ization of i or ii, which employs the poor acetate leaving group. Without experimental verification, however, we cannot dismiss this possibility.

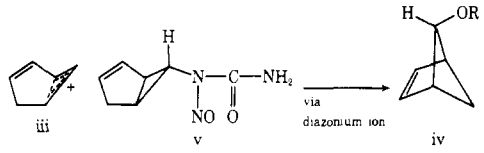
(9) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); (b) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (c) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965); (d) G. H. Whitham and M. Wright, *J. Chem. Soc. C*, 891 (1971).

(10) This is a major process in the ionization of *exo*-bicyclo[4.1.0]hept-7-yl tosylate. See ref 1a.

(11) K. Yano, *J. Org. Chem.*, **40**, 414 (1975).

(12) K. Yano, personnal communication.

(13) A referee has suggested that partially opened cation iii, which receives vertical stabilization due to the double bond, could account for the observed



rates and products. This intermediate remains a possibility in the acetolysis of **8**, in which the forcing conditions necessary for solvolysis precluded isolation of **22**. However iii alone cannot account for the formation of products with the bicyclo[2.1.1]hex-2-en-5-yl ring system (iv) in the decomposition of *N*-nitroso-*N*-*exo*-bicyclo[3.1.0]hex-2-en-6-yl urea[14] (v). Our suggestion, as a result of the solvent effect study, is that the transition state for solvolysis of cyclopropyl triflates occurs quite early along the reaction coordinate. As such, little nuclear motion will have occurred and the major stabilization of this transition state is probably vertical. However, we believe that in the first cationic intermediates, derived from the k_Δ processes for ionization of **5** and **8**, there is significant nuclear reorganization.

(14) Products of this ring structure and rearranged ring structure have been observed in the decomposition of *N*-nitroso-*N*-*exo*-bicyclo[3.1.0]hex-2-en-6-yl urea: see W. Kirmse and F. Scheidt, *Angew. Chem., Int. Ed. Engl.*, **10**, 263 (1971). Similar intermediates have been proposed, but data does not allow evaluation of the extent of neighboring-group participation.

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(16) A complete product analysis study of solvolysis products from **10** was not undertaken due to the contamination of **10** with endo isomer **11**, the inability to produce large amounts of **10**, and the expected instability of the alcohol products at the temperatures necessary for solvolysis.

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(19) U. Schöllkopf, J. Paust, and M. R. Patsch, "Organic Synthesis", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 859.

(20) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.* **29**, 2813 (1964).

(21) An *m* value of 0.45 has been reported for cyclopropyl triflate (**26**) in aqueous ethanol solvents: see P. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Am. Chem. Soc.*, **94**, 125 (1972).

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Effect of Surfactant Micelles on the Stereochemistry and Rate of "Amsylate" Solvolytic Displacement Reactions in Water[1]

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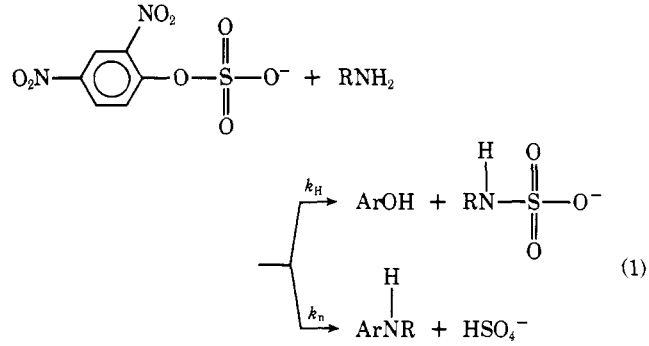
Abstract: A study of the effect of micelles on the aqueous solvolysis of alkyl *p*-trimethylammonium benzenesulfonates ("amsylates") has revealed that anionic micelles strongly inhibit the rate, and in some cases modify the stereochemistry, of the reaction. The mechanism of these solvolyses has been examined in detail. The results suggest that the rate inhibition is due to the squeezing out of water from the Stern layer of the mixed cationic-anionic micelles involved and the stereochemical changes are due to direct attack of the surfactant head group upon the reactive amsylate carbon atom, leading to a short-lived covalent dialkyl sulfate intermediate.

Though the first record of catalysis by surfactants dates back to 1906,[3a] the fact that micelles were the catalytically active species was not recognized until 1942[3b,c] and detailed investigations of micellar catalysis did not emerge until the late 1950's. Thus, the growth of micelle-related research during the past 20 years has been quite spectacular. Fortunately, the field has recently been the subject of numerous review articles[4a-d] and books.[4e,f]

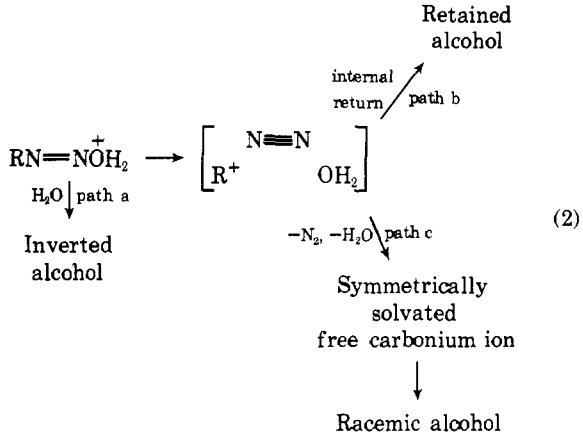
Most chemical studies have concentrated on the effect of micelles on reaction rates and very few attempts have been made to look at the effect micelles might have in altering reaction products. The synthetic chemist has shown limited interest,[5] despite the recent impressive developments in phase-transfer catalysis.[6] To date only a few systems have been examined in which a micellar medium has been shown to affect the partitioning of an organic reaction. For example, in studying the competitive hydrolysis and aminolysis of aryl sulfates, Fendler et al.[7] were able to use cationic micelles of hexadecyltrimethylammonium bromide (CETAB) to alter the balance between k_n and k_H (eq 1). Under nonmmicellar conditions C-O bond cleavage (k_n) accounts for 75-98% of the observed reactions. They found that cationic micelles can induce "complete suppression of aniline formation".[7] The authors acknowledged the micelle's ability to alter the relative extent of competing reactions, but as an explanation suggested only that "[The above effects] may be primarily due to changes in the micro-environment of both the substrates and the transition states by a contribution of electrostatic and hydrophobic interactions".[7]



(1)

A second example of the use of micelles to alter a delicate balance between reaction pathways is found in the effect of micellization on the stereochemistry of alkyl amine deamination reactions.[8] It is argued[8a] that the diazotic acid reaction

intermediate can partition itself among three stereochemically distinct pathways as shown in (eq 2). The contention is made



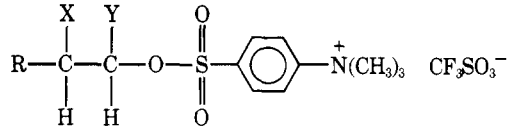
(2)

that whereas normal stereochemistry (for the conversion of 2-octylamine to 2-octanol) is 24% net *inversion*, micellization generates a water-poor environment, which enhances path b and results in 6% net *retention*. This same argument has been adapted to a study of micellar control of 1,2-hydride shifts in deaminations.[8b] These studies stand as the best examples of micelle-induced partitioning of a reactive intermediate.[9]

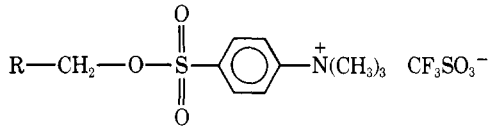
Many studies in micelle chemistry have been primarily directed towards examining events which take place in the Stern layer, the highly charged interface between the micelle's hydrophobic core and the bulk aqueous solution.[10] Much of the work that has been done to date on micellar systems can be fairly well explained in the following terms. The reaction substrate is partitioned between micellar and bulk aqueous phases by hydrophobic binding of a substrate to a micelle. Then, by simple electrostatics, this complex either attracts (rate acceleration) or repels (rate retardation) an incoming ionic reagent. We felt that a better probe of the nature of the Stern layer itself might result from generating a charged reactive species (e.g., a carbonium ion or carbanion) inside that environment and comparing its reactions (i.e., unimolecular, bimolecular with a charged reagent, or bimolecular with a neutral reagent) with the analogous processes in bulk aqueous solution.

