(dd, $^2J_{F,F}$ = 247 Hz, $^3J_{F,H}$ = 10 Hz, 1 F), -116.6 (dd, $^2J_{F,F}$ = 247 Hz, $^3J_{F,H}$ = 10 Hz, 1 F). ^{1}H NMR ($CDCl_3$): 6.01-5.42 (m, 5 H), 2.13 (s, 1 H), 2.03-1.05 (m, 6 H). FT-IR (CCl_4): 3611 (s), 2946 (s), 1689 (m), 1653 (w), 1169 (s), 1072 (s). MS: 156 ($M^+ - H_2O$, 0.1), 97 (100), 79 (17.7), 77 (16.8), 67 (9.4).

Reaction of 1 with 2-Cyclohexenone and Zinc in the Presence of Cuprous Iodide. Similarly, reaction of 5.5 g (35 mmol) of 1, 2.9 g (30 mmol) of 2-cyclohexenone, 4.5 g (70 mmol) of zinc, and 0.7 g (3.5 mmol) of cuprous iodide in 30 mL of THF at room temperature for 4.5 h gave a residue, which was distilled to give 2.3 g (44%) of **14**.

Preparation of 4,4-Difluoro-1-phenyl-1,5-hexadien-3-ol (15). Similarly, **15** was prepared from 3.6 g (55 mmol) of zinc, 4.0 g (30 mmol) of cinnamaldehyde, and 5.5 g (35 mmol) of 1. Usual workup gave a residue, which was purified by column chromatography (silica gel, 200-425 mesh; hexane/ethyl acetate, 8:2) to afford 4.7 g (75%) of **15**.[25b] ^{19}F NMR ($CDCl_3$): -107.7 (dt, $^2J_{F,F}$ = 247 Hz, $^3J_{F,H}$ = 10 Hz, 1 F), -111.5 (dt, $^2J_{F,F}$ = 249 Hz, $^3J_{F,H}$ = 10 Hz, 1 F). ^{1}H NMR ($CDCl_3$): 7.28 (s, 5 H), 6.85-5.45 (m, 5 H), 4.44 (m, 1 H), 2.69 (s, 1 H). IR (CCl_4): 3580 (s), 3030 (m), 1650 (w), 1550 (s), 1165 (s), 1080 (s). MS: 211 (M^+ + 1, 0.3), 210 (M^+, 1.6), 133 (100), 115 (34.7), 105 (8.5), 103 (11.8), 77 (20.3), 55 (13.4), 51 (7.8).

Reaction of 1 with Benzaldehyde and Cadmium or Tin. Similarly, reaction of 3.1 g (20 mmol) of 1 with 4.2 g (40 mmol) of benzaldehyde and 4.4 g (40 mmol) of cadmium (**CAUTION: Toxic!**) in 30 mL of DMF at room temperature overnight gave a residue, which was distilled to give 2.7 g (75%) of **3**.

Similarly, reaction of 3.1 g (20 mmol) of 1, 4.2 g (40 mmol) of benzaldehyde, and 4.7 g (40 mmol) of tin in 20 mL of THF at room temperature gave 2.5 g (67%) of **3**.

Reaction of 1 with Benzaldehyde and Tin Dichloride in the Presence of Aluminum. A flask fitted with a stir bar and a nitrogen inlet was charged with 0.57 g (3 mmol) of tin dichloride, 0.87 g (30 mmol) of aluminum, 0.5 mL of acetic acid, 2.5 mL of water, and 5 mL of ethanol. The reaction mixture was stirred for 10 min, and then 1.6 g (15 mmol) of benzaldehyde and 4.7 g (30 mmol) of 1 were added via syringe. The resultant mixture was stirred at room temperature for 20 h. ^{19}F NMR (vs $PhCF_3$) indicated the formation of **3** in 56% yield.

