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**Formic Acid Reduction. XV.¹⁾ Reaction of N-Methyl and N-Formyl
Derivatives of *p*-Phenylenediamine with Formates.
N-Methylation of Formanilides**

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Conversion of varied N-methyl and N-formyl derivatives of *p*-phenylenediamine to other kinds of analogous compounds with increase and decrease of N-methyl has been found to occur on heating at 175—180° with the high-boiling liquid formates composed of formic acid and trialkylamine. From investigation on this reaction the formate reagents have been introduced to affect N-methylation of formanilides in a course entirely different from the known demethylation by the same reagents.

The distillable salt-like materials composed of formic acid and trialkylamine have been known⁴⁻⁷⁾ and recently developed as good reagents mainly for organic reduction reactions.^{4,5)} In an earlier paper⁷⁾ it was reported in this laboratory that the dealkylation of N,N-dialkylanilines can be effected to give N-alkylformanilides on heating with these reagents.

In a continuing study, it was found that conversions of varied N-methyl and N-formyl derivatives of *p*-phenylenediamine to mixtures of other kinds of analogous compounds with increase and decrease of the N-methyl group occur on heating with the reagents. Beginning with an investigation into this interesting reaction, the present paper deals with a new N-methylation reaction of formanilides induced by the formate reagents.

Substrate compounds, N-methyl and N-formyl derivatives of *p*-phenylenediamine, for the formate reaction are those, I—VI, listed in Table I together with their physical and spectral data. Among these *p*-phenylenediamine derivatives, N,N'-diformyl-N,N'-dimethyl-*p*-phenylenediamine (IV),⁸⁾ which has not been known, and N,N'-diformyl-N-methyl-*p*-phenylenediamine (V)⁹⁾ were prepared by the methods not reported previously.

- 1) Part XIV: M. Sekiya and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **20**, 2128 (1972).
- 2) M. Sekiya initiated this study when he was enjoying the hospitality of Dr. N.J. Leonard's laboratory in the Department of Chemistry at the University of Illinois, Urbana, Illinois, U.S.A.
- 3) Location: 2-2-1 Oshika, Shizuoka.
- 4) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964); M. Sekiya, K. Ito, A. Hara, and J. Suzuki, *ibid.*, **15**, 802 (1967); M. Sekiya, Y. Harada, and K. Tanaka, *ibid.*, **15**, 833 (1967); M. Sekiya and S. Takayama, *ibid.*, **18**, 2146 (1970); K. Mori, H. Sugiyama and M. Sekiya, *ibid.*, **19**, 1722 (1971).
- 5) K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966); M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 738 (1969); *idem, ibid.*, **17**, 747 (1969); M. Sekiya, C. Yanaihara, and J. Suzuki, *ibid.*, **17**, 752 (1969); M. Sekiya and C. Yanaihara, *ibid.*, **17**, 810 (1969); M. Sekiya and K. Suzuki, *ibid.*, **18**, 1530 (1970); *idem, ibid.*, **19**, 1531 (1971); *idem, ibid.*, **19**, 1540 (1971); *idem, ibid.*, **20**, 343 (1972).
- 6) Farbenfabriken Bayer A.G., Neth. Patent 6503120 (1965) [*C.A.*, **64**, 6501 (1966)]; K. Wagner, *Angew. Chem.*, **82**, 73 (1970).
- 7) M. Sekiya, M. Tomie, and N.J. Leonard, *J. Org. Chem.*, **33**, 318 (1968).
- 8) This compound was directly prepared by a new reaction proceeding on heating *p*-nitro-N,N-dimethylaniline with TMAF. Details will be reported in the near future.
- 9) This compound appeared in a patent [S.R. Buc and S.A. Glickmann, U.S. Patent 2647815 (1953) [*C. A.*, **48**, 1017 (1954)], but was prepared referring to the method reported by M. Sekiya and K. Ito [*Chem. Pharm. Bull.* (Tokyo), **14**, 1007 (1966)] through N-(*p*-acetamidophenylaminomethyl)phthalimide from N-acetyl-*p*-phenylenediamine. See Experimental.