Our interest in such systems was further stimulated by a statement made by E. H. Cordes in a discussion of carbonium ion reactions taking place in a micelle.[4e] While a variety of carbonium ion systems had been studied, in most cases the results were consistent[9] with the above simple understanding of micellar behavior. He noted, however, that a simple dissociation of R–X to R^+ and X^- in a micellar medium had never been investigated. Furthermore, he contended that it was impossible to predict the effect that micellization would have on such a process. We therefore began our research with the goal of designing a system that would (a) generate carbonium ions by a dissociative process taking place in the micellar Stern layer, (b) allow the carbonium ion to partition itself among a variety of both unimolecular and bimolecular reaction pathways, and (c) allow us to compare the reactions of this carbonium ion or carbonium ion-like transition state, in terms of kinetics, product distribution, and stereochemistry in simple aqueous solution, to those in both homogeneous and mixed micellar environments.[11]

In order to achieve as many of these goals as possible, we chose to study the solvolysis of I in aqueous solution. We chose I as the system for study because we expected that these compounds would be water soluble and thus allow us to study their behavior alone in dilute aqueous solution.[12] They are also structurally similar to the water-insoluble sulfonates more traditionally used in solvolytic studies. Since simple solvolysis reactions have been so extensively studied, their behavior would be a good probe for the specific effects of the micellar environment. Furthermore, the electron-withdrawing power of $^+N(CH_3)_3$ [$\sigma_p = 0.86$[13]] would make this system very reactive even under mild conditions (25 °C in aqueous solution) and probably impart a great deal of carbonium ion character to the solvolysis transition state. Finally, varying the R group in I



	R	X	Y
Ia	C_5H_{11}	H	H
b	C_5H_{11}	CH_3	H
c	C_5H_{11}	H	CH_3
d	C_6H_{13}	H	H
e	C_2H_5	H	H
f	CH_3	H	CH_3



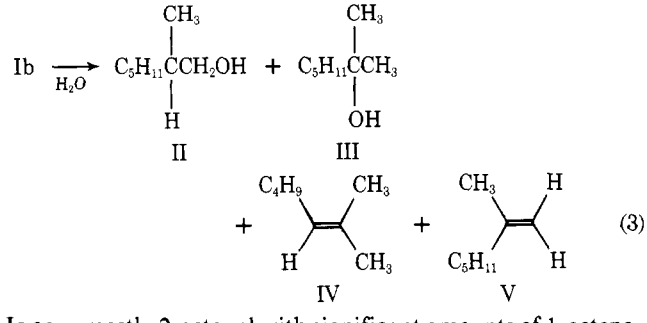
Ig, R = H
h, R = -CH=CH$_2$

allows us to control the ability of a given substrate to self-micellize or hydrophobically bind to micelles composed of other surfactants.

Results—I

We were able to readily synthesize I by the alkylation of the corresponding dimethylaminobenzenesulfonate esters with methyl trifluoromethanesulfonate (methyl triflate). These esters in turn were prepared from the appropriate alcohols and *p*-dimethylaminobenzenesulfonyl chloride. The use of the triflate alkylating agent is notable for two reasons. We found that less-reactive reagents [i.e., CH_3I, $(CH_3)_3SO^+I^-$, $Et_3O^+BF_4^-$] did not work as well, presumably due to deactivation by the SO_3R unit. Furthermore, the triflate anion is extremely nonnucleophilic, preventing its direct interference in our solvolysis reactions. The resulting alkylated sulfonates were all readily purified white powders. They were easily handled and could be stored indefinitely in a desiccator at room temperature or below.

The simple nonmmicellar behavior of I is consistent with the properties suggested above. They are water soluble and hydrolyze in aqueous solution at room temperature to give the kinds of mixtures of alcohols and olefins that one might expect from the solvolysis of a sulfonate in water. Ia, d, e, f, g, and h gave good yields (≥70%) of their unrearranged precursor alcohols; traces of the 1-olefin were detected for Ia and d. No effort was made to find the volatile butenes expected from Ie and f. Ib gave a mixture of the products indicated in eq 3 and



(3)

Ic gave mostly 2-octanol with significant amounts of 1-octene, *cis*-2-octene, *trans*-2-octene, and 3-octanol.

Table I. Effect of Cationic Micelles on Solvolysis Product Distribution of I in Water at 25 °C

Substrate	Concentration relative to its own cmc[c]	[Alcohol][b] / [Olefin]	Rearranged[b] alcohol / Unrearranged alcohol
Id	Below	92/1	≪0.01
	Above	92/1	≪0.01
Ic	Below	5/1	0.04
	Above	2/1	0.04
	Below[a]	2/1	
Ib	Below	14/1	2.5
	Above	8/1	2.5

[a] 2 × cmc CETAB added. [b] Product ratios determined VPC integration. [c] Critical micelle concentration (cmc).

A summary of the effects of cationic micelles, the compounds themselves,[14] or added CETAB on the distribution of solvolysis products of Id, b, and c (i.e., alcohol vs. olefin and rearranged vs. unrearranged alcohol) is given in Table I. These effects, although apparently real, were not very large and were very difficult to reproduce with good accuracy.

A better characterization of system I, as well as a better probe of the effects of micelles on the hydrolysis of I, resulted from a study of reaction kinetics. The results of this study are summarized in Table II. First, these results confirm that trimethylammonium benzenesulfonate ("amsylate") is a very reactive leaving group.[15] The relative order of reactivity of alkyl amsylates is allyl ≥ secondary ≫ primary and the observed secondary/primary rate ratio of $>3.5 \times 10^2$ is among the largest known.[16] These results suggest a substantial degree of carbonium ion character in the transition state of the solvolysis reaction. The most significant effect of micelles on the rate of solvolysis of I is that cationic micelles (either of the reactant itself[14a] or CETAB) do not significantly change the rate of reaction, while *anionic micelles (sodium lauryl sulfate (SLS) or sodium dodecanoate (NaDd)) strongly inhibit the solvolysis reaction.*[14b]

A further probe of the behavior of our system in a micellar medium is the study of the stereochemistry of the solvolysis of these sulfonates. We therefore synthesized optically active Ic using optically active 2-octanol. As might have been expected,[17] the production of 2-octanol from this solvolysis proceeded with complete inversion of configuration at the secondary carbon. The observed 100% inversion persisted regardless of the starting concentration of Ic and in spite of the presence of an added cationic surfactant (micellar CETAB) or an added anionic carboxylate surfactant (micellar NaDd). However, *in the presence of micellar SLS, the observed stereochemistry could be modified to a value as low as 54% net inversion.* The effect of SLS on the reaction stereochemistry was investigated as a function of the concentration of SLS and the concentration of Ic. These results, as well as the results of other stereochemical experiments, are summarized in Table III.

Discussion—I

The most clear-cut result arising from the above data is that amsylate solvolysis is strongly inhibited by anionic micelles. This requires a very strong binding of I to the anionic micelle, presumably by both hydrophobic and electrostatic forces. Thus, while homogeneously charged cationic micelles, with our cationic substrates, undoubtedly have several molecules of water incorporated between surfactant head groups that would otherwise repel each other, the anionic micelles use the tightly bound cationic substrate to help neutralize their effective charge and squeeze out water from the microscopic environment. This effect is quite comparable to the effect postulated by Moss et al.[8a] in micelle-mediated deamination systems; they surmised that tightly bound anions were squeezing out water from the surface of a cationic micelle. Our system thus presents some insight into the behavior of a mixed cationic–anionic micellar catalyst and strongly suggests that the micellar Stern layer in these systems is not as "wet" as the Stern layer of a homogeneous-charge micelle.[18] This is particularly important, since in nearly all cases of catalysis by mixed micelles investigated to date, the components have been either similarly charged or charged and uncharged surfactants.[19]

The above picture of the nature of the interaction of I with anionic micelles is consistent with the observed effect of SLS on the reaction stereochemistry. As can be seen from Table III, the results with added SLS are surprisingly regular. These results allow us to contend that the actual solvolysis in the micellar SLS–Ic system is taking place on the micelle, rather than by combination of a highly inverting, fast solvolysis of a small instantaneous concentration of unbound monomeric Ic along with a highly retaining, but slower, micellar reaction. If this latter combination were in effect, the total observed stereochemistry would depend directly on the total concentration of SLS above some critical level for this system (an operational cmc). The results show it does not; a plateau at 55% inversion is observed.