Preparation of 1,1-Difluoro-3-iodopropene (2). A flask fitted with a stir bar and an isopropyl alcohol condenser with nitrogen inlet was charged with 11.3 g (75 mmol) of sodium iodide and 25 mL of acetone. After a Neslab Cryocool 100 was used to cool the isopropyl alcohol to -40 °C, 7.8 g (50 mmol) of 1 was added via a syringe and the mixture was stirred at room temperature for 2 days. The reaction mixture was then poured into a beaker with water, and the organic lower layer was separated, washed with saturated sodium sulfite solution and water, and dried over molecular sieves. Distillation of the crude material gave 7.7 g (75%) of a mixture of **2** and **2b**, bp 93 °C. ^{19}F NMR and GLPC analysis of the product showed it to be a 23:1 mixture of 3-iodo-1,1-difluoropropene (**2**) and 3-iodo-3,3-difluoropropene (**2b**). ^{19}F NMR ($CDCl_3$) **2**: -84.1 (d, $^2J_{F,F}$ = 27 Hz, 1 F), -85.3 (dd, $^2J_{F,F}$ = 27 Hz, $^3J_{F,H\text{-trans}}$ = 23 Hz, 1 F). ^{19}F NMR ($CDCl_3$) **2b**: -41.9 (d, $^3J_{F,H}$ = 12 Hz). ^{1}H NMR ($CDCl_3$) **2**: 4.69 (dt, $^3J_{F,H\text{-trans}}$ = 23 Hz, $^3J_{H,H}$ = 12 Hz, 1 H), 3.81 (d, $^3J_{H,H}$ = 12 Hz, 2 H). FT-IR (CCl_4): 3103 (w), 1733 (s), 1335 (s), 1244 (s), 1161 (s). MS: 204 (M^+, 5.2), 127 (16.0), 77 (100), 75 (9.4), 51 (20).

Preparation of 3 from 2 and 2b. A mixture of 2.2 g (10 mmol) of **2** and **2b**, 1.1 g (10 mmol) of benzaldehyde, and 1.3 g (20 mmol) of zinc in 20 mL of THF was reacted at 0 °C for 2 h. Usual workup gave 1.1 g (61% isolated yield) of **3**.

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Supplementary Material Available: ^{19}F and/or ^{1}H NMR spectra for compounds **2-15** (29 pages). Ordering information is given on any current masthead page.

Micellar Catalysis of Organic Reactions. 29.[1] S_NAr Reactions with Neutral Nucleophiles

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The reaction of a number of nitroactivated halobenzoates (**1-4**) with some primary and tertiary amines has been studied in the presence of micelles of cetyltrimethylammonium bromide (CTAB) and in water. With primary amines aminodehalogenation was observed, and it was found that if the reaction center of the aromatic substrate was located at the micelle water interface (compounds **1** and **2**) the reaction was catalyzed by CTAB, but if the reaction center was more deeply buried into the micellar interior the reaction with aniline was inhibited by micelles of CTAB (compounds **3** and **4**), while CTAB had little effect on the reaction of *n*-propylamine with compound **4**. With the more sterically bulky tertiary amines, hydroxydehalogenation was observed rather than aminodehalogenation, and the reactions were all catalyzed by CTAB, but for the substrate with a more deeply buried reaction center (compound **4**), the catalysis was stronger than for that with a reaction center at or near the interface (compound **2**). The mechanism of hydroxydehalogenation was found to be specific base catalysis by the tertiary amine. Thus the observation of micellar catalysis or inhibition of these reactions depends on the orientation of the organic substrate within the micellar aggregate and the reaction product, amine or phenol, depends on the steric bulk of the amine at least for the compounds investigated here which contain two substitutents ortho to the reaction center.