TABLE I. Physical and Spectral Data of *p*-Phenylenediamine Derivatives

No.	Compound				Appearance (recryst. solvent)	mp (°C)	IR $\nu_{\text{C=O}}^{\text{KBr}}$ (cm ⁻¹)	UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (log ϵ)
	R ₁	R ₂	R ₃	R ₄				
I	CH ₃	CH ₃	CH ₃	CH ₃	plates (dil. EtOH)	50 ^{a)}		263 (4.24)
II	CH ₃	CH ₃	CH ₃	CHO	needles (ether)	102—103	1665	266 (4.30)
III	CH ₃	CH ₃	CHO	H	plates (benzene)	108 ^{b)}	1675	278 (4.24)
IV	CH ₃	CHO	CH ₃	CHO	needles (EtOH)	201—202	1670	254 (4.27)
V	CH ₃	CHO	CHO	H	prisms (EtOH)	138—141 ^{c)}	1700 1650	259 (4.28)
VI	CHO	H	CHO	H	needles (H ₂ O)	204—205 ^{d)}	1720	268 (4.29)

a) A. Mangini and R. Passerini [*J. Chem. Soc.*, 1956, 4945] reported mp 51°

b) J. Pinnow and G. Pistor [*Ber.*, 26, 1314 (1893)] reported mp 108°

c) S.R. Buc and S.A. Glickman [U.S. Patent, 2647815 (1953)] reported mp 138—141°

d) E. Wundt [*Ber.*, 11, 830 (1878)] reported mp 203.5—204°

Each of them was submitted to heating with TMAF under standardized conditions: 175—180°, 30 hr, and substrate to TMAF (as HCO₂H) molar proportion of 1:25. In the course of the reaction drop of the refluxing temperature, due to the formation of water by decomposition of some part of formic acid, had to be avoided by topping from the end of the long air condenser tube fitted on the reaction flask. As shown in Table II, other series of *p*-phenylenediamine derivatives were obtained as products, in amounts varying with the substrate. After several trials, the general procedures for isolation of the products (see Experimental) were established with accuracy above 90% yield.

TABLE II. TMAF Reaction^{a)} of *p*-Phenylenediamine Derivatives

Substrate	Product and Yield ^{b)} (%)						Total	Increase of methyl group ^{c)}
	I	II	III	IV	V	VI		
I	24 ^{d)}	59	0	10	0	0	93	-79
II	4	72 ^{d)}	0	22	0	0	98	-18
III	4	15	61 ^{d)}	4	10	0	94	+13
IV	1	6	0	93 ^{d)}	0	0	100	+8
V	1	5	2	8	80 ^{d)}	0	96	+23
VI	0	trace	0	1	5	89 ^{d)}	95	+7

a) substrate (0.05 mole) to TMAF (as HCO₂H) molar proportion; 1:25, reaction temperature; 175—180°, reaction time; 30 hr. General procedure is given in Experimental.

b) yield based on the product isolated

c) increase of N-methyl group on the products isolated, based on their yields

d) recovery of the substrate

Although the demethylation of N,N,N',N'-tetramethyl-*p*-phenylenediamine (I) with TEAF was reported in the previous paper,⁷⁾ its TMAF reaction shown in Table II was recognized to give N-formyl-N,N',N'-trimethyl-*p*-phenylenediamine (II) and IV in 59% and 10% yields, respectively. In view of the results shown in Table II it is noticeable that not only such demethylations mainly with the higher methylated substrates but also methylations with the lower methylated substrates were observed. Amount of increase of the N-methyl was

shown to grow as the reaction time was extended. This and the product composition are shown in Table III with the reaction of N-formyl-N',N'-dimethyl-*p*-phenylenediamine (III).