Table II. Rates of Solvolysis of I in Water with and without Added Surfactant

Substrate	Initial concn, M	Additive (molar concn)	Temp, °C	$k \times 10^5$, s^{-1}	$T_{1/2}$, min
Ib	2.7×10^{-3}		22	3.8[b]	300
Ib	8.3×10^{-3}		22	4.0[b]	290
Ib	1.3×10^{-3}	CETAB (1.4×10^{-3})	22	4.4[b]	270
Ib	3.8×10^{-3}	SLS (1.97×10^{-2})	22	*a*	*a*
Ic	0.2×10^{-3}		25	1600[c]	0.7
Ic	4.3×10^{-3}	SLS (1.97×10^{-2})	22	22.4[b]	52
Ic	2.5×10^{-3}	SLS (2.1×10^{-2})	22	16.8[b]	69
Ic	5.45×10^{-3}	NaDd (5.2×10^{-2})	22	28.5[b]	41
Ia	1.0×10^{-3}		40	29.0[c]	40
Ie			25	7.7[b]	150
Ie	1.7×10^{-2}		40	19.3[b]	60
If	3.4×10^{-2}		25	1600[b,d]	0.7
Ig			25	1900[b,d]	0.6
Ih			25	13.8[b]	84
IIh	3.8×10^{-2}		40	22.2[b]	52

[a] Less than 5% reaction in 17 h in NMR probe. [b] Rate measured by NMR. [c] Rate measured titrimetrically. [d] Values are approximate due to rapidity of reaction. Note: rate constants were measured for reactions run to ≥80% completion. Error <10%.

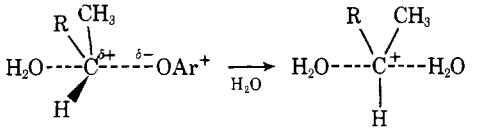
Table III. Dependence of Stereochemistry of Solvolytic Displacement of Ic on Concentration of Ic and on Concentration and Nature of Added Surfactant

Qualitative conditions	Additive × 10^2	Ic × 10^2	Stereochemistry (% net inversion)
High [SLS]; low to moderate	2.8	1.1	56
[Ic] (cmc SLS = 0.8 × 10^{-2} M)	2.8	1.5	57
	2.1	0.6	55
	1.7	1.0	54
Moderate [SLS]; moderate [Ic]	1.6	1.6	63
Moderate [SLS]; high [Ic]	1.7	2.1	81
	1.7	2.8	85
Low [SLS]; low to moderate [Ic]	0.7	1.0	88
	0.7	1.6	93
No additive; moderate [Ic]		1.7	101
		1.4	100
No additive; low [Ic]		0.6	99
		0.6	101
2.2 × cmc [NaDd]; low [Ic]	3.0	1.4	100
2 × cmc [CETAB]; low [Ic]	0.14	0.6	99
	0.14	0.6	101

The results show that with respect to the SLS–Ic interaction there is a simple relationship of catalytic significance. As long as the absolute concentration of SLS is relatively high and [SLS] ≥ [Ic], our postulated tight binding of Ib to SLS micelles by both electrostatic and hydrophobic forces persists. As the relative concentration of Ic rises, presumably the substrate molecules become surrounded by an ever increasing fraction of solvent molecules instead of anionic surfactant head groups. Thus the reaction approaches the situation found with the cationic micelles alone; i.e., a return to aqueous rate and stereochemistry.

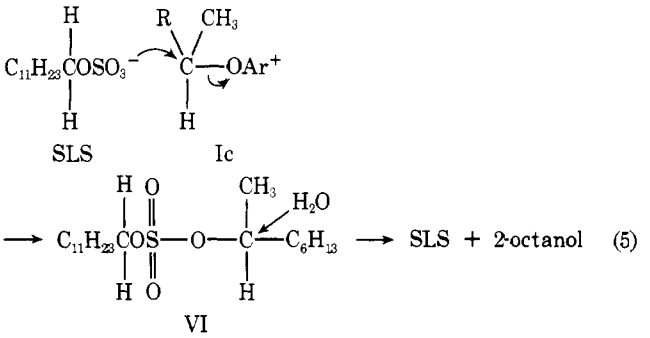
It must be pointed out, however, that while the above explanation treats the results of I with SLS rather well, it leaves two very difficult questions: (1) Why do anionic SLS micelles change both reaction rate and stereochemistry, while anionic NaDd micelles change only the rate? (2) What is the precise mechanism whereby SLS surfactant molecules induce less than complete inversion in this seemingly straightforward solvolysis reaction? Clearly these questions are related. They both require a better understanding of the microscopic details of the reaction going on in the micelle Stern layer.

It would seem that a good starting point for the analysis of these questions is the realization that there are at least three reasonable mechanistic possibilities that could explain the effect of SLS on the stereochemistry of the solvolysis of Ic. They are the following. (1) The highly charged environment at the surface of the mixed cationic–anionic micelle stabilizes the ion pair initially formed in the solvolysis of I and allows for internal return of the tight ion pair back to starting material. It has been amply demonstrated[20] that internal return in a solvolysis reaction can racemize the starting material either partially or completely. Thus our results would be consistent with a simple back-side displacement by water competing with internal return. In total this would account for a product of reduced stereochemical integrity. (2) The incipient carbonium ion or ion pair is sufficiently stabilized by the ionic medium present in the Stern layer to allow water to replace the leaving group on the front side of the reactive species, as shown in eq 4. This process would also lead to increased racemization of



(4)

the observed displacement product. (The reader is asked to note that this postulate would be a corollary to the more intuitive statement that the micelle should protect the back side of the ionizing species and thus retard back-side attack by H_2O.) (3) The alkyl sulfate anion of SLS actually attacks Ic and forms a dialkyl sulfate (VI), as shown in eq 5. This species is hydro-



SLS Ic VI

(5)

lyzed by water in what is formally a second displacement step, thus regenerating the SLS along with doubly inverted 2-octanol. Our observed reduction in net inverted product would thus be the result of a catalytic displacement by SLS competing with a direct displacement by H_2O.

In some reaction systems these possibilities are relatively easy to distinguish. For example, a simple reisolation of starting material at partial conversion would easily prove or rule out hypothesis 1. However, the extreme reactivity of Ic in the absence of SLS and the difficulty of recovering it pure (but unfractionated) from the reaction mixture made this approach unworkable here. Similarly, the common probe of measuring an in situ k_α vs. k_t was impossible due to the rather unpredictable extrinsic effects that micellar environments have on optical rotation,[21] as well as the relatively low observed rotations of our reaction solutions. We therefore devised a series of experiments that would attempt to indirectly resolve the above mechanistic question as well as explain the difference in stereochemical behavior induced by SLS and NaDd.

