CTAB micelles. It is of course hard to estimate in how far orientation of the reactants in the micelles contributes to or hampers the overall catalytic efficiency of the micellar reaction. For instance, it is likely that the nonionic perchlorate 1 will penetrate deeper into the hydrophobic core of the micelles than the ionic reactants 2a–d. Nevertheless it is highly possible that one of the important factors responsible for the pronounced micellar effects will be concentration of the reactants into a relatively small volume element in the micellar pseudophase.[2,15] The finding that binding constants as well as k_m values are only modestly influenced by the nature of X in the series 2a–d is consistent with this rationalization but constitutes no proof for it. We emphasize—as pointed out repeatedly[2,15,16]—that it is at the moment hardly feasible to separate "concentration" and "medium" effects on k_m/k_w.

The main conclusion to be drawn from the kinetic data in Table I is that the k_m/k_w values for 2a–d are within a small range, implying that the substituent effect of X on the kinetic basicity of the sulfinate ions in the micellar-catalyzed process is small and not governed by the hydrophobicity of X.

In view of the unexpected observation[1] that the rate of the formate-catalyzed hydrolysis of 1 is also greatly accelerated by CTAB, we have also determined the effect of CTAB micelles on k_m/k_w for the more hydrophobic butyrate anions. The kinetic analysis was carried out by means of eq 1 employing butyric acid concentrations in the range 2.38×10^{-4}–11.9×10^{-4} M. The rate acceleration was linear with the butyrate anion concentration for ten kinetic runs at different butyrate concentrations. As shown in Table I, k_m/k_w amounts to 9×10^3 which is three times larger than the corresponding value for formate anions. This dependence of the catalytic factor on the chain length of the reactants has been noted before,[2,15] but in the absence of information on the binding of both carboxylate anions to CTAB micelles, a detailed explanation is premature.

Experimental Section

Materials. *p*-Tolylsulfonylmethyl perchlorate (1) was prepared as described previously.[3] Cetyltrimethylammonium bromide (CTAB; Merck, p.a. quality) was purified by the method of Duynstee and Grunwald.[17] The sodium arenesulfinates 2c and 2d were obtained via reduction of the corresponding sulfonyl chlorides with sodium sulfite. The water content of the sulfinates was determined by means of potentiometric titration with sodium nitrite (for 2a and 2b) or by oxydimetric titration[18] with potassium permanganate (for 2c and 2d). The water used in all experiments was demineralized and distilled twice in an all quartz distillation unit.

Spectroscopic Measurements. Ultraviolet (UV) spectra (25.0 °C) were measured on a Zeis PMQ II spectrophotometer using 2-cm quartz cells (10–12 mL). The sulfinate concentration was kept constant at 10^{-3} M for all series and the CTAB concentration was varied by adding up to 100 μL of a concentrated (0.1 M) solution of CTAB containing 10^{-3} M sulfinate. The NMR spectra were recorded on a Varian XL-100 spectrometer (probe temperature 34.6 °C) locked on the HOD signal. All samples were D$_2$O solutions (5 mL) containing 10 μL of H$_2$O in a 12-mm probe. The sulfinate concentration was 2×10^{-2} M in all cases and the CTAB concentration was varied between 0 and 0.1 M.

Kinetic Measurements. The rate of hydrolysis of 1 was determined by monitoring the change in the absorption at 235 nm. The initial pH of the reaction mixtures was brought to ca. 3.5 by addition of HCl. Pseudo-first-order kinetics were observed for at least 2–3 half-lives. The reactions were carried out in 2-cm quartz cells which were placed in the thermostated (±0.05 °C) cell compartment of a Zeiss PMQ II spectrophotometer.[19] Rate constants were reproducible to within 3%. In the presence of the sulfinates 2c and 2d, there was no suitable wavelength for monitoring the hydrolytic reaction. Therefore conductivity measurements were employed by means of a Philips PW 9501 conductivity meter. The accuracy of this method was, however, somewhat less satisfactory (see Table I).

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(13) The fact that during our kinetic runs constant values for k_{obsd} are obtained should be rationalized in terms of compensation effects in the second and third term in the expression for k_{obsd} (see ref 1). Moreover, k_{obsd} values were largely obtained for the second half of the reaction, so that [product] is not too different from the final product concentration.
(14) As done before, we assume that the pK_A of the rather hydrophobic sulfinic acids[4] 2a–d is decreased by 0.5 pK_A unit as a result of binding to CTAB micelles. No correction is applied to the pK_A of formic acid and butyric acid; compare ref 11.
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(19) All rate constants in this paper pertain to reactions in unstirred solutions (compare ref 1).