Introduction

Previous studies of the effects of substrate orientation in micelles on the magnitude of catalysis[2a,b] have been hampered by the small catalysis observed for the selected reactions. In most cases substrates containing charged substituents (e.g. carboxylate groups) have been used because the orientation of these compounds in micelles is known from NMR studies of chemical shift changes of the aromatic protons on transfer from water to micelles of cetyltrimethylammonium bromide (CTAB). The presence of the charged substituent serves two purposes. Firstly it provides sufficient water solubility to obtain an NMR

(1) For part 28, see: Broxton, T. J.; Christie, J. R.; Wright, S. *J. Phys. Org. Chem.*, in press.

(2) (a) Broxton, T. J.; Christie, J. R.; Chung, R. P.-T. *J. Org. Chem.* **1988**, *53*, 3081. (b) Broxton, T. J.; Christie, J. R.; Chung, R. P.-T. *Aust. J. Chem.* **1989**, *42*, 855.

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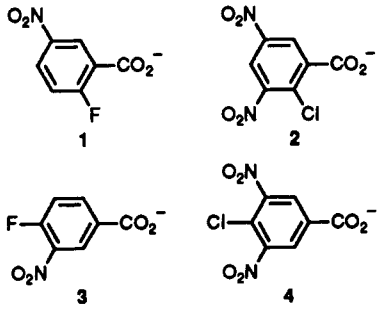
spectrum of the substrate in aqueous solution (D_2O) for comparison with that obtained in the presence of CTAB. Secondly it plays a role in orienting the substrate molecule in the micelle since the carboxylate group prefers to protrude from the micelle into the more polar aqueous intermicellar pseudophase.[3,4] The orientation taken by the substrate in the micelle is governed jointly by this preference of the charged carboxylate group to be in the aqueous intermicellar pseudophase and the preference of nitro group to be buried into the less polar regions of the micellar aggregates. By using this rationale substrates 1–4 were selected such that the reaction centers of substrates 1 and 2, in which the halogen nucleofuge is ortho to the carboxylate group, are at the micelle water interface. Coversely the reaction centers of substrates 3 and 4, in which the halogen nucleofuge is located para to the carboxylate group, are more deeply buried into the micellar core.



Thus, it seems reasonable that for attack of an anionic nucleophile which is located either in the aqueous intermicellar pseudophase or at the micelle water interface the orientation of substrates 1 and 2 is more favorable than that of substrates 3 and 4. The effects of micelles of CTAB on the rates of S_NAr hydroxydehalogenation and azidodehalogenation of substrates 1–4 are small because the reactions involve the attack of anionic nucleophiles (azide or hydroxide ions) on substrates containing an anionic substituent (carboxylate) leading to the production of a dianionic intermediate (i.e. the concentration of charge in the rate-determining transition state). Since the polarity of micelles even in the polar Stern region is less than that of water,[5] these reactions are hindered by the transfer from water to the micellar environment as predicted by the Hughes Ingold solvent theory.[6] Analysis of these reactions of compounds 1–4 using the pseudophase ion-exchange PPIE model[1,7,8] has shown that for hydroxydehalogenation the rate of reaction within the micelle (k_2^M) is less than that in water (k_2^W) for all compounds. For the azidodehalogenation of compound 2 k_2^M is significantly larger than k_2^W but for the other substrates the rates are similar in water and in the micelle. Thus the observed catalysis in most of these reactions is due only to concentration of the substrate within the micelle as indicated by the large values of the substrate–micelle binding constant K_s. Consequently only small catalytic effects are observed for these reactions on transfer from water to the micellar environment. Accordingly the differences between the catalysis for the reactions of substrates with a favorable orientation and those with less favorable orientations are not large because the catalysis is due primarily to concentration effects.

