Dealkylation of Aromatic Tertiary Amines with Formates

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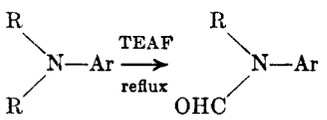
Triethylammonium formate, TEAF, and trimethylammonium formate, TMAF, both $5HCOOH \cdot 2NR_3$, have been introduced as reagents for the dealkylation of aromatic tertiary amines, $ArNR_2$. The dealkylation reaction is facilitated by the presence of electron-releasing *para* (or *ortho*) substituents such as $N(CH_3)_2$, OH, OCH_3, and OC_2H_5 on the aromatic ring. An N-benzyl group is removed more readily than N-methyl and N-propyl. Almost no reaction occurs when the *para* substituent is electron attracting, such as NHCHO, Cl, $COCH_3$, and SO_2NH_2.

A survey of the literature reveals that the dealkylation of aromatic tertiary amines can be brought about by the direct action of mineral acids or organic acids at high temperature.[4-10] In selected examples, thermal eliminations have been found to occur during the heating of hindered aliphatic amine salts,[11] and amides have been obtained by intramolecular reaction between carboxylic acid and tertiary amine groups.[12,13] With the development, as reducing agents,[14,15] of several saltlike compounds of formic acid, which may be represented by the general formula $5HCOOH \cdot 2NR_3$ and which are polar liquids of constant, high boiling point, it became of interest to investigate other potential uses of this type of reagent.

Using triethylammonium formate,[15,16] it has now been found that the dealkylation of N,N-dialkylanilines can be effected with this reagent at the reflux temperature to give N-formyl-N-monoalkylanilines.



The result of substitution on the aromatic ring, with respect to both type and position of substituent, has been studied by comparison of yields under standardized conditions, and the relative ease of different C–N bond cleavages has been investigated by varying the R and R′ groups.

In general, the reactions were carried out in a flask fitted with a very long air condenser under the following uniform conditions: 175–180°, 30 hr, and an N,N-dialkylaniline to TEAF (as HCOOH) molar proportion of 1:25. As the reaction proceeded, the reflux temperature dropped because of the consumption of formic acid; accordingly, the excess triethylamine was topped from the end of the condenser tube. When the escape of part of the TEAF could not be avoided during the course of the reaction, additional reagent was added. The N-formyl-N-alkylaniline produced was isolated and identified in each case, and unchanged N,N-dialkylaniline was also recovered in most cases.

The results of the experiments with representative *para*-substituted N,N-dimethylanilines are summarized in Table I. Since N,N-dimethylaniline was demethylated in only 4% yield under the standard reaction conditions, the reaction was shown to be facilitated by the presence of electron-releasing *para* substituents such as $N(CH_3)_2$, OH, OCH_3, and OC_2H_5. Almost no reaction occurred when the *para* substituent was electron attracting, such as NHCHO, Cl, $COCH_3$, and SO_2NH_2. The substituent effect is noticeably in contrast with that observed for the previously reported dealkylation with hydrogen bromide, where an electron-attracting substituent in the aromatic ring increases the rate of dealkylation.[9] N,N-Dimethyl-*p*-phenylenediamine did not undergo demethylation, but N,N-dimethyl-N′-formyl-*p*-phenylenediamine was formed readily, which was then inert to the demethylation.

TABLE I
THE DEALKYLATION OF SUBSTITUTED N,N-DIMETHYLANILINES WITH TEAF[a]

Substituent	Yield,[b] %	Substituent	Yield,[b] %
p-$N(CH_3)_2$	48	*p*-$COCH_3$	0
p-OH	20	*p*-SO_2NH_2	0
p-OCH_3	18	*o*-$N(CH_3)_2$	50
p-OC_2H_5	19	*o*-OCH_3	55
H	4	*m*-OCH_3	3
p-NH_2	0	*o*-Cl	9
p-NHCHO	0	*m*-Cl	0
p-Cl	0		

[a] General method and specific conditions given in the Experimental Section. [b] Yield based on the N-formyl-N-methylaniline actually isolated.

