  Bull. Chem. Soc. Jpn., 60, 3597—3601 (1987) 

# Alkaline Hydrolysis of *N*-Methyl-2,4-dinitroacetanilide and *N*-Alkyl-*N*-(5-nitro-2-pyridyl)acetamides

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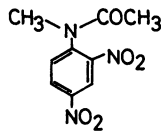
(Received November 21, 1986)

The kinetics of the alkaline hydrolysis of *N*-methyl-2,4-dinitroacetanilide (**2**), *N*-ethyl- (**3**), and *N*-methyl-*N*-(5-nitro-2-pyridyl)acetamide (**4**) was carried out. The reaction path consists of two stages: the first one is the rate-limiting formation of the first tetrahedral intermediate (monoanionic) and the second one the fast decomposition of the intermediate. The latter fast decomposition of the intermediate (monoanionic) involves two processes: one is the direct decomposition of the intermediate to the products and the other is a proton abstraction of the hydroxyl group of the intermediate by $^-$OH giving the second tetrahedral intermediate (dianionic), followed by its deconposition to the products. For the alkaline hydrolysis of **2**—**4**, the decomposition of the first intermediate occurred predominantly via the latter process.

Many reports and reviews have so far appeared on the alkaline hydrolysis of amides.[1] In particular the alkaline hydrolysis of acetanilides has been extensively studied by Schowen et al.,[2-6] Pollack and Bender,[7] Dewolfe and Newcomb,[8] and Eriksson et al.[9] The alkaline hydrolysis of amides is generally considered to be sensitive to both polar and steric effects of acyl substituents. We have already reported the alkaline hydrolysis of *N*-ethyl-2,4-dinitroacetanilide (**1**) and found that the substituents on the amido nitrogen atom and on the phenyl moiety considerably affect its rate of hydrolysis.[10] Although previous studies involved the effects of substituents on the amido nitrogen atom and ring carbon atom of acetanilides, there have been few cases in which both effects are considered[2-9] simultaneously.

This paper reports the effects of substituents of the following acetanilide and *N*-pyridylacetamides on their rates of alkaline hydrolyses to elucidate the nature of these effects (inductive or steric).



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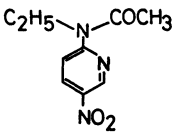

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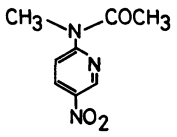

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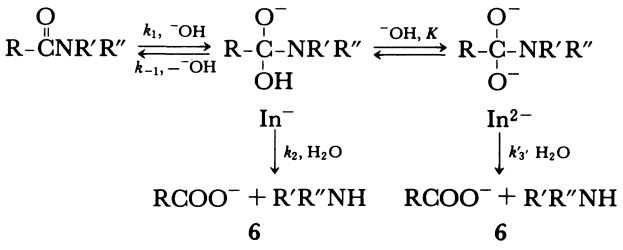
## Results and Discussion

**Absorption Spectra.** The time-dependent spectral changes were measured in the reactions of **2** with excess NaOH (Fig. 1). The spectral change was found to be moderate for the reaction rate to be measured, where the absorption (d) was due to *N*-methyl-2,4-dinitroaniline (Fig. 1). For **3** and **4**, similar changes were observed (not shown).

From these results and much information obtained so far,[1-10] the reaction sequence is shown in Scheme 1 in unbuffered solutions.

**Order of Reaction.** The kinetic order with respect to [NaOH] is important for considering the reaction




Scheme 1.

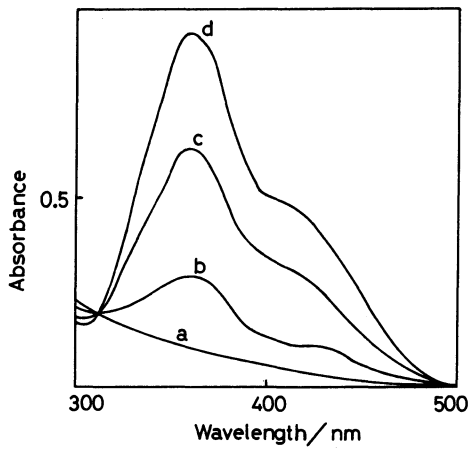



Fig. 1. Time-dependent spectral change in the alkaline hydrolysis of *N*-methyl-2,4-dinitroacetanilide (**2**) at 30°C {[$^-$OH] 0.1 M}: a **2** ($3.0\times10^{-5}$ M); b 10 min after addition of NaOH; c 45 min; d 19 h.

