apparatus to afford a yellow solid (4.1 g). GC analysis of the distilled product showed only one isomer. The crude product from the 80 °C run (5.0 g) was distilled to afford a yellow solid (2.75 g). Recrystallization of the solid from absolute alcohol afforded a white crystalline solid, mp 120–121 °C (lit.[19] mp 120 °C for 6-acetyl-2-(methylthio)naphthalene: ^{1}H NMR ($CDCl_3$) δ 8.37–7.37 (m, 6 H), 2.70 (s, 3 H) and 2.59 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.71, 140.1, 135.93, 133.61, 129.93, 129.49, 127.02, 125.93, 124.72, 121.86, 26.53 and 15.08; IR (KBR) 1668 (vs), 1612 (s), 1280 (s), 1270 (s), 865 cm^{-1}.

Phenyl Disulfide with Acetic Anhydride. The reaction of phenyl disulfide at 80 °C for 3 h and workup afforded an oil (22.9 g). CG analysis of the product indicated the presence of **5** (8%), **6** (12%), **7** (10%), and **14** (65%).

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Registry No. 2a, 1778-09-2; **2b**, 53207-58-2; **5**, 108-98-5; **6**, 934-87-2; **7**, 14859-20-2; **8**, 18889-01-5; **9**, 100-68-5; **10a**, 91-60-1; **11**, 135455-69-5; **12**, 831-23-2; **13**, 62759-49-3; **14**, 882-33-7; acetic anhydride, 108-24-7; isobutyryl chloride, 79-30-1.

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Micellar Catalysis of Organic Reactions. 32. S_NAr Reactions of 1,5-Difluoro-2,4-dinitrobenzene and Related Compounds in the Presence of Cationic Micelles

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Introduction

The effects of cationic micelles on the S_NAr reactions of hydroxide ions with DNFB, one of the classic substrates for this type of reaction, have been widely studied. For example, micelles of CTAB significantly catalyze the hydroxydefluorination of this substrate[1] and a 60-fold optimum catalysis was observed at 20 mM CTAB.

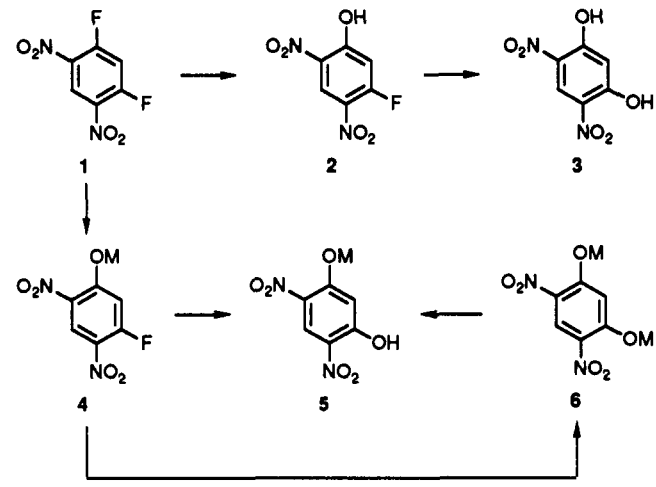
Monohydroxy-functionalized micelles, e.g., CHEDAB and 2-OH-CTAB also catalyze the reaction, in this case by a nucleophilic mechanism in which an aryl micellar ether is formed during the reaction. This aryl micellar ether is subsequently converted, by a second S_NAr reaction, into 2,4-dinitrophenol, the normal product of the hydroxydefluorination reaction.[2]

β-Cyclodextrin also catalyzes the reaction by a similar mechanism,[2] although in this case an arylcyclodextryl ether is formed and subsequently decomposed during the reaction.