Comparative effects of substituents at the *ortho*, *meta*, and *para* positions were examined with the representative OCH_3, $N(CH_3)_2$, and Cl groups, with the results also shown in Table I. In the case of methoxyl substitution, the reactivity toward dealkylation clearly followed the order $o > p > m$, suggestive of a possible combination of electron-releasing and

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(16) Triethylammonium formate, $5HCOOH \cdot 2N(C_2H_5)_3$, bp 95° (15 mm), TEAF; trimethylammonium formate, $5HCOOH \cdot 2N(CH_3)_3$, bp 91–93° (18 mm), TMAF.[14]

steric effects. In certain other cases the order $o > p$ was observed.

Control experiments included an examination of the stability of the triethylammonium formate reagent itself. When TEAF was heated at 175–180° for 30 hr, the triethylamine component was converted in only 2% yield into N,N-diethylformamide. Tribenzylamine was 5% debenzylated with TEAF to N,N-dibenzylformamide under the standard reaction conditions. If in place of TEAF the allied TMAF[16] was used under the same conditions, the dealkylation of some representative substrates (N,N-dimethylaniline with *o*- and *p*-OCH_3, *o*- and *p*-$N(CH_3)_2$ substitution) proceeded with equal or greater efficiency. Using an autoclave but otherwise the same conditions, N,N-dimethyl-*p*-anisidine was 10% demethylated with glacial acetic acid alone.

The substrate N,N-dimethylanilines listed in Table I, where not readily available, were prepared by previously reported methods, but details have been added and improvements made (see Experimental Section) for a number of these, including N,N-dimethyl-*o*-, *m*-, and *p*-anisidine, N,N-dimethyl-*p*-phenetidine, N,N,N′,N′-tetramethyl-*o*- and *p*-phenylenediamine, *p*-dimethylaminophenol, *p*-dimethylaminoacetophenone, and *o*-, *m*-, and *p*-chloro-N,N-dimethylamine. Additional N,N-disubstituted *p*-anisidines were prepared, with variation in the N-alkyl groups as shown in Table II. When these compounds

TABLE II
THE DEALKYLATION OF *p*-ANISIDINES HAVING TWO DIFFERENT N-SUBSTITUENTS WITH TEAF[a]

N-Substituent		
R retained	R′ removed	Yield,[b] %
CH_3	CH_3	18
CH_3	$C_6H_5CH_2$	26
n-C_3H_7	$C_6H_5CH_2$	27
$C_6H_5CH_2$	$C_6H_5CH_2$	20

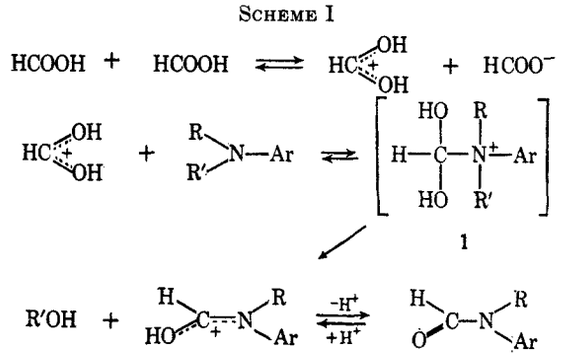
[a] General method and specific conditions given in the Experimental Section. [b] Yield based on the N-alkyl-N-formyl-*p*-anisidine actually isolated.

were subjected to the standard dealkylation conditions with TEAF, it was found that the N-benzyl group was removed more readily than N-methyl and N-propyl.

In order to follow the fate of the eliminated group in the dealkylation reaction, N,N-di(2-phenylethyl)-*p*-anisidine was used as a substrate. It was prepared from *p*-anisidine and 2-phenylethyl bromide in the presence of sodium amide in two steps, the first to produce N-2-phenylethyl-*p*-anisidine[17] and that succeeding to N,N-di(2-phenylethyl)-*p*-anisidine. It was less active to dealkylation with TEAF than either N,N-dimethyl- or N,N-dibenzyl-*p*-anisidine. N-Formyl-N-2-phenylethyl-*p*-anisidine was obtained in 17% yield after 120 hr. The oily product resulting from the 2-phenylethyl moiety was also isolated from the reaction mixture and was subjected to gas–liquid partition chromatography, leading to identification of 1-phenylethanol and 2-phenylethanol in the mixture. Since no isomerization of 2-phenylethanol was found to occur when it was heated with TEAF under the same conditions and styrene did not yield 1-phenylethanol under these conditions, it was concluded that the 2-phenylethanol formed was a product of solvolysis and the 1-phenylethanol was probably formed following rearrangement of the intermediate phenethyl carbonium ion.

