2-Methyl-3-phenyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (21). The above general procedure was followed on dithiane (0.6 g, 5 mmol) and allylic chloride **4** (0.7 g, 3.2 mmol) to give after flash column chromatography the desired cyclopentenone **21** as a yellow viscous oil (0.4 g, 45%). IR (neat): 1700, 1650, 1600, and 1500 cm^{-1}. Mass spectrum: *m/e* 276 (M^+), 243 (base peak). ^{13}C NMR: 204.06, 159.34, 134.92, 129.86, 128.56, 127.65, 128.17, 46.48, 45.32, 26.36, 24.14, and 10.25. ^1H NMR: 7.50 (s, 5 H, Ar H), 3.95 (2 H, dt, J = 14, 2.5 Hz, 7- and 9-axial H's), 2.95 (2 H, d, J = 2.5 Hz, 4-CH_2), 2.60 (2 H, dm, J = 14 Hz, 7- and 9-equatorial H's), 2.10 (2 H, m, 8-CH_2's), and 1.95 (3 H, s). Anal. Calcd for $C_{15}H_{16}S_2O$: C, 65.21; H, 5.79; S, 23.18. Found: C, 65.02; H, 5.94; S, 22.96.

2,3-Dimethyl-2-cyclopenten-1-one (22). A solution of **20** (0.84 g, 4 mmol) in ethanol (25 mL) was treated carefully with a slurry of Raney nickel[40] (1.2 mL) and refluxed for 1 h. The mixture was then cooled, filtered through Celite, and concentrated. Flash column chromatography of the resulting oil gave the cyclopentenone **22** (0.3 g, 70%) eluting in 50% EtOAc/hexane as a colorless oil. IR (neat): 1700, 1650 cm^{-1}. ^1H NMR: 2.38 (m, 4 H), 2.10 (s, 3 H), and 1.68 (s, 3 H). Mass spectrum: *m/e* 110 (M^+), 67 (base peak). ^{13}C NMR: 209.15, 169.30, 135.80, 33.50, 30.96, 16.10, and 7.20.

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(40) Obtained from Aldrich Chemical Company.

Micellar Catalysis of Organic Reactions. 27.† Micellar Bound Meisenheimer Complexes

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Reactions of nitro activated aryl halides with base in the presence of dihydroxy micelles of cetyl(2,3-dihydroxypropyl)dimethylammonium bromide (CDHPDAB) give rise to spiro Meisenheimer complexes that are covalently bound to the micelles. From the large fluorine/chlorine rate ratios observed for these reactions, we conclude that the initial attack on the aryl halide by the micellar hydroxyl group is the rate-determining step for the formation of the Meisenheimer complex. For the subsequent decomposition of the complex the rate of reaction is dependent on hydroxide concentration if the complex contains only one ortho substituent. This indicates that the breakdown of the aryl micellar ether formed in the first step of the decomposition is the rate-determining step. However, for complexes containing two ortho substituents, the rate of decomposition is almost independent of the hydroxide concentration, indicating for these complexes that the rate-determining step is the initial unimolecular breakdown of the Meisenheimer complex to form the micellar ether. It is proposed that this change is caused by the built-in solvation effect of Bunnett et al. in which the positive charge on the side chain of the complex is stabilized by an electrostatic interaction with either the negatively charged carboxylate group or the dipolar nitro group.

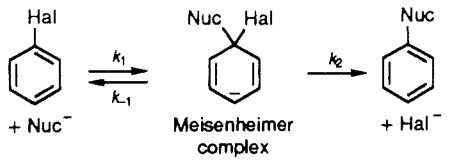
Introduction

The currently accepted mechanism for the nucleophilic aromatic substitution of activated aromatic substrates (see Scheme I) is a two-step process in which carbon–nucleophile bond formation precedes carbon–nucleofuge bond breakage.[1-4] An anionic intermediate termed a Meisenheimer complex[5-7] is formed during this reaction. In most reactions the formation of this complex is rate determining since the presence of a good nucleofuge makes the breakdown of the complex fast. This conclusion is supported by the large fluorine/chlorine rate ratios observed.