Reaction in the presence of dihydroxy micelles of CDHPDAB resulted in the transient formation of a micellar-bound spiro-Meisenheimer complex from the intermediate aryl micellar ether.[3]

We now report the results of a study of the reaction of DFDNB and related compounds, with hydroxide ions, in the presence of the above micelles. This substrate is of interest because it contains two potential nucleofuges (fluoride), both of which are activated by nitro groups at ortho and para positions.

Scheme I[a]



[a] M = micelle.

Results and Discussion

(a) Reactions with Hydroxide Ions in CTAB. The reaction of DFDNB with hydroxide ions, in the presence of micelles of CTAB, occurs in two distinct phases. At 30 °C, in the presence of 0.01 M NaOH, an instantaneous reaction leads to the production of 5-fluoro-2,4-dinitrophenol (**2**), λ_{max} 345 (A = 0.8) and 395 nm (A = 0.95). The UV–vis spectrum of this product was identical with that of an authentic sample prepared in water. This product was stable at 30 °C, but on heating the reaction mixture to 66 °C a slow reaction leading to 4,6-dinitroresorcinol (**3**), λ_{max} 335 (A = 1.3) and 424 nm (A = 0.97), was observed.

4,6-Dinitroresorcinol had previously been reported[4] as the product of a slow reaction of 1,5-diiodo-2,4-dinitrobenzene with a boiling aqueous solution of dilute hydroxide ions, although there was no report of an intermediate product in that case.

The difference in the rates of these two stages of reaction can be rationalized after a consideration of the substituent effects operational on each reaction. The first stage of reaction is rapid because of the presence of a good nucleofuge (fluoride) and nitro groups at the ortho and para positions relative to the nucleofuge. The corresponding reaction of 2,4-dinitrofluorobenzene, with hydroxide ions in CTAB, is also rapid[1] for the same reasons, with a first-order rate constant, $k_1 = 7.2 \times 10^{-2}$ s^{-1}, and a half-life of 10 s. In the second stage of reaction a good nucleofuge (fluoride) is still present, but the accelerating effect of the two nitro groups is now opposed by the strong electron-releasing effect of the ionized phenolic hydroxyl group at the meta position ($\sigma_{m\text{-}O^-} = -0.71$).[5] On the other hand, the extra fluorine present in DFDNB has only a small electronic effect on the reaction center ($\sigma_{m\text{-}F} = 0.06$) during the first stage of reaction.[5]

The corresponding reaction of (BrDNFB) also occurred in two distinct phases, a very fast reaction at 30 °C in which the fluoride was displaced and a very slow reaction at 66 °C in which the bromide was displaced. The difference in rates of the slow reactions of these two substrates at 66 °C is typical of the large F/Br rate ratios

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Table I. First-Order Rate Constants ($10^5 \times k_1$, s^{-1}) for (a) the Decomposition of the Dimicellar Ether 6 to Compound 5 and for the Corresponding Reaction of DNFB at 30 °C with 0.01 M NaOH in Several Hydroxy-Functionalized Micelles and (b) for the Decomposition of Meisenheimer Complexes Obtained from Reactions of DNFB and BrDNFB

[micelle] (mM)	[OH^-] (M)	6	DNFB[a]	BrDNFB
(a) Decomposition of Dimicellar Ethers				
CHEDAB, 2	0.01	614		
CHEDAB, 5	0.01	405		
CHEDAB, 8	0.01		205	
CHPDAB, 2	0.01	33.4		
CHPDAB, 5	0.01	26.9		
CHPDAB, 8	0.01		8.7	
2-OH CTAB, 8	0.01		13	
CDHPDAB, 2	0.01	34.6		
CDHPDAB, 5	0.01	29.5		
analyte λ, nm		400	358	
(b) Decomposition of Meisenheimer Complexes				
CDHPDAB, 2	0.001		5.3	
CDHPDAB, 2	0.005		26.8	303
CDHPDAB, 2	0.01		42	361
CDHPDAB, 2	0.02			435
CDHPDAB, 2	0.04			490
CDHPDAB, 2	0.05		89	517
analyte, λ, nm			490	480

[a] Part a, ref 2; part b, ref 3.

usually observed in S_NAr reactions.[6]

(b) Reactions with Hydroxide Ions in Monohydroxy-Functionalized Micelles. The first stage of the reaction of DFDNB with hydroxide ions in the presence of monohydroxy-functionalized micelles is also rapid for the above reasons. In this stage the reactant 1 is partitioned (see Scheme I between reaction with hydroxide ion leading to 2 and reaction with the ionized hydroxyl group of the micelle leading to 4).