While we wish to put forward this use of the TEAF or TMAF reagent chiefly on the basis of its novelty and possible application to selective degradation, it is interesting to speculate on a mechanism of the dealkylation which will explain the assembled observations. It is possible that the reaction proceeds *via* equilibrium protonation of the aromatic amine and displacement of its N-alkyl group as postulated by Chambers and Pearson[9] for the dealkylation of aromatic tertiary amines by passing hydrogen bromide through the molten salt; however, the observed effect of electron-attracting groups was to increase the rate of dealkylation under their conditions. An attractive alternative is to regard TEAF or TMAF as a high-boiling vehicle for formic acid and to take into account the high autoprotolysis constant of formic acid, which implies that it has a strong tendency both to donate and to accept a proton.[18] Reaction of the amine to form an adduct intermediate (1) (Scheme I) could be

SCHEME I



followed by an N^+–C cleavage step dependent upon the nature of the groups R and R′. With the assumption of adduct formation as the slow step, this formal sequence fits the observations that the reaction is facilitated by electron-releasing *para* substituents and that the extent of reaction is diminished by groups R and R′ of increased steric requirement. Moreover, the greater extent of dealkylation of *ortho*- compared with *para*-substituted dimethylanilines is in agreement with the stronger basicities of the *ortho*-substituted isomers (pK_a's: N,N-dimethylanisidines, *o*, 6.27 ± 0.07, *p*, 5.95 ± 0.13 (uv); N,N,N′,N′-tetramethylphenylenediamines, *o*, 6.96 ± 0.15, *p*, 6.24 ± 0.01 (potentiometric); chloro-N,N-dimethylanilines, *o*, 4.21 ± 0.02; *p*, 4.16 ± 0.04 (uv)). The preference for N-benzyl cleavage in a mixed adduct 1 reflects the resonance stabilization of the developing benzyl carbonium ion, although the benzyl group must be regarded as base weakening as well (see Table II).

Most of the dealkylation products, the N-formylated secondary aromatic amines obtained in the present work, have not been previously described. They were isolated mainly by vacuum distillation and identified by elemental analysis.

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Experimental Section

Preparation of N,N-Dialkylanilines. N,N-Dimethyl-*o*-, -*m*-, and -*p*-anisidine, N,N-Dimethyl-*p*-phenetidine, and N,N,N′,N′-Tetramethyl-*o*- and -*p*-phenylenediamines.—The general procedure[19] used was as follows. To 60 ml of water, 0.2 mole of the aromatic primary amine and 76 g (0.6 mole) of dimethyl sulfate were added. To the vigorously stirred mixture was added 66 ml of 30% aqueous sodium hydroxide drop by drop at such a rate that the mixture was kept slightly basic, while the temperature was maintained below 30°. After addition of the entire sodium hydroxide solution, in most cases a clear and strongly basic solution was obtained. In the runs with *p*-anisidine and with N,N-dimethyl-*p*-phenylenediamine, since solid material was deposited at this time, sufficient water was added to effect solution. To the resulting basic solution in each case 34 g of potassium iodide dissolved in 30 ml of water was added, whereupon the quaternary ammonium iodide precipitated. The precipitate was collected by filtration, dried, and weighed to ascertain satisfactory yield. This material was added to a solution of 1.5 molar equiv amount of sodium hydroxide dissolved in *n*-amyl alcohol. The suspension was refluxed with stirring for 5 hr and the insoluble material was removed by filtration. The filtrate was washed with an aqueous solution saturated with sodium chloride and the organic layer was dried over calcium oxide. After evaporation of *n*-amyl alcohol, the residual liquid was distilled under reduced pressure to give each of the N,N-dimethylated products. In the procedure for the tetramethylation of *o*-phenylenediamine more than twofold the normal amount of the reagents, dimethyl sulfate, and the sodium hydroxide solution, etc., were necessary to give the bisquaternary ammonium hydroxide, for which the yield was lower than for the other compounds, presumably owing to the steric factor. The identification of each product was based on comparison with physical properties previously reported and upon the correct elemental analysis in each case (analyses are not reported for known compounds): N,N-dimethyl-*o*-anisidine, yield 67%, bp 120° (50 mm) (lit.[20] bp 93° (6 mm)); N,N-dimethyl-*m*-anisidine, yield 63%, bp 96° (3 mm) (lit.[20] bp 118° (6 mm)); N,N-dimethyl-*p*-anisidine, yield 79%, mp 48° (lit.[21] mp 48°); N,N-dimethyl-*p*-phenetidine, yield 68%, mp 35° (lit.[20] mp 34°); N,N,N′,N′-tetramethyl-*o*-phenylenediamine, yield 48%, bp 93° (15 mm) (lit.[22] bp 92° (10 mm)); N,N,N′,N′-tetramethyl-*p*-phenylenediamine, yield 78%, mp 50° (lit.[21] mp 51°).