TABLE III. TMAF and TBAF Reaction^{a)} of N-Formyl-N',N'-dimethyl-*p*-phenylenediamine (III)

Reagent	Reaction time (hr)	Product and yield ^{b)} (%)							Increase of methyl group ^{d)}
		I	II	III ^{c)}	IV	V	VI	Total	
TMAF ^{e)}	5	trace	3	93	trace	3	0	99	0
	10	2	6	78	3	5	0	94	+ 5
	30	4	15	61	4	10	0	94	+13
	100	13	21	18	21	19	0	92	+28
TBAF ^{e)}	30	0	12	82	0	5	0	99	+ 7
	60	0	17	77	0	5	0	99	+12
	90	0	26	68	0	5	0	99	+21
	120	0	32	59	0	6	0	97	+26

a) reaction temperature: 175—180°. General procedure is given in Experimental.

b) yield based on the product isolated

c) recovery of the substrate (III)

d) increase of N-methyl group on the products isolated, based on their yields

e) substrate (III) (0.05 mole) to the formate (as HCO₂H) molar proportion; 1:25

Comparative experiments included examinations of efficiencies of some other reagents. Using III as a substrate, reactions with the formate reagents such as TEAF and TBAF and with 99% formic acid were carried out under the same condition as in the foregoing TMAF reaction. The TBAF, bp 108—109° (20 mmHg), abbreviated from "tributylammonium formate", was first prepared for the present work. Elemental analysis and potentiometric titration of the tributylamine component showed the composition 7HCO₂H·3N(C₄H₉)₃. As the results are shown in Table IV, the reactions with these reagents proceeded in the mode

TABLE IV. Formate Reaction^{a)} of N-Formyl-N',N'-dimethyl-*p*-phenylenediamine (III)

Substrate	Reagent	Product and yield ^{b)} (%)							Increase of methyl group ^{d)}
		I	II	III ^{c)}	IV	V	VI	Total	
III	TMAF ^{e)}	4	15	61	4	10	0	94	+13
III	TEAF ^{e)}	0	9	79	0	8	0	96	+ 1
III	TBAF ^{e)}	0	12	82	0	5	0	99	+ 7
III	HCO ₂ H ^{f)}	0	8	62	0	20	0	90	-12

a) reaction temperature: 175—180°, reaction time: 30 hr

b) yield based on the product isolated

c) recovery of the substrate (III)

d) increase of N-methyl group on the products isolated, based on their yields

e) substrate (III) (0.05 mole) to the formate (as HCO₂H) molar proportion; 1:25. General procedure is given in Experimental.

f) substrate (III) (0.1 mole) to HCO₂H molar proportion; 1:40. The reaction was carried out in a zirconium-lined autoclave.

similar to the TMAF reaction. In the reaction with 99% formic acid which was carried out in a zirconium-lined autoclave, the demethylation was shown to be predominant over the methylation. In the TMAF reaction, possible participation of trimethylamine component of TMAF in the methylation is entirely excluded from the results of the reactions shown in Table IV.

Since there was considered another possibility of migration of the N-methyl of *p*-phenylenediamine derivatives to the other nitrogen in the formate reaction, an attempt to carry out the TMAF reaction with N,N-diethyl-N'-formyl-*p*-phenylenediamine on heating at 175—

180° for 50 hr was made in order to see the possible N-ethyl migration. However, no ethyl-migrating product was detected at all, and only the methylated products, N,N-diethyl-N'-formyl-N'-methyl-*p*-phenylenediamine and N,N-diethyl-N',N'-dimethyl-*p*-phenylenediamine, were obtained in 17% and 3% yields, respectively. In view of this fact migration of the N-methyl to the other nitrogen is not likely to occur.