mechanism. The relationships between log $k_\psi$ (pseudo first-order rate constant) and log[$^-$OH] (Table 1), therefore, are shown in Fig. 2, together with those of **1** and 4-nitroacetanilide (**7**).[7]

For **7**, the slope varied from ca. 2 at log [$^-$OH] $\leqslant$ ca. $-1.0$ to ca. 1 at log [$^-$OH] $\geqslant$ ca. $-1.0$, which shows that at lower log [$^-$OH] the decomposition of $In^-$ to $In^{2-}$ is rate-limiting, whereas at higher log [$^-$OH] the addition of $^-$OH to the carbonyl carbon atom of an amido group is rate-limiting (refer to Eq. 1).

On the other hand, for **1**—**4** the slope was ca. 1 in the

Table 1. Dependence of Pseudo First-Order Rate Constants on Hydroxide Ion Concentrations in the Alkaline Hydrolyses of *N*-Methyl-2,4-dinitroacetanilide (**2**), and *N*-Methyl- (**3**) and *N*-Ethyl-*N*-(5-nitro-2-pyridyl)acetamide (**4**)[a]

| [⁻OH] / M | $k_\psi$ / min⁻¹ Obsd[b] | $k_\psi$ / min⁻¹ Calcd[c] | [⁻OH] / M | $k_\psi$ / min⁻¹ Obsd[b] | $k_\psi$ / min⁻¹ Calcd[c] |
|---|---|---|---|---|---|
| | **2** 50 °C | | | **2** 60 °C | |
| 0.0095 | 0.0055 | 0.0055 | 0.00185 | 0.0017 | 0.0013 |
| 0.0190 | 0.0112 | 0.0113 | 0.00090 | 0.0037 | 0.0033 |
| 0.0285 | 0.0171 | 0.0172 | 0.00585 | 0.0056 | 0.0055 |
| 0.0380 | 0.0232 | 0.0231 | 0.00780 | 0.0079 | 0.0079 |
| 0.0475 | 0.0292 | 0.0291 | 0.00975 | 0.0099 | 0.0103 |
| 0.0570 | 0.0352 | 0.0351 | 0.0117 | 0.0128 | 0.0127 |
| 0.0665 | 0.0412 | 0.0412 | 0.0136 | 0.0151 | 0.0151 |
| 0.0760 | 0.0478 | 0.0473 | 0.0156 | 0.0177 | 0.0176 |
| 0.0855 | 0.0531 | 0.0533 | 0.0176 | 0.0197 | 0.0201 |
| 0.0950 | 0.0598 | 0.0594 | 0.0195 | 0.0226 | 0.0225 |
| 0.145 | 0.0924 | 0.0916 | 0.0214 | 0.0251 | 0.0249 |
| | | | 0.0254 | 0.0296 | 0.0300 |
| | **2** 70 °C | | 0.0292 | 0.0354 | 0.0348 |
| | | | | **3** 50 °C | |
| 0.00205 | 0.00351 | 0.00408 | | | |
| 0.00306 | 0.00552 | 0.00611 | | | |
| 0.00386 | 0.00720 | 0.00769 | 0.00469 | 0.0063 | 0.0070 |
| 0.00621 | 0.0122 | 0.0124 | 0.00657 | 0.0099 | 0.0099 |
| 0.0133 | 0.0265 | 0.0266 | 0.00844 | 0.0128 | 0.0128 |
| 0.0201 | 0.0405 | 0.0404 | 0.00938 | 0.0146 | 0.0143 |
| 0.0482 | 0.0980 | 0.0980 | 0.0188 | 0.0292 | 0.0293 |
| 0.0676 | 0.138 | 0.138 | 0.0281 | 0.0443 | 0.0445 |
| 0.0772 | 0.158 | 0.158 | 0.0375 | 0.0605 | 0.0601 |
| 0.0965 | 0.198 | 0.198 | 0.0563 | 0.0915 | 0.0915 |
| | | | 0.0750 | 0.123 | 0.123 |
| | **3** 60 °C | | 0.0938 | 0.155 | 0.154 |
| | | | | **4** 60 °C | |
| 0.00657 | 0.0191 | 0.018 | | | |
| 0.00844 | 0.0231 | 0.0237 | | | |
| 0.00938 | 0.0271 | 0.0266 | 0.00201 | 0.0189 | 0.0194 |
| 0.00188 | 0.0561 | 0.0558 | 0.00302 | 0.0287 | 0.0299 |
| 0.0281 | 0.0852 | 0.115 | 0.00402 | 0.0395 | 0.0405 |
| 0.0375 | 0.116 | 0.146 | 0.00503 | 0.0510 | 0.0512 |
| 0.0469 | 0.146 | 0.176 | 0.00603 | 0.0609 | 0.0618 |
| 0.0563 | 0.176 | 0.236 | 0.00704 | 0.0715 | 0.0726 |
| 0.0750 | 0.238 | 0.298 | 0.0101 | 0.1030 | 0.1052 |
| 0.0938 | 0.298 | 0.327 | 0.0121 | 0.1253 | 0.1266 |
| 0.103 | 0.328 | | 0.0141 | 0.1453 | 0.1479 |
| | | | 0.0161 | 0.1691 | 0.1693 |