As for the reaction in CTAB, compound 2 is stable at 30 °C due to the ionization of the phenolic hydroxyl group of 2 in basic solution. Compound 4, however, is reactive, since it contains a good nucleofuge, fluoride, and two nitro groups at the ortho and para positions and since the alkoxy group at the meta position has only a small electronic effect on the reaction center ($\sigma_{m\text{-}OCH_3} = 0.11$).[5] Thus, the partitioning of 4 also occurs in the fast initial phase of the reaction.

The partitioning of compound 4 between reaction with hydroxide ion leading to 5 and reaction with the ionized hydroxyl group of the micelle leading to 6 is shown in Scheme I. Spectroscopically, in the presence of CHEDAB at 30 °C, this is manifested in an instantaneous reaction leading to the production of maximum absorbances at 340 and 400 nm, due to the dinitrophenol chromophores of 2 and 5, and at 275 nm, due to the dinitroaryl micellar ether chromophore of 4 and 6. The reaction of DFDNB with methoxide ions in methanol resulted in an instantaneous production of a maximum absorbance at 266 nm (A = 1.14), which we attribute to the production of 1,5-dimethoxy-2,4-dinitrobenzene, which also has a dinitroaryl ether chromophore. A second, slower reaction in CHEDAB at 30 °C, resulting in an increase of the absorbance at 340 and 400 nm, was attributed to the conversion of 6 to 5. First-order rate constants, for this stage of reaction of DFDNB, in a number of hydroxy-functionalized micelles, are in Table Ia. This reaction is slower than the partitioning of either compound 1 or 4, observed in the first phase, because an alkoxide ion nucleofuge MO^- is a poorer nucleofuge than fluoride ion. At 66 °C, a very slow reaction, leading to an increase in the absorbance at 424 nm, was attributed to a subsequent reaction of compound 2, as observed for the reaction in CTAB. The absorbance at 275 nm, due to the aryl micellar ether, did not decrease in the time allowed at 66 °C because compound 5 is relatively unreactive, presumably because of the combined effects of having a poor nucleofuge (OM^-) and the strong electron-releasing electronic effect of the ionized phenolic hydroxyl group at the meta position.

(c) Reactions with Hydroxide Ions in a Dihydroxy-Functionalized Micelle (CDHPDAB). Reaction of DNFB with hydroxide ions,[3] in the presence of micelles of CDHPDAB, led to the production of a Meisenheimer complex, as shown by the production of an absorbance in the UV–vis spectrum at 490 nm (A = 0.33). However, reaction of DFDNB under these conditions only resulted in the production of a small absorbance at this wavelength (A_{490} = 0.03). This indicates that little Meisenheimer complex is formed in the reaction of DFDNB under these conditions.

The initial spectrum of the reaction mixture had a strong absorbance at 275 and 331 nm, indicating the production of a diether such as compound 6. Little phenol was detected in this reaction mixture, since the absorbance at 400 nm was small (0.1). This indicates that the partitioning of compound 1 strongly favored the production of compound 4 (Scheme I) and that the subsequent partitioning of compound 4 strongly favored the production of compound 6 (Scheme I). Subsequently, this diether decomposed, with the production of a hydroxy ether 5, as shown by the production of a strong absorbance (A = 0.77) at 340 and 400 nm and the loss of absorbance at 275 nm.