Taking account of simplicity of the product composition in the reaction with TBAF compared with the other reagents, we then conducted the TBAF reactions with the same

TABLE V. TBAF Reaction^{a)} of *p*-Phenylenediamine Derivatives

Substrate	Product and yield ^{b)} (%)							Increase of methyl group ^{c)}
	I	II	III	IV	V	VI	Total	
I	62 ^{d)}	18	0	1	0	0	81	—20
II	0	91 ^{d)}	0	7	0	0	98	— 7
III	0	26	68 ^{d)}	0	5	0	99	+21
IV	0	15	0	84 ^{d)}	0	0	99	+15
V	0	5	6	6	79 ^{d)}	0	96	+22
VI	0	trace	0	2	24	73 ^{d)}	99	+28

a) substrate (0.05 mole) to TBAF (as HCO₂H) molar proportion; 1:25, reaction temperature: 175—180°, reaction time: 90 hr. General procedure is given in Experimental.

b) yield based on the product isolated

c) increase of N-methyl group on the product isolated, based on their yields

d) recovery of the substrate

substrates as those in the TMAF reactions shown in Table II under the conditions of heating at 175—180° for 90 hr. The more simplified results were obtained as shown in Table V, although these product formations showed tendency similar to those obtained in the TMAF reactions shown in Table II. From these results directions of the methylations and of the demethylations may be deduced to follow as shown in Chart 1. That is, the methylation proceeds with the nitrogen types, -NHCHO and $\text{-N} \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$, and, because of no conversions of II to III, IV to V, and V to N,N'-diformyl-*p*-phenylenediamine (VI), the demethylation proceeds only with the $\text{-N} \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$ type. In the formation of the tetramethylated product, I, the TMAF reactions are distinguished from the TBAF reactions. Since the topping liquid is obtained during the course of the TMAF reactions, the volatile I formed escapes in the topping vapor, avoiding the demethylation. On the other hand, because of lower volatility of TBAF, the topping liquid was not obtained during the course of its reaction.

The results described thus far show that the reactions of the formates and formic acid with such N-methyl- and N-formyl-substituted *p*-phenylenediamines cause simultaneously the N-methylation and the demethylation. Of these two the demethylation can be referred to as the reaction similar to the demethylation of N,N-dialkylanilines with the formates, which has previously reported⁷⁾ from this laboratory. However, the formates and formic acid have now been found simultaneously to affect the N-methylation of the *p*-phenylenediamine derivatives in the mode shown in Chart 1. In view of the accumulated facts, it appears that the methylation and the demethylation are not reversible and entirely different each other in their courses and the N-methyl produced comes from the N-formyl of the substrate or formic acid component of the reagents.

When considered from the N-methylation which was effected in part by interaction of formates or formic acid with the *p*-phenylenediamine derivatives, other formanilides are likely to suffer N-methylation under similar reaction condition. Extensive experiments were conducted with a number of formanilides possessing varied substituents and using TMAF as a formate. The reaction was carried out under the following uniform conditions: substrate

TABLE VI. TMAF Reaction^{a)} of Formanilides

Substrate:

Run No.	Substituent X	Product and yield ^{b)} (%)

1	<i>p</i> -N	20	—
2	<i>o</i> -OCH ₃	trace ^{c)}	—
3	<i>m</i> -OCH ₃	7	—
4	<i>p</i> -OCH ₃	7	0.5
5	<i>p</i> -OH	—	1
6	<i>o</i> -CH ₃	7	—
7	<i>m</i> -CH ₃	4	—
8	<i>p</i> -CH ₃	7	—
9	H	—	—
10	<i>p</i> -Cl	8	—
11	<i>p</i> -CO ₂ H	3 ^{d)}	—

a) substrate (0.1 mole) to TMAF (as HCO₂H) molar proportion; 1:25, reaction temperature: 175—180°, reaction time: 30 hr. General procedure is given in Experimental.

b) yield based on the product isolated

c) detected by GC method

d) the decarboxylated product

to TMAF (as HCO_2H) molar proportion of 1:25 and $175\text{--}180^\circ$, 30 hr. The results of the experiments are summarized in Table VI. As can be seen, N-monomethylation in most runs and N,N-dimethylation in some runs were found to proceed to some extent to give N-methylformanilides and N,N-dimethylanilines, respectively. In the run with *p*-formamidobenzoic acid simultaneous decarboxylation occurred to give N-methylformanilide as monomethylation product. Thus the N-methylation of formanilides by interaction of formates, which has not been known, was generally realized, where the N-methyl would be derived from the N-formyl of the substrate or formic acid component of the formate reagents as inferred in the reaction with *p*-phenylenediamine derivatives. Mechanistic study on this new type of the reaction will be reported in a succeeding paper.