For the formation of the complex the polarization of the carbon–halogen bond is important in determining the reactivity (electrophilicity) of the aromatic carbon atom under attack. The greater electronegativity of fluorine than that of chlorine[8a] thus results in the observed F/Cl rate ratios. On the other hand, the decomposition of the complex involves carbon–halogen bond breakage, and in this case the mobility of the halogens should depend on the carbon–halogen bond strength as is the case for both S_N1 and S_N2 reactions.[8b]

Attempts to isolate the Meisenheimer complexes formed in these S_NAr reactions failed because the decomposition

Scheme I



of the complex (k_2 or k_{-1} in Scheme I) was too fast.

To overcome this problem it has become common to study the reactions of activated aryl ethers with alkoxide ions for which decomposition of the complex is slow because alkoxide ions are poor nucleofuges. In suitably stabilized compounds, e.g., 1-ethoxy-2,4,6-trinitrobenzene, the Meisenheimer complex formed by reaction with methoxide ions has been isolated. In less stabilized systems, e.g., the 2,4-dinitrobenzene and the mononitrobenzene derivatives, the corresponding intermediate has

† Part 26: Broxton, T. J.; Christie, J. R.; Chung, R. P.-T. *Aust. J. Chem.* **1989**, *42*, 855.

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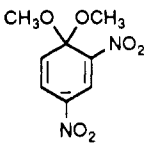
0022-3263/90/1955-3886$02.50/0

been detected spectroscopically both by UV–visible and by NMR spectroscopy.[9] Optically the formation of a Meisenheimer complex is indicated by the production of a red coloration at λ_{max} 495 nm for compounds **1** and **2** in methanol and at 564 nm for compound **3** in methanol.[7]



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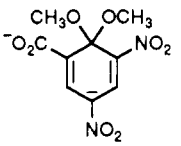

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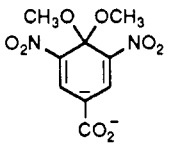

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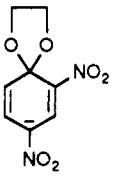

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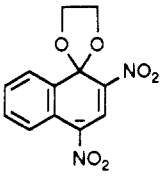


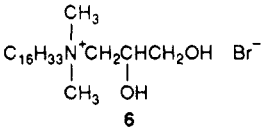
5

More recently[10-12] spiro Meisenheimer complexes **4** and **5** have been formed using bifunctional nucleophiles such as ethanediol. For complex **4**, a λ_{max} at 493 nm was observed[7] which is similar to that observed for the corresponding 1,1-dimethoxy compound **1**. It has been found that these spiro complexes are much more stable than their 1,1-dialkoxy analogues presumably because of the rigidity of the cyclic substituent perpendicular to the benzene ring.[11]

The effect of micelles of cetyltrimethylammonium bromide (CTAB) on nucleophilic aromatic substitutions has recently been widely studied.[13-15] The effect of micelles on the stability of both normal and spiro Meisenheimer complexes has also been studied.[11] It has been found that micelles of CTAB enhance the equilibrium constant for the formation of the Meisenheimer complex by retarding the breakdown (k_{-1}) of the complex.

Results and Discussion

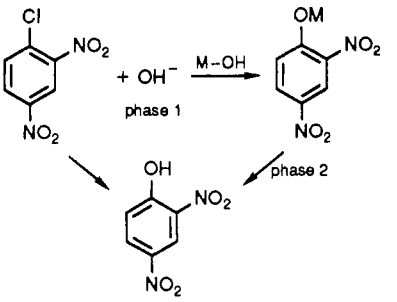
We now report the first examples of Meisenheimer complexes covalently bound to micelles. These complexes were obtained by using micelles of cetyl(2,3-dihydroxypropyl)dimethylammonium bromide (CDHPDAB) (**6**) with



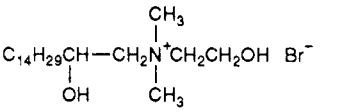
6

1-chloro-2,4-dinitrobenzene (**7**), 1-fluoro-2,4-dinitrobenzene (**8**), 1-chloro-2,6-dinitrobenzene (**9**), sodium 2-chloro-3,5-dinitrobenzoate (**10**), and sodium 4-chloro-3,5-dinitrobenzoate (**11**) as substrates in basic solution.

Scheme II. Reaction in Monohydroxy Micelle



Other dihydroxy micelles (**12** and **13**) were also prepared, but no evidence of Meisenheimer complexation was found for these micelles with any of the substrates used.