a) [Substrate]$_0$ $2.5\times10^{-5}$ M; $\mu$ 0.8 M (NaCl); solvent $H_2O$–$CH_3CN$ (99.95/0.05 v/y). b) Estimated limit of error ±0.5% for observed $k_\psi$. c) These $k_\psi$ values were calculated by substituting the data in Table 2 into Eq. 1.

range of [⁻OH] studied, indicating the addition of ⁻OH to the carbonyl carbon atom to be rate-limiting. As will be discussed later, **1**—**4** have an alkyl group on the amide nitrogen atom. This is also expected to exert steric hindrance, in addition to the inductive effect, toward the carbonyl carbon atom in the transition state for formation of In⁻. These effects, therefore, would be expected to make In⁻ less stable.

**Rate Constants.** According to Scheme 1, the alkaline hydrolysis is catalyzed by ⁻OH to produce the tetrahedral intermediate (In⁻), followed by its decomposition to the products. By applying the steady-state approximation to the concentration of In⁻, the mechanism leads to Eq. 1 for the observed pseudo first-order rate constant, $k_\psi$, for alkaline hydrolysis (Table 1). In Eq. 1, $k_3$ (Table 2) means $Kk_3'$. At present, it is not clear whether the $K$ and $k_3'$ steps are stepwise or simultaneous. Eq. 2 is derived by dividing both sides of Eq. 1 by [⁻OH]. Therefore, the relationship between $k_\psi$/[⁻OH] and [⁻OH] should be convex upward (not shown),

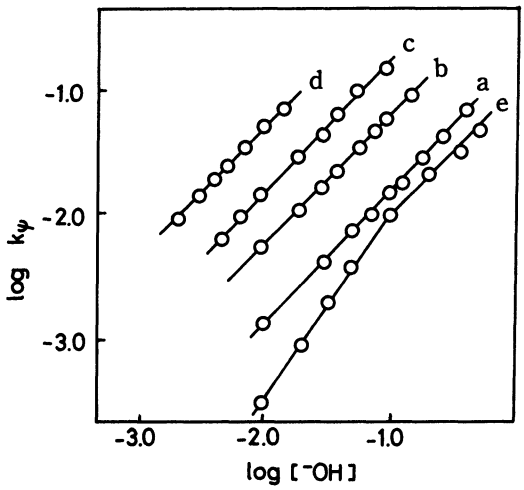



Fig. 2. Relationship between $\log k_\psi$ and $\log[^-OH]$ in the alkaline hydrolyses of acetanilides and pyridylacetamides; a **1** (20°C); b **2** (60°C); c **3** (50°C); d **4** (60°C); e **7** (25°C).

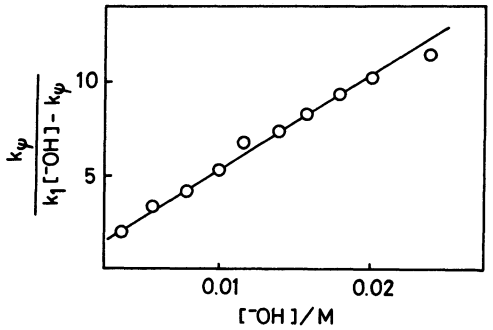



Fig. 3. Relationship between $k_\psi/(k_1[^-OH]-k_\psi)$ and $[^-OH]$ in the alkaline hydrolysis of *N*-methyl-2,4-dinitroacetanilide (**2**) at 60°C [$\mu$ 0.8 M (NaCl)].