***p*-Dimethylaminophenol.**—A mixture of 25 g of *p*-methylaminophenol suspended in 142 g of methyl iodide was refluxed carefully for a few hours. The solid was collected by filtration, pulverized, and added, with 13 g of sodium carbonate, to 300 ml of *n*-amyl alcohol. The mixture was refluxed for 5 hr with stirring. Following filtration the filtrate was washed twice with a saturated aqueous sodium chloride solution and then dried over calcium oxide. The *n*-amyl alcohol was removed by distillation and the *p*-dimethylaminophenol was distilled at 161–164° (28 mm) and solidified: mp 75–77° (lit.[21] mp 77–78°); yield 13.2 g (48%).

***o*- and *m*-Chloro-N,N-dimethylaniline.**—To 100 ml of water 26 g (0.21 mole) of either *o*- or *m*-chloroaniline, 67.2 g (0.8 mole) of sodium bicarbonate, and 76.5 g (0.6 mole) of dimethyl sulfate were added. The mixture was stirred at about 10° for 2 hr and then warmed at 50–60°. After the insoluble material was filtered, the filtrate was rendered strongly basic with sodium hydroxide and subjected to steam distillation. The oily material in the distillate was extracted into chloroform and the solution was concentrated. To the residual liquid was added 40 ml of acetic anhydride and the mixture was refluxed for 1 hr to remove monomethylated material. The resulting solution was concentrated and the residual liquid was washed with aqueous sodium hydroxide and taken up in petroleum ether (bp 40–60°). After drying over potassium carbonate and removal of the solvent, distillation under reduced pressure gave the dimethylated product: *o*-chloro-N,N-dimethylaniline, bp 102–104° (20 mm) (lit.[23] bp 98–99° (18 mm)), yield 92%; *m*-chloro-N,N-dimethylaniline, bp 113–114° (15 mm) (lit.[20] bp 90° (2 mm)), yield 83%. *p*-Chloro-N,N-dimethylaniline was made as previously described.[24]

***p*-Dimethylaminoacetophenone.**—N,N-Dimethylation of *p*-aminoacetophenone, for which a completely satisfactory method had not been reported previously, was performed by a procedure similar to that described above: yield 84%; bp 132° (3 mm) (lit.[25] bp 172–175° (11 mm)); mp 104–105° (lit.[26] mp 105.5°).

N,N-Di(2-phenylethyl)-*p*-anisidine.—A suspension of 3.3 g (0.085 mole) of sodamide in a solution of 16 g (0.07 mole) of N-2-phenylethyl-*p*-anisidine[17] in 100 ml of dry toluene was heated at reflux, with stirring, for 3 hr. Then, 19.5 g (0.105 mole) of 2-phenylethyl bromide was added dropwise to the refluxing mixture and, after the addition, the refluxing and the stirring were continued for an additional 16 hr. The solid material was filtered and washed with benzene. After the washings were combined with the filtrate, the solution was washed with 5% aqueous sodium hydroxide and then dried over potassium carbonate. Under reduced pressure the solvent and the excess 2-phenylethyl bromide were distilled from the solution. To the resulting residue a fivefold amount of acetic anhydride was added and the mixture was refluxed for 2 hr. After removal of the excess acetic anhydride the residue was extracted with dry ether. Through the ethereal solution dry hydrogen chloride was passed. The resulting precipitate was collected, washed with ether, and dried. The crude product weighed 15.8 g (62%). The N,N-di(2-phenylethyl)-*p*-anisidine hydrochloride was recrystallized from benzene–ethanol as needles, mp 171–172°.