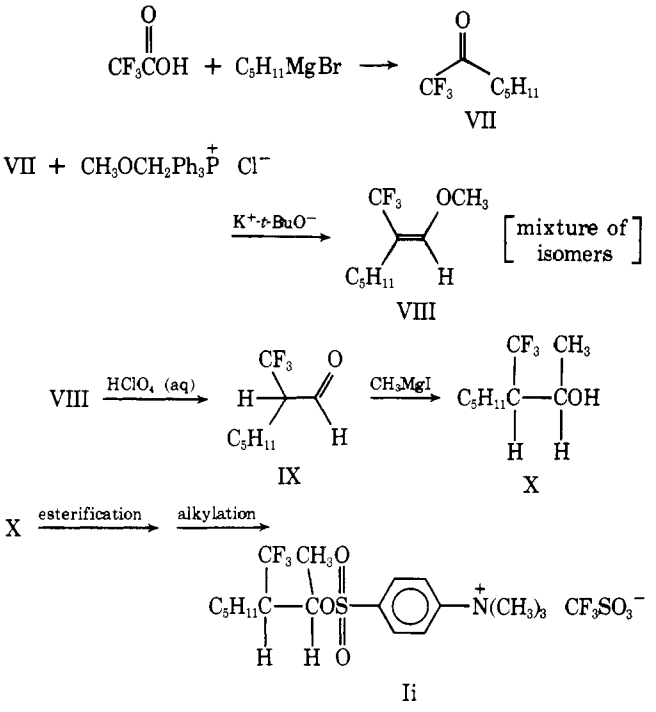
Results—II

Two lines of investigation were employed to resolve the questions discussed in the preceding section. The first involved a study of fluorinated amsylate Ii; in the second, we examined the effect of a secondary sulfate on the solvolysis of Ic.

The primary difficulty in probing the source of the stereochemical effect of SLS was the lack of a convenient way to monitor the stereochemical fate of our starting material as the reaction progressed. The ability to do this might allow us to make some decision about hypothesis 1—the partial racemization of the starting material. We therefore synthesized Ii by the route indicated in Scheme I. We were able to separate the diastereomeric alcohols X by VPC and further enhance the stereochemical purity of this system by recrystallization of the *p*-dimethylaminobenzenesulfonate esters. By identification of the elimination products of each diastereomer of Ii we were able to establish their configurations. The major diastereomer was a mixture of *R,S* and *S,R* and the minor diastereomer was *R,R* and *S,S* (see the Experimental Section for details of this correlation). The presence of the diastereomeric CF_3 groups and the fact that their ^{19}F NMR signals were easily distinguishable would allow us to observe any racemization of starting material. Racemization of diastereomerically pure starting material might manifest itself in the transient appearance of the ^{19}F signals due to the other diastereomer as one observed the progress of the solvolysis in the NMR probe.

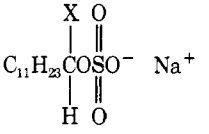
The solvolytic behavior of Ii can best be summarized as follows. In aqueous solution it reacted very slowly to give alcohol X as its primary product (along with some olefin and no rearranged alcohol). Ii was so unreactive relative to all other

Scheme I



compounds I that while their rates could be monitored conveniently near ambient temperatures, Ii required ≥70 °C.[22] As indicated in Table IV the solvolysis of Ii is still significantly inhibited by the addition of micellar SLS even at this relatively high temperature.[23] However, as is also indicated in Table IV, micellar SLS did *not* alter the stereochemistry of the solvolysis of Ii. Both in the absence and presence of SLS the observed stereochemistry of the alcohol X produced is ≥98% inversion of configuration[22b] (this was determined by VPC analysis, since the two diastereomers of X are easily separated). This maintainance of stereochemical integrity precluded any possible starting material racemization for this substrate and thus obviated the possibility of looking for diastereomer interconversion.

In the second approach, we synthesized sodium 2-tridecyl sulfate (XI) and determined its effect on the reactions of Ic. The advantages of such a system are: (a) it would allow us to better define the uniqueness of the stereochemical effect in the SLS–Ic system; and (b) if there were a nucleophilic displace-



SLS, X = H; XI, X = CH_3

ment by $ROSO_3^-$ occurring (hypothesis 3) the XI–Ic system would yield the following mechanistic probe: whereas, in the case of the primary–secondary dialkyl sulfate (VI) generated from SLS–Ic, decomposition would always occur at the more reactive site and regenerate SLS and doubly inverted 2-octanol, in the XI–Ic system, the dialkyl sulfate intermediate would be chemically symmetric (secondary–secondary) and should decompose equally well from either side.

We observed the following effects when Ic was solvolyzed in the presence of micellar XI.[24] The rate of reaction of Ic was inhibited to approximately the same extent as it was inhibited by SLS and NaDd; the observed rate constant at 22 °C was 18×10^{-5} s^{-1} (compare with Table II). The stereochemistry of the 2-octanol isolated from this reaction was only 86% inverted (as compared to 56% inversion for SLS, but 100% inversion for NaDd or no surfactant). We also noted in the VPC

Table IV. Solvolysis of Ii

Additive	Temp, °C	$k \times 10^5$, s^{-1}	Stereochemistry
None	74	79.5	≥98% inversion
SLS (2–3 × cmc)	74	5.1	≥98% inversion

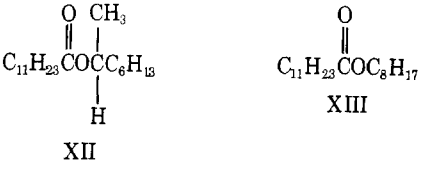
analyses of the reaction mixture of XI–Ic the presence of a variety of new products. *These were shown by comparison to the solvolysis products of Ij* ($R = C_{10}H_{21}$, $X = H$, $Y = CH_3$), *to be 1-tridecene, cis- and trans-2-tridecene, and 2-tridecanol.* These "new products" were present in sufficient quantities such that, depending on the relative concentrations of XI and Ic in the starting reaction mixture, each mole of 2-octanol could be accompanied by, for example, 0.09 mol of tridecyl olefins and 0.28 mol of 2-tridecanol.[25]

Further verification of a micelle-dependent stereochemical effect resulted from the solvolysis of optically active Ic in the presence of $NaClO_4$ and $NaEtSO_4$. In both cases the isolated 2-octanol was completely inverted.

Because of its possible implication in our mechanistic schemes, we attempted to directly probe the nucleophilic behavior of our surfactants. While this was not readily done with the alkyl sulfates due to the inherent instability of the dialkyl sulfates, we were able to directly measure the nucleophilicity of carboxylate towards I. We solvolyzed a variety of substrates I in water in the presence of known concentrations of sodium acetate and analyzed for the ratio of acetate to alcohol product. The results of this study are shown in Table V.

These data indicate that as the carbonium ion character of the reaction transition state increases, trapping of nucleophiles from solution becomes less selective. Thus, as the amsylate substrate is changed from methyl to primary to secondary, the effective enhanced nucleophilicity of acetate over water drops from a factor of 300 to 90 to 5.1.[26]

Based on the behavior of acetate we would expect that the amount of ester product resulting from trapping by carboxylate in the NaDd–I systems would be very small, since the concentration of NaDd used is only about 0.05 M. In fact, when Ic and d were each solvolyzed in the presence of NaDd and the products analyzed by VPC, we found the expected esters in both cases, XII for Ic and XIII for Id. (The stability of these



compounds to our reaction conditions was independently demonstrated.) More importantly the amount of ester found in each case correlated well with the acetate system. Ic and NaDd gave 0 < XII < 1% and Id and NaDd gave XIII = 9 ± 3%. Based on the concentration of NaDd used and the acetate model we would have predicted a 0.48% yield of XII and an 8.2% yield of XIII.

Discussion—II

A mechanism consistent with all the above data must provide answers to the following questions: (1) Why do we observe (in the reaction of XI and Ic) 2-tridecyl solvolysis products when XI itself is stable to our reaction conditions? (2) Why is XI just as effective as SLS at inhibiting the *rate* of hydrolysis of Ic, but significantly less effective at perturbing its *stereochemistry?* (3) How does SLS inhibit the rates of solvolysis of both Ic and Ii, while only changing the stereochemistry of

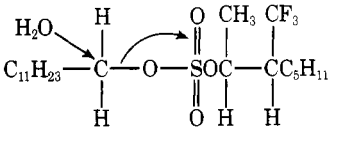
Table V. Solvolyses of I in the Presence of Added Sodium Acetate

Substrate type	Substrate	Substrate concn, M	Concn NaOAc, N	Obsd [OAc]/[OH] products[a]	Corrected[b] product ratios
Me	Ih	0.07	1.0	5.4[c]	300
Primary	Ie	0.02	1.0	1.9[c]	104
	Id	0.01	0.1	0.16[d]	90
	Id	0.01	1.0	1.33[d]	74
Secondary	If	0.03	1.0	≤0.1[c]	≤5.4
	Ic	0.01	0.1	0.01[d]	4.2
	Ic	0.01	1.0	0.11[d]	5.9

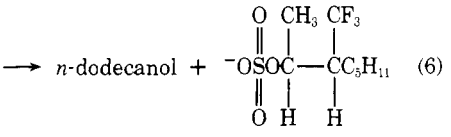
[a] Products identified by comparison with independently synthesized material. [b] Corrected for 55.4 M water vs. [OAc^-]. [c] Measured by NMR integration in D_2O. [d] Measured by integration of VPC analysis of reaction mixture.

