Summary

1-Acylaminoarylmethylation of ethyl malonate was effected in several cases by interaction of N-arylmethylene-1-acylamino-1-arylmethylamine in refluxing toluene solution with suspended sodium hydroxide powder. Ethyl cyanoacetate, phenylacetonitrile and malononitrile formed arylmethylene derivatives under the same condition as with ethyl malonate.

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96. Minoru Sekiya and Keiichi Ito: Reduction with Formic Acid. I. Reduction of N-Acylaminomethyl and N-Sulfonamidomethyl Compound.

(*Shizuoka College of Pharmacy*[*1])

Previously,[1] the catalytic reduction of N-acylaminomethyl compounds was shown in some examples to result in a reductive fission of the carbon bond connecting to amide nitrogen. Lately, a similar mode of the reduction was also found to occur in formic acid reduction.

$$RCON\text{-}CH_2\text{-}N\langle \xrightarrow{HCOOH} RCONH + CH_3N\langle$$

On formic acid reduction of compound of alkylidenediamine type there have been some reports indicating the reductive fission of the carbon-nitrogen bond, in which reductions of 1,1′-benzylidenedipiperidine,[2] 1,1′-methylenedipiperidine,[3] and N,N,N′,N′-tetrabenzylmethylenediamine[3] were examined, however, no report has been made in the case of monoacylated alkylidenediamine. The present paper reports the studies on the formic acid reduction reaction with a series of N-acylaminomethyl and N-sulfonamidomethyl compounds, which have been developed in this laboratory.

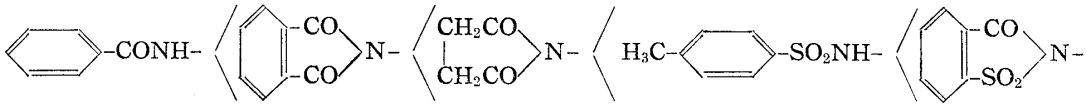
In this work the trimethylammonium formate, which was previously reported[4] to be constant-boiling liquid salt given by $5HCOOH \cdot 2N(CH_3)_3$, was employed as a reducing agent. Though there was another paper[5] in which salt of formic acid with aliphatic tertiary amine was reported to be a 2:1 addition product, the above composition of trimethylammonium formate was reaffirmed by analyses and the same 5:2 proportion of formic acid and tertiary amine was also analyzed correctly with the salts of 1-methylpiperidine and of 4-methylmorpholine, which were shown to be constant-boiling liquid of $b.p_{20}$ 100.5° and of $b.p_{20}$ 89~90° respectively. On the use of trimethylammonium formate as a reducing agent, its constant high boiling point and very weak acidity appeared to

*1 Oshika, Shizuoka (関屋 実, 伊藤敬一).

1) M. Sekiya, K. Ito: This Bulletin, **11**, 892 (1963).
2) E. Staple, E. C. Wagner: J. Org. Chem., **14**, 565 (1949).
3) H. T. Clarke, H. B. Gillespie, S. Z. Weisshaus: J. Am. Chem. Soc., **55**, 4572 (1933).
4) M. G. André: Compt. rend., **126**, 1106 (1898).
5) P. L. deBenneville, J. H. Macartney: J. Am. Chem. Soc., **72**, 3074 (1950).

be convenient to carry out the reaction at high temperature in weak acidic medium. It was recognized that hydrolysis of the starting material in the reaction with formic acid was inhibited in larger extent in that with trimethylammonium formate. Comparative data between the experiments with trimethylammonium formate and 98% formic acid are shown in Table I (run 1, 2, and 7) with respect to three representative N-acylaminomethyl compounds, *i.e.*, N-(piperidinomethyl)benzamide, N-(piperidinomethyl)-phthalimide, and N-(N-methyl-*p*-toluidinomethyl)phthalimide. As can be seen, every yield on these runs with 98% formic acid was lower than that with trimethylammonium formate, a side reaction giving N-formylated amine which is formed through formylation of hydrolyzed amine.

