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2. K.-J. Lee, D. O. Choi, S. Kim, J. U. Jeong, and H. Park, *Synthesis* 455 (1990).
3. During our studies on the synthesis of 1,3-benzodiazepines, a very similar method was reported, see: J. Kurita, T. Iwata, W. Yasuike, and T. Tsuchiya, *J. Chem. Soc. Chem. Commun.*, 81 (1992).
4. Selected data for **2a** (89%): mp. 195-196℃ (EtOAc); ^{1}H-NMR ($CDCl_3$/DMSO-d_6) δ 4.86 (s, 2H, CH_2), 7.60-8.20 (m, 8H, Ar); **2b** (62%): mp. 89℃ (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 4.47 (s, 2H, CH_2), 6.88 (s, 2H, vinyl H), 7.20-8.40 (m, 4H, Ar); **2c** (87%): mp. 151℃ (Et_2O); ^{1}H-NMR ($CDCl_3$/DMSO-d_6) δ 2.82 (s, 4H, CH_2CH_2), 4.73 (s, 2H, CH_2Br), 7.26-8.23 (m, 4H, Ar).
5. The compounds **1a-c** were prepared conventionally from the *o*-aminoacetophenone with the corresponding anhydride, and selected data for **1a** (84%): mp. 134℃ (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 2.50 (s, 3H, CH_3), 7.30-8.10 (m, 8H, Ar); **1b** (84%): mp. 112℃ (Et_2O); ^{1}H-NMR ($CDCl_2$) δ 2.50 (s, 3H, CH_3), 6.85 (s, 2H, vinyl H), 7.20-8.00 (m, 4H, Ar); **1c** (82%): mp. 212℃ (EtOAc); ^{1}H-NMR ($CDCl_3$) δ 2.53 (s, 3H, CH_3), 2.85 (s, 4H, CH_2CH_2), 7.13-8.02 (m, 4H, Ar).
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7. For the different synthetic method of 1,5-dihydropyrrolo [1,2-a]quinoline-1,5-diones, see: L. W. Deady and D. M. Werden, *J. Org. Chem.*, **52**, 3930 (1987); selected data for **5**: mp. 218-219℃ (Et_2O); ^{1}H-NMR ($CDCl_3$) δ 6.48 and 7.37 (two d, each 1H, J=6.1 vinyl H), 7.42-8.82 (m, 4H, Ar).
8. For the different synthetic method of 6-chloro-5,11-dihydroisoindolo[2,1-a]quinoline-5,11-dione, see: H. Vorbruggen, B. D. Bohn, and K. Krolikiewicz, *Tetrahedron* **46**, 3489 (1990); selected data for **4a**: mp. 234-235℃ ; ^{1}H-NMR ($CDCl_3$/DMSO-d_6) δ 7.30-8.30 (m, 8H, Ar); MS (relative intensity) m/z 327 ($M+2^+$, 19), 325 (M^+, 22), 297 (17), 246 (12), 190 (100).
9. Selected data for **3a**: mp. 137-139℃ (Et_2O); ^{1}H-NMR ($CDCl_3$/DMSO-d_6) δ 4.48 (s, 2H, CH_2), 7.50-8.20 (m, 8H, Ar); **3c**: mp. 101-102℃ (Et_2O); ^{1}H-NMR ($CDCl_3$/DMSO-d_6) δ 2.85 (s, 4H, CH_2CH_2), 4.53 (s, 2H, CH_2N_3), 7.22-7.92 (m, 4H, Ar).
10. For the different synthetic method of same heterocyclic system, see: (a) reference 8; (b) Y. Ishihara, Y. Kiyota, and G. Goto, *Chem. Pharm. Bull.*, **38**, 3024 (1990); (c) G. Goto and Y. Ishihara, JP 90 42,078 (1990); C. A. 1990, **113**, 40431z; selected data for **4b**: mp. 122-124℃ (dec); ^{1}H-NMR ($CDCl_3$) δ 7.30-9.20 (m, 8H, Ar); MS (relative intensity) m/z 288 (M^+, 2), 260 (76), 205 (11), 204 (100), 203 (30), 177 (29), 102 (43); IR (KBr) ν_{N_3} (cm^{-1}) 2124.
11. For the different synthetic method of 1,2,3,5-tetrahydropyrrolo[1,2-a]quinoline-1,5-diones, see: L. W. Deady and D. M. Werden, *Synth. Commun.*, **17**, 319 (1987) and reference 7; selected data for **6a**: mp. 139℃ (dec); ^{1}H-NMR ($CDCl_3$) δ 2.92 (m, 2H, CH_2), 3.14 (m, 2H, CH_2), 7.45-9.06 (m, 4H, Ar).
12. Selected data for **4c**: mp. 308-310℃ ; ^{1}H-NMR ($CDCl_3$) δ 7.15-9.24 (m, 23H, Ar); ^{31}P-NMR ($CDCl_3$/H_3PO_4) δ 17.6; MS (relative intensity) m/z 522 (M^+, 97), 470 (30), 469 (32), 207 (29), 183 (100); **4d**: mp. 255-256℃ (toluene); ^{1}H-NMR (DMSO-d_6) δ 5.89 (s, 2H, NH_2), 7.37-9.15 (m, 8H, Ar); MS (relative intensity) m/z 262 (M^+, 100), 234 (27), 178 (38), 103 (33), 76 (40).
13. Selected data for **6b**: mp. 250-251℃ (dec); ^{1}H-NMR ($CDCl_3$) δ 2.93 (m, 2H, CH_2), 3.47 (m, 2H, CH_2), 7.25-9.14 (m, 19H, Ar); ^{31}P-NMR ($CDCl_3$/H_3PO_4) δ 9.94: MS (relative intensity) m/z 474 (M^+, 27), 288 (25), 184 (27), 183 (100), 130 (28).
14. Selected data for **4e**: mp. 249-251℃ ; ^{1}H-NMR ($CDCl_3$) δ 6.74 (s, 1H, CH), 7.27-9.12 (m, 8H, Ar); MS (relative intensity) m/z 247 (M^+, 40), 219 (100), 190 (47), 163 (22), 101 (17).
15. Mp. 190-192℃ (EtOH, lit.[11] 192-193℃).