which shows the validity of Scheme 1. As a result, $k_1$ can be obtained as $k_\psi/[^-OH]$ ($\equiv k_1$), when $[^-OH]$ is much higher in Eq. 1. Eq. 2 is further derived by rearranging

$$k_\psi = k_1[^-OH]\cdot\frac{k_2+k_3[^-OH]}{k_{-1}+k_2+k_3[^-OH]} \quad (1)$$

$$\frac{k_\psi}{[^-OH]} = k_1\cdot\frac{a+b[^-OH]}{1+a+b[^-OH]} \quad (2)$$

$$a=\frac{k_2}{k_{-1}}\ ;\ b=\frac{k_3}{k_{-1}}\ ;\ k_3=Kk_3'$$

Eq. 1. Then, the relationship between $k_\psi/(k_1[^-OH]-k_\psi)$ and $[^-OH]$ is expected to be linear (Fig. 3). By substituting the $k_1$ value determined above into Eq. 2, $a$ and $b$ can be estimated from the intercept and slope of the straight line. These $k_1$, $a$, and $b$ values were used as the initial ones to calculate $k_1$, $a$, and $b$ more accurately. The $k_1$, $a$, and $b$ values in Table 2 were derived from Eq. 2 by using the initial values ($k_1$, $a$, and $b$), obtained above, and the non-linear least squares method (Program: SALT Model-F[11]).

By applying a similar method to **3** and **4**, the rate constants were determined.

**(1) $k_1$ Values.** The $k_1$ ratio (**2**/**1**) is ca. 2.8, being comparable to ca. 3.3 for that (**4**/**3**) (Run 1, 3, 5, and 6), from which it was found that on changing from an ethyl to a methyl group on the amido nitrogen atom the extent of release of steric compression is similar in both the *N*-pyridylacetamide and the acetanilide. These values are close to the $k_1^{CH_3}/k_1^{C_2H_5}$ values for the alkaline hydrolysis of methyl and ethyl acetates (ca. 2.3 at 0.6—20 °C in 62% acetone-$H_2O$[12]) and of methyl and ethyl lactates (2.4 at 0 °C in $H_2O$).[13] These rate ratios are due almost entirely to the inductive effect of the alkyl groups.[12]

As for the $k_1$ ratio due to the change in the acyl component of esters, Evans et al.[14] showed the $k_1^{CH_3}/k_1^{C_2H_5}$ values of ca. 1.6—1.7 for the alkaline hydrolyses of ethyl acetate and propanoate, and Taft[15] reported 2.0 as a statistical value for the rate ratio of the same esters, which are a little smaller than those described above.

From Table 2 the $k_1$ value for acetanilide is smaller than that for the corresponding *N*-pyridylacetamide: the $k_1$ ratio is 7.0 (**3**/**1**) and 8.3 (**4**/**2**) (Run 5 and 1, and 6 and 3). These rate ratios are clearly due to the steric hindrance of 2-substituent toward the steric crowding in the transition state for formation of $In^-$.[10]

On the other hand, Pratt[16] has reported the $k_1$ value for the alkaline hydrolysis of *N*-methyl-4-nitroacet-

Table 2. Rate Constants and Rate Ratios for the Alkaline Hydrolyses of *N*-Methyl-2,4-dinitroacetanilide (**2**) and *N*-Alkyl-*N*-(5-nitro-2-pyridyl)acetamide (**3** and **4**)

| Run No. | Substrate | Temp °C | $k_1$[a] $M^{-1}min^{-1}$ | $a(k_2/k_{-1})$[a] | $b(k_3/k_{-1})$[a] $M^{-1}$ |
|---|---|---|---|---|---|
| 1 | **1**[b] | 60 | 0.460 | 2.03 | 5.25 |
| 2 | **2** | 50 | 0.649 | 6.95 | 209 |
| 3 | | 60 | 1.28 | 0.255 | 459 |
| | | 70 | 2.11 | — | — |
| 4 | **3**[c] | 50 | 1.71 | 6.12 | 238 |
| 5 | | 60 | 3.26 | 3.22 | 376 |
| 6 | **4**[d] | 60 | 10.7 | 2.23 | 3484 |

a) Estimated limit of error ±1.0% for $k_1$; ±1.3% for $a$ and $b$. b) *N*-Ethyl-2,4-dinitroacetanilide; cited from Ref. 10. c) *N*-Ethyl-*N*-(5-nitro-2-pyridyl)acetamide. d) *N*-Mehyl-*N*-(5-nitro-2-pyridyl)acetamide.

anilide (**8**) to be 0.0408 $M^{-1}$ $min^{-1}$ ($1m^{-1}$ mol $dm^{-3}$) at 25 °C, which is smaller than the $k_1$ value (0.119 $M^{-1}$ $min^{-1}$ at 25 °C) for **2**, derived from the temperature-dependence of log $k_1$ ($E_a$=54.8 kJ $mol^{-1}$).