Ic? (4) Why does NaDd effect only the rate, but not the stereochemistry, of the solvolysis of Ic?

The observation that all anionic micelles strongly inhibit amsylate solvolyses, whereas stereochemical effects seem to be both surfactant and substrate specific, seems to indicate that while our "water exclusion medium effect" may be adequate to account for the reaction kinetics, it is insufficient in accounting for the observed stereochemical effects. It is, however, reasonable to contend that the stereochemical effect of SLS on Ic and the decomposition of XI (along with its lessened stereochemical effect on Ic) are all consistent with, and even suggestive of, the intermediacy of a dialkyl sulfate. Attack at the reactive 2-octyl center by monoalkyl sulfate anion would result in a dialkyl sulfate that itself is capable of hydrolysis, either to doubly inverted 2-octanol or to surfactant decomposition products. This hypothesis nicely handles questions 1 and 2 (above) and leaves open two possible answers to question 3: either (1) the SLS–Ii dialkyl sulfate (XIV) never forms; or (2) it forms, but always cleaves on the SLS side to give dodecanol and XV, but not doubly inverted alcohol X[27] (eq 6). Since we



XIV



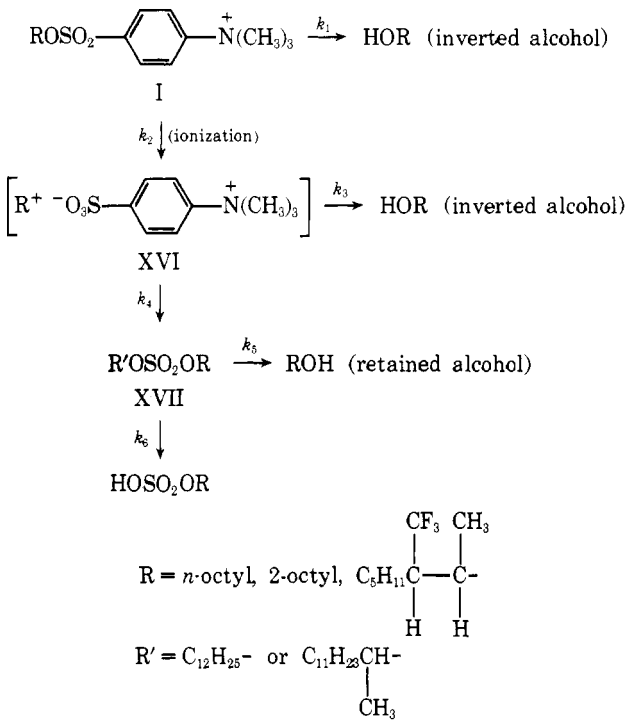
(6)

XV

could find no evidence for increased dodecanol formation in the reaction of SLS–Ii and any attempts to locate XV by ^{19}F NMR were at best ambiguous,[28] we believe that XIV is never formed. Furthermore, in a reaction of SLS–Id, where the hypothetical dialkyl sulfate would be primary-primary (and should thus cleave on both sides), we could find no evidence for increased SLS decomposition. We therefore contend that an overall mechanistic picture as depicted in Scheme II may be operative.

When R is such that R^+ would be a very unstable species (i.e., primary or CF_3-substituted), the SN2 path predominates (i.e., $k_1 \gg k_2$) and only inverted alcohol is formed regardless of the medium or the presence of surfactants. When R^+ is energetically accessible, the intimate ion pair XVI is generated. This species will be of very high energy relative to I and will thus be a much less *selective* nucleophile trap (analogous to the above reduced selectivity in trapping acetate over H_2O as R was changed from methyl to primary to secondary). Therefore, XVI will now react with any nucleophilic species that is in its immediate proximity. Since we have already

Scheme II



postulated, based on the reaction kinetics, that the anionic micellar Stern layer around our cationic species (I) is relatively water free with strongly interacting ionic species, this forced intimacy of RSO_4^- and XVI makes k_4 a reasonable process despite the relatively poor "normal" nucleophilicity of RSO_4^-. It must be noted that the intermediacy of intimate ion pairs in solvolysis reactions has firm precedent.[29] Furthermore, the distinction made here between reaction pathways based on the relative stabilities of R^+ as R loses a reactive leaving group is identical with the mechanistic distinction postulated for the deamination of primary vs. secondary alkylamines.[30]

We believe that the above scheme is consistent with all the data herein reported. There remains only one unanswered question. Since the micelle Stern layer is able to impose unusual nucleophilic properties on alkyl sulfates, why does it not do the same for alkyl carboxylates? Why was the observed amount of dodecanoate ester in the reactions of I with NaDd only that which could be explained by the normal nucleophilic behavior of carboxylates? This contrasting behavior of carboxylate and sulfate head groups in our system can best be understood by reference to a number of independent physical studies.

A wide range of properties of ions and their ability to interact with hydrophobic species in water have been correlated in what is known as a lyotropic series. The most extensive such series,

Table VI. Enthalpies and Free Energies of Hydration (kcal/mol) at 25 °C[34]

	F^-	OH^-	Cl^-	Br^-	I^-	BF_4^-	ClO_4^-	I_3^-
$-\Delta H_{298}$	121.9	110	87.6	79.8	69.7	71.2	57.1	43.8
$-\Delta G_{298}$	112.5		82.3	75.2	67.1	65.8		

for monovalent anions, based on their interaction with a variety of gels and proteins in water and their "salting out" ability, was compiled by Voet[31] and is indicated below.

$$F^- < IO_3^- < H_2PO_4^- < HCO_3^- < CH_3CO_2^- < BrO_3^- < NO_2^- < Cl^- < ClO_3^- < Br^- < NO_3^- < ClO_4^- < I^- < CNS^- \quad (7)$$

A more specific example of sequencing of anions with respect to only one property was compiled by Reiman.[32] He ordered monovalent anions in terms of their affinity for an ammonium resin.

$$OH^- < F^- < CH_3CO_2^- < H_2PO_4^- < Cl^- < NO_2^- < HSO_3^- < CN^- < Br^- < NO_3^- < HSO_4^- < I^- < ClO_4^- \quad (8)$$

Similar to this, Larsen and Magid[33] have measured, by calorimetry as well as by competition studies, the relative affinities of series of anions for the surface of CETAB micelles.

$$CH_3COO^- < F^- < OH^- < HCO_2^- < Cl^- < NO_3^- < Br^- < Tos^- \quad (9)$$

Interestingly, these sequences to a large extent seem to parallel not only each other, but also the hydration energies of the ions, a few values of which are indicated in Table VI.

An obvious corollary to the above sequences is the statement that the more interaction there is between a particular ion and water, the less interaction there will be between that ion and other ions. We would thus contend that, while carboxylate at the surface of the micelle is tightly bound to its hydration sphere as it would be in bulk solution, the sulfate head group is interacting much more strongly with the cations present in the Stern layer. In view of the observation by Larsen and Magid[33] that SLS binds NH_4^+ much more tightly than it binds Na^+, it is furthermore reasonable that both SLS and XI would be very tightly associated with the $^+N(CH_3)_3$ group of I. This situation would serve to generate an alkyl sulfate anion which is unusually well disposed to react with our incipient carbonium ion center, thus accounting for the "uncharacteristically high" observed nucleophilicity of SLS and XI.