The Effect of Medium on the α-Effect for the Reaction of *p*-Nitrophenyl Acetate with Benzohydroxamates

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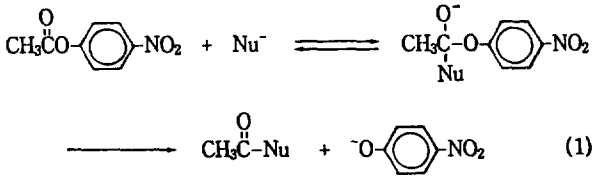
The term α-effect has been given to a positive deviation on a Broensted plot which is often observed in the reaction of the nucleophile containing a hetero atom adjacent to the reaction center (the α-position).[1] Although, numerous studies have been performed to investigate the origin of the α-effect, it has not been completely understood.[2]

Recently, a series of systematic studies has demonstrated that the effect of medium on the α-effect is significantly important for the acyl-transfer reaction of *p*-nitrophenyl acetate (PNPA) with anionic nucleophiles in various reaction medium, such as aqueous dimethyl sulfoxide (DMSO),[3] aqueous acetonitrile (MeCN),[4] and aqueous micellar solutions.[5] In our preceding paper on this series, we reported that benzohydroxamate (**1**) shows a large α-effect in pure H_2O, but the α-effect nucleophile (**1**) becomes less reactive than the corresponding normal-nucleophile (**4**) upon the addition of cethyltrimethylammonium bromide (CTAB) in H_2O.[6] Some explanations were suggested for the disappearance of the α-effect, but they were speculative and not conclusive.[6] Thus, we have now performed a systematic study for the following reactions in order to obtain some solid evidences.

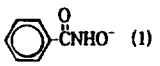
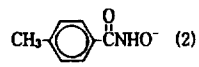


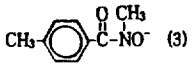
(1)

Table 1. Summary of the pK_a Values of the Conjugate Acids of Nucleophiles in H_2O and in Micellar Solution (20 mM CTAB in H_2O)

Nu^-	pK_a		K_s^c, M^{-1}
	in pure H_2O	in CTAB solution	
(1)	8.88[a]	8.20	650
(2)	8.90[a]	8.11	870
(3)	8.50[b]	8.12	630
(4)	9.02[a]	7.92	7460

[a] ref. 12a, [b] ref. 12b. [c] The binding constant values (K_s) taken from ref. 6.