The first-order rate constants for this process are in Table Ia. Comparison of this rate constant with those of other diethers leads us to conclude that the initial interaction of DFDNB with CDHPDAB to form a micellar ether occurs at the secondary hydroxyl group of the micelle. The rate of decomposition of this diether is very similar to that of the diether derived from CHPDAB, which also contains a secondary hydroxyl group, while it is much slower than that of the diether derived from CHEDAB, which contains a primary hydroxyl group.

The reaction of DFDNB with the secondary hydroxyl group of CDHPDAB, rather than with the usually more reactive primary hydroxyl group, is probably because the secondary hydroxyl group is closer to the cationic nitrogen than is the primary hydroxyl group and hence is more easily ionized than is the primary hydroxyl group because the inductive electron-withdrawing effect of the quaternary ammonium group decreases with distance. Furthermore, alkoxide ions are much more nucleophilic than unionized alcohols.

One possible reason for the reduction in the yield of Meisenheimer complex from DFDNB compared to that from DNFB is that both of the available fluorines of DFDNB are displaced by micellar alkoxide ions, producing a sterically crowded species 6 in which the intramolecular reaction, leading to a sterically crowded Meisenheimer complex, is less favorable than a competing reaction in which one of the bulky alkoxide ions is displaced by hydroxide ion, producing a less sterically crowded species 5 (see Scheme I).

The corresponding reaction of BrDNFB is instructive because for that compound only one fluorine is available and the bromide ion is displaced very slowly, even at 66 °C. Consequently, a monomicellar ether similar to com-

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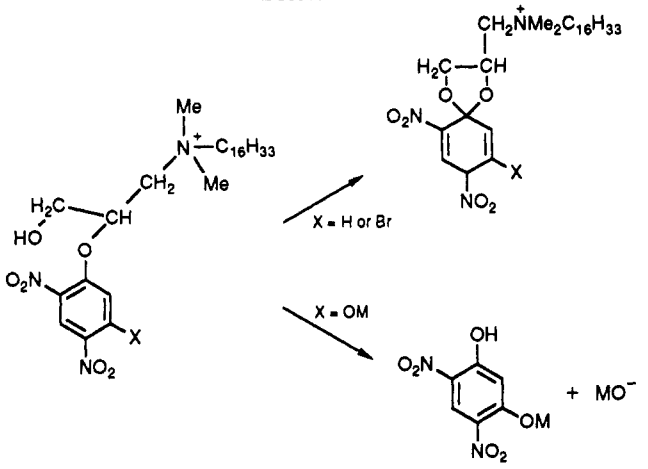
Scheme II



pound 4 with the fluoro group replaced by a bromo group is produced. This compound is less sterically crowded than the dimicellar ether 6 and the intramolecular reaction leading to the corresponding Meisenheimer complex should be favored compared to reaction with hydroxide ion. This is confirmed by the rapid production of a strong absorbance at 480 nm (A = 0.8).

The Meisenheimer complex formed from BrDNFB decomposed slowly at 30 °C in a reaction that had a slightly less than first-order dependence on the hydroxide ion concentration. This is typical of second-order reactions carried out under pseudo-first-order conditions in the presence of micelles.[7,8]

The rate constants for this reaction are in Table Ib. Since these rate constants for the decomposition of the Meisenheimer complex depend on the hydroxide concentration, we conclude that ring opening of the Meisenheimer complex to form the aryl micellar ether is fast and the decomposition of the micellar ether is the rate-determining step, as is the case for DNFB.[3]

Experimental Section

Materials. (a) Substrates. DFDNB (1, Aldrich) and BrDNFB (Alfred Bader Library of Rare Chemicals/Aldrich) were commercially available. 5-Fluoro-2,4-dinitrophenol (2), mp 78–80 °C (lit.[9] mp 80 °C) was prepared from DFDNB (1) by treatment with a solution containing 0.5 M NaOH at reflux temperature for 2 h. The reaction solution was cooled to room temperature, extracted with Et_2O (3 × 50 mL) to remove residual 1 and then acidified with dilute HCl. This solution was then extracted again with Et_2O (3 × 50 mL). The extract was dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallized (EtOH/water) to give 2, which was pure by TLC (SiO_2/2:1 petroleum ether–$CHCl_3$).