Mechanism of Azo Coupling in Nonpolar Media

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The coupling of aryldiazonium cations with activated aromatic compounds is one of the most widely studied reactions of organic chemistry.[1] A preponderance of literature on the subject concerns reactions conducted in aqueous or highly polar organic solvents, such as acetonitrile, nitromethane, and nitrobenzene,[2–4] in which arenediazonium salts are soluble. Reports of azo coupling in nonpolar media are rare.[5–7]

Aryldiazonium tetrafluoroborates and hexafluoro phosphates have been solublized in solvents of low polarity by: (1) attaching a lipophilic alkyl group to the aryl ring;[5,6,8] (2) metathetical gegen ion exchange with tetraalkylammonium chlorides to yield the chlorocarbon-soluble aryldiazonium chlorides;[7] and (3) complexation with crown ethers in chlorocarbon solvents.[9,10] The first two methods have been employed to solublize aryldiazonium ions for azo coupling reactions in nonpolar solvents. Thus, Bradley and Thompson[5,6] coupled *p*-decyloxybenzenediazonium tetrafluoroborate with 2-naphthol in benzene in the presence of pyridine. Very recently, Korzeniowski and Gokel[7] treated chloroform-soluble para-substituted benzenediazonium chlorides with *N,N*-dimethylaniline and produced the corresponding azo coupling products.

Mechanistic information concerning azo coupling in sol-

Table I. Observed Pseudo-First-Order Rate Constants for the Coupling of *p-tert*-Butylbenzenediazonium Tetrafluoroborate[a] (1) with *N,N*-Dimethylaniline (2) and 4-Deuterio-*N,N*-dimethylaniline (3) in 1,2-Dichloroethane at 25.0 °C

[2] × 10³, M	[3] × 10³, M	k_obsd × 10³, s⁻¹ [b]	$k_{obsd}/[2]^2 \times 10^{-2}$, s⁻¹ L² mol⁻²	$k_{obsd}/[3]^2 \times 10^{-2}$, s⁻¹ L² mol⁻²	k_H/k_D
0.594[c]		0.238 ± 0.007	6.73		
	0.594	0.120		3.40	1.98
0.762[c]		0.416 ± 0.037	7.16		
0.928		0.584	6.77		
	0.928	0.310		3.60	1.88
1.09		0.782	6.53		
1.18		1.00	7.23		
1.34		1.28	7.14		
	1.34	0.645		3.59	1.98
1.50[c]		1.69 ± 0.08	7.48		
1.67[c]		2.06 ± 0.16	7.40		
	1.67	1.02		3.66	2.02
1.18[d]		0.0938			

[a] [ArN₂⁺BF₄⁻] = 5.88–5.97 × 10⁻⁵ M. [b] Estimated uncertainty in individual run is ±5%. [c] Duplicate runs. [d] 18-Crown-6, 6.00 × 10⁻⁵ M, present.

vents of low polarity is almost entirely absent. For this reason, we have undertaken a kinetic investigation of the reaction of *p-tert*-butylbenzenediazonium ion with *N,N*-dimethylaniline in 1,2-dichloroethane.
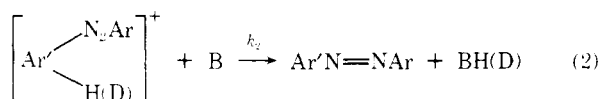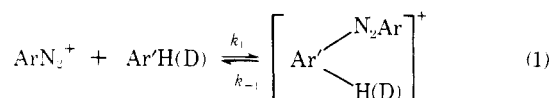
Results

Kinetics of the azo coupling reactions of *p-tert*-butylbenzenediazonium tetrafluoroborate (1) with *N,N*-dimethylaniline (2) or 4-deuterio-*N,N*-dimethylaniline (3) were followed under pseudo-first-order conditions (2 or 3 in at least a tenfold excess) by monitoring the appearance of an absorption band due to the product 4-*tert*-butyl-4'-*N,N*-dimethylaminoazobenzene (4) at 410 nm. Excellent pseudo-first-order kinetic plots covering at least 2 half-lives were obtained. Quantitative yields of the azo coupling product were determined by comparison of the absorption at 410 nm in infinity samples with that calculated using the extinction coefficient of an authentic sample of 4.

Observed pseudo-first-order rate constants are recorded in Table I. Since $k_{obsd}/[2]^2$ and $k_{obsd}/[3]^2$ are constant within experimental error, a second-order dependence in *N,N*-dimethylaniline is demonstrated. Therefore, the rate equation is: rate = $k[1][2 \text{ or } 3]^2$. Values of the primary kinetic deuterium isotope effect at four concentrations of amine are also presented in Table I. An average k_H/k_D value of 1.96 ± 0.05 is calculated.

Reaction of 1, 2, and 18-crown-6 in 1,2-dichloroethane at 25.0 °C also exhibited excellent pseudo-first-order kinetics and produced a quantitative yield of 4. The observed pseudo-first-order rate constant for this reaction appears as the last entry in Table I.