These results show that the inductive effect (accelerating effect) of 2-$NO_2$ group is superior to its steric hindrance (retarding effect).

**(2) *a* and *b* Values.** The $b/a$ value ($k_3/k_2$) is 2.5 (60 °C) for **1**, and 30 (50 °C) and 1800 (60 °C) for **2**. It is 39 (50 °C) and 117 (60 °C) for **3**, and 1562 (60 °C) for **4**.

From these results, the decomposition of $In^-$ is seen to take place predominantly via the $K$ and $k_3'$ stages, together by considering the $b/a$ value (138 at 30 °C in $H_2O$) of 4-nitroacetanilide (**7**)[8] and other related acetanilides with electron-withdrawing 4-substituents.[17]

In the case of acetanilide or *N*-pyridylacetamides with electron-withdrawing substituents on the aniline or pyridine moiety, the acidity of the hydroxyl group of $In^-$ becomes stronger,[6] which would make $In^-$ decompose via the $K$ and $k_3'$ stages more often than via the $k_2$ stage.

Further, on changing from an ethyl to a methyl group on the amido nitrogen atom, the $k_3/k_2$ ($b/a$) value increases (2.5 for **1** to 1800 for **2**, and 117 for **3** to 1562 for **4** at 60 °C).

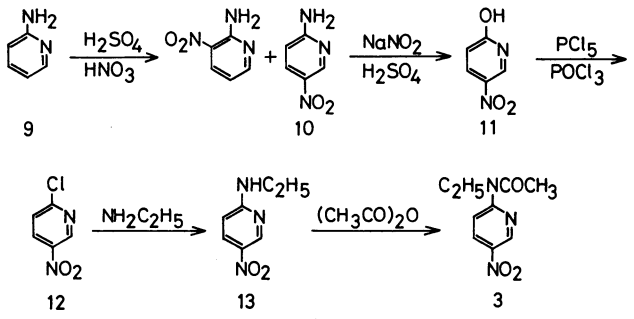
These results indicate that $In^-$ of the substrate with an *N*-methyl group is more stable than $In^-$ of the one with an *N*-ethyl group, because in the former the steric compression is less. Then, proton abstraction of $In^-$ by $^-OH$ could occur more frequently, that is, the possibility that $In^-$ decomposes to products via the $K$ and $k_3'$ stages would increase.

In conclusion it is found that in the alkaline hydrolysis of nitro-substituted acetanilides or *N*-pyridylacetamides the substituents on the amido nitrogen atom electronically affect the rate of hydrolysis, and those at the 2-position of a ring do so sterically, as well as electronically.

## Experimental

**Materials. *N*-Methyl-2,4-dinitroacetanilide (2).** *N*-Methyl-2,4-dinitroaniline (NMDA) was synthesized from 2,4-dinitrochlorobenzene and methylamine according to the method of Bogoslovskii and Tsil'man[18] (yield 75.1%; recryst. solvent ethanol), mp 174—175 °C (lit,[18] 176—177 °C). The compound **2** was synthesized from NMDA and acetic anhydride in the presence of a small amount of concd. $H_2SO_4$ (three or four drops) as described in the literature:[10] Yield 63.4%; mp 75—76 °C; $^1H$ NMR (DMSO-$d_6$, 60 MHz) $\delta$= 2.17 (3H, s, acetyl $CH_3$), 3.48 (3H, s, N-$CH_3$), 7.07 (1H, d, $J$=4 Hz, ring $H^6$), and 8.70 (2H, m, ring $H^3$ and $H^5$ overlapped). Anal. ($C_9H_9N_3O_5$) C, H, N.

***N*-Ethyl-*N*-(5-nitro-2-pyridyl)acetamide (3).** The synthetic sequence was shown in Scheme 2.




Scheme 2.

**9 → 10.** Into a 120 ml solution of concd $H_2SO_4$ was dissolved 2-aminopyridine (27 g, 0.29 mol) by portions under stirring below 90 °C, and the solution was cooled to 0 °C. Then, into this stirred solution was added the cooled mixed acid (concd $HNO_3$ 19.5 ml and concd $H_2SO_4$ 21 ml) at 10 to 20 °C. Stirring was continued and the temperature rose to 65 °C. The mixture was then poured onto 500 ml of ice water and neutralized with $Na_2CO_3$, giving the precipitate (raw **10**). It was separated by filtration and dried. Althogh it included a small amount of 2-amino-3-nitropyridine, it was used in the next procedure without purification.

