 Hz, $>NC\underline{H}_2CH_2CH_3$), 6.79 (3H, s, $>N\text{-}CH_3$), 8.15—8.80 (2H, m, $>NCH_2C\underline{H}_2CH_3$), 9.16 (3H, t, J=6.9 Hz, $>NCH_2CH_2C\underline{H}_3$).

Reaction with *p*-Dimethylamino-*p*′-methylazobenzene with Formic Acid (Run 9 in Table III)——In a zirconium-lined autoclave, a mixture of 23.9 g of *p*-dimethylamino-*p*′-methylazobenzene and 151 ml (4.0 mole) of 99% formic acid was heated at 175—180° for 1.5 hr. The reaction solution was concentrated under reduced pressure. The resulting residue was shown to contain nine products, N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N-methyl-*p*-phenylenediamine, N,N-dimethylaniline, N-methylformanilide, N,N-dimethyl-*p*-toluidine, N-methyl-*p*-formotoluidide and *p*-formotoluidide. Isolation procedures are as follows.

To the resulting residue benzene was added so as to remove small amount of an insoluble resinous material. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing.

The petr. ether extract, after evaporation, was subjected to careful fractional distillation under reduced pressure to give four oily distillates; 0.3 g of N,N-dimethylaniline, bp 80—83° (20 mmHg), 1.4 g of N,N-dimethyl-*p*-toluidine, bp 100—103° (20 mmHg), 0.2 g of N-methylformanilide, bp 120—125° (15 mmHg), 1.9 g of N-methyl-*p*-formotoluidide, bp 140—146° (15 mmHg). The distillation residue obtained was subjected to recrystallization from ether to give 1.1 g of N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine.

The insoluble residue obtained by the foregoing extraction with petr. ether was subjected to extraction with ether and ethereal extract, after removal of ether, was subjected to distillation under reduced pressure to give *p*-formotoluidide, bp 161—165° (3 mmHg), and N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, bp 155—160° (0.2 mmHg), after purification, weighing 8.0 g and 4.6 g, respectively. The insoluble residue obtained by the above extraction with ether was then extracted with benzene. Evaporation of benzene and fractional recrystallization of the residue form EtOH gave 2.0 g of N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine and 6.4 g of N,N′-diformyl-N-methyl-*p*-phenylenediamine.

Identities of the products obtained above were made by the following data.

The products, N,N-dimethylaniline, N-methylformanilide, N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, N-formyl-N′,N′-dimethyl-*p*-phenylenediamine, N,N′-diformyl-N,N′-dimethyl-*p*-phenylenediamine and N,N′-diformyl-N-methyl-*p*-phenylenediamine showed the IR spectra consistent with the authentic specimens obtained in the foregoing.

N,N-Dimethyl-*p*-toluidine: Colorless oil, bp 100—103° (20 mmHg). n_D^{20} 1.5362 (lit.[14]) n_D^{20} 1.5460). *Anal.* Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.71; H, 9.69; N, 10.82.

N-Methyl-*p*-formotoluidide: Colorless oil, bp 140—146° (15 mmHg). n_D^{20} 15500. *Anal.* Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found: C, 73.07; H, 7.45; N, 9.39. IR $\nu_{CO}^{liq.}$ cm^{-1}: 1678.

p-Formotoluidide: Needles (from ether–petr. ether), mp 50—51° (lit.[15] mp 52°). *Anal.* Calcd. for C_8H_9ON: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.13; H, 6.74; N, 10.24. IR ν_{CO}^{KBr} cm^{-1}: 1688.

Reaction of *p*-Dimethylamino-*p*′-methoxyazobenzene with Formic Acid (Run 10 in Table III)——In a zirconium-lined autoclave a mixture of 25.5 g (0.1 mole) of *p*-dimethylamino-*p*′-methoxyazobenzene and 151 ml (4.0 mole) of 99% formic acid was heated at 175—180° for 1 hr. The reaction solution was con-

13) H. Bader, *J. Chem. Soc.*, **1956**, 3293.
14) H. Ley and G. Pfeiffer, *Ber.*, **54B**, 363 (1921).
15) S. Sugasawa and H. Shigehara, *J. Pharm. Soc. Japan*, **62**, 531 (1942).

centrated under reduced pressure. The resulting residue was shown to contain nine products, N-formyl-N,N',N'-trimethyl-*p*-phenylenediamine, N-formyl-N',N'-dimethyl-*p*-phenylenediamine, N,N'-diformyl-N,N'-dimethyl-*p*-phenylenediamine, N,N'-diformyl-N-methyl-*p*-phenylenediamine, N,N-dimethylaniline, N-methylformanilide, N,N-dimethyl-*p*-anisidine, N-methyl-*p*-formanisidide and *p*-formanisidide. Isolation procedures are in the following.

The resulting residue was treated with benzene where small amount of an insoluble resinous material was removed. The benzene solution was concentrated and the resulting residue was extracted with petr. ether several times on refluxing.