Discussion

Coupling reactions of aryldiazonium ions with activated aromatic compounds in polar media proceed by formation of a σ complex followed by proton transfer from the σ complex to a base[1,11] (eq 1 and 2). Whether the first or second step of this SE2 mechanism is rate limiting depends upon the relative

$$\text{ArN}_2^+ + \text{Ar'H(D)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\text{Ar}' \diagup \overset{\text{N}_2\text{Ar}}{\underset{\text{H(D)}}{\diagdown}} \right]^+ \quad (1)$$

$$\left[\text{Ar}' \diagup \overset{\text{N}_2\text{Ar}}{\underset{\text{H(D)}}{\diagdown}} \right]^+ + \text{B} \overset{k_2}{\longrightarrow} \text{Ar'N}{=}\text{NAr} + \text{BH(D)} \quad (2)$$

magnitudes of k_{-1} and $k_2[\text{B}]$. In aqueous buffers, the rate-determining step for azo coupling of aryldiazonium ions with naphthols depends upon the structure of the naphthol.[11] A dependence of rate-limiting step upon the nature of the coupling component has also been reported in reactions of *p*-methoxybenzenediazonium tetrafluoroborate with anilines and naphthylamines in nitrobenzene.[4] For coupling of 4-toluenediazonium salt with *N,N*-dimentylaniline, the rate-limiting step changes in going from water to acetonitrile or nitromethane.[3]

In order to probe the mechanism of azo coupling in nonpolar media, *p-tert*-butylbenzenediazonium tetrafluoroborate (1) was employed. Swain[8] has reported the solubility of this diazonium salt in chlorocarbon solvents.

Kinetic studies of the coupling reaction between 1 and excess *N,N*-dimethylaniline (2) in 1,2-dichloroethane at 25.0 °C reveal that the reaction is first order in diazonium salt and second order in 2. These results are consistent with the two-step mechanism presented in eq 1 and 2 if the rate-limiting step is proton transfer from the σ complex to a second molecule 2. In agreement, when 4-deuterio-*N,N*-dimethylaniline is used as the coupling component, a k_H/k_D value of 1.96 ± 0.05 is observed. Apparently, the two methyl groups of 2 provide sufficient steric hindrance so that proton abstraction from the σ complex by 2 is rate limiting. The rather low magnitude of the primary deuterium isotope effect indicates either an asymmetrical transition state for the proton transfer or a close balance between $k_2[\text{B}]$ and k_{-1}.[12] The present experimental data do not allow for differentiation between these two possibilities.

Our results are similar to those which have been reported for the coupling of *p*-methoxybenzenediazonium tetrafluoroborate with *N,N*-dimethylaniline in a considerably more polar solvent, nitrobenzene.[4] Overall third-order kinetics and a k_H/k_D value of 1.5 at 50 °C were found. Therefore, the azo coupling of aryldiazonium tetrafluoroborates with *N,N*-dimethylaniline occurs via the same mechanism in nitrobenzene and in 1,2-dichloroethane. Furthermore, the similarity of deuterium isotope effect values indicates transition states with approximately the same structure in the two aprotic solvents of differing polarity.

It is conceivable that crown ethers could be used to effect solubilization of aryldiazonium tetrafluoroborates and hexafluorophosphates in chlorocarbon solvents for azo coupling reactions. In order to assess the effects of crown ether upon the azo coupling rate of 1 and 2, the reaction of 1 and an equivalent amount of 18-crown-6 with an excess of 2 in 1,2-

dichloroethane was conducted. As may be seen in Table I (compare the penultimate and last entries), the presence of 1 equiv of crown ether reduces the coupling reaction rate to approximately 10% of its value under comparable conditions in the absence of crown ether. Therefore, azo coupling reactions are subject to the same aryldiazonium ion deactivation recently reported for thermolysis,[13] photolysis,[14] and nucleophilic replacement of para substituents[15] in crown ether complexed arenediazonium ions. Despite the rate retardation, reaction of 1 with excess 2 in the presence of 1 equiv of 18-crown-6 produced a quantitative yield of azo coupling product 4.

An attempt to study the azo coupling of *p-tert*-butylbenzenediazonium chloride (produced from the corresponding diazonium tetrafluoroborate and tetraethylammonium chloride) with excess 2 in 1,2-dichloroethane at 25.0 °C was unsuccessful. Curved kinetic plots and lower (60%) yields of azo coupling product 4 were observed.

Experimental Section

Materials. *p-tert*-Butylbenzenediazonium tetrafluoroborate was prepared according to Swain.[8] *N,N*-Dimethylaniline was Mallinckrodt reagent grade and was used directly. Gold label 1,2-dichloroethane from Aldrich was used directly. 4-Deuterio-*N,N*-dimethylaniline (98% D) was obtained from Merck.