This analysis is corroborated by an NMR study of Gustavsson and Lindman[35] which directly compares physical properties of micellar sodium octanoate and sodium octyl sulfate. By looking at changes in relaxation times for ^{23}Na counterions, they concluded that "the mode of counterion binding may be different for octanoate and octyl sulfate micelles".[35] They propose that "for carboxylate head groups, hydrogen bonding between the surfactant end group and the water of counterion hydration should be important, whereas [it] should not be significant for alkyl sulfates".[35] They further demonstrate this difference by showing that the weakly hydrated Rb^+ ion is bound more tightly to sulfate head groups than to carboxylate head groups. Thus, our ability to distinguish between the chemical behavior of carboxylate and sulfate surfactants seems to be quite consistent with the wide variety of physical studies cited above.

In conclusion, it is interesting to speculate as to the relevance of our results to related systems. In particular, it may be possible to re-evaluate the results in the deamination system[8] in light of our findings. The stereochemical perturbation of both amsylate solvolyses and aqueous deamination reactions is anion dependent. In both cases, hydrophobic, poorly hydrated anions are more effective at changing the overall reaction stereochemistry. Since in both systems the reaction centers are at secondary carbons, the possibility of trapping available nucleophiles should be comparable. Moreover, the carbonium ion generated under deamination conditions should be a very reactive and nonselective electrophile. We therefore suggest that it may be possible that the increased retention observed in the deamination systems may also be due to a double displacement process. Since the explanation proposed by Moss et al.[8a] seems to be based on a "medium effect" which promotes increased retention by increasing internal return of H_2O (see discussion in introduction above), a simple ^{18}O labeling experiment would distinguish these two mechanistic possibilities.

Experimental Section

A. General. Proton NMR spectra were obtained on Varian A-60A, T-60, XL-100-15, and HR-220 spectrometers. ^{19}F NMR were obtained at 94.7 MHz on the Varian XL-100-15. Ir spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer and are reported in centimeters^{-1}. All melting and boiling points are uncorrected. Analyses were performed either by Spang Microanalytical Laboratory, Ann Arbor, Mich. or by the Caltech Analytical Laboratory (as indicated). Preparative vapor-phase chromatography was performed on a Varian Aerograph 90-P3 gas chromatograph using ⅜ in. o.d. stainless steel columns; analytical VPC was performed on a HP-5750 Research chromatograph using ⅛ in. o.d. stainless steel columns (flame-ionization detector). Integration of analytical VPC output was accomplished by use of an Autolabs System I computing integrator. Optical rotations were recorded at five wavelengths on a Perkin-Elmer Model 141 polarimeter using a water-jacketed cell with a volume of 0.95 ml and a path length of 10.001 cm. Surface tensions of micellar solutions (for cmc determinations) were measured by use of a Fisher automatic surface tensiomat equipped with a 6-cm platinum–iridium ring and a thermostated cell. All surfactants (CETAB, SLS, NaDd, XI) were purified by recrystallization from acetone or ethanol. The H_2O used for all reactions was first distilled, then deionized, then distilled again.

B. Synthesis. Alkyl *p*-Trimethylammonium Benzenesulfonate Trifluoromethanesulfonates ("Amsylates"). Details of the synthesis of *p*-dimethylaminobenzenesulfonyl chloride have been described elsewhere, as has the conversion of this material to salts Ig and h by reaction with the appropriate alcohol followed by alkylation with methyl trifluoromethanesulfonate (triflate).[36]

The neutral dimethylaminobenzenesulfonate ester precursors of compounds Ia–f and Ii were prepared by reaction of *p*-dimethylaminobenzenesulfonyl chloride with the appropriate alcohol in pyridine, as described[36] for the synthesis of the precursors of Ie and f. These esters were converted to the corresponding trimethylammonium salts by alkylation with methyl triflate as described[36] for Ig and h. The yields in the sulfonyl chloride esterifications were all in the 70–90% range; alkylation yields were >90%. Both steps have been performed on a scale ranging from 10 mg to 10 g of material. The only useful modification to be noted is that the esterification of unreactive alcohols (i.e., X) can be aided by heating the reaction mixture to approximately 55 °C for 2 days after a day at ambient temperature. This resulted in yields >80%.

Following is a listing of characteristic data for new compounds in the series I, as well as for their dimethylamino precursors.

***n*-Heptyl *p*-dimethylaminobenzenesulfonate:** mp 42 °C (recrystallized from petroleum ether); NMR (CCl_4) δ 2.90 (ABq, 4 H), 6.15 (t, J = 6 Hz, 2 H), 6.97 (s, 6 H), 8.8 (m, 13 H).

Anal. Calcd for $C_{15}H_{25}NO_3S$: C, 60.0; H, 8.66; N, 4.66; S, 10.66. Found (Spang): C, 60.23; H, 8.61; N, 4.57; S, 10.63.

Trimethylammonium ester Ia: NMR ($CDCl_3$) δ 1.91 (s, 4 H), 5.90 (t, J = 6 Hz, 2 H), 6.27 (s, 9 H), 8.75 (m, 13 H).

2-Methylheptyl *p*-dimethylaminobenzenesulfonate: mp 54.5–56.0 °C (recrystallized from ether); NMR ($CDCl_3$) δ 2.8 (ABq, 4 H), 6.19 (d, J = 5.5 Hz, 2 H), 6.94 (s, 6 H), 8.9 (m, 15 H).

Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.34; H, 8.63; N, 4.47. Found (Caltech): C, 61.35; H, 8.37; N, 4.55.

Trimethylammonium ester Ib: NMR ($CDCl_3$) δ 1.91 (s, 4 H), 6.06 (d, J = 5.5 Hz, 2 H), 6.27 (s, 9 H), 8.8 (m, 15 H).

Anal. Calcd for $C_{18}H_{30}NF_3O_6S_2$: C, 45.28; H, 6.29; N, 2.94. Found (Caltech): C, 45.13; H, 6.25; N, 2.82.

2-Octyl *p*-dimethylaminobenzenesulfonate: racemic mp 90.5–92.0 °C, optically active mp 76.0–77.5 °C; NMR ($CDCl_3$) δ 2.82 (ABq, 4 H), 5.47 (m, J = 6 Hz, 1 H), 6.95 (s, 6 H), 8.8 (m, 16 H).

Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.34; H, 8.63; N, 4.47; S, 10.2. Found (Spang): C, 61.41; H, 8.59; N, 4.56; S, 10.14.

Trimethylammonium ester Ic: NMR ($CDCl_3$) δ 1.90 (s, 4 H), 5.28 (m, J = 6.5 Hz, 1 H), 6.27 (s, 9 H), 8.8 (m, 16 H). No analysis was obtained because it is too reactive.

***n*-Octyl *p*-dimethylamino benzenesulfonate:** mp 33.0–34.5 °C (recrystallized from ether; NMR ($CDCl_3$) δ 2.81 (ABq, 4 H), 6.03 (t, J = 6 Hz, 2 H), 6.96 (s, 6 H), 8.8 (m, 15 H).

Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.34; H, 8.63; N, 4.47. Found (Caltech): C, 61.54; H, 8.49; N, 4.42.

Trimethylammonium ester Id: NMR (CD_2Cl_2) δ 1.89 (s, 4 H), 5.87 (t, J = 6.3 Hz, 2 H), 6.24 (s, 9 H), 8.78 (m, 15 H).

Anal. Calcd for $C_{18}H_{30}NF_3O_6S_2$: C, 45.28; H, 6.29; N, 2.94. Found (Caltech): C, 45.41; H, 6.22; N, 2.88.

***n*-Butyl *p*-trimethylammonium benzenesulfonate trifluoromethanesulfonate (Ie):** NMR (D_2O) δ 1.90 (s, 4 H), 5.80 (t, J = 6.0 Hz, 2 H), 6.32 (s, 9 H), 8.6 and 9.2 (m, 7 H) (Note: On standing, this NMR sample solvolyzed to butanol).

Anal. Calcd for $C_{14}H_{22}F_3NO_6S_2$: C, 39.91; H, 5.23; N, 3.33. Found (Caltech): C, 39.85; H, 5.18; N, 3.19.