(b) Detergents. CTAB was commercially available (BDH), while CHEDAB,[10] CHPDAB,[10] 2-OHCTAB,[10] and CDHPDAB[3] were prepared as previously described.

CTAB was purified by the method of Mukerjee and Mysels.[11] Distilled water was further purified by a Millipore system to achieve a resistivity of at least 10 MΩ cm^{-1}.

Kinetics. Stock solutions (0.01 M) of the substrates were prepared in HPLC-grade acetonitrile. Stock solutions of NaOH (0.5 M) and the detergents (20 mM) were prepared in purified water. Rate measurements were carried out at the temperatures indicated in the tables in a cuvette kept at constant temperature in the cell compartment of a Varian 635 UV–vis spectrophotometer. Solutions for kinetic studies were prepared by mixing appropriate volumes of NaOH and detergent with dilution as required. The mixed solutions were placed into cuvettes and allowed 30 min in the constant temperature cell holder of a Varian 635 UV–vis spectrophotometer to reach thermal equilibrium. The temperature within the cuvette was measured with a Jenco Thermistor thermometer. Then, a sample of the stock solution of the required substrate (20 μL) was added and the contents were mixed thoroughly to initiate the reaction. The rate of change of absorbance at the desired wavelength (see tables) was followed by means of a National VP 6511 A X-T recorder. Reactions were followed to infinity (10 half-lives) where possible or, alternatively for very slow reactions or for 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 2 half-lives. Good agreement was obtained between rate constants and infinity measurements obtained by the two methods. Rate constants were all obtained in duplicate and average results (within ±2%) are presented in the tables.

All reactions were first studied using an X-Y recorder to determine the spectral changes occurring during the reaction. Substrate solution (20 μL) was added to the desired detergent/NaOH mixture in a cuvette, and the reaction mixture was scanned between 550–250 nm at appropriate time intervals.

Abbreviations. DNFB, 2,4-dinitrofluorobenzene; CTAB, cetyltrimethylammonium bromide; CHEDAB, cetyl(2-hydroxyethyl)dimethylammonium bromide; 2-OH-CTAB, (2-hydroxycetyl)trimethylammonium bromide; CDHPDAB, cetyl(2,3-dihydroxypropyl)dimethylammonium bromide; DFDNB, 1,5-difluoro-2,4-dinitrobenzene; BrDNFB, 5-bromo-2,4-dinitrofluorobenzene; CHPDAB, cetyl(2-hydroxypropyl)dimethylammonium bromide.

Registry No. DFDNB, 327-92-4.

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Phosphonium Ions Rather Than Phosphenium Ions from the Reaction of Secondary Phosphines with Trityl Cation

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Introduction

Phosphenium and nitrenium ions ($R_2P:^+$ and $R_2N:^+$) are isoelectronic with silylenes and carbenes ($R_2Si:$ and $R_2C:$) but possess the positive charge of silylenium and carbenium ions (R_3Si^+ and R_3C^+). All of these species have only a sextet of valence electrons and hence possess an empty p orbital. The two neutral species and the nitrenium ion are generally regarded as reactive intermediates, available for study only on a brief time scale. Carbenium ions have been known as stable species for decades, and silylenium ions also have been found to be long-lived under selected conditions of solvent.[1] Phosphenium ions were reported as stable species in solution during the 1970s.[2] Essentially all reported examples of phosphenium ions have at least one heteroatom, usually nitrogen, directly attached to phosphorus.

The most common method for preparation of phosphenium ions is chloride abstraction from chloro-

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