Furthermore for substrates 1 and 2, with the reaction center at the micelle water interface, the presence of the charged carboxylate group ortho to the reaction center leads to unfavorable electrostatic repulsion between the attacking nucleophile and the substituent. Thus, the orientation favorable to attack by an anionic nucleophile present in the aqueous intermicellar pseudophase is hindered by an unfavorable electrostatic effect. For substrates 3 and 4 the reaction center is more buried inside the micelle and hence less accessible to a nucleophile present in the aqueous intermicellar pseudophase or at the micelle water interface. However, this unfavorable orientation is not as susceptible to electrostatic effects because the electrostatic repulsion between the attacking nucleophile and the charged substituent is less than for the compounds 1 and 2 above since in this case the charged substituent is further from the reaction center. Thus the differences between favorable and unfavorable orientations of substrates 1–4 for reactions with anionic nucleophiles in the aqueous intermicellar pseudophase or at the micelle water interface are masked by differential electrostatic effects in the two cases.

In an attempt to overcome these problems we now report the effects of micelles of CTAB on the reactions of neutral nucleophiles (amines) with substrates 1–4. S_NAr reactions of amine nucleophiles have been widely studied,[9] and in some cases general base catalysis by a second molecule of amine has been detected by the observation of a second-order term in amine concentration. More recently Bunton[10] has reported the catalytic effects of micelles of CTAB on the reaction of aniline with both 1-chloro-2,4-dinitrobenzene and 1-fluoro-2,4-dinitrobenzene. With neutral nucleophiles the problems of small catalysis due to the concentration of charge in the rate-determining step and the compensating effects of different electrostatic repulsions for the reactions of the different substrates are overcome. Consequently the true effects of substrate orientation in micelles are able to be detected without complication by these other factors.

Results and Discussion

A number of different amines were chosen for this work including aniline and *n*-propylamine as examples of primary amines and 1,1,2,2-tetramethylethylenediamine (TMED) and dimethylaminoethanol (DMAE) as examples of tertiary amines.

Rate constants for the reactions of substrates 2 and 4 are in Table I while those for the aminodefluorination of substrates 1 and 3 are in Table II.

Primary Amines. With primary amines product studies have shown that the reaction observed was aminodehalogenation. The UV–vis spectra of the reaction products obtained in water or in CTAB were identical with those of the authentic products or aminodehalogenation obtained from reaction in ethanol as solvent. These UV–vis spectra had identical shapes and absorbance at the wavelength of maximum absorbance. Furthermore they were different from the spectra of the phenolic products obtained from the basic hydrolysis of the above substrates. On viewing Table I it can be seen that for both substrates 2 and 4 reaction with the primary amines was significantly faster than reaction with the tertiary amines. It can also

(3) Manohar, C.; Rao, U. R. K.; Valaulikar, B. S.; Iyer, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 379.
(4) Rao, U. R. K.; Manohar, C.; Valaulikar, B. S.; Iyer, R. M. *J. Phys. Chem.* **1987**, *91*, 3286.
(5) Kalyanasundaram, K.; Thomas, J. K. *J. Phys. Chem.* **1977**, *81*, 2176.
(6) Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1935**, 244.
(7) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.
(8) Bunton, C. A. *Catal. Rev.-Sci. Eng.* **1979**, *20*, 1.
(9) Suhr, H. *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 544.
(10) Bunton, C. A.; Robinson, L. *J. Am. Chem. Soc.* **1970**, *92*, 356.

Table I. Pseudo-First-Order Rate Constants (10^4k_1, s^{-1}) for the Reaction of Substrates 2 and 4 in the Presence of 0.05 M Amine[a]

[CTAB], mM	amine $PhNH_2$	n-$PrNH_2$	TMED	DMAE
	2-Cl Compound (2)			
0	2.01	3.05	0.351	0.138
1	28.1	25.8	0.264	0.177
2	34.9	35.5	–	0.935
3	36.8	–	2.09	–
4	36.6	39.6	–	1.16 (1.14)
5	36.0	–	2.03	–
7	37.0	–	2.25	–
8	–	41.4	–	1.12
16	–	42.3	–	0.997
20	34.4	–	2.14	–
catalysis[b]	18.4	14	6.4	8.4
wavelength	390	377	380	380
temp, °C	31	31	73	57
	4-Cl Compound (4)			
0	1.95 (0.89)	14.1	0.872	0.352
0.4	1.00	–	–	–
1	0.447	14.9	0.747	1.97
2	0.383	14.7	–	4.85
3	0.373	–	11.6	–
4	0.358	14.1	12.8 (13.1)	4.55 (3.98)
7	0.335	–	11.3	–
8	0.325	14.1	–	3.75
10	0.317 (0.148)	–	–	–
16	–	13.3	–	2.69
20	0.266	–	7.76	–
catalysis[b]	0.14[c]	1.06	13.3	13.8
temp, °C	31	31	73	57
wavelength	425	434	444	443