2-Butyl *p*-trimethylammonium benzenesulfonate trifluoromethanesulfonate (If): NMR (CD_2Cl_2) δ 1.96 (s, 4 H), 6.36 (q, J = 6.0 Hz, 1 H), 6.27 (s, 9 H), 8.44 (q, J = 7.0 Hz, 2 H), 8.75 (d, J = 6.0 Hz, 3 H), 9.20 (t, J = 7.0 Hz, 3 H). Compound was too reactive for analysis.

3-Trifluoromethyl-2-octyl *p*-dimethylaminobenzenesulfonates: minor diastereomer, mp 54.0–55.5 °C (recrystallized from ether); major diastereomer, oil; NMR ($CDCl_3$) δ 2.84 (ABq, 4 H), 5.25 (m, 1 H), 6.97 (s, 6 H), 7.22 (m, 1 H), 8.70 (m, 14 H).

Anal. Calcd for $C_{17}H_{26}F_3NO_3S$ (minor): C, 54.54; H, 6.82; N, 3.68. Found (Caltech): C, 53.52; H, 6.77; N, 3.59.

Trimethylammonium esters Ii: NMR ($CDCl_3$) δ 1.88 (s, 4 H), 5.02 (m, 1 H), 6.23 (s, 9 H), 7.79 (m, 1 H), 8.67 (m, 14 H).

Anal. Calcd for $C_{19}H_{29}F_6NO_6S_2$: C, 41.84; H, 5.32; N, 2.57. Found (major, Caltech): C, 41.44; H, 5.13; N, 2.50. Found (minor, Caltech): C, 41.41; H, 5.15; N, 2.44.

^{19}F NMR of Ii. The dimethylamino esters in $CDCl_3$ each showed a doublet with J = 10 Hz with the major diastereomer being 30-Hz downfield of the minor.

Trimethylammonium esters in D_2O each showed a singlet for $CF_3SO_3^-$ and doublets for each diastereomer, J = 9.5 Hz. The relative positions of these signals in hertz downfield from a sample of HCF_3SO_3 in D_2O were as follows: $CF_3SO_3^-$ = 10; major diastereomer = 1087; minor diastereomer = 1209 Hz.

2-Tridecyl *p*-dimethylaminobenzenesulfonate: solid at low temperature (0 °C), melts to oil at room temperature: NMR ($CDCl_3$) δ 2.80 (ABq, 4 H), 5.5 (m, 1 H), 6.97 (s, 6 H), 8.78 (m, 26 H).

Trimethylammonium ester Ij: NMR ($CDCl_3$) δ 1.89 (s, 4 H), 5.27 (m, 1 H), 6.24 (s, 9 H), 8.75 (m, 26 H).

1,1,1-Trifluoro-2-heptanone (VII). Using the procedure of Dishart and Levine,[37a] a 1-l. three-neck flask equipped with a reflux condenser, addition funnel, N_2 inlet, and magnetic stirrer was flame dried and charged with 14.6 g of oven dried magnesium metal and 400 ml of dry ether. *n*-Pentyl bromide (75 ml, 91 g) (Aldrich) was added dropwise at a rate sufficient to maintain a gentle ether reflux. After the addition was complete the reaction was allowed to stir for 1 h at room temperature to guarantee complete reaction. Trifluoroacetic acid (14.9 ml, 22.8 g) (MCB) was mixed with 50 ml of dry ether and this solution was added dropwise to the Grignard reagent over a period of 1 h. The reaction was heated at reflux for an additional 2 h after the acid addition was complete and it was then poured onto a mixture of ice and 100 ml of concentrated HCl. This mixture was extracted exhaustively with ether and the combined ether fraction was washed with saturated aqueous $NaHCO_3$, H_2O, and saturated aqueous NaCl. The ether solution was dried over Na_2SO_4, then filtered, and the ether was removed under reduced pressure at room temperature. The remaining liquid was distilled through a 10-in. Vigreux column. The desired ketone (VII) distilled over at 100 °C at atmospheric pressure [lit.[37b] bp 112 °C] and continued distillation at reduced pressure gave significant amounts of the alcohol corresponding to the reduction of VII. Yield of VII = 17 g (51% yield). Yield of alcohol was between 20 and 25%: NMR ($CDCl_3$) δ 7.28 (t, J = 6.5 Hz, 2 H), 8.65 (m, 9 H); ir (neat) 1770 (>C=O), 1150, 1250 (CF_3) cm^{-1}.

Methoxymethylenetriphenylphosphonium Chloride.[38] *Caution:* the chloromethyl methyl ether used in this preparation is a very volatile, very potent carcinogen. It should therefore be used with extreme care in a well ventilated hood and all glassware should be thoroughly base washed after use.

A one-neck 500-ml 24/40 round-bottom flask equipped with a magnetic stirrer and an N_2 inlet was charged with 100 g of Ph_3P and 225 ml of CH_2Cl_2 (distilled from $CaCl_2$ and stored over molecular sieves). Chloromethyl methyl ether (30.5 ml, 32.4 g) (Aldrich) was added in one portion and the flask was fitted with a reflux condenser, under N_2, and allowed to reflux overnight. The next day 100 ml of dry (distilled from $LiAlH_4$) benzene was added and all of the CH_2Cl_2 and unreacted chloromethyl methyl ether were distilled off at atmospheric pressure. Using a Schlenk-type apparatus consisting of a metal tube with filter paper on the end and a rubber septum, the white solid was repeatedly slurried in fresh benzene which was then filtered off. This process was repeated four times with 100-ml portions of benzene and after the last solvent removal the flask containing the white solid product (the original reaction flask) was attached to a vacuum line and dried for 10 h. The resulting white powder (122.5 g, 92.6% yield) was stored in a desiccator: NMR ($CDCl_3$) δ 2.2 (m, 15 H), 4.16 (d, J = 4 Hz, 2 H), 6.29 (s, 3 H).

***(E)*- and *(Z)*-1-Methoxy-2-trifluoromethyl-1-heptene (VIII).** A three-neck 2-l. flask, equipped with an N_2 inlet, magnetic stirrer, and an addition funnel was flame dried and charged with 47.2 g of methoxymethylenetriphenylphosphonium chloride and 750 ml of dry ether. While this slurry was being vigorously stirred, 15.5 g of K^+t-BuO^- (Ventron) was added in three or four portions. Within 15 min a red solution resulted and it was allowed to stir for another 1.5 h. Trifluoromethyl ketone VII (11 g, 92% pure by VPC) was diluted to 450 ml with dry ether and this solution was added over 2.5 h to the reaction mixture. The reaction was then allowed to stir at room temperature for 26 h, at which time 200 ml of H_2O, followed by 100 ml of pentane, was added. The aqueous layer was separated and the organic layer was washed three times with 200 ml of H_2O. The combined aqueous layers were back washed once with 100 ml of pentane, which was added to the organic solution (volume = 1400 ml). Most of the ether and pentane solvents were removed under reduced pressure. This solution (300 ml) was filtered to remove Ph_3PO and then dried over Na_2SO_4. After drying, removal of the rest of the solvent yielded 20 ml (18 g) of black-red oil. This was distilled through a 6-in. Vigreux at 20-mm pressure to yield a main fraction (~10 ml) at 92–94 °C and approximately 1 ml of a higher boiling afterrun. By VPC analysis (⅛ in. × 12 ft, 15% Carbowax 20 M on Chromosorb W) the first fraction (9.42 g) was shown to be a 2.6:1 ratio of isomer 1/isomer 2. Fraction 2 was 0.43 g of pure isomer 2. Total yields of distilled material was therefore 9.85 g (83% yield). This mixture of isomers was used as is for the next step in the reaction sequence: ir (neat mixture of isomers) 1680, 1455, 1350, 1295, 1250, 1215, 1110, 1050 cm^{-1}.