An authentic sample of 4-*tert*-butyl-4'-*N,N*-dimethylaminoazobenzene (4) was prepared by dropwise addition of a solution of 1 (1 equiv) in 1,2-dichloroethane to a solution of 2 (1 equiv) and pyridine (10 equiv) in the same solvent. The reaction mixture was stirred at room temperature for 45 min. The solvent was removed in vacuo and diethyl ether was added to the residue. Filtration afforded a yellow ether layer which was reduced in volume and absorbed onto a small amount of basic alumina which was then placed on top of a basic alumina column (Fisher-Brockman activity I). The column was eluted with diethyl ether and the product was isolated by removal of diethyl ether in vacuo from the eluent. A yellow-orange solid was obtained: mp 137–137.5 °C; λ_{max} (1,2-dichloroethane) 410 (log ϵ 5.44). Anal. Calcd for $C_{18}H_{23}N_3$: C, 76.87; H, 8.18; N, 14.95. Found (Chemalytics, Tempe, Arizona): C, 76.62; H, 8.18; N, 14.85.

Kinetic Measurements. The rates of reaction of 1 and 2 or 3 were determined under pseudo-first-order conditions (2 or 3 in at least a tenfold excess) by measuring the rate of appearance of absorption at 410 nm due to 4. Plots of log $(A_\infty - A_t)$ vs. time were linear over at least 2 half-lives.

Registry No.—**1**, 52436-75-6; **2**, 121-69-7; **3**, 19125-73-6; **4**, 24596-41-6.

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# Orientation in Base-Promoted Dehydrohalogenation of N-(Chlorobenzyl)-n-butylamine[1]

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Although the mechanisms of olefin formation by base-promoted dehydrohalogenation have been extensively investigated,[3,4] the removal of hydrogen halide across C-N bonds has received little attention. The only kinetic studies of imine-forming dehydrohalogenation involve the reactions of alkyldifluoroamines, RCH_2NF_2, in water–diglyme at 25–75 °C reported by Braumann and Hill.[5,6] In contrast to the strongly basic conditions required for alkene formation by dehydrofluorination of closely related 1,1-difluoro-2-arylethanes,[7] water was a sufficiently strong base to induce eliminations from the alkyldifluoroamines. These observations underscore the marked facility of carbon–heteroatom multiple bond forming eliminations when compared with analogous processes leading to alkenes or alkynes.

In order to rationalize the differences between imine- and alkene-forming dehydrohalogenations, it is important to assess the extent of double-bond formation in concerted, imine-producing eliminations. The kinetic data for alkyldifluoroamine dehydrofluorination[5,6] were interpreted by Braumann and Hill in terms of a concerted E2 elimination having extensive C_β–H bond scission, N_α–F bond rupture, and carbon–nitrogen double bond formation in the transition state. However, elimination rates of 1 and 2 were found to be
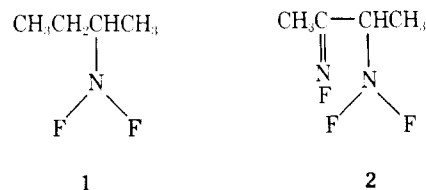
nearly the same. Significant transition state double bond character is seemingly inconsistent with the negligible conjugative effect of an unsaturated linkage attached to the β carbon.

To gain insight into the degree of double bond character in transition states for imine-forming dehydrohalogenation, we have measured positional orientation for reactions of *N*-chlorobenzyl-*n*-butylamine (3) with several base–solvent
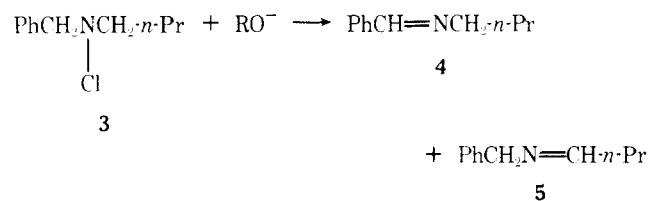
systems.[8] The *N*-chloroamine 3 was prepared by chlorination of benzyl-*n*-butylamine with *N*-chlorosuccinimide in pentane, followed by solvent exchange. Conceivable dehydrohalogenation products are *N*-benzylidene-*n*-butylamine (4) and *N*-*n*-butylidenebenzylamine (5). Results are recorded in Table I. The percentage yields are calculated based upon the starting amine.

Reactions of MeONa–MeOH, EtONa–EtOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–hexane with 3 at room temperature are regiospecific, producing 91–95% yields of the conjugated imine 4.[9] The positional isomer 5 could not be detected as a reaction product by either gas chromatography or proton magnetic resonance spectroscopy. The small deviations of measured product yields from 100% are attributed to minor losses attending the in