Nu^- : α-effect-nucleophile ;  (1)  (2)

 (3)

normal-nucleophile ;  (4)

Since the basicity of nucleophiles influences directly the nucleophilicity,[7] one might attribute the disappearance of the α-effect to an unusual basicity change upon the addition of CTAB in the reaction medium. In order to examine whether the α-effect nucleophile becomes significantly less basic than the corresponding normal-nucleophile, we have measured the pK_a values of the nucleophiles in the presence of CTAB using a titration method.[8]

In Table 1 are summarized the pK_a values of three benzohydroxamic acids and *m*-chlorophenol (*m*-ClPhOH) in the absence and presence of CTAB. In cationic micellar solutions, anionic bases have been generally believed to the more stabilized than the respective conjugate acids due to the coulombic interaction between the positively charged micelles and the anionic bases.[9] Thus, the pK_a of an acid decreases in a cationic micellar solution. Such a micellar effect is considered to be more significant for the anionic base having stronger interactions with the cationic micelles. This is consistent with the present result that the base showing the larger binding constant (**4**) exihibits the more decrease in the pK_a value upon the addition of CTAB into H_2O. As shown in Table 1, the pK_a value of each conjugate acid of the anionic nucleophiles decreases as the medium changes from pure H_2O to the micellar solution of CTAB. However, the decrease in the pKa value is more significant for *m*-ClPhOH than hydroxamic acids. For example, the pK_a values of *m*-ClPhOH and benzohydroxamic acid are 9.02 and 8.88 in pure H_2O, and 7.92 and 8.20 in the presence of CTAB, respectively. Consequently, the normal nucleophile (**4**) becomes less basic than the α-effect nucleophiles (**1**, **2**, **3**) upon the addition of CTAB in H_2O. Such a basicity order is contrary to what would have been expected based on the previous rate behavior shown by **1** and **4** in the presence of CTAB. Therefore, the disappearance of the α-effect in the micellar solution can not be attributed to any unusual pK_a change between **1** and **4** upon the addition of CTAB.

Hydroxamates (I) with an N-H bond have often been suggested to form an equilibrium with their isomeric forms,

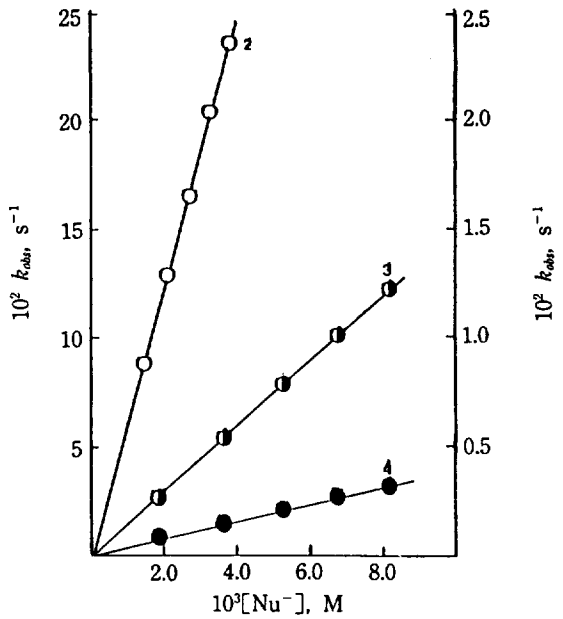
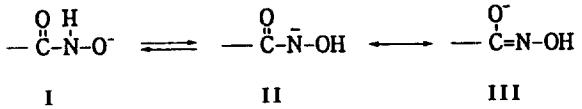


Figure 1. Plots showing dependence of k_{obs} on the nucleophile concentration for the reactions of PNPA with bezohydroxamates (**2** and **3**: left hand side scale) and *m*-chlorophenoxide (**4**: right hand side scale) in H_2O at 25.0℃.

