on silica gel (25 g) with AcOEt-MeOH-Et_3N (20:1:2, v/v) to give **5** (361 mg, 64%) as crystals. Recrystallization from AcOEt-hexane gave colorless prisms: mp 142-143 °C; $[\alpha]^{20}_D$ -54.8° (*c* 1.0, $CHCl_3$), -41.1° (*c* 1.0, EtOH); IR (KBr) 3265, 3170, 2925, 1440, 1300, 985, 735 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.48-7.08 (m, 4 H), 5.54 (q, *J* = 6.8 Hz, 1 H), 4.07 (s, 2 H), 4.04-4.03 (m, 1 H), 3.35-3.27 (m, 2 H), 2.99-2.92 (m, 1 H), 2.74-2.70 (m, 2 H), 2.39-2.34 (m, 2 H), 2.10-2.04 (m, 1 H), 1.80-1.72 (m, 1 H), 1.65 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.0, 136.1, 127.9, 122.5, 121.7, 119.6, 118.2, 110.9, 109.3, 68.5, 52.9, 42.3, 33.3, 24.7, 22.8, 13.3.

Anal. Calcd for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.36; H, 8.26; N, 10.16.

(*E*)-(*S*)-(-)-Deplancheine [(*E*)-4]. A solution of 200 mg (0.74 mmol) of **22** in 5 mL of acetonitrile was treated with triphenylphosphine (291 mg, 1.11 mmol), carbon tetrachloride (228 mg, 1.48 mmol), and triethylamine (150 mg, 1.48 mmol). The mixture was stirred at room temperature for 12 h under argon and concentrated in vacuo. The residue was chromatographed on silica gel (15 g) with Et_2O-Et_3N (15:1, v/v) to give **4** (149 mg, 80%) as crystals. Recrystallization from Et_2O-hexane gave colorless crystals: mp 140.5-141.5°; $[\alpha]^{20}_D$ -52.0° (*c* 1.0, $CHCl_3$), -64.9° (*c* 1.0, EtOH); IR ($CHCl_3$) 3440, 2840-2770, 1435, 1300 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.75 (br s, 1 H), 7.48-7.08 (m, 4 H), 5.42 (q, *J* = 6.8 Hz, 1 H), 3.42-3.31 (m, 2 H), 3.1-2.98 (m, 3 H), 2.83-2.63 (m, 3 H), 2.19-2.13 (m, 1 H), 1.98 (br t, 1 H), 1.62 (d, *J* = 6.8 Hz, 3 H), 1.65-1.53 (m, 1 H); ^{13}C NMR ($CDCl_3$, ppm) 136.5, 135.0, 134.5, 127.9, 121.5, 119.6, 119.1, 118.3, 110.8, 108.7, 63.6, 60.3, 53.0, 30.4, 26.0, 21.8, 12.6.

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.76; H, 8.12; N, 11.06.

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Micellar Catalysis of Organic Reactions. 19. Basic Hydrolysis of Carbamates in the Presence of Hydroxy-Functionalized Micelles

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A number of hydroxy-functionalized micelles were prepared, and their effects on the basic hydrolysis of a number of carbamates are compared. For reactions proceeding by the E1cB mechanism, the intermediate *p*-nitrophenyl isocyanate was trapped by the hydroxy group of the functional micelles. The efficiency of trapping by the different micelles was compared, and it was found that primary hydroxyl groups were more active than secondary ones. Furthermore, hydroxy groups bonded to the ethyl or propyl groups of detergent molecules **7** and **9** were more effective than those attached to the cetyl chain of **8**. The effects of the various micelles on the rate of E1cB hydrolysis and on $B_{Ac}2$ hydrolysis of carbamates and on the decarboxylation of aryl carbamate ions in basic solution were also compared.