Experimental

Preparation of N,N'-Diformyl-N-methyl-*p*-phenylenediamine (V)—In 160 ml of EtOH 14.7 g of phthalimide and 8.5 g of 37% formaline were dissolved and to this solution an ethanolic hydrogenation solution of N-acetyl-*p*-phenylenediamine, obtained by catalytic hydrogenation of 18.0 g of N-acetyl-*p*-nitroaniline over Raney nickel catalyst, was added. The mixture was refluxed for 40 min. After standing overnight the deposited crystals were collected by filtration. This material was almost pure without recrystallization and was identified as N-(*p*-acetamidophenylaminomethyl)phthalimide. Additional small amount of crystals was also obtained by concentration of the filtrate. Total yield, 30.5 g (99%). Yellow prisms, mp $204\text{--}205^\circ$. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3$: C, 66.01; H, 4.89; N, 13.59. Found: C, 65.97; H, 5.00; N, 13.51.

In an autoclave 15.5 g of the material prepared above, 250 ml of EtOH-dioxane of 1:9 proportion, and Raney nickel catalyst prepared from 2 g of 50% alloy were placed. Under 83 kg/cm² (at 20°) of initial hydrogen pressure the whole was heated at $100\text{--}110^\circ$ and shaken. After uptake of hydrogen the reaction solution was concentrated under reduced pressure. Phthalimide was deposited in the concentrated solution and filtered. An oily residue obtained by further concentration of the filtrate was extracted with benzene, and the benzene solution was washed with 3% NaOH solution and dried. Evaporation followed by distillation under reduced pressure gave a distillate, bp $157\text{--}158^\circ$ (0.2 mmHg), weighing 6.6 g (82%). This viscous liquid crystallized after standing for a week. Recrystallization from benzene gave prisms, mp $102\text{--}103^\circ$, which were identified as N-acetyl-N'-methyl-*p*-phenylenediamine. *Anal.* Calcd. for $\text{C}_9\text{H}_{12}\text{ON}_2$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.83; H, 7.35; N, 16.78.

From N-acetyl-N'-methyl-*p*-phenylenediamine obtained, N-methyl-*p*-phenylenediamine dihydrochloride,¹⁰ mp $226\text{--}228^\circ$, was prepared by refluxing with 20% HCl solution. A mixture of 25.0 g of this dihydrochloride and 175 g of TMAF was heated at $110\text{--}120^\circ$ for 3 hr. The reaction solution was concentrated under reduced pressure and the residue was extracted with CHCl_3 . The extract was washed with H_2O and dried. After evaporation the crystalline residue was recrystallized from EtOH to give V, prisms, mp $138\text{--}141^\circ$, weighing 18.2 g (80%). *Anal.* Calcd. for $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$: C, 60.65; H, 5.65; N, 15.72. Found: C, 60.51; H, 5.55; N, 15.61.

Preparation of TBAF—To 518 g of 80% HCO_2H 556 g of tributylamine was added in small portion on cool. Distillation of this mixture under reduced pressure gave a nearly constant-boiling fraction after removal of H_2O and of excess of HCO_2H . After drying over MgSO_4 , redistillation gave a liquid of bp $108\text{--}109^\circ$ (20 mmHg) and of n_D^{25} 1.4381, which was analyzed almost as $7\text{HCO}_2\text{H}\cdot 3\text{N}(\text{C}_4\text{H}_9)_3$. *Anal.* Calcd. for $\text{C}_{43}\text{H}_{95}\text{O}_{14}\text{N}_3$: C, 58.96; H, 10.76; N, 4.79. Found: C, 58.96; H, 10.63; N, 4.91.

A solution of this material dissolved in CHCl_3 -AcOH was titrated potentiometrically with a 0.01N standard solution of HClO_4 in dioxane. Content of tributylamine: Calcd. for $7\text{HCO}_2\text{H}\cdot 3\text{N}(\text{C}_4\text{H}_9)_3$; 63.3%. Found: 62.9%.