II or III.[10] Particularly, in dipolar aprotic solvents such as DMSO and MeCN, it has been recognized that hydroxamate (I) exists mainly as II or its resonance structure III.[10] A similar equilibrium would be expected to occur in the micellar pseudophase. Since II or III would be considered to be less reactive than I due to their structures, one would suggest that an equilibrium of I with II or III is responsible for the absence of the α-effect in the micellar solution. In order to examine this hypothesis, we have chosen **3** as another α-effect nucleophile reacting with PNPA (see equation 1). Since **3** has no N-H bond, the equilibrum of I with II or III is not possible. Thus, the reaction of **3** with PNPA would not exhibit any rate retardation from such an equilibrium in the presence of CTAB.



I II III

In Figure 1 are graphically demonstrated the kinetic results in the absence of CTAB for the reaction of PNPA with **2**, **3**, and **4** in H_2O. As shown in the Figure, the observed rate constants for each nucleophile show a good linear correlation with the concentration of the respective nucleophile. However, the α-effect nucleophiles (**2** and **3**) are much more reactive than the corresponding normal nucleophile (**4**) in pure H_2O, although their basicities are comparable in H_2O. This clearly implies that an α-effect is operative for the present reaction system in H_2O.

The kinetic data in the presence of CTAB are summarized in Table 2, and plotted in Figure 2. As shown in the Table and the Figure, the observed rate constant (k_{obs}) increases with increasing the concentration of CTAB in the reaction medium up to near 6 mM of CTAB. Such a reactivity trend

Table 2. Summary of Observed Rate Constants (k_{obs}, min^{-1}) for the Reaction of *p*-Nitrophenyl Acetate with *m*-Chlorophenoxide and Benzohydroxamates in 0.1 M Borate Buffer (pH=9.27) Containing Various Concentrations of CTAB at 25.0℃[a]

10^4[CTAB], M	k_{obs}, min^{-1}			
	(1)	(2)	(3)	(4)
0.0	.037	.038	.148	.028
4.0	.059	.085	1.47	.115
8.0	.097	.139	3.37	.192
14.0	.133	.193	6.33	.237
20.0	.164	.218	7.59	.264
28.0	.185	.233	9.25	.266
36.0	.198	.248	10.2	.267
48.0	.208	.247	11.4	.267
60.0	.207	.246	12.1	—
76.0	.213	.246	12.0	.265

[a][PNPA]=1.0×10^{-5} M, [NuH]=2.00×10^{-4} M.

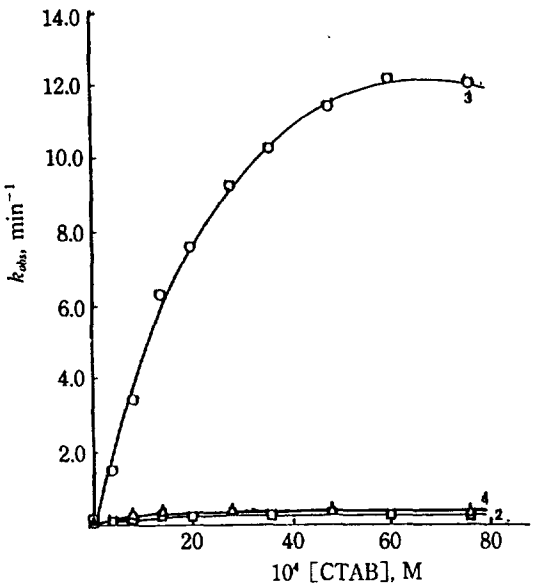


Figure 2. Plots showing micellar effect on rates for reactions of PNPA with *m*-chlorophenoxide (**4**) and benzohydroxamates (**2**, **3**) in 0.1 M borate buffer (pH=9.27) at 25.0℃.

is typical of nucleophilic substitution reactions with anionic nucleophiles in cationic micellar solutions.[4,6,11] However, the rate enhancement is most significant for the reaction of **3** and, therefore, the α-effect shown by **3** in pure H_2O retains in the presence of CTAB. This result is quite opposite from the one for the reaction of the hydroxamates having an N-H bond (**1** and **2**).

Therefore, the present study would lead to a conclusion that an equilibrum of I with II or III for the hydroxamates having an N-H bond appears to be responsible for the disappearance of the α-effect in the previous system. However, more systematic studies are required for a complete understanding of the present results.

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Theoretical Study of the Nonlinear Optical Properties of Nonsubstituted-, Methyl-fluoro-, and Amino-nitro-Polyenes

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Development of highly nonlinear optical materials is currently an area of intense interest in photonics or optoelectro-