Thus, using trimethylammonium formate as reducing agent, a variety of N-acylaminomethyl and N-sulfonamidomethyl compounds were submitted to the reduction. As shown in Table I, the reduction of N-acylaminomethyl and N-sulfonamidomethyl compounds attached to aliphatic secondary amine such as piperidine and morpholine proceeded in almost theoretical yield in every case giving N-methylated amine and amide (run 1a, 2a, 3, 4, 5, and 6). So, this process appears to be very available for the N-methylation of aliphatic secondary amine. By taking account of the time required for the reaction, relative reactivities of these compounds are also deduced from the table to increase in the following order with respect to their acylamino and sulfonamido group.



This order is in agreement with the decreasing order of the electron densities of their amido nitrogen. So it can be said that ease of the reduction increases with lowering the electron density of the nitrogen atom.

As N-acylaminomethyl compound attached to aromatic secondary amine, some phthalimidomethyl homologs were employed for the reduction with trimethylammonium formate (run 7, 8, 9, and 10). As can be seen in comparison between run 7a and 2a or 3, at 90~100°, N-(N-methyl-*p*-toluidinomethyl)phthalimide took the reaction time about twice as long as N-piperidino or N-morpholinomethylphthalimide, even on 65% of the reduction. As also shown in other runs (8, 9, and 10), the compounds attached to aromatic secondary amine were generally less reactive than the aliphatic secondary amine homologs and in every case hydrolysis of the material took place as a side reaction resulting in the formation of N-formylated amine. In the cases of run 9 and 10, in addition to this side reaction, formation of the *p,p'*-diarylmethane possessing a methylene bridge between two N-methylated amines also proceeded to very considerable extent as shown in Table I. While a part of this methylene formation is considered to result from the methylene group of the starting N-phthalimidomethyl compound, such a great deal of the formation can be explained to be led through a reaction with formic acid in reaction environment. The similar type of the reaction was previously reported,[6] in which the formation of bis(*p*-dimethylaminophenyl)methane resulted by heating N,N-dimethylaniline with formic acid. As can be seen in run 7a, 7b, and 8, in which the *para* positions are occupied by substituent, no diarylmethane formation was observed and in higher yield N-methylated amine was obtained.

With a view to reduce the formation of diarylmethane, the method was improved for the reaction with N-(N-methylanilinomethyl)phthalimide (run 9b) and with 1-phthalimidomethyl-1,2,3,4-tetrahydroquinoline (run 10b). The improved method is that during

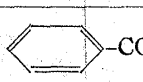
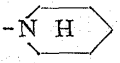
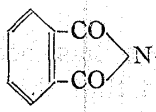
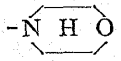
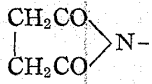
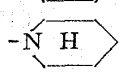
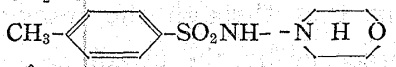
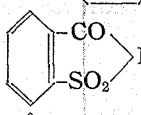
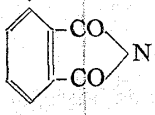
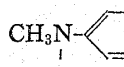
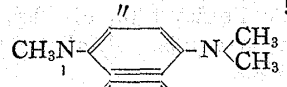
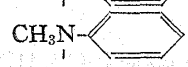
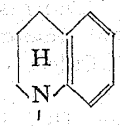
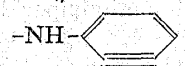
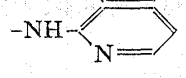
6) E. Votoček, C. Krauz : Ber., **42**, 1604 (1909).

the reaction the reaction mixture was allowed to be boiled simultaneously with a dropwise addition of trimethylammonium formate, while N-methylated amine was distilled together with the formate. As shown in Table I, this method gave N-methylated amine in yield of about 20% more than the usual method (12% in 9a and 11% in 10a).

Reduction of N-phthalimidomethyl compounds attached to aromatic primary amine (run 11 and 12) resulted in no formation of the reduction product, resinous product accompanied by some amount of hydrolysis product, N-formylated amine, was obtained