General Procedure for Reactions of *p*-Phenylenediamine Derivatives with Formates—Formate reactions of *p*-phenylenediamines shown in Tables II, III, IV, and V, *i.e.*, I, II, III, IV, V, and VI with TMAF and with TBAF, and III with TEAF, were processed by the following general procedure. In a flask provided with a thermometer and a long air condenser tube (*ca.* 195×1.6 cm), the end of which was connected to a receiver, were placed 0.05 mole of the substrate and the formate (1.25 mole based on HCO_2H). The mixture was heated at $175\text{--}180^\circ$ with constant stirring. Since, as the reaction proceeded, HCO_2H was consumed and decomposition of a small part of HCO_2H proceeded at the temperature, the refluxing temperature became lower. Accordingly, the resulting H_2O and triethylamine in the case of TEAF were topped from the end of the condenser tube. In most cases with TMAF and TEAF, escape of a part of the formate could not be avoided and additional formate was added. In the runs with TBAF processed for a long reac-

10) R. Willstätter and A. Pfannenstiel, *Chem. Ber.*, **38**, 2244 (1905). Its melting point is not described.

tion period, consumption of HCO_2H was balanced by addition of 99% HCO_2H . Nevertheless, in runs with the relatively volatile I escape of this substrate could not be avoided during the course of the reaction. In this case the topped substrate was placed back in the reaction flask. Heating was continued for the requisite hours shown in the Tables.

Each of the products was isolated by the following general procedures. The reaction mixture was subjected to distillation under reduced pressure, whereupon excess of formate was removed. The distillate was accompanied by the recovered I when this was used as the substrate. When I was produced this was obtained mainly from the topping liquid by saturation with KOH followed by extraction with ether. The residue obtained by distillation of the reaction solution was thoroughly extracted with petr. ether several times on refluxing. Evaporation of the extract gave II, when it was produced, which formed needles, mp 102—103°, on recrystallization from ether. When substrate III was used the extraction residue was subjected to high vacuum distillation to give recovered III as a solid distillate, bp 155—157° (0.12 mmHg). When III was produced as minor product, extraction with ether was preferable to obtain this product. After trial of extraction with ether the above distillation residue or the foregoing extraction residue was subjected to recrystallization from EtOH to give IV. When both IV and V were produced, fractional recrystallization from EtOH was also used to separate them, IV being less soluble than V. Recrystallization from EtOH gave IV as needles, mp 201—202° and V as prisms, mp 138—141°. Identities of the products I, II, III, IV, V, and VI were made by noting good correspondence of their infrared (IR) spectra with those of authentic samples (see Table I) and by mixed melting point determination with the same samples.

Reaction of N-Formyl-N',N'-dimethyl-*p*-phenylenediamine (III) with Formic Acid shown in Table IV—In a zirconium-lined autoclave were placed 16.4 g (0.1 mole) of III and 184 g (4.0 mole) of 99% HCO_2H . The mixture was heated at 175—180°. As the decomposition of HCO_2H proceeded, the pressure of the content increased. Sometimes, in the case of danger, the decomposing gas was released through the valve. After heating for 30 hr the reaction mixture was concentrated under reduced pressure to remove excess of HCO_2H . The resulting residue was treated by the same manner as described in the preceding formate reactions. Yields of the products are recorded in Table IV.

General Procedure for Reaction of Formanilides with TMAF shown in Table VI—The formanilides possessing the following substituents, prepared as shown with their melting points, were employed as substrates for the formate reaction: *p*- $\text{C}_5\text{H}_{10}\text{N}$ -, mp 137—139° (This new compound was prepared by catalytic reduction of N-(*p*-nitrophenyl)piperidine¹¹) with palladium-on-charcoal catalyst followed by N-formylation with HCO_2H . *Anal.* Calcd. for $\text{C}_{12}\text{H}_{16}\text{ON}_2$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.63; H, 7.91; N, 13.73); *o*- OCH_3 ,¹² mp 83—84°; *m*- OCH_3 ,¹³ mp 57—58°; *p*- OCH_3 ,¹⁴ mp 80—81°; *p*-OH,¹⁵ mp 137—139°; *o*- CH_3 ,¹⁶ mp 58—59°; *m*- CH_3 ,¹⁷ bp 183—185° (20 mmHg); *p*- CH_3 ,¹⁸ mp 49—51°; *p*-H, mp 46—47°; *p*-Cl,¹⁹ mp 100—101°; *p*- CO_2H ,²⁰ mp 266° (decomp.).