The petr. ether extract was subjected to fractional distillation under reduced pressure to give 0.3 g of N,N-dimethylaniline, 2.2 g of N,N-dimethyl-*p*-anisidine, which was shown to contain trace amount of N-methylformanilide by VPC and 2.7 g of N-methyl-*p*-formanisidide as fractions boiling at 70—75° (14 mmHg), 112—118° (14 mmHg) and 130—135° (2 mmHg), respectively. The distillation residue obtained was subjected to recrystallization from ether to give 0.3 g of N-formyl-N,N',N'-trimethyl-*p*-phenylenediamine.

The insoluble residue obtained by the foregoing extraction with petr. ether was subjected to extraction with ether and ethereal extract was distilled under reduced pressure to give 8.4 g of *p*-formanisidide, bp 140—145° (0.3 mmHg), and 5.2 g of N-formyl-N',N'-dimethyl-*p*-phenylenediamine, bp 170—175° (0.5 mmHg). The insoluble residue obtained by the above extraction with ether was then extracted with benzene and the benzene extract, which solidified after removal of benzene, was fractionally recrystallized from EtOH to give 2.3 g of N,N'-diformyl-N,N'-dimethyl-*p*-phenylenediamine and 8.0 g of N,N'-diformyl-N-methyl-*p*-phenylenediamine.

Identities of the products obtained were made by the following data.

The products, N,N-dimethylaniline, N-formyl-N,N',N'-trimethyl-*p*-phenylenediamine, N-formyl-N',N'-dimethyl-*p*-phenylenediamine, N,N'-diformyl-N,N'-dimethyl-*p*-phenylenediamine and N,N'-diformyl-N-methyl-*p*-phenylenediamine, showed the IR spectra consistent with the authentic specimens obtained in the foregoing.

N,N-Dimethyl-*p*-anisidine: Plates (from EtOH), mp 46—47° (lit.[16] mp 48°), bp 112—118° (14 mmHg). Vapor phase chromatogram of this material showed a peak at the corresponding retention time, but other very small peak of a material appeared, of which retention time corresponds to N-methylformanilide. *Anal.* Calcd. for $C_9H_{13}ON$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.97; H, 8.77; N, 9.30.

N-Methyl-*p*-formanisidide: Colorless oil, bp 130—135° (2 mmHg). n_D^{19} 1.5602. *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.01; H, 7.07; N, 8.25. IR $\nu_{max}^{liq.}$ cm^{-1}: 1670 (CO), 1248 (ether).

p-Formanisidide: Plates (from benzene), mp 80° (lit.[14] mp 80—81°). *Anal.* Calcd. for $C_8H_9O_2N$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.78; H, 5.97; N, 9.17. IR ν_{max}^{KBr} cm^{-1}: 1650 (CO), 1248 (ether).

Reaction of *p*-Methyl-*p'*-piperidinoazobenzene with Formic Acid——In a zirconium-lined autoclave, a mixture of 28.0 g (0.1 mole) of *p*-methyl-*p'*-piperidinoazobenzene and 151 ml (4.0 mole) of 99% formic acid was heated at 175—180° for 2.5 hr. The reaction solution was concentrated under reduced pressure. To the resulting residue benzene was added where small amount of an insoluble resinous material was removed. Concentration of the benzene solution followed by distillation under reduced pressure gave 1.0 g of N-phenylpiperidine, bp 115—125° (15 mmHg), which was shown to contain trace amount of N-formylpiperidine by VPC and 12.6 g of *p*-formotoluidide, bp 170—173° (15 mmHg).

The residue obtained by the above distillation was extracted with benzene where small amount of a resinous material remained undissolved. Removal of benzene followed by recrystallization of the solid residue from aq. EtOH gave 18.0 g of N-(*p*-formylaminophenyl)piperidine.

Identities of the products obtained by the above procedures were made by the following data.

N-(*p*-Formylaminophenyl)piperidine: Prisms (from 60% EtOH), mp 135—138°. *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, 13.73. IR ν_{CO}^{KBr} cm^{-1}: 1680. NMR (7% solution in $CDCl_3$) τ: 1.44 (1H, s, >NH), 1.80 (1H, s, -CHO), 2.50—3.30 (4H, m, aromatic protons), 6.80—7.10 (4H, m, C_2 and C_6-H_2), 8.13—8.57 (6H, m, C_3, C_4 and C_5-H_2).

p-Formotoluidide: Needles (from ether–petr. ether), mp 48—50° (lit.[15] mp 52°).

N-Phenylpiperidine: Colorless oil, bp 115—125° (15 mmHg). n_D^{21} 1.5617 (lit.[17] n_D^{23} 1.5606). *Anal.* Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.66; H, 9.57; N, 8.75. This material was contaminated with trace amount of N-formylpiperidine which was detected by VPC.

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17) J.F. Bunnett and T.K. Brotherton, *J. Org. Chem.*, **22**, 832 (1957).