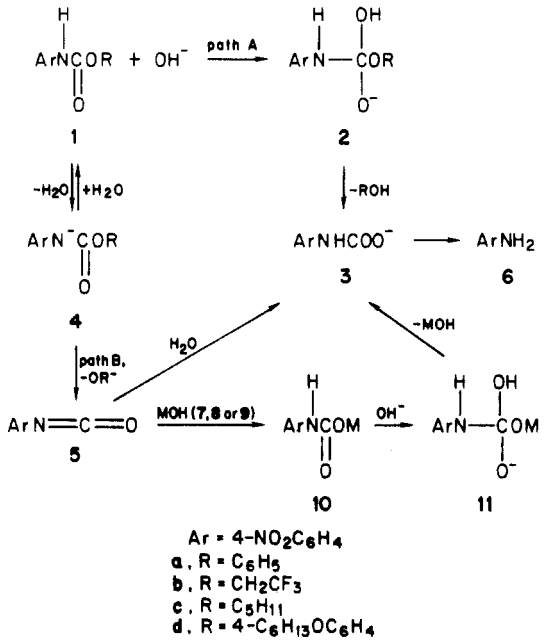
The basic hydrolysis of carbamates is of current interest.[1-5] One reason for this interest is the competition between the E1cB (path B) and $B_{Ac}2$ (path A) mechanisms for the basic hydrolysis of carbamates (Scheme I).

Good evidence for the occurrence of the E1cB mechanism in the basic hydrolysis of the phenyl and 2,2,2-trifluoroethyl compounds **1a,b** was obtained[6] by trapping the intermediate *p*-nitrophenyl isocyanate (**5**) with the hydroxy group of the functional micelle cetyl(2-hydroxyethyl)dimethylammonium bromide (chedab) (**7**). Since this intermediate **5** is not formed on path A, this result confirms that the mechanism operating for the hydrolysis of compounds **1a,b** is the E1cB mechanism (path B). The micellar carbamate **10** thus formed, subsequently decomposed slowly via the $B_{Ac}2$ mechanism (**10** → **11** → **3** → **6**).

For the *n*-pentyl compound **1c**, hydrolysis occurred by the $B_{Ac}2$ mechanism (**1c** → **2c** → **3** → **6**), but the catalysis provided by the functional micelles of chedab and by nonfunctional micelles of cetyltrimethylammonium bromide (ctab) was very similar.[6]

It is now of interest to vary the nature of the hydroxy group in the functional micelle (e.g., primary vs. secondary)

Scheme I



and also to vary the position at which the hydroxy group is bonded to the micelle. In this paper we report the preparation of two other hydroxy-functionalized micelles: 2-hydroxycetyltrimethylammonium bromide (**8**) and cetyl(2-hydroxy-1-propyl)dimethylammonium bromide (**9**).

(1) Hegarty, A. F.; Frost, L. N. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1719.
(2) Broxton, T. J. *Aust. J. Chem.* **1984**, *37*, 47.
(3) Broxton, T. J. *Aust. J. Chem.* **1984**, *37*, 2005.
(4) Hill, S. V.; Thea, S.; Williams, A. *J. Chem. Soc., Perkin Trans 2* **1983**, 437.
(5) Mindl, J.; Sterba, V.; Kaderabek, V.; Klicnar, J. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1577.
(6) Broxton, T. J. *Aust. J. Chem.* **1985**, *38*, 77.

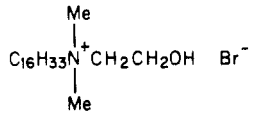
0022-3263/86/1951-3112$01.50/0

Table I. ^{13}C Chemical Shifts Expected for C-1 and C-2 of 1-Bromo-2-hydroxyhexadecane (I) and for 2-Bromo-1-hydroxyhexadecane (II) and Found for Bromohydrin Product[a]

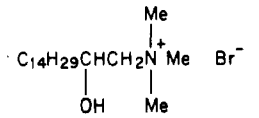
	^{13}C chemical shifts, ppm		
	I		
C	expected for I[b]	found	expected for II[c]
C-1	70.0	71.06	63.1
C-2	34	40.66	52.6

[a] Reference 8. [b] Using data for cyclohexanol and 1-bromooctane. [c] Using data for bromocyclohexane and 1-octanol.

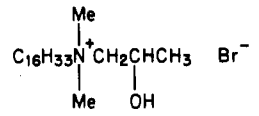
Both of these compounds contain secondary hydroxy groups, thus allowing a comparison of the reactivity of primary and secondary hydroxy groups in micelles.