Table I. Formic Acid Reduction of N-Acylaminomethyl and N-Sulfonamidomethyl Compound

$$X\text{-}CH_2\text{-}Y \longrightarrow XH + CH_3Y$$

Run	Substituent X	Substituent Y	Reducing agent	Reaction temp. (°C)	Reaction time (hr.)	Yield of CH_3Y (%)
1a			$5HCOOH \cdot 2N(CH_3)_3$	90~100	12	97
1b	〃	〃	HCOOH	90~100	8	76
2a		〃	$5HCOOH \cdot 2N(CH_3)_3$	90~100	8	96
2b	〃	〃	HCOOH	90~100	5	93
3	〃		$5HCOOH \cdot 2N(CH_3)_3$	90~100	8	95
4			〃	90~100	3	93
5		〃	60~70	2	97
6		〃	〃	50~60	1.5	95
7a			〃	90~100	17	65
7b	〃	〃	HCOOH	90~100	15	33
7c	〃	〃	$5HCOOH \cdot 2N(CH_3)_3$	160~170	1.5	68
8	〃		〃	160~170	2	69
9a	〃		〃	160~170	2	12
9b	〃	〃	〃	160~170	1.5	31
10a	〃		〃	160~170	2	11
10b	〃	〃	〃	160~170	1.5	29
11	〃		〃	160~170	4	—
12	〃		〃	160~170	6	—

In the following runs, the following by-products were obtained in yields written in parentheses: 1b) 1-Formylpiperidine (18) and N,N′-methylenebisbenzamide (20), 7a) N-Methyl-N-*p*-tolylformamide (24), 7b) N-Methyl-N-*p*-tolylformamide (59), 7c) N-Methyl-N-*p*-tolylformamide (18), 8) N-Formyl-N,N′,N′-trimethyl-*p*-phenylenediamine (21), 9a) N-Methyl-N-phenylformamide (7) and bis(*p*-dimethylaminophenyl)methane (59), 9b) N-Methyl-N-phenylformamide (10) and bis(*p*-dimethylaminophenyl)methane (47), 10a) 1-Formyl-1,2,3,4-tetrahydroquinoline (9) and 1,1′-dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-6,6′-methylenediquinoline (65), 10b) 1-Formyl-1,2,3,4-tetrahydroquinoline (12) and 1,1′-dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-6,6′-methylenediquinoline (43), 11) N-Phenylformamide (10) accompanied with resinous product, 12) 2-Aminopyridine (53) accompanied with resinous product.

instead. N,N'-Methylenebisbenzamide was resistant to the reduction even after as long as 90 hours at 160~170°.

The foresaid facts concerning nature of the reduction can be summarized as follows: Reactivity increases with lowering the electron density of the amido nitrogen of N-acylaminomethyl compound and with raising the electron density of amine nitrogen of the compound. In addition, it was also known that representative O-acylaminomethyl compounds such as N-(methoxymethyl)benzamide and N-(phenethyloxymethyl)phthalimide did not undergo the formic acid reduction at any condition. A general reaction path for the formic acid reduction of N-acylaminomethyl compound which accounts for these facts can be proposed. The compound first forms quaternary ammonium ion by protonation at amine nitrogen and then hydride of the formate ion becomes attached with a subsequent release of carbon dioxide.

$$\mathrm{ArCON(H)\text{-}CH_2\text{-}N<} \underset{}{\overset{\mathrm{H^{\oplus}\ or\ NHR_3^{\oplus}}}{\rightleftharpoons}} \mathrm{ArCON(H)\text{-}CH_2\text{-}\overset{\oplus}{N}H<}$$

$$\xrightarrow[-CO_2]{HCOO^{\ominus}} \mathrm{ArCON^{\ominus}} + \mathrm{CH_3\text{-}\overset{\oplus}{N}H<} \xrightarrow{\text{acid medium}} \mathrm{ArCONH} + \mathrm{CH_3\text{-}\overset{\oplus}{N}H<}$$

In relation to the mechanism for the formic acid reduction, there has been the paper[7] concerning the reduction of enamine, in which it was established that the reduction proceeds through the intermediate ternary iminium formate as follows.

$$\mathrm{>C{=}C\text{-}N<} \underset{}{\overset{HCOOH}{\rightleftharpoons}} \mathrm{[>CH\text{-}\overset{\oplus}{C}{=}\overset{\oplus}{N}<]HCOO^{\ominus}} \longrightarrow \mathrm{>CH\text{-}CH\text{-}N<} + CO_2$$

This pathway agrees with the above one on the point that through the intermediate possessing $>\overset{\oplus}{N}<$ the reduction with the formate ion proceeds by the attachment of the hydride.