In a flask provided with a thermometer and a long air condenser tube connected to a receiver were placed 0.01 mole each of formanilides and 2.5 mole (based on HCO_2H) of TMAF. The mixture was heated at 175—180° for 30 hr with constant stirring. When the refluxing temperature became lower with increase of the reaction time, low-boiling liquid was topped from the end of the condenser tube. In most cases with TMAF escape of some part of the formate could not be avoided and additional TMAF was needed. Nevertheless, simultaneous escape of relatively volatile substance could not be avoided during the course of the reaction. The reaction mixture was concentrated under reduced pressure. The residue and the distillate combined with the topping liquid were separately treated for product isolation as in the following. The residue was composed of N-methylformanilides and the starting formanilides. The former product was separated from the latter by extraction with petr. ether. Physical and analytical data of the N-methylformanilides obtained are recorded in Table VII. The foregoing distillate combined with the topping liquid was diluted with H_2O and in this enough amount of KOH was dissolved so as to liberate an oily material, which was extracted with benzene. After drying over K_2CO_3 dry HCl was passed through the benzene solution, while aniline hydrochlorides precipitated. The precipitates were collected by filtration and recrystallized from EtOH or treated with K_2CO_3 solution to give free anilines which were purified by distillation. Removal of benzene from the above benzene solution, after washing with NaHCO_3 solution and drying over K_2CO_3 , gave a small amount of both N-methylformanilides and the starting formanilides. In

- 11) J.E. LuValle, D.B. Glass, and A. Weissberger, *J. Am. Chem. Soc.*, **70**, 2223 (1948).
- 12) E. Diepolder, *Chem. Ber.*, **32**, 3514 (1899).
- 13) F. Reverdin and A. DeLuc, *Chem. Ber.*, **47**, 1537 (1914).
- 14) L.A. Cort and R.G. Pearson, *J. Chem. Soc.*, **1960**, 1682.
- 15) A.T. Shulgin and H.O. Kerlinger, *J. Org. Chem.*, **25**, 2037 (1960).
- 16) H.R. Hirst and J.B. Cohen, *J. Chem. Soc.*, **67**, 829 (1895).
- 17) V. Niementowski, *Chem. Ber.*, **20**, 1892 (1887).
- 18) E. Bamberger and P. Wurcz, *Chem. Ber.*, **24**, 2077 (1891).
- 19) E.E. Slosson, *Am. Chem. J.*, **29**, 289 (1903).
- 20) A. Zehara, *Chem. Ber.*, **23**, 3625 (1890).

the cases (run 4 and 5) that the oily free base contained N,N-dimethylanilines, this was separated from anilines by extraction with petr. ether. Physical and analytical data of N,N-dimethylanilines are also recorded in Table VII.

In the case of using *p*-formamidobenzoic acid (run 11), simultaneous decarboxylation occurred to give N-methylformanilide

Yields of N-methylformanilides and N,N-dimethylanilines are shown in Table VI. Recovery of the substrate was estimated by summing up yield of the free anilines and recovery of the formanilides. In every run percentage of summation of the yields of the products and the recovery of the substrate attained to above 90%.