7



8



9

Furthermore, it is possible that the hydroxy group of 8 may be more embedded into the surface of the micelle than those of either chedab (7) or the propyl compound 9. Thus, we may be able to detect differences in reactivity of the secondary hydroxyl groups in micelles of 8 and 9. We thus compare the effects of the nonfunctionalized ctab with the hydroxy-functionalized micelles 7–9 on the trapping of intermediate 5 formed during the hydrolysis of compounds **1a,b** and on the rate of various steps involved in the overall hydrolysis of compounds **1a–c**, e.g., the conversion of the nitranion **4b** to intermediate **5**, k_{4-5}, the decarboxylation of the carbamate ion **3** to *p*-nitroaniline (**6**), k_{3-6}, the decomposition of the micellar carbamate, $k_{10-11-3-6}$, and the rate of the $B_{Ac}2$ hydrolysis of compound **1c**, $k_{1c-2c-3-6}$.

Results and Discussion

(a) Micelles. (2-Hydroxycetyl)trimethylammonium bromide (8) was prepared from 1-hexadecene via the bromohydrin[7] which was reacted with trimethylamine in methanol. The structure of the bromohydrin, i.e., 1-bromo-2-hydroxyhexadecane, was confirmed by ^{13}C NMR spectroscopy in $CDCl_3$. Signals δ 71.06 (d, ORD, CHOH) and 40.66 (t, ORD, CH_2Br) were compared to the literature values[8] for primary and secondary alcohols and alkyl bromides (Table I). Cetyl(2-hydroxy-1-propyl)dimethylammonium bromide (**9**) was prepared by quaternization of 1-(dimethylamino)-2-propanol with cetyl bromide.

Critical micelle concentrations (CMC) of 8 (1.31×10^{-3} M) and 9 (1.01×10^{-3} M) in neutral solution were determined by conductance measurements. The CMC of chedab (7) in neutral solution was reported to be 8×10^{-4} M.[9] Thus, the CMC for each of the functional micelles are similar. Presumably, in basic solution, the CMC would be reduced, as found for chedab,[9] because of ionization of the hydroxy groups.

Table II. The Percentage of Trapping of Intermediate 5 Produced in the Hydrolysis of Compound 1a in the Various Functional Micelles at 29.4 °C

[detergent], mM	[OH^-], M	% trapping in micelle[a] 7	8	9
4	0.1	88 (92)	30 (28)	47 (49)
	0.05	90	31	48
	0.01	93	30	49
	0.001	90	25	47
2	0.1	89 (91)	29 (25)	48 (46)
1	0.1	93 (100)	15 (27)	43 (52)
	0.001	91 (100)	21 (16)	45 (56)

[a] Results in parentheses for hydrolysis of compound **1d**.

Table III. Molar Absorptivity of *p*-Nitrophenyl Carbamate Ion 3 and Micellar Carbamate 10 under Various Conditions

conditions		molar absorptivity at 350 nm (400 nm)	
[detergent], mM	[OH^-], M	carbamate ion 3	micellar carbamate 10
4	0.1	14710 (3009)	7000 (17167)
4	0.05	14750 (3150)	7523 (17887)
4	0.01	14660 (3060)	7523 (16884)
4	0.001	14250 (3000)	7573 (12638)
2	0.1	14544 (3375)	7422 (17887)
1	0.1	13758 (4200)	7472 (17553)
1	0.001	13300 (3800)	7523 (12956)

(b) Trapping Studies. To study the efficiency of trapping the *p*-nitrophenyl isocyanate intermediate (**5**) by the different micelles, the phenyl **1a** and 4-(hexyloxy)-phenyl **1d** compounds were chosen because for these compounds, the production of (**5**) was essentially instantaneous. Under most conditions, intermediate **5** was only partially trapped, leading to a mixture of carbamate ion **3** and micellar carbamate **10**. The proportion of **3** and **10** produced in each case was determined by a spectrophotometric technique that involved taking absorbance measurements at two wavelengths (350 nm, λ_{max} for **3**, and 400 nm, λ_{max} for **10** in basic solution). Provided the molar absorptivity of the products **3** and **10** were known at these wavelengths (Table III), the concentration of each product could be calculated. The carbamate ion **3** was obtained from reaction of the phenyl compound **1a** in ctab. Under these conditions, no trapping is possible and the molar absorptivity of carbamate ion **3** was calculated from the absorbance at 350 and 400 nm and the concentration of the phenyl compound precursor used. The micellar carbamates **10** formed by trapping intermediate **5** with the functional micelles **7** and **9** were prepared, and their absorbances at 350 and 400 nm were measured in basic solutions of the appropriate micelles. Attempts to prepare the micellar carbamate corresponding to 2-OH ctab (8) were unsuccessful. Consequently, molar absorptivity for the micellar carbamate based on functional micelle **7** were used in the calculations of the percentage of trapping in the presence of 2-OH ctab (8).