Anal. Calcd for $C_{23}H_{26}ClNO$: C, 75.06; H, 7.12; N, 3.81. Found: C, 74.92; H, 6.84; N, 3.90.

The corresponding base was isolated by treatment of the salt with 50% aqueous potassium hydroxide, extraction with benzene, drying, removal of the benzene, and distillation *in vacuo:* bp 206–209° (0.14 mm); $n^{18}D$ 1.5982.

Anal. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.16; H, 7.72; N, 4.19.

N-Benzyl-N-*n*-propyl-*p*-anisidine was obtained in a manner similar to that described above from N-benzyl-*p*-anisidine, sodamide, and *n*-propyl bromide in 92% crude yield and isolated as the **hydrochloride,** prisms from ethanol, mp 172–173°.

Anal. Calcd for $C_{17}H_{22}ClNO$: C, 69.98; H, 7.60; N, 4.81; Cl, 12.15. Found: C, 69.98; H, 7.56; N, 4.54; Cl, 12.55.

The free base was obtained on basification of the hydrochloride: bp 159–163° (4 mm); $n^{23}D$ 1.5749.

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.74; H, 8.20; N, 5.37.

N-Benzyl-N-methyl-*p*-anisidine was obtained in 90% yield by the catalytic reductive alkylation[27] of N-benzyl-*p*-anisidine with formaldehyde using Raney nickel in ethanol–acetic acid: bp 160–162° (3 mm) (lit.[28] bp 220–222° (30 mm)); $n^{31}D$ 1.5878.

The **picrate** separated as yellow plates from ethanol, mp 114–115°.

Anal. Calcd for $C_{21}H_{20}N_4O_8$: C, 55.26; H, 4.39; N, 12.28. Found: C, 55.39; H, 4.55; N, 12.36.

N,N-Dibenzyl-*p*-anisidine was obtained in 89% yield by the alkylation of N-benzyl-*p*-anisidine in toluene with sodamide and benzyl bromide and was recrystallized as prisms from ethanol, mp 81–82° (lit.[29] mp 81.5–82°).

N,N-Dimethylaminobenzenesulfonamide was made as previously described.[30]

Partial Decomposition of TEAF on Heating.—In a flask fitted with a long air condenser, 200 ml of TEAF, $5HCOOH \cdot 2N(C_2H_5)_3$, was heated at 175–180° for 30 hr, while evolution of a slight amount of CO_2 was observed. On cooling in ice–water, the liquid was diluted with water and saturated with potassium hydroxide, whereupon the triethylamine layer separated. The layer was dried over potassium carbonate and then concentrated under reduced pressure. The resulting residual liquid was purified by distillation under reduced pressure to give a liquid, bp 63–65° (15 mm), weighing 2 g

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(2% yield), which was identified as N,N-diethylformamide by its infrared spectrum.

Partial Dibenzylation of Tribenzylamine.—In a flask fitted with a long air condenser, a mixture of 20.0 g (0.07 mole) of tribenzylamine and 150 g of TEAF was heated at 175–180° for 30 hr. Unchanged tribenzylamine was removed in part by crystallization and in part as the hydrochloride and the final separation of pure N,N-dibenzylformamide was by chromatography through a silica gel column using chloroform as the eluent, identified by mp 52° (lit.[31] mp 52°) and by infrared spectrum, yield 5%.

Demethylation of N,N-Dimethyl-*p*-anisidine with Acetic Acid.—In an autoclave a mixture of 15.1 g (0.1 mole) of N,N-dimethyl-*p*-anisidine and 200 ml of acetic acid was heated at 175–180° for 30 hr. After evaporation, the residue was distilled under reduced pressure. Unchanged N,N-dimethyl-*p*-anisidine was first collected and then a solid distillate, bp 142–144° (6 mm), mp 51–53°, weighing 1.7 g (10% yield), was obtained, which was recrystallized from ether–petroleum ether, mp 57–58° (lit.[32] mp for N-acetyl-N-methyl-*p*-anisidine, 57–59°).