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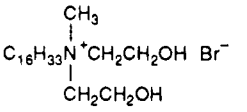
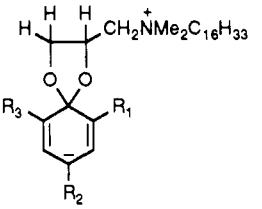


13

We note that Meisenheimer complexes formed with micelles **12** and **13** would involve eight-membered rings, and so the well-known medium-ring effect[8c] may be the reason for this difference in behavior.

(a) Formation of the Meisenheimer Complex. The production of Meisenheimer complexes from the interaction of the dihydroxy micelle **6** with various substrates was indicated from an inspection of the changes in the UV–visible spectrum during the course of the reaction. By comparison reaction of hydroxide ions in micelles of CTAB with, for example, substrates **7** and **8** was a monophasic reaction with concurrent loss of absorbance at 260 nm due to reactant loss, and formation of absorbance at 358 nm due to 2,4-dinitrophenolate ion production. Reaction of the same substrates in the presence of monohydroxy micelles of cetyl(2-hydroxyethyl)dimethylammonium bromide (CHEDAB) was biphasic.[16] The production of a transient species with λ_{max} 300 nm was attributed to the production and subsequent decomposition of an aryl micellar ether (Scheme II). Reaction in the presence of dihydroxy micelles (**6**), however, was characterized by the rapid production and subsequent loss of a red coloration (λ_{max}) at 490 nm. This was attributed to the formation of a spiro Meisenheimer complex (**14**) which is similar in structure and visible spectrum to complex **4**.



14: $R_1 = NO_2$, $R_2 = NO_2$, $R_3 = H$
15: $R_1 = NO_2$, $R_2 = H$, $R_3 = NO_2$
16: $R_1 = NO_2$, $R_2 = NO_2$, $R_3 = CO_2^-$
17: $R_1 = NO_2$, $R_2 = CO_2^-$, $R_3 = NO_2$

Likewise substrate **9** gave rise to a coloration at λ_{max} 585 nm which was attributed to complex **15** which is similar in structure and UV–visible spectrum to the spiro complex reported by Crampton[17] (λ_{max} 575 nm), while substrate **10** gave rise to a coloration with λ_{max} 486 nm which was at-

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Scheme III. Formation of the Meisenheimer Complex

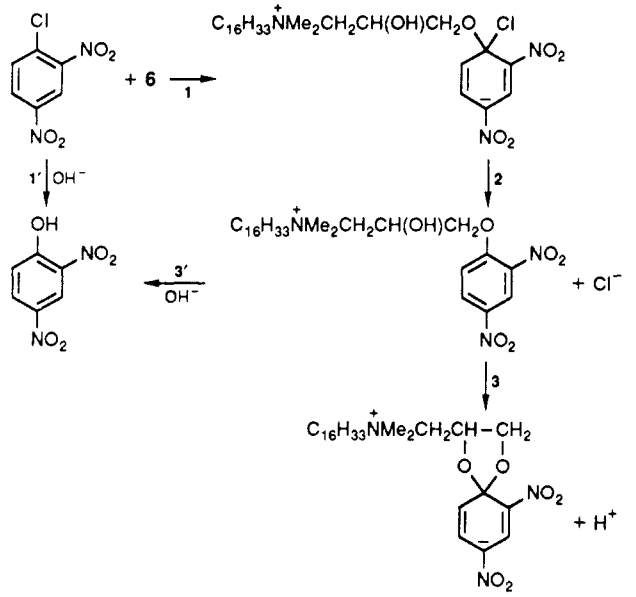

Table I. First-Order Rate Constants ($10^5 k_\psi/s^{-1}$) as a Function of Hydroxide Concentration for the Formation of the Meisenheimer Complex Indicated in Micelles of CDHPDAB at 30 °C

[NaOH], M	complex substrate	14 7	14 8	15 9	16 10	17 11
0.001		148		7.83	6.06	36.1
0.005		841		69.4	47.4	393
0.01		1368	465 000	117	87.7	619
0.05		4170	1 190 000		149	1050
0.1			1 820 000	337	171	1295
[CDHPDAB], mM		8	6	8	8	8
analyte λ, nm		490	490	585	486	553

tributed to complex **16** which is similar in structure to the 1,1-dimethoxy complex **2** reported by Pollitt[7] (λ_{max} 495 nm). Substrate **11** produced a coloration having λ_{max} 553 nm which was attributed to complex **17** which is similar in structure and UV–visible spectrum to the 1,1-dimethoxy complex **3** reported by Pollitt[7] (λ_{max} 564 nm).