The percentage trapping was determined by the following method. The detergent solution was allowed to reach thermal equilibrium in the jacketed cell holder of

(7) Langman, A. W.; Dalton, D. R. *Organic Syntheses*; Coates, R. M., Ed.; Wiley: New York, 1980; Vol. 59, p 16.
(8) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer Verlag: Berlin, 1983.
(9) Bunton, C. A.; Paik, C. H. *J. Org. Chem.* **1976**, *41*, 40.

Table IV. Pseudo-First-Order Rate Constants for the Conversion of the Equilibrium Mixture of Carbamate 1b and Nitranion 4b into Isocyanate 5 at 29.4 °C

[NaOH], M	[detergent], mM	$10^4 k_1$ in micelles, s^{-1} ctab	chedab (7)	2-OH ctab (8)	9
0.1	8	20.2	18.0	17.4	17.8
0.1	4	21.0	17.4	18.1	18.1
0.1	2	20.6	16.6	17.9	18.0
0.05	4	20.6	18.4	16.7	19.0
0.01	4	20.0	19.0	16.0	19.1

spectrophotometer. A sample of a stock solution of carbamate **1a** or **1d** was added. The sodium hydroxide solution was added, and the contents were mixed thoroughly. Absorbance measurements at 350 and 400 nm were taken.

$$A_{obsd}^{350} = \sum_{10}^{350} [\mathbf{10}] + \sum_{3}^{350} [\mathbf{3}] \quad (1)$$

$$A_{obsd}^{400} = \sum_{10}^{400} [\mathbf{10}] + \sum_{3}^{400} [\mathbf{3}] \quad (2)$$

With eq 1 and 2, the concentrations of **3** and **10** were calculated and hence the percentage of trapping was obtained in each case. The percentage trapping for each functional micelle under various conditions is given in Table II.

It can be seen that the most efficient micelle for trapping the intermediate **5** is chedab (**7**). The least effective is 2-OH ctab (**8**). The lower efficiency of 2-OH ctab could be due either to the fact that it contains a secondary alcohol group, while chedab (**7**) contains a primary alcohol group, or alternatively due to the fact that the hydroxy group of **8** is bonded to the cetyl chain, whereas that of **7** is bonded to an ethyl group which may be more mobile at the micelle water interface. To try to determine which of these effects is more important we also studied reaction in micelle **9**, which contains a secondary hydroxy group bonded to a propyl group which should behave similarly to the hydroxy ethyl group of chedab (**7**). The propyl compound **9** is less effective than chedab (**7**), but more effective than 2-OH ctab (**8**). Thus, it appears that both factors are important. Primary alcohols are more effective traps for intermediate **5** than secondary alcohols, and a hydroxy group bonded to a short alkyl chain is more effective than one bonded to the cetyl chain.

Variations of either the detergent concentration (between 1–4 mM at 0.1 M OH^-) or the hydroxide concentration (between 0.001–0.1 M at 4 mM detergent) were insignificant compared to differences between the micelles.

(c) Kinetic Studies. (i) E1cB Reaction of Nitranion 4b (i.e., k_{4b-5}). For the trifluoroethyl compound **1b**, which reacts by the E1cB mechanism,[1,2] it was possible to determine the rate of loss of nitranion **4b**. Since the conversion of the isocyanate intermediate **5** to **3** and/or **10** is instantaneous, the reaction actually being followed is the slow step, i.e., the conversion of nitranion **4b** to isocyanate **5**, i.e., k_{4b-5}.

The experimental method used for this kinetic measurement was as described above for trapping studies except that carbamate **1b** was used and that the rate of change of absorbance at 400 nm was monitored.

Pseudo-first-order rate constants for the conversion of carbamate **1b**/nitranion **4b** into isocyanate **5**, i.e., k_{4b-5}, are in Table IV.