Experimental

Formate of Aliphatic Tertiary Amines

Trimethylammonium Formate——To the ice cooled 80% $HCO_2H \cdot N(CH_3)_3$ gas was introduced until the solution became basic. The solution was concentrated on a water bath under reduced pressure to remove H_2O and the residue was distilled to give a liquid, $b.p_{18}$ 91~93°, n_D^{25} 1.4107. The composition of this liquid was shown to be $5HCO_2H \cdot 2N(CH_3)_3$ by analysis. *Anal.* Calcd. for $C_{11}H_{28}O_{10}N_2$: C, 37.92; H, 8.10; N, 8.04. Found: C, 38.00; H, 8.12; N, 7.89.

Its yield on this preparation was almost theoretical.

1-Methylpiperidinium Formate——To 24 ml. of the ice cooled 80% HCO_2H, 24 g. of 1-methylpiperidine was added. The solution was concentrated to remove H_2O. The residual liquid was submitted to distillation under reduced pressure to give the almost theoretical amount of the formate of a liquid, $b.p_{20}$ 100.5°, n_D^{30} 1.4394, analyzed for $5HCO_2H \cdot 2CH_3NC_5H_{10}$. *Anal.* Calcd. for $C_{17}H_{36}O_{10}N_2$: C, 47.66; H, 8.47; N, 6.54. Found: C, 47.57; H, 8.46; N, 6.40.

4-Methylmorpholinium Formate——A mixture of 24 ml. of 80% HCO_2H and 24 g. of 4-methylmorpholine was treated in the same manner as described for 1-methylpiperidinium formate. The formate was obtained in almost theoretical yield as a liquid, $b.p_{20}$ 89~90°, n_D^{17} 1.4442, analyzed for $5HCO_2H \cdot 2CH_3N(C_2H_4)_2O$. *Anal.* Calcd. for $C_{15}H_{32}O_{12}N_2$: C, 41.66; H, 7.46; N, 6.48. Found: C, 41.31; H, 7.28; N, 6.16.

Preparation of N-Acylaminomethyl Compound

1-Phthalimidomethyl-1,2,3,4-tetrahydroquinoline——In 170 ml. of EtOH 26.5 g. of phthalimide, 18 ml. of 37% CH_2O, and 25.2 g. of 1,2,3,4-tetrahydroquinoline were dissolved and the solution was refluxed for 30 min. After cool, the deposited crystals were collected. Recrystallization from EtOH gave leaves, m.p. 119~120°, weighing 45.5 g. (86% yield). *Anal.* Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.97; H, 5.62; N, 9.26.

7) N. J. Leonard, R. R. Sauers: J. Am. Chem. Soc., **79**, 6210 (1957).

N-Phthalimidomethyl-N,N′,N′-trimethyl-*p*-phenylenediamine——In 140 ml. of EtOH 14.7 g. of phthalimide, 10 ml. of 37% CH_2O, and 16.5 g. of N,N,N′-trimethyl-*p*-phenylenediamine were dissolved and the solution was refluxed for 30 min. The reaction solution was concentrated under reduced pressure, the residue was washed with Et_2O, and the deposited crystals were collected and recrystallized from EtOH to prisms, m.p. 87~89°, weighing 21.9 g. (71% yield). *Anal.* Calcd. for $C_{18}H_{19}O_2N_3$: C, 69.88; H, 6.19; N, 13.58. Found : C, 69.53; H, 6.58; N, 13.22.

Formic Acid Reduction of N-Acylaminomethyl and N-Sulfonamidomethyl Compound

General Procedure——All the runs in Table I, in which trimethylammonium formate (TMAF for short) was used as reducing agent, were worked up as described in the following, with the exception of run 9b and 10b.

In a flask provided with a long air condenser tube, 0.1 mole of N-acylaminomethyl or N-sulfonamidomethyl compound and 50 g. (0.7 mole as HCO_2H) of TMAF were placed and the mixture was heated or refluxed at the desired temperature with constant stirring until the evolution of CO_2 was ceased.