General Procedure for Dealkylation of Aromatic Tertiary Amines with TEAF or TMAF.—In a flask provided with a thermometer and a long air condenser (195 × 1.6 cm), the end of which was connected to a receiver, were placed 0.1 mole of the N,N-dialkylaniline and TEAF (or TMAF) (2.5 moles based on formic acid). The mixture was heated at 175–180° for 30 hr with stirring. As the reaction proceeded and the formic acid was consumed, the refluxing temperature became lower because of the increase in triethylamine present in the reaction mixture. Accordingly, triethylamine was topped from the end of the condenser tube. As in most cases escape of TEAF, and in some cases escape of the relatively volatile substrate, could not be avoided during the course of the reaction, additional TEAF was added. In the runs with TMAF, some trimethylamine was lost below the reflux temperature. After 30 hr the reaction mixture was subjected to distillation under reduced pressure, whereupon excess TEAF was removed, accompanied by part of the substrate when the relatively volatile dialkylanilines were used. The resulting distillation residue was further distilled under higher vacuum. In general the N-alkyl-N-formylaniline products of dealkylation were found to be separable from the lower boiling N,N-dialkylanilines and distillable under high vacuum. The distillates were checked by infrared spectra and were purified further by distillation or recrystallization. No product other than the N-alkyl-N-formylaniline was obtained. In a run with N,N-dimethyl-*p*-phenylenediamine, demethylation did not result, but N,N-dimethyl-N′-formyl-*p*-phenylenediamine was formed in almost theoretical yield. The following section gives the yields and identification data for each of the products.

N-Formyl-N,N′,N′-trimethyl-*p*-phenylenediamine was obtained as a solid distillate: bp 170–175° (15 mm); yield 48% (run with TEAF), 49% (run with TMAF). Recrystallization from ether gave needles: mp 102–103°; ν_{max}^{KBr} 1670 cm^{-1} (amide C=O).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.26; H, 7.62; N, 15.73.

N-Formyl-N,N′,N′-trimethyl-*o*-phenylenediamine was obtained as a liquid: bp 145–147° (16 mm); yield 50% (run with TEAF), 54% (run with TMAF); ν_{max}^{liq} 1660 cm^{-1} (C=O); n^{30}D 1.5470.

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 66.99; H, 8.27; N, 15.52.

N,N,N′-Trimethyl-*o*-phenylenediamine hydrochloride was obtained by hydrolysis, prisms from ethanol, mp 178–179° dec.

Anal. Calcd for $C_9H_{16}Cl_2N_2$: C, 48.44; H, 7.23; N, 12.56. Found: C, 48.66; H, 7.34; N, 12.52.

N-Formyl-N-methyl-*p*-hydroxyaniline was obtained as a solid distillate: bp 143–146° (0.005 mm); yield 20%. Recrystallization from ethanol gave needles: mp 108–109° (lit.[33] mp 105–106°); ν_{max}^{KBr} 3200 (O–H), 1650 cm^{-1} (C=O).

N-Formyl-N-methyl-*p*-anisidine was obtained as a liquid distillate: bp 155–157° (17 mm); yield 18% (run with TEAF), 24% (run with TMAF); ν_{max}^{liq} 1665 (C=O), 1250 cm^{-1} (ether); n^{17}D 1.5645.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.01; H, 7.07; N, 8.25.

N-Methyl-*p*-anisidine hydrochloride, mp 119–120° (lit.[34] mp 119–120°), was obtained on hydrolysis.

N-Formyl-N-methyl-*o*-anisidine was obtained as a liquid distillate: bp 146–148° (20 mm); yield 55% (run with TEAF), 54% (run with TMAF); ν_{max}^{liq} 1665 (C=O), 1250 cm^{-1} (ether).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.04; H, 7.14; N, 8.41.

N-Methyl-*o*-anisidine hydrochloride, prisms from ethanol–ether, mp 117–118° (lit.[35] mp 118–120°), was obtained on hydrolysis.

N-Formyl-N-methyl-*m*-anisidine was obtained as a liquid distillate, bp 105–108° (0.05 mm), yield 3%, ν_{max}^{liq} 1660 (C=O), 1230 cm^{-1} (ether), and converted by treatment, following liberation of the base, with phenyl isothiocyanate into **N-methyl-N-*m*-methoxyphenyl-N′-phenylthiourea**: needles from ethanol, mp 97°; ν_{max}^{KBr} 3360 (N–H), 1345 (>NC(=S)–, 1230 cm^{-1} (ether).