A proposed scheme for the production of the Meisenheimer complex from substrate **7** is shown in Scheme III.

First-order rate constants for the production of the appropriate Meisenheimer complexes from substrates **7–11** as a function of [hydroxide] at constant [CDHPDAB] are given in Table I and as a function of [CDHPDAB] at constant [NaOH] in Table II. The critical micelle concentration (cmc) of CDHPDAB in neutral aqueous solution (0.9 mM) was determined from conductance measurements. This is very similar to the cmc of CTAB in neutral solution. It has previously been shown[18] that the cmc of CTAB is reduced to 0.3 mM in the presence of sodium hydroxide (0.02–0.1 M). We believe that a similar effect is also operating in CDHPDAB because we have spectral evidence of the production of Meisenheimer complexes at concentrations as low as 0.2 mM for compounds **10** and **11** (Table VI). Indeed from the data in Table II it can be seen that the rate of production of complex **17** is also significant at 0.2 mM CDHPDAB. The observed rate increases up to a maximum at between 4 and 20 mM depending on the substrate. Above the maximum rate attained for each substrate the rate decreased with further

(18) Broxton, T. J.; Christie, J. R.; Chung, R. P.-T. *J. Org. Chem.* **1988**, *53*, 3081.

Table II. First-Order Rate Constants ($10^5 k_\psi/s^{-1}$) as a Function of CDHPDAB Concentration at Constant [NaOH] for the Production of the Indicated Meisenheimer Complexes at 30 °C

[CDHPDAB], mM	complex substrate	14 7	14 8	15 9	16 10	17 11
0.2					21	442
0.4		341			46.7	906
0.6				71		1120
0.8		685		94	76	1205
1		785	136 000	118		1225
2		1220	217 000	199	126	1285
4				278	154	1320
6		1453	465 000			
8		1368		337	171	1295
10		1446	492 000			
13.3				352	175	1148
15		1257	489 000			
20		1049	431 000	356	174	1118
30			346 000	334	172	1014
40			243 000		166	949
[NaOH], M		0.01	0.01	0.1	0.1	0.1
analyte λ, nm		490	490	585	486	553

increases in CDHPDAB concentration as is normal for bimolecular reactions in the presence of micelles. From the results in Tables I and II it can be seen that the rate of production of the complex depends on the [hydroxide] for each complex, and also the rate for substrate **8**, the fluoro compound, is significantly faster than that for substrate **7**, the corresponding chloro compound at the same temperature (30 °C). This large fluorine/chlorine rate ratio allows us to pinpoint the rate-determining step for the production of the complex (step 1 in Scheme III) since step 1 is the only reaction in Scheme III for which a large F/Cl rate ratio would be expected. If step 2 was the rate-determining step, we would expect k_F less than k_{Cl}, while if step 3 was rate-determining we would expect equal rates for both halogens.

Yield of Complex. The estimated yields of the complexes obtained in the reactions of the various substrates with base in the presence of micelles of **6** are in Table VI. For substrates **8**, **10**, and **11** the yield of Meisenheimer complex at constant hydroxide concentration (0.01 M) increased to a maximum as the concentration of CDHPDAB was increased and subsequently decreased if the concentration of CDHPDAB was further increased. This may reflect the increasing extent of solubilization of the substrates as the micelle concentration was increased. For substrate **9**, an essentially quantitative yield of complex **15** was formed at all micelle concentrations used.

At constant CDHPDAB concentration the yield of complex formed from all the above substrates increased as the concentration of sodium hydroxide was increased. This may reflect the increasing extent of ionization of the second hydroxyl group within the micellar ether as the hydroxide concentration was increased. It can be seen that the yields of complexes from substrates **9–11** are comparable and are much higher than that from compound **8**.

The yield of complex is dependent upon the partitioning of the substrate to produce the micellar ether by step 1 (Scheme III) rather than reaction with hydroxide ions to form dinitrophenolate ions by step 1′ (Scheme III) and also by the partitioning of the micellar ether itself between intramolecular attack by the second hydroxyl group to form the Meisenheimer complex by step 3 (Scheme III) rather than attack by an external hydroxide ion to form 2,4-dinitrophenolate ions (step 3′; Scheme III).