**10 → 11.** To a solution of 24.9 ml of concd. $H_2SO_4$ in 358 ml of $H_2O$ was added 23.1 g (0.166 mol) of crude **10**, into which 98 g of ice was added. Subsequently a solution of 12.8 g (0.186 mol) of $NaNO_2$ in 40 ml of $H_2O$ was added dropwise under stirring at 0 °C, the solution was stirred for an additional 30 min, and filtered. Recrystallization of the precipitates from $H_2O$ gave 11.9 g (51.2%) of pure **11**: mp 182.5—183.5 °C. Anal. ($C_5H_4N_2O_3$) C, H, N.

**11 → 12.** To a mixture of 11.9 g (0.085 mol) of **11** and 35 g (0.168 mol) of $PCl_5$ was added sufficient $POCl_3$ to just cover the mixture. After the mixture was refluxed (at 110 °C) for 3 h, the $POCl_3$ was distilled off under reduced pressure. To the residue was added 144 ml of cooled $H_2O$, and it was neutralized with NaOH. After the mixture was filtered off, recrystallization of the precipitate from ethanol gave 12.0 g (89.1%) of pure **12**: mp 106—108 °C. Anal. ($C_5H_3ClN_2O_2$) C, H, N.

**12 → 13.** A solution of 7.9 g (0.05 mol) of **12** in 150 ml of DMSO was added dropwise to a stirred solution of 120 ml $C_2H_5NH_2$ (0.725 mol) in 82.8 ml of DMSO. After the mixture was stirred for 5 h at room temperature, it was neutralized by pouring into a cooled aqueous solution of dilute $H_2SO_4$ and filtered. Recrystallization of the precipitate from ethanol gave 5.9 g (71.1%) of pure **13**: mp 117—119 °C. Anal. ($C_7H_9N_2O_2$) C, H, N.

**13 → 3.** After a mixture of 1.5 g (0.009 mol) of **13**, 2 ml of acetic anhydride, and 2 ml of gracial acetic acid was refluxed for 9.5 h, and then the solvent was distilled off under reduced pressure. Recrystallization of the residue from ethanol gave 1.55 g (93%) of **3**: mp 60—61 °C; $^1H$ NMR (DMSO-$d_6$, 60 MHz) $\delta$=1.17 (3H, t, *N*-ethyl $CH_3$), 2.27 (3H, s, acetyl $CH_3$), 4.05 (2H, q, *N*-ethyl $CH_2$), 7.87 (1H, d, $J_{H^3\text{-}H^4}$=7.0 Hz, ring $H_3$), 8.66 (1H, d with each peak finely and doubly split, $J_{H^3\text{-}H^4}$=7.0 Hz, ring $H^4$), and 9.28 (1H, finely-split d, $J_{H^4\text{-}H^6}$=2 Hz, ring $H^6$). Anal. ($C_9H_{11}N_3O_3$) C, H, N.

***N*-Methyl-*N*-(5-nitro-2-pyridyl)acetamide (4).** According to the similar method to **3**, **4** was synthesized: mp 96.5—97 °C; $^1H$ NMR (DMSO-$d_6$, 60 MHz) $\delta$=2.25 (3H, s, acetyl $CH_3$), 3.30 (3H, s, N-$CH_3$), 7.70 (1H, d, $J_{H^3\text{-}H^4}$=7.0 Hz, ring $H^3$), 8.51 (1H, d with each peak finely and doubly split, $J_{H^3\text{-}H^4}$=7.0 Hz, ring $H^4$), and 9.11 (1H, finely-split d, $J_{H^4\text{-}H^6}$=2 Hz, ring $H^6$). Anal. ($C_8H_9N_3O_3$) C, H, N.

**Rate Measurements.** A sample solution was prepared as follows: After 1.5 μl of an acetonitrile solution of an amide

(0.1 M) was added to a quartz cell containing 3 ml of the prescribed concentration of an aqueous sodium hydroxide solution kept at the constant ionic strength (0.8 M NaCl), the time-dependent increase in the absorption maximum of the corresponding aniline formed were measured with a Hitachi 124 spectrophotometer.

Rate constants were calculated by the Guggenheim method.[19]

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11) This program was contrived by Dr. T. Nakagawa, Department of Chemistry, Faculty of Science, Tokyo University, to whom the auther (s.s.) is indebted very much.

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