At 4 mM detergent, there was no significant variation of rate with [OH^-], and thus we conclude that in the range 0.01–0.1 M OH^-, carbamate **1b** is completely ionized to nitranion **4b** in the presence of micelles. Furthermore, at 0.1 M OH^- there is no significant variation in rate with [detergent] for any of the detergents studied. Thus, we conclude that the nitranion is fully solubilized within the micelle at these detergent concentrations. There is a barely discernible difference between the micelles. For example, at 0.1 M OH^- and 2 mM detergent, the reactivity order is ctab > 2-OH ctab ≈ **9** > chedab; however, there is only a 20% change in rate over this series.

Table V. First-Order Rate Constants for the Decarboxylation of Carbamate Ion 3 at 29.4 °C

[NaOH], M	[detergent], mM	$10^4 k_1$ in micelles, s^{-1} ctab	chedab (7)	2-OH ctab (8)	9
0.1	8	1.08	1.20	0.58	1.33
0.1	4	1.00	1.17	0.57	1.23
0.1	2	0.92	1.11	0.50	1.19
0.1	1	0.78	0.84		0.95
0.05	4	0.93	1.13	0.53	1.11
0.01	4	0.96	1.04		1.08

Table VI. Pseudo-First-Order Rate Constants for the Decomposition of the Micellar Carbamates in the Appropriate Micelles at 29.4 °C

[OH^-], M	[detergent], mM	$10^4 k_1$, s^{-1} propyl model in 9	chedab model in 7
0.1	13.3		0.85
0.1	8.0	0.095	0.95
0.1	6.7		0.97
0.1	6.0		0.95
0.1	4.0	0.120	1.06
0.1	3.3		1.16
0.1	2.0	0.121	1.40
0.1	1.0	0.112	1.72
0.05	4.0	0.098	1.13
0.01	4.0	0.137	1.26

(ii) Decarboxylation (k_{3-6}). The effects of the various micelles on the rate of decarboxylation of the carbamate ion (i.e., k_{3-6}) was studied next. The carbamate ion **3** was generated in situ by adding the phenyl carbamate **1a** to a solution of sodium hydroxide in water. When the yellow coloration (due to nitranion **4a**) had faded completely, a sample of the required detergents **7**, **8**, **9**, or ctab was added, and the rate of decarboxylation was followed at 380 nm (*p*-nitroaniline production). Rate constants for the decarboxylation of the carbamate ion **3** i.e., k_{3-6}, are in Table V.

It can be seen that the rate of decarboxylation is much slower (×20) than the rate of production of carbamate ion from nitranion **4b** (see results for ctab in Table IV). It has previously been reported[2] that the decarboxylation rate is significantly catalyzed by micelles of ctab. However, the hydroxy-functionalized micelles do not provide significantly greater catalysis than ctab. In fact, reaction in 2-OH ctab (**8**) is slower than in ctab itself. The rate of decarboxylation in 0.1 M NaOH increased slightly as the detergent concentration was increased from 1 to 8 mM. An optimum rate is probably achieved at 8 mM since the rate at 4 and 8 mM is very similar.

At 4 mM detergent, the rate of decarboxylation is essentially independent of [NaOH]. In the various micelles, the reactivity order is propyl compound **9** > chedab (**7**) > ctab > 2-OH ctab (**8**).

(iii) $B_{Ac}2$ Hydrolysis of Micellar Carbamates (i.e., $k_{10-11-3-6}$). The rates of decomposition of the micellar carbamates **10** in the appropriate micelle were studied for chedab (**7**) and for the propyl compound **9**. A sample of the micellar carbamate **10** was added to a premixed solution containing NaOH and the required micelle. The rate of loss of micellar carbamate was followed at 395 nm. Pseudo-first-order rate constants for the decomposition of the micellar carbamates are in Table VI.

Table VII. Pseudo-First-Order Rate Constants for the Basic Hydrolysis of Pentyl Carbamate 1c by the $B_{Ac}2$ Mechanism at 46.1 °C

[OH^-], M	[detergent], mM	$10^4 k_1$ for micelles, s^{-1}			
		ctab	chedab (7)	2-OH ctab (8)	9
0.1	8	1.07	1.01	1.43	0.94
0.1	4	1.07	1.07	1.46	0.98
0.1	2	1.13	1.08	1.49	0.97
0.05	8	0.99	0.98	1.40	0.90
0.01	8	0.79	0.81	1.20	0.78
0.005	8	0.62	0.69	1.06	0.65