In some cases, a part of the amide product deposited in the reaction mixture was removed by filtration. The reaction solution was submitted to distillation under reduced pressure whereupon the N-methylated amine product was distilled. The N-methylated aliphatic amines in run 1a, 2a, 3, 4, 5, and 6 were obtained as a constant-boiling liquid salt given by $5HCO_2H \cdot 2NR_3$, while the aromatic amines in run 7a, 7c, 8, 9a, 10a, 11, and 12 were distilled together with TMAF. The distillate was treated with KOH on cool as usual, the liberated oil was extracted with Et_2O and dried over K_2CO_3. After removal of Et_2O, distillation of the residual liquid gave the N-methylated amine as a constant-boiling liquid, which was identified as its picrate. The N-formylated amine, when it was formed through a side reaction, was also distilled as a part of the above distillate of the reaction solution. This was separated by fractional distillation of the Et_2O extract.

A part of the amide product, in some cases, was obtained when the reaction mixture was cooled and filtered. Usually, distillation of the reaction solution gave the amide product as the residue. Its yield was almost theoretical.

The *p,p′*-diarylmethane formed in run 9a and 10a took a part of the residue on the distillation of the reaction solution and was separated from the accompanying amide by Et_2O extraction of the residue.

In the cases of HCO_2H reduction shown in run 1b, 2b, and 7b, 0.7 mole of 98% HCO_2H was used in place of TMAF. The procedure of run 1b and 2b is the same as described above. In run 7b, the separation of the amine products was accomplished by fractional distillation of the reaction solution.

Improved Procedure——The procedure of run 9b and 10b is as follows. In a flask provided with a distillation tube, 0.1 mole of N-(N-methylanilinomethyl)phthalimide or 1-phthalimidomethyl-1,2,3,4-tetrahydroquinoline and 50 g. (0.7 mole as HCO_2H) of TMAF were placed and the mixture was boiled at 160~170° simultaneously with a dropwise addition of further 200 g. of TMAF, while the N-methylated amine product was distilled together with the formate. The process was discontinued when there was no insoluble oily material in the distillate. The distillate and the residual solution were separately treated in the same manner as described in the general procedure.

Identification of the Amine Products

Formic Acid Reduction of N-(Piperidinomethyl)benzamide[8]——1-Methylpiperidine : b.p. 102~104°. Picrate, m.p. 220~222°, undepressed on admixture with an authentic sample.

1-Formylpiperidine : $b.p_{15}$ 99~103°. IR ν_{max}^{liquid} 1655 cm^{-1} (-CON<). By hydrolysis with 10% HCl, this was converted to piperidine. 1-Phenyl-3,3-pentamethylenethiourea, m.p. 98~100°, undepressed on admixture with an authentic sample. *Anal.* Calcd. for $C_{12}H_{16}N_2S$: C, 65.43; H, 7.32; N, 12.72. Found : C, 65.41; H, 7.44; N, 12.58.

N,N′-Methylenebisbenzamide : m.p. 224~222°, undepressed on admixture with an authentic sample.

Formic Acid Reduction of N-(Piperidinomethyl)phthalimide[9] **and TMAF Reduction of N-(Piperidinomethyl)benzamide, N-(Piperidinomethyl)phthalimide, or N-(Piperidinomethyl)succinimide**[10]——1-Methylpiperidine : b.p. 102~104°. Picrate, m.p. 220~222°, undepressed on admixture with an authentic sample.

TMAF Reduction of N-(Morpholinomethyl)phthalimide,[11] **N-(Morpholinomethyl)-*p*-toluenesulfonamide,**[12] **or N-(Morpholinomethyl)saccharin**[13]——4-Methylmorpholine : b.p. 111~115°. Picrate, m.p. 221~223°, undepressed on admixture with an authentic sample. *Anal.* Calcd. for $C_{11}H_{14}O_8N_4$: C, 40.00; H, 4.27; N, 16.97. Found : C, 39.92; H, 4.27; N, 16.82.

8) A. Einhorn : Ann., **343**, 207 (1905).
9) H. W. Heine, M. B. Winstead, R. P. Blairs : J. Am. Chem. Soc., **78**, 672 (1956).
10) J. R. Feldman, E. C. Wagner : J. Org. Chem., **7**, 45 (1942).
11) H. Hellmann, I. Löschmann : Chem. Ber., **87**, 1688 (1954).
12) W. J. Weavers, J. K. Simons, W. E. Baldwin : J. Am. Chem. Soc., **66**, 222 (1944).
13) H. Zinner, U. Zelck, G. Rembarz : J. prakt. Chem., 8, 150 (1959).