For substrates **10** and **11** which contain substituents at both ortho positions, it is conceivable that the intramolecular reaction leading to the Meisenheimer complex is more sterically favorable than the alternative intermolecular reaction with an external hydroxide ion. We thus

Table III. First-Order Rate Constants ($10^5 k_\psi/s^{-1}$) for the Decomposition of the Meisenheimer Complexes Indicated as a Function of the Sodium Hydroxide Concentration

[NaOH], M	complex substrate	14 7	14 8	15 9	15 9	16 10	17 11
0.001			5.3		41.8	13.5	43.4
0.005		24.7	26.8		42.9	17.0	54.2
0.01			42	0.68	41.0	17.8	
0.05		84.7	89			17.0	59.6
0.1			119	0.57	32.2	16.6	62.1
analyte λ, nm		490	490	585	585	486	553
[CDHPDAB], mM		8	8	8	8	8	8
temp, °C		30	30	30	56	56	56

Table IV. First-Order Rate Constants ($10^5 k_\psi/s^{-1}$) for the Decomposition of the Indicated Meisenheimer Complexes as a Function of Detergent Concentration

[CDHPDAB], mM	complex substrate	14 8	15 9	16 10	17 11	17 11
0.2				6.97	34.9	
0.4		55.6		13.8	53.3	
0.8			31.4	15.8	62.1	
1		72.6	31.9			
2			31.7	17.0		
4		55.6	34.0	16.7	64.3	1.46
8		42	32.2	16.6	62.1	1.37
10		38.7				
13.3			31.8	15.1	60.3	1.21
20			32.1	16.3	55.8	1.15
30			32.2	15.8	53.0	
40				15.4	50.6	
[NaOH], M		0.01	0.1	0.1	0.1	0.1
temp, °C		30	56	56	56	30
analyte λ, nm		490	585	486	553	553

conclude that it is the presence of two ortho substituents which influence the partitioning of the micellar ether in favor of the Meisenheimer complex that is responsible for the high percentage yields of Meisenheimer complexes from compounds **9–11**.

(b) Decomposition of the Meisenheimer Complex. First-order rate constants for the decomposition of the Meisenheimer complexes **14–17** as a function of hydroxide concentration at constant CDHPDAB concentration are in Table III, while those as a function of CDHPDAB concentration at constant hydroxide concentration are in Table IV. Once again significant rates are detectable down to as low as 0.2 mM CDHPDAB for complexes **16** and **17**. The observed rate increased to a maximum and then decreased as the CDHPDAB concentration was increased. It is interesting that the optimum rates of decomposition of the complexes are obtained at lower concentrations (1–4 mM) of CDHPDAB than was observed for their production. This is a result of the complexes being covalently bound to the micelles while the initial substrates were not. A proposed mechanism for the decomposition of the Meisenheimer complexes is shown in Scheme IV.

Of particular interest is the different dependence of the rate of decomposition of the complexes on the sodium hydroxide concentration. For complex **14** the rate of decomposition at 30 °C increased significantly as the sodium hydroxide concentration was increased. We thus conclude that the rate-determining step for the decomposition of this complex is step 2, the decomposition of the micellar ether, in Scheme IV; i.e., step 1, the unimolecular breakdown of the Meisenheimer complex, is fast.

For complex **15** the rate of decomposition was very slow at 30 °C, but the rate actually decreased slightly as the concentration of NaOH was increased. A similar effect of hydroxide concentration was observed for this complex at 56 °C, but a much faster reaction was observed at the

Scheme IV. Decomposition of the Meisenheimer Complex

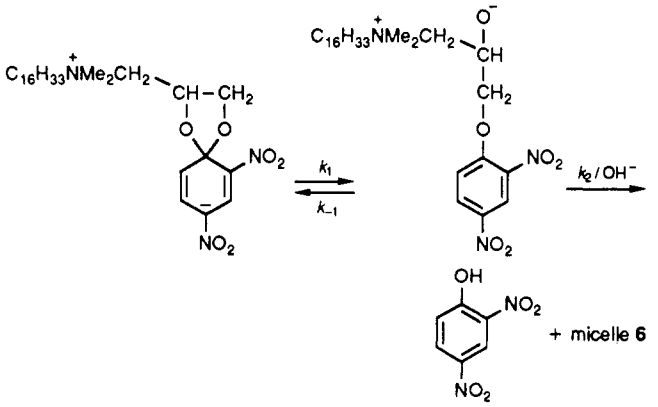

Table V. First-Order Rate Constants ($10^5 k_\psi/s^{-1}$) for the Decomposition of Meisenheimer Complexes and Model Micellar Ethers at 30 °C in the Presence of 0.1 M NaOH[a]

substrate (ArX)	Meisenheimer complex	micellar ether (ArM)[b]
8	119 (490)	424 (358)
9	0.57 (585)	87 (444)
10	0.39 (486)	32 (373)
11	1.37 (553)	132 (442)
	8 mM CDHPDAB	8 mM 3-CHPDAB