Anal. Calcd for $C_{15}H_{16}N_2OS$: C, 66.12; H, 5.85; N, 10.28; S, 11.76. Found: C, 65.74; H, 5.74; N, 10.20; S, 11.69.

N-Formyl-N-*n*-propyl-*p*-anisidine was obtained as a liquid distillate: bp 125–127° (2 mm); yield 27%; ν_{max}^{liq} 1665 (C=O), 1250 cm^{-1} (ether); n^{17}D 1.5400.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.63; H, 8.15; N, 7.00.

N-*n*-Propyl-*p*-anisidine hydrochloride was obtained by hydrolysis with hydrochloric acid, needles from ethanol, mp 123–124° (lit.[33] mp 125°).

N-Benzyl-N-formyl-*p*-anisidine was obtained as a solid distillate: bp 183–185° (0.6 mm); mp 45°; yield 20%; ν_{max}^{KBr} 1670 (C=O), 1250 cm^{-1} (ether).

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.78; H, 6.22; N, 5.76.

N-Formyl-N-(2-phenylethyl)-*p*-anisidine was obtained as a liquid distillate: bp 115–117° (*ca.* 0.005 mm); yield 17% after 120 hr; ν_{max}^{liq} 1670 (C=O), 1250 cm^{-1} (ether); n^{18}D 1.5730.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.73; H, 7.05; N, 5.76.

N-(2-Phenylethyl)-*p*-anisidine hydrochloride was obtained by hydrolysis, plates from ethanol–ether, mp 142–143° (lit.[17] mp 127–128°).

Anal. Calcd for $C_{15}H_{18}ClNO$: C, 68.31; H, 6.87; N, 5.31. Found: C, 68.09; H, 6.86; N, 5.56.

In the dealkylation of N,N-di(2-phenylethyl)-*p*-anisidine, an attendant product was also isolated from the reaction mixture and identified by gas–liquid chromatography through a 2 m × 2.2 mm column of 15% diethylene glycol succinate polyester on 60/80 Chromosorb P at 164–165°, using nitrogen as the carrier gas at 3 kg/cm^2, in a Perkin-Elmer F11 apparatus, as a mixture of **1-phenylethanol**, residence time 2.1 min, and **2-phenylethanol**, 3.5 min.

N-Formyl-N-methyl-*p*-phenetidine was obtained as a solid distillate: bp 130–132° (4 mm); prisms from ether, mp 51–52°; yield 19%; ν_{max}^{KBr} 1660 (C=O), 1250 cm^{-1} (ether).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.65; H, 7.21; N, 7.80.

N-Methyl-*p*-phenetidine hydrochloride was obtained by hydrolysis, needles from ethanol, mp 126–127°.

Anal. Calcd for $C_9H_{14}ClNO$: C, 57.59; H, 7.52; N, 7.46; Cl, 18.89. Found: C, 57.10; H, 7.32; N, 7.31; Cl, 18.83.

N-Formyl-N-methylaniline was obtained as a liquid distillate: bp 121–123° (15 mm) (lit.[36] bp 130–132° (22 mm)); ν_{max}^{liq} 1670 cm^{-1} (C=O); n^{20}D 1.5583.

The hydrolysis product was characterized as **N-methylaniline hydrogen oxalate**, mp 108°.

Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.85; H, 5.72; N, 7.23.

***o*-Chloro-N-formyl-N-methylaniline** was obtained as a liquid distillate: bp 141–143° (20 mm); yield 9%; ν_{max}^{liq} 1670 cm^{-1} (C=O).

Anal. Calcd for C_8H_8ClNO: C, 56.65; H, 4.75; N, 8.26; Cl, 20.91. Found: C, 57.07; H, 5.08; N, 8.05; Cl, 91.65.