The rate of basic hydrolysis of the propyl model **10** (M = $CH(Me)CH_2N^+Me_2C_{16}H_{33}Br^-$) in the propyl micelle **9** was considerably slower than that for the chedab model **10** (M = $CH_2CH_2N^+Me_2C_{16}H_{33}Br^-$) in chedab (**7**). This presumably is due to steric hindrance provided by the extra methyl group in the propyl model. At 0.1 M NaOH, optimal rates were observed at low detergent concentrations (1–2 mM), reflecting the hydrophobic nature and hence ease of solubilization of the micellar carbamates. As the detergent concentration was increased above that level, the observed rate decreased, presumably because of dilution of the substrate as the volume of the micellar pseudophase was increased beyond that required to achieve complete solubilization.

(iv) $B_{Ac}2$ Hydrolysis of the Pentyl Carbamate (i.e., $k_{1c-2c-3-6}$). Rate constants for the basic hydrolysis of the pentyl carbamate **1c**, which reacts via the $B_{Ac}2$ mechanism, were obtained for each of the micelles. A sample of the pentyl carbamate **1c** was added to a solution of the detergent in water. Then sodium hydroxide was added, and the rate of basic hydrolysis was followed at 430 nm, which corresponds to the loss of the reactant (carbamate **1c**–nitranion **4c** equilibrium mixture). Rate constants for this reaction are in Table VII.

The basic hydrolysis of compound **1c** is much slower than that for the trifluoroethyl compound **1b**, and consequently to achieve convenient reaction times it was studied at 46.1 °C. At 0.1 M NaOH the maximum rate observed was at 2 mM detergent, except for the propyl compound **9** (4 mM). This reflects the hydrophobicity of the pentyl carbamate. At 8 mM detergent, the rate of reaction increased as the hydroxide concentration was increased from 0.005 to 0.1 M. For micelles of ctab, chedab (**7**), and the propyl compound **9**, reaction occurred at approximately the same rate. However, for 2-OH ctab, the rate of reaction was approximately 50% faster than for the other detergents.

Conclusions

Although there are many examples[10-13] in the literature of significantly larger catalysis of organic reactions by functional micelles, e.g., chedab (**7**), than by ctab, no such effects were obtained in any of the reactions associated with the basic hydrolsyis of carbamates. Thus, it was not possible to obtain a meaningful comparison of the reactivity of **7–9**. Further work on reactions more susceptible to functional catalysis is under way.

As far as trapping *p*-nitrophenyl isocyanate (**5**) formed during the E1cB hydrolysis of some carbamates is concerned, it seems that chedab is the most effective micelle, and an order **7** > **9** > **8** was obtained. Thus, it appears that the greater nucleophilicity of a primary alcohol than a secondary alcohol and the site at which the alcohol group is bonded to the detergent molecule are both important factors.

Experimental Section

Materials. The carbamates **1a–c** were available from previous studies.[2] The 4-(hexyloxy)phenyl carbamate **1d**, mp 168–170 °C (EtOH), was prepared from *p*-(hexyloxy)phenol (Aldrich) and *p*-nitrophenyl isocyanate in benzene containing a catalytic amount of triethylamine.[2] Found: C, 63.7; H, 6.1; N, 7.7. $C_{19}H_{22}N_2O_5$ requires: C, 63.7; H, 6.1; N, 7.8. The chedab micellar carbamate **10** (M = $CH_2CH_2N^+Me_2C_{16}H_{33}Br^-$) was available from previous work.[6] The propyl micellar carbamate **10** (M = $CH(CH_3)CH_2N^+Me_2C_{16}H_{33}Br^-$) (mp 160–162 °C (EtOH). Found: C, 58.7; H, 8.8; N, 7.2; Br, 13.7. $C_{28}H_{50}BrN_3O_4$ requires: C, 58.7; H, 8.7; N, 7.3; Br, 14.0) was prepared by quaternization of 1-(dimethylamino)-2-propyl *N*-(4-nitrophenyl)carbamate with cetyl bromide in ethanol (16 h at reflux). 1-(Dimethylamino)-2-propyl *N*-(4-nitrophenyl)carbamate, mp 156–158 °C ($CHCl_3$–petroleum ether) was prepared from *p*-nitrophenyl isocyanate and 1-(dimethylamino)-2-propanol in benzene containing a catalytic amount of triethylamine.[2] CTAB (BDH) was purified by the method of Mukerjee and Mysels.[14] Chedab was freshly prepared as before.[6] The propyl compound **9** was prepared by quaternization of 1-(dimethylamino)-2-propanol with cetyl bromide in ethanol (16 h at reflux). Recrystallization from EtOH–Et_2O gave white crystals, mp 73–74 °C. Found: C, 62.1; H, 11.5; N, 3.7; Br, 19.5. $C_{21}H_{46}BrNO$ requires: C, 61.8; H, 11.3; N, 3.4; Br, 19.6. (2-Hydroxycetyl)trimethylammonium bromide (**8**) (mp 111–112 °C) was prepared by quaternization of 1-bromo-2-hydroxyhexadecane with trimethylamine in methanol. Found: C, 59.6; H, 10.9; N, 4.0; Br, 21.4. $C_{19}H_{42}BrNO$ requires C, 60.0; H, 11.1; N, 3.7, Br, 21.0. 1-Bromo-2-hydroxyhexadecane, mp 48–49 °C (petroleum ether), was prepared by the reaction of 1-hexadecene with *N*-bromosuccinimide in wet dimethyl sulfoxide:[7] ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H, CH_3), 1.35 (m, 26 H, 13 × CH_2), 1.9 (d, 2 H, CH_2Br); ^{13}C NMR ($CDCl_3$) δ 71.06 (d, ORD, CH), 40.66 (t, ORD, CH_2).