[a] Underlined results in D_2O; italicized results in 0.02 M amine. [b] Ratio of highest observed rate in CTAB to rate in water. [c] Inhibition, ratio of lowest observed rate in CTAB to rate in water.

Table II. Pseudo-First-Order Rate Constants (10^4k_1, s^{-1}) for the Aminodefluorination of Compounds 1 and 3 in the Presence of 0.05 M Aniline at 73 °C

[CTAB], mM	1	3
0	0.123	0.206
1	0.120	0.208
5	0.287	0.0624
wavelength	403	425
catalysis[a]	2.33	0.30[b]

[a] Ratio of highest observed rate in CTAB to rate in water. [b] Inhibition, ratio of lowest observed rate in CTAB to rate in water.

be seen that the reaction of aniline with the chlorodinitro substrates 2 and 4 was significantly faster than reaction with the fluoronitro substrates 1 and 3.

For the primary amine nucleophiles, reactions with compounds 1 and 2 which have reaction centers at or near the micelle/water interface, are catalyzed by CTAB, while the reaction of aniline with compounds 3 and 4 with reaction centers more buried inside the micelle is inhibited. However the reaction of n-propylamine with compound 4 is not affected by micelles of CTAB.

Before attempting to explain the different effects of micelles of CTAB observed in the reactions of each of these amine nucleophiles, it is necessary to consider the location of each amine within the micelle. Aniline has been reported to be located at the micelle water interface,[11,12] and this explains why the reactions of aniline with compounds 1 and 2 are catalyzed by micelles of CTAB while the reactions with compounds 3 and 4 are inhibited. Khan et al.[13] concluded that n-propylamine was located in the nonpolar interior of sodium dodecyl sulfate (SDS) micelles. It is quite possible that the location of n-propylamine in cationic and in anionic micelles may differ because of specific interactions between the primary amine group and the micellar head groups. We find that the reaction of propylamine with compound 2 is catalyzed by micelles of CTAB while the rate of reaction with compound 4 is not affected by CTAB. These results are difficult to explain because the similar catalysis of the reactions of aniline and n-propylamine with compound 2 indicate a similar location of the two amines in the micelle probably at the micelle water interface. However the inhibition of the reaction of aniline with compound 4 and the lack of any effect of CTAB on the reaction of propylamine with compound 4 suggests that the two amines are located in different regions of the micelle.

Tertiary Amines. Product studies have indicated that for reactions in the presence of tertiary amines, quaternary ammonium salts are not formed either in water or in the presence of micelles of CTAB. Authentic samples of these quaternary ammonium salts formed by the reaction of the tertiary amines with substrates 2 and 4 in ethanol as solvent had little absorbance above 350 nm in the UV–vis spectrum. This presumably is because the lone pair of the nitrogen atom is used in bonding to the aromatic carbon atom and consequently through conjugation between the amino and nitro groups present in the secondary amine products from the reaction of primary amines is absent in the quaternary ammonium salts. The products formed in the reactions of tertiary amines when carried out in water or in the presence of CTAB had a strong absorbance in the region between 350 and 450 nm. Comparison of these products with the phenols formed during the basic hydrolysis of these substrates showed that the UV–vis spectra were identical. We thus conclude that the products formed from the reaction of substrates 2 and 4 in the presence of tertiary amines were the corresponding phenols. No reaction was observed in the absence of the tertiary amine, so we conclude that the amine is involved probably as a base catalyst. The absence of a solvent isotope effect for the reaction of DMAE with the 2-Cl substrate 2 and the lack of dependence of the rate of reaction of the 4-Cl substrate 4 with TMED on the concentration of TMED rules out the occurrence of general base catalysis. This leads us to suggest the occurrence of specific base catalysis by the teritary amine, i.e. a fast preequilibrium formation of hydroxide ion from water followed by rate-determining attack of hydroxide on the aromatic substrate.