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Registry No.—TEAF, 15077-13-1; TMAF, 2738-94-5; N,N-di(phenylethyl)-*p*-anisidine hydrochloride, 15020-04-9; N,N-di(phenylethyl)-*p*-anisidine, 14924-80-2; N-benzyl-N-*n*-propyl-*p*-anisidine hydrochloride, 15020-02-7; N-benzyl-N-*n*-propyl-*p*-anisidine, 14924-81-3; N-benzyl-N-methyl-*p*-anisidine picrate, 15020-03-8; N-formyl-N,N′,N′-trimethyl-*p*-phenylenediamine, 2739-06-2; N-formyl-N,N′,N′-trimethyl-*o*-phenylenediamine, 14924-65-3; N,N,N′-trimethyl-*o*-phenylenediamine hydrochloride, 2427-05-6; N-formyl-N-methyl-*p*-hydroxyaniline, 14924-67-5; N-formyl-N-methyl-*p*-anisidine, 5279-51-6; N-formyl-N-methyl-*o*-anisidine, 14924-69-7; N-formyl-N-methyl-*m*-anisidine, 14924-70-0; N-formyl-N-*m*-propyl-*p*-anisidine, 14924-71-1; N-benzyl-N-formyl-*p*-anisidine, 14924-72-2; N-formyl-N-(2-phenylethyl)-*p*-anisidine, 15038-88-7; N-formyl-N-methyl-*p*-phenetidine, 5635-30-3; N-methyl-*p*-phenetidine hydrochloride, 15206-42-5; N-formyl-N-methylaniline, 93-61-8; N-methylaniline hydrogen oxalate, 14924-75-5; *o*-chloro-N-formyl-N-methylaniline, 14924-76-6; *p*-dimethylaminophenol, 619-60-3; N-methyl-N-*m*-methoxyphenyl-N′-phenylthiourea 14924-78-8.

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Diimide Formation in the Basic Decomposition of N,N-Dimethyl-N-phenylhydrazinium Chloride[1]

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The basic decomposition of N,N-dimethyl-N-phenylhydrazinium chloride in the presence of phenylpropiolic acid causes hydrogenation of the latter exclusively to *cis*-cinnamic acid, a stereospecificity consistent with the postulated transient formation of diimide.

Hydrazinium salts of the form, $(R_3N-NH_2)^+Cl^-$, can be prepared in excellent yields by reacting tertiary amines with gaseous chloramine (eq 1).[3] The anhydrous chloramine required for this reaction is made from ammonia and chlorine in a generator such as that described by Sisler.[4]

$$R_3N + NH_2Cl \longrightarrow (R_3N-NH_2)^+Cl^- \quad (1)$$

These hydrazinium salts are generally stable, hygroscopic substances, unaffected by neutral solvents. In the presence of bases, however, a rather complex decomposition takes place. For example, N,N-dimethyl-N-phenylhydrazinium chloride (I) reacts with sodium ethylate in anhydrous tetrahydrofuran to yield, as identifiable products, nitrogen, hydrogen, ammonia, dimethylaniline, and N-methyl-N-phenylhydrazine. The first step in this basic decomposition is likely a deprotonation (eq 2) to the trisubstituted amine–imine II. By carrying out the

$$\underset{\text{I}}{(PhN(CH_3)_2NH_2)^+Cl^-} + NaOEt \longrightarrow \underset{\text{II}}{PhN^+(CH_3)_2N^-H} + NaCl + EtOH \quad (2)$$

deprotonation of trimethylhydrazinium chloride with potassium amide in liquid ammonia, it was possible to isolate trimethylamine–imine.[5] Similar imines of phosphorus[6] and of arsenic[7] have also been prepared, using sodamide as the deprotonating base in liquid ammonia.

When triphenylphosphine is allowed to react with the amine–imine II, the imino group is transferred to the phosphine (eq 3) to give triphenylphosphine–imine (III). It appears doubtful, however, that this

$$II + Ph_3P \longrightarrow \underset{\text{III}}{Ph_3P{=}NH} + PhN(CH_3)_2 \quad (3)$$

reaction proceeds *via* the intermediate formation of the imine radical, since numerous attempts to detect NH by addition across double bonds have failed.[5] The formation of large amounts of nitrogen and hydrogen during the deprotonation of I suggests, instead, that another compound of nitrogen and hydrogen forms which then easily decomposes, especially in alkaline solutions, to give nitrogen and hydrogen. Such reactivity has been observed for diimide, N_2H_2, which is formed, for example, by the careful oxidation of hydrazine. Hünig[8] and Corey[9] have demonstrated that the hydrogenation reactions observed with hydrazine in the presence of an oxidizing agent occur *via* diimide as the hydrogenating species. They showed that the hydrogenation of phenylpropiolic acid under these conditions leads exclusively to *cis*-cinnamic acid, probably through an unstable, cyclic intermediate, IV. Such a structure is consistent with the observed stereospecificity of the reaction. We

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