[a] Analytical wavelength (nm) in parentheses. [b] Where M = $OCH_2CH_2CH_2N^+Me_2C_{16}H_{33}$.

higher temperature. For convenience, the decompositions of complexes **16** and **17** were also studied at 56 °C. For complexes **15**, **16**, and **17** the rate of decomposition appears to be almost independent of the hydroxide concentration. We thus conclude that step 1 in Scheme IV is rate determining for the decomposition of these complexes. This change in rate-determining step could in principle be due either to a decrease in the rate of step 1 for complexes **15–17** or to an increase in the rate of step 2. Step 2 resembles the breakdown of the micellar ether formed in monohydroxy micelles. As a guide to the rate of the second step of the breakdown of the Meisenheimer complex, we have measured the rate of decomposition of some model micellar ethers produced during the reaction of substrates (**8–11**) with micelles of cetyl(3-hydroxypropyl)dimethylammonium bromide (3-CHPDAB). The rate constants are in Table V.

For compound **8** the overall rate of decomposition of the Meisenheimer complex **14** for which step 2 is rate determining is slower by a factor of ~3 than that for the model micellar ether presumably because the model micellar ether does not have the O^- substituent which would slow the attack of hydroxide ion on the micellar ether derived from the Meisenheimer complex for electrostatic reasons. For compounds **9–11** the rate-determining step changes from step 2 to step 1. Looking now at the model micellar ethers, the rate of decomposition, Table V, actually decreases as we pass from compound **8** to compounds **9**, **10**, and **11**. It is therefore unlikely that the change of rate-determining step for the decomposition of the Meisenheimer complexes **15**, **16**, and **17** compared to complex **14** is due to an increase in the rate of step 2. We therefore conclude that it must be due to a decrease in the rate of step 1. Consequently the rate of decomposition of the Meisenheimer complex is slower by a factor of ~100 than the rate of the decomposition of the model micellar ether for substrates **9–11**.

This decrease in the rate of step 1 for the decomposition of complexes **15–17** compared to complex **14** is possibly

due to the stabilization of the Meisenheimer complexes 15–17 by an intramolecular electrostatic interaction between the positively charged nitrogen atom of the complex and either the negatively charged carboxylate group in 16 or the dipolar nitro group of complexes 15 and 17. This interaction is analogous to Bunnett's built-in solvation observed in the reactions of piperidine with aromatic substrates having either a nitro group[20] or a carboxylate group[21] at the ortho position.

For complexes 15–17 nitro or carboxylate groups are present at both ortho positions leading to efficient stabilization of the positive charge irrespective of the conformation of the complex. For complex 14, however, a nitro group is present at only one ortho position while a proton is at the other ortho position.

In this case efficient stabilization of the positive charge by built-in solvation requires both the long alkyl chain and the nitro group to be in close proximity, and this is unlikely for steric reasons since a more favorable conformation is available with the nitro group on one side of the molecule and the alkyl chain on the other as shown in Scheme IV.

Experimental Section

Materials. Substrates 7–9 were commercially available from Aldrich (7 and 8) and Lancaster Synthesis (9). Substrates 10 and 11 were available from previous work.[19]

Surfactant 6, mp 65–66 °C. (Anal. Calcd for $C_{21}H_{46}BrNO_2$: C, 59.4; H, 10.9; Br, 18.9; N, 3.3. Found: C, 59.2; H, 10.8; Br, 19.0; N, 3.1), was prepared by the quaternization of cetyl bromide with 3-dimethylaminopropane-1,2-diol (Aldrich) in ethanol at reflux for 20 h. The critical micelle concentration (cmc) of surfactant 6, 0.9 mM, in neutral solution was determined by conductance measurements.