Stock solutions of the carbamates **1a–d** (0.01 M in dioxane), the micellar carbamates **10** (0.01 M in dry MeOH), the detergents (ctab and **7–9**) (0.02 M in water), and sodium hydroxide (0.5 M in H_2O) were prepared. The sodium hydroxide was standardized by titration against hydrochloric acid using bromocresol green indicator. Distilled water was further purified by using a Millipore system to achieve a resistivity of, at least, 10 M Ω cm.

Kinetics and trapping experiments were carried out by methods described above (Results section), using a Varian 635 UV–vis spectrophotometer and a National VP 6511A X-T recorder for kinetics or a Hewlett-Packard 7041A X-Y recorder for repetitive scans of the reaction mixture.

Reactions were followed for at least 10 half-lives where possible, or, alternatively, for very slow reactions or consecutive reactions an infinity value was calculated by using a computer program designed to give the best straight line fit to data collected over at least two half-lives. Good agreement was obtained between rate constants obtained by the two methods. Reactions were carried out in a cuvette kept at constant temperature in the jacketed cell holder of the spectrophotometer. The temperature within the cell was measured with a Jenco thermistor thermometer.

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Registry No. **1a**, 6465-01-6; **1b**, 405-59-4; **1c**, 90429-36-0; **1d**, 102831-88-9; **3**, 74401-81-3; **5**, 100-28-7; **7**, 20317-32-2; **8**, 102831-87-8; **9**, 68796-83-8; **10** (M = $CH_2CH_2NMe_2C_{16}H_{33}^+Br^-$), 96042-14-7; **10** (M = $CH(CH_3)CH_2NMe_2C_{16}H_{33}^+Br^-$), 102831-89-0; $CH_3(CH_2)_{13}CH{=}CH_2$, 629-73-2; $CH_3(CH_2)_{13}CH(OH)CH_2Br$, 86579-61-5; NMe_3, 75-50-3; $Me_2NCH_2CH(OH)CH_3$, 108-16-7; $CH_3(CH_2)_{15}Br$, 112-82-3; 4-$C_6H_{13}OC_6H_4OH$, 18979-55-0; 4-$NO_2C_6H_4NHCO_2CH(CH_3)CH_2NMe_2$, 102831-90-3.

(10) Meyer, G. *Tetrahedron Lett.* **1972**, 4581.
(11) Bunton, C. A.; Ionescu, L. G. *J. Am. Chem. Soc.* **1973**, *95*, 2912.
(12) Minch, M. J.; Chen, S.-S.; Peters, R. *J. Org. Chem.* **1978**, *43*, 31.
(13) Fornasier, R.; Tonellato, U. *J. Chem. Soc., Perkin Trans. 2* **1982**, 899.
(14) Mukerjee, P.; Mysels, K. J. *J. Am. Chem. Soc.* **1955**, *77*, 2937.