TABLE VII. Physical and Analytical Data of the Product in the TMAF Reaction with Formanilides

Product	Appearance (Recryst. solvent)	bp (°C/mmHg) or mp (°C)	n_D (°C)	IR $\nu_{C=O}$ (cm ⁻¹)	Formula	Analysis (%)		
							Found	Calcd.	
							C	H	N
<i>m</i> -OCH ₃	CH ₃	liquid	96/3 ^{a)}	1.5610 (12)		C ₉ H ₁₃ ON	71.54 (71.49)	8.86 (8.67)	9.46 (9.26)
<i>p</i> -OCH ₃	CH ₃	plates (dil. EtOH)	mp 48 ^{b)}			C ₉ H ₁₃ ON	71.79 (71.49)	8.57 (8.67)	9.40 (9.26)
<i>p</i> -C ₅ H ₁₀	CHO	prisms (ether-petr. ether)	mp 80—81		1675	C ₁₃ H ₁₈ ON ₂	71.64 (71.52)	8.33 (8.31)	12.64 (12.83)
<i>o</i> -OCH ₃	CHO	liquid	150—153/21 ^{c)}	1.4859 (30)	1665	C ₉ H ₁₁ O ₂ N	65.71 (65.51)	6.88 (6.71)	8.56 (8.48)
<i>m</i> -OCH ₃	CHO	liquid	113—116/1 ^{d)}	1.4565 (30)	1660	C ₉ H ₁₁ O ₂ N	65.71 (65.51)	6.83 (6.71)	8.55 (8.48)
<i>p</i> -OCH ₃	CHO	liquid	165—168/20 ^{e)}	1.5654 (17)	1665	C ₉ H ₁₁ O ₂ N	65.45 (65.51)	6.87 (6.71)	8.52 (8.48)
<i>o</i> -CH ₃	CHO	liquid	145—147/28 ^{f)}	1.5495 (25)	1678	C ₉ H ₁₁ ON	72.41 (72.45)	7.39 (7.43)	9.48 (9.39)
<i>m</i> -CH ₃	CHO	liquid	135—138/25 ^{g)}	1.5501 (24)	1662	C ₉ H ₁₁ ON	72.44 (72.45)	7.46 (7.43)	9.51 (9.39)
<i>p</i> -CH ₃	CHO	liquid	145—147/18 ^{h)}	1.5512 (20)	1678	C ₉ H ₁₁ ON	72.55 (72.45)	7.34 (7.43)	9.55 (9.39)
<i>p</i> -Cl	CHO	leaflets (petr. ether)	mp 51—52 ⁱ⁾		1645	C ₈ H ₈ ONCl	56.60 (56.64)	4.87 (4.75)	8.42 (8.25)
H	CHO	liquid	121—123/15 ^{j)}	1.5538 (20)	1670	C ₈ H ₉ ON	71.28 (71.09)	6.67 (6.71)	10.54 (10.37)

a) H.P. Crocker and B. Jones [*J. Chem. Soc.*, **1959**, 1808] reported bp 118° (6 mmHg)

b) A. Mangini and R. Passerini [*J. Chem. Soc.*, **1956**, 4954] reported mp 48°

c) M. Sekiya, M. Tomie, and N.J. Leonard [*J. Org. Chem.*, **33**, 318 (1968)] reported bp 146—148° (20 mmHg)

d) M. Sekiya, M. Tomie, and N.J. Leonard [*J. Org. Chem.*] reported bp 105—108° (0.05 mmHg)

e) M. Sekiya, M. Tomie, and N.J. Leonard [*J. Org. Chem.*] reported bp 155—157° (17 mmHg)

f) L. Marion and W. Ashford [*Can. J. Research*, **23B**, 26 (1945)] reported bp 85—90° (1 mmHg)

g) R.M. Robert and P.J. Vogt [*J. Am. Chem. Soc.*, **78**, 4778 (1956)] reported bp 163—164° (40 mmHg)

h) M. Sekiya and K. Ito [*Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964)] reported bp 160—163° (25 mmHg)

i) R.M. Robert and P.J. Vogt [*J. Am. Chem. Soc.*, **78**, 4778 (1956)] reported mp 51°

j) L.F. Fieser and J.E. Jones [*Organic Syntheses*, Coll. Vol. III, p. 590 (1955)] reported bp 130—132° (15 mmHg)

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