On comparing the magnitude of catalysis for the reaction of substrates 2 and 4 with sodium hydroxide in CTAB,[1] we find that the catalysis was greater for the 2-Cl compound (70.4-fold) than for the 4-Cl compound (48-fold). However for the specific base-catalyzed hydrolysis of these substrates we find greater catalysis for the 4-Cl compound (13–14-fold) than for the 2-Cl compound (6–8-fold). This may arise from the location of the tertiary amine in the micellar aggregate.

It is likely that the hydrophobic tertiary amines are located in the micellar interior as suggested by Khan et al.[13] Thus the larger catalysis of the reaction of the 4-Cl substrate 4 with its buried reaction center than of the reaction of the 2-Cl substrate 2 with its reaction center at the micelle water interface is understandable. The action

(11) Stilbs, P. *J. Colloid Interface Sci.* **1983**, *94*, 463.
(12) Graglia, A.; Pramauro, E.; Pelizzetti, E. *Ann. Chim.* **1984**, *74*, 41.
(13) Khan, M. N.; Dahiru, M.; Naaliya, J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 623.

of these amines as specific base catalysts in the micellar interior, however, indicates the presence of some water in the micellar interior in these systems. The presence of water in the micellar interior has been the subject of speculation for some years.[14,15]

Conclusions

On the basis of our kinetic studies it appears likely that the magnitude of catalysis of reactions by micelles is influenced firstly by the orientation of substrates solubilized by the micelles, as shown by the different effects of micelles of CTAB on the reactions of primary amines with substrates 2 and 4 and secondly by the location of reagents, as shown by the different order of the catalyses of the reactions of these substrates with sodium hydroxide and with the tertiary amines.

Experimental Section

Materials. The aromatic substrates were available from previous studies.[1,2] The amines were all commercially available and were redistilled before use. CTAB was purified by the method of Mukerjee and Mysels.[16] Distilled water was furthe purified by using a Millipore system to achieve a resistivity of at least 10 MΩ cm. Stock solutions of both the aromatic substrates (0.01 M) and the amines (1 M) were prepared in HPLC grade acetonitrile (Mallinkrodt). Stock solutions of CTAB were prepared in purified water.

Kinetics. Reaction solutions containing the required volumes of CTAB and amine stock solutions were prepared in a volumetric flask and diluted with purified water. The mixture was pipetted into a cuvette (3 mL) and allowed to reach thermal equilibrium in the jacketed cell compartment of a Varian 635 UV–vis spectrophotometer. The reaction was initiation by the addition (microsyringe) of substrate (20 μL). After mixing, the absorption of the reaction mixture at the analytical wavelength (see tables) was followed for at least 2 half-lives with a National VP 6511A X-T recorder. The infinity value for each reaction was calculated by a computer program designed to give the best straight-line fit to data collected over at least 2 half-lives. Where possible experimental infinity values were also determined, and good agreement was obtained between the calculated and experimental infinity values and rate constants. The rate constants in Tables I and II are all the averages of at least two determinations with a reproducability of ±2%.