Formic Acid or TMAF Reduction of N-(N-Methyl-*p*-toluidinomethyl)phthalimide[9]——N,N-Dimethyl-*p*-toluidine : b.p_{25} 103～105°. Picrate, m.p. 130～131°. *Anal.* Calcd. for $C_{15}H_{16}O_7N_4$: C, 49.45; H, 4.43; N, 15.38. Found : C, 49.44; H, 4.64; N, 15.56.
N-Methyl-N-*p*-tolylformamide : b.p_{25} 160～163°. *Anal.* Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found : C, 72.41; H, 7.59; N, 9.18.

By hydrolysis with 10% HCl, N-methyl-*p*-toluidine·HCl, m.p. 115～116°, was obtained. The melting point was not depressed on admixture with an authentic sample.

TMAF Reduction of N-Phthalimidomethyl-N,N′,N′-trimethyl-*p*-phenylenediamine——N,N,N′,N′-tetramethyl-*p*-phenylenediamine : b.p_{15} 128～130°, leaves (from ligroin), m.p. 50～51°, undepressed on admixture with an authentic sample. *Anal.* Calcd. for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found : C, 73.41; H, 9.77; N, 16.95.
N-Formyl-N,N′,N′-trimethyl-*p*-phenylenediamine : b.p_{15} 170～172°, prisms (from EtOH), m.p. 99～100°. *Anal.* Calcd. for $C_{10}H_{14}ON_2$: C, 67.38; H, 7.92; N, 15.72. Found : C, 67.28; H, 8.27; N, 15.33.

By hydrolysis with 10% HCl, N,N,N′-trimethyl-*p*-phenylenediamine·2HCl, m.p. 219°(decomp.), was obtained. *Anal.* Calcd. for $C_9H_{16}N_2Cl_2$: C, 48.44; H, 7.23; N, 13.79. Found : C, 48.01; H, 7.20; N, 13.63.

TMAF Reduction of N-(N-Methylanilinomethyl)phthalimide[9]——N,N-Dimethylaniline : b.p_{20} 87～90°. Picrate, m.p. 155～157°, undepressed on admixture with an authentic sample.
N-Methyl-N-phenylformamide : b.p_{23} 132～136°. By hydrolysis with 10% HCl, N-methylaniline·HCl, m.p. 121～122°, was obtained. The melting point was not depressed on admixture with an authentic sample.
Bis(*p*-dimethylaminophenyl)methane : b.$p_{0.05}$ 200～210°, leaves (from EtOH), m.p. 89～92°, undepressed on admixture with an authentic sample. *Anal.* Calcd. for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.07; H, 8.72; N, 10.74.

TMAF Reduction of 1-Phthalimidomethyl-1,2,3,4-tetrahydroquinoline——1-Methyl-1,2,3,4-tetrahydroquinoline : b.p_{24} 140～143°. Picrate, m.p. 134～135°. *Anal.* Calcd. for $C_{16}H_{16}O_7N_4$: C, 51.06; H, 4.29; N, 14.89. Found : C, 51.25; H, 4.25; N, 15.13.
1-Formyl-1,2,3,4-tetrahydroquinoline : b.p_5 147～149°. *Anal.* Calcd. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69. Found : C, 74.34; H, 6.63; N, 8.56.

By hydrolysis with 10% HCl, 1,2,3,4-tetrahydroquinoline·HCl, m.p. 180～181°, was obtained. The melting point was not depressed on admixture with an authentic sample.
1,1′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-6,6′-methylenediquinoline : b.$p_{0.07}$ 216～218°. *Anal.* Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.14. Found : C, 82.56; H, 8.66; N, 9.37.

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Summary

A number of N-acylaminomethyl and N-sulfonamidomethyl compounds were subjected to formic acid reduction using trimethylammonium formate as a reducing agent. The reduction was found to lead to a fission of the carbon bond connecting to the amide nitrogen. Ease of the reduction increased with lowering the electron density of the amide nitrogen. The compounds attached to aliphatic amine underwent the reduction almost quantitatively and, on the other hand, the aromatic amine homologs were less reactive. A possible mechanism for the reduction was proposed.

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