Surfactant 13, mp 82–4 °C (lit.[22] 85 °C), was prepared by quaternization of cetyl bromide with *N*-methyldiethanolamine (Aldrich) in ethanol at reflux for 24 h. Surfactant 12, mp 78–9 °C. (Anal. Calcd for $C_{20}H_{44}BrNO_2$: C, 58.5; H, 10.7; N, 3.4; Br, 19.5. Found: C, 58.1; H, 10.9; N, 3.3; Br, 19.3), was prepared by quaternization of 1-bromo-2-hydroxyhexadecane with dimethylaminoethanol in ethanol at reflux for 18 h. 1-Bromo-2-hydroxyhexadecane was prepared as described previously.[23] 3-CHPDAB, mp 86 °C (lit.[24] 85 °C), was prepared by quaternization of cetyl bromide with 3-dimethylamino-1-propanol (Aldrich) in ethanol at reflux for 16 h.

Stock solutions of surfactants (20 and 60 mM) and of sodium hydroxide (0.5 M) were prepared in purified water. Distilled water was further purified by using a Millipore system to achieve a resistivity of at least 10 MΩ cm. Stock solutions of substrates 7–11 (0.01 M) were prepared in HPLC grade acetonitrile (Mallinkrodt).

Kinetics. A solution of the required concentration of surfactant and sodium hydroxide was thermally equilibrated in a cuvette in the sample compartment of either a Varian 635 or DMS 70 UV–vis spectrophotometer. The reaction was initiated by the addition of the substrate solution (18 μL) and followed at the indicated wavelength (see Tables I–IV) using a National VP6511A X-T recorder. The temperature inside the cuvette was measured with a Jenco Thermistor thermometer. An inifinity 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 obtained, and good agreement was obtained between experimental and calculated rate constants and infinity values. Rate constants for fast reactions, e.g., those of compound 7, were obtained by a stopped-flow technique using equipment described by Grant[25] and the method of Scopes.[26] The rate constants reported in the tables are all the averages of duplicate runs with reproducibility within ±2%.

Table VI. Estimated Percentage Yields of Complexes from Substrates 8–11

(A) At 8 mM CDHPDAB as a Function of [NaOH]

[NaOH], M	product / substrate	14 / 8	15 / 9	16 / 10	17 / 11
0.001		4	67	67	60
0.005		9	98	89	72
0.01		12	100	92	72
0.05		17		91	72
0.10		19	100	89	70

(B) At Constant Hydroxide Concentration as a Function of CDHPDAB Concentration

[DCHPDAB], mM	product / substrate	14 / 8	15 / 9	16 / 10	17 / 11
0.2		8		53	57
1		16	99		70
4		13	100	92	71
8		12		89	70
20		10	100	90	75
30		9	99	89	72
40		8		87	71
[NaOH], M		0.01	0.10	0.10	0.10

Product Analyses. The estimated yields of Meisenheimer complexes reported in Table VI were determined from an examination of the UV–vis spectra of the product after allowing sufficient time for the yield of Meisenheimer complex to optimize, i.e., after the absorbance/time plot at the wavelength corresponding to the complex had levelled out, i.e., A_∞. For compounds 9–11 for which only one product is reported, the analysis was carried out at the wavelength of maximal absorbance using molar absorptivity (ϵ) reported in the literature for similar compounds. The percentage yield was calculated using the equation

$$\% \text{ yield} = (A_\infty/[\text{substrate}]\epsilon) \times 100 \quad (1)$$

The molar absorptivity used was 27 000 L mol^{-1} cm^{-1} for complex 15 from the 2,6-dinitro compound and for complex 17 from substrate 11. We assume that the presence of the extra carboxylate group in complex 17 would have little effect on the UV–vis spectrum. This value of ϵ is based on that obtained in methanol for the spiro complex formed from compound 9.[10] For complex 16 from compound 10 we used a value of ϵ = 21 000 L mol^{-1} cm^{-1} based on that reported for the spiro complex 4 by Crampton.[10] Once again we are assuming that the presence of the additional carboxylate group in complex 16 would have little effect on the spectrum. This assumption is based on the similarity in the molar absorptivity of Meisenheimer complexes containing either a hydrogen or a nitro group at either the 4- or 6-position.[7]

For complex 14 formed from substrate 8 we have used a similar method with ϵ = 21 000 L mol^{-1} cm^{-1} as reported by Crampton.[10]

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