Products. Authentic products expected from the nucleophilic reactions of aniline with substrates 1–4 and of propylamine with substrates 2 and 4 were obtained from reaction of the appropriate amine and substrate in ethanol at reflux. The mixture was then cooled to room temperature, and water was added to dissolve any amine hydrochloride precipitated. The product was filtered and washed with dilute HCl and water. The residue was recrystallized from aqueous ethanol to give 2-anilino-3,5-dinitrobenzoic acid, mp 213–5 °C (lit.[17] mp 214 °C); 4-anilino-3,5-dinitrobenzoic acid, mp 238–40 °C (lit.[18] mp 239 °C); 4-anilino-3-nitrobenzoic acid, mp 257–60 °C (lit.[19] mp 254 °C); 2-anilino-5-nitrobenzoic acid, mp 250–52 °C (lit.[20] mp 247–8 °C); 2-(propylamino)-3,5-dinitrobenzoic acid, mp 137–8 °C [^{1}H NMR ($CDCl_3$) δ 1.4 (t, 3 H, terminal methyl), 2.0 (m, 2 H, $CH_2CH_2CH_3$), 3.3 (t, 2 H, NCH_2CH_2), 9.0 (d, 1 H, Ar-H_6), 9.1 (d, 1 H, Ar-H_4)]; 4-(propylamino)-3,5-dinitrobenzoic acid, mp 171–5 °C [^{1}H NMR [$(CD_3)_2CO$] δ 1.2 (t, 3 H, terminal methyl); 2.0 (m, 2 H, $CH_2CH_2CH_3$), 3.2 (2 H, NCH_2CH_2), 8.7 (s, 2 H, Ar-H)]. Authentic products expected from the nucleophilic reactions of the tertiary amines with substrates 2 and 4 were obtained from reaction of the appropriate amine and substrate in ethanol at reflux. The solvent was then removed, and ether was added to the residue to precipitate the quaternary ammonium salt which was filtered and recrystallized from ethanol/ether to give 4-(dimethyl(2′-hydroxyethyl)ammonio)-3,5-dinitobenzoic acid: mp 125–6 °C; ^{1}H NMR δ 2.8 (s, 6 H, N^+Me_2), 3.2 (t, 2 H, N^+CH_2), 3.9 (t, 2 H, CH_2O), 8.4 (s, 2 H, ArH), 8.3 (br s, OH). Anal. Calcd for $C_{11}H_{14}N_3O_7Cl$: C, 39.3; H, 4.2; N, 12.5; Cl, 10.6. Found: C, 39.5; H, 4.1; N, 12.3; Cl, 10.7:

2-(Dimethyl(2′-hydroxyethyl)ammonio)-3,5-dinitrobenzoic acid: mp 125 °C. Anal. Calcd for $C_{11}H_{14}N_3O_7Cl$: C, 39.3; H, 4.2; N, 12.5. Found: C, 39.6; H, 4.3; N, 12.2.

Solutions for each of these products were prepared in CH_3CN (0.01M). The UV–vis spectra of the authentic nucleophilic substitution products from the reactions of the primary amines obtained using a Hewlett-Packard 7041-AX-Y recorder were identical with actual kinetic products formed during the reactions in either water or in CTAB. However the UV–vis spectra of the quaternary ammonium salts had little absorbance above 350 nm, while the actual kinetic products from the reactions of substrates 2 and 4 in the presence of tertiary amines in both water and CTAB had a strong absorbance in the region between 350 and 450 nm. Comparison of the spectra of these products with the products of basic hydrolysis (with sodium hydroxide in CTAB) indicated that phenolic products were also formed during the reaction in the presence of tertiary amines.

(14) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.
(15) Menger, F. M.; Doll, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 1109.
(16) Mukerjee, P.; Mysels, K. J. *J. Am. Chem. Soc.* **1955**, *77*, 2937.
(17) Cohn, P. *Monatschefte* **1891**, *22*, 389.
(18) Jackson, C. L.; Ittner, M. H. *J. Am. Chem. Soc.* **1897**, *19*, 18.
(19) Schopff, M. *Ber.* **1889**, *22*, 3281.
(20) Schopff, M. *Ber.* **1890**, *23*, 3440.