The mixture of isomers could be separated by preparative VPC (15 ft × ⅜ in. 10% DEGS on Chromosorb P). At 140 °C isomer 1 had a retention time of 8 min and isomer 2 a retention time of 14 min. Their ^{19}F NMR (Varian XL-100-15) show each CF_3 group to be a singlet. The two signals are separated by 366 Hz (≈3.9 ppm). Their proton NMR spectra (60 MHz), with a tentative assignment of isomers, are indicated below: isomer 1 (OCH_3 and CF_3 *trans*) NMR ($CDCl_3$) δ 3.4 (m, 1 H), 6.30 (s, 3 H), 7.85 (t, J = 7 Hz, 2 H), 8.7 (m, 9 H); isomer 2 (OCH_3 and CF_3 *cis*) NMR ($CDCl_3$) δ 3.9 (br s, 1 H), 6.30 (s, 3 H), 7.96 (t, J ≈6.0 Hz, 2 H), 8.7 (m, 9 H).

2-Trifluoromethylheptanal (IX). In a 1-l. separatory funnel with a teflon stopcock were combined 550 ml of dry ether and 150 ml of 60% perchloric acid. This very exothermic process evaporated about 50 ml of ether, which was replaced. Neat enol ether VIII (9.85 g) was added and the funnel was shaken a few times to guarantee complete homogeneity. The hydrolysis proceeded slowly and it was necessary

to let this mixture stand in the stoppered separatory funnel for at least 3 days. After 3 days a saturated aqueous Na_2CO_3 solution was added, *slowly*, in 100-ml portions. After each addition of base the aqueous layer was drained off. This process was repeated until the resulting aqueous layer was of neutral pH. The ether solution was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure at room temperature. The aldehyde product was a clear liquid which could be used as is for the next step: ir (neat) 1740 (>C=O), 1255, 1175, 1145, 1100 cm^{-1}; NMR ($CDCl_3$) δ 0.34 (m, 1 H), 7.08 (m, H), 8.8 (m, 11 H).

3-Trifluoromethyl-2-octanol (X). A flame-dried three-neck 14/20 100-ml round-bottom flask was equipped with a reflux condenser, magnetic stirrer, septum, and N_2 inlet. It was charged with 1.1 g of magnesium metal and 20 ml of dry ether. CH_3I (2.8 ml, distilled) was added by syringe at a rate sufficient to maintain a gentle reflux. The reaction was allowed to stir at room temperature for 2 h after the addition of CH_3I was complete. Aldehyde IX (4 g) was added as a 50% solution in ether over a period of 10 min. The reaction was then refluxed for 2 h, after which it was quenched by pouring onto a mixture of ice and HCl. This mixture was repeatedly extracted with ether and the combined ether extracts were washed once with H_2O and once with saturated aqueous NaCl. The ether solution was dried over Na_2SO_4 and the solvent was removed under reduced pressure at room temperature. The resulting 4.2 g of light yellow liquid was about 81% product by VPC (27 ft × ⅛ in. 15% Carbowax 20 M at 141 °C), indicating a crude yield of 3.4 g (79%). This material consisted of two species in the ratio of 55:45, which could be analyzed using the above VPC conditions (retention times: major = 17; minor = 20 min). Pure samples of each diastereomer were obtained by preparative VPC (15 ft × ⅜ in., 10% DEGS on Chromosorb P, at 155 °C and flow of 100 ml/min). Each diastereomer had the following physical properties: major diastereomer, NMR ($CDCl_3$) δ 5.82 (d of q, J_{CH_3-H} = 6.5, J_{H-H} = 3.0 Hz, 1 H), 7.85 (m, 1 H), 7.93 (s, 1 H), 8.62 (m, 11 H); ir (neat) 3390, 2960, 2870, 1463, 1375, 1260, 1168, 1140 cm^{-1}.

Anal. Calcd for $C_9H_{17}F_3O$: C, 54.55; H, 8.59. Found (Caltech): C, 54.26; H, 8.39.

Minor diastereomer: NMR ($CDCl_3$) δ 5.86 (d of q, J_{CH_3-H} = 6.5, J_{H-H} = 4.5 Hz, 1 H), 7.80 (m, 1 H), 7.91 (s, 1 H), 8.63 (m, 11 H); ir (neat) 3390, 2960, 2875, 1465, 1376, 1255, 1170, 1095, 1058 cm^{-1}.

The ^{19}F NMR of each of the above showed a doublet (J = 9.75 Hz) and the signals for the minor diastereomer were 110 Hz (1.17 ppm) downfield of those for the major diastereomer.

3-Trifluoromethyl-2-octene (Mixture of *E* and *Z* Isomers). Ethyltriphenylphosphonium bromide was prepared from ethyl bromide (Aldrich) and triphenylphosphine (MCB) in dried distilled benzene and was used as is for the next step. A three-neck, 24/40 round-bottom flask equipped with a magnetic stirrer, reflux condenser, N_2 inlet, and a septum was flame dried and charged with 46.2 g of $EtPh_3P^+Br^-$ and 300 ml of dry ether. While this slurry was being rapidly stirred, 52 ml of a 2.4 M solution of *n*-BuLi in hexane (Ventron) was added by syringe over 20 min. After stirring for 1 h at room temperature the clear red solution was cooled to 0 °C and 17 ml of ketone VII was added via syringe over 10 min. The reaction mixture was stirred at room temperature for 1 h and then refluxed for 4 h, at which time it was diluted with pentane and quenched by the addition of H_2O. The organic solution was filtered and then washed with saturated aqueous sodium bisulfite, H_2O, and saturated aqueous NaCl. After drying over anhydrous Na_2SO_4 the volume of the organic solution was reduced from 600 to 100 ml, which was filtered and then distilled through a 15-in. Vigreux to give 15 ml of 80% pure product. This material was redistilled carefully to yield approximately 10 ml of 90% pure product, bp 118–119 °C. VPC analysis of this material (50 °C on a 27 ft × ⅛ in., 15% Carbowax 20M) indicated the presence of both isomers (ratio 1.5:1) with the earlier eluting olefin predominating: ir (mixture of olefins, neat) 2940, 2860, 1670, 1460, 1390, 1315, 1260, 1165, 1115 cm^{-1}; major product (early eluting), NMR ($CDCl_3$) δ 4.2 (q, J = 7.5 Hz, 1 H), 7.83 (m, 2 H), 8.19 (m, 3 H), 8.72 (m, 9 H); minor product (later eluting), NMR ($CDCl_3$) δ 3.8 (q, J = 6.5 Hz, 1 H), remainder of spectrum assumed to be the same as above, but the isomers were *not* preparatively separated.

The above compounds were assigned stereochemistry based on the chemical shift difference of the vinyl protons. By analogy to other systems[37b] it was assumed that a proton cis to the CF_3 group resonate further downfield. The major olefin product is the *Z* isomer (CF_3 and CH_3 on same side) and the minor, later eluting olefin is the *E* isomer.

^{19}F NMR showed a singlet for each compound and they were separated by 709 Hz, approximately 7.5 ppm. These peaks were not assigned.

Carboxylate Esters. Methyl acetate was obtained commercially (MCB). *n*-Butyl, 2-butyl, *n*-octyl, and 2-octyl acetates were prepared by the following procedure. A 50-ml Erlenmeyer flask was charged with 10 ml of acetic anhydride (reagent grade) and either 5 ml of butanol or 8 ml of octanol (reagent grade). After standing at room temperature for 24 h the reaction mixtures were each poured onto 50 g of ice. The organic material was extracted into ether and the ether layer was washed successively with: dilute aqueous HCl, H_2O, saturated aqueous $NaHCO_3$, H_2O, and saturated aqueous NaCl. The resulting ether solution was further dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure to yield products which were pure by NMR and ≥98% pure by VPC (12 ft × ⅛ in., 15% Carbowax 20M, Chromosorb W). Yield = 7.2 g of *n*-octyl acetate, 7.4 g of 2-octyl acetate, 4.7 g of *n*-butyl acetate, and 3.5 g of 2-butyl acetate.

n-Dodecyl esters XII and XIII were prepared by reaction of their respective alcohol precursors with *n*-dodecanoyl chloride, which was prepared from NaDd and oxalyl chloride, all by standard procedures.[40] The resulting esters were purified by chromatography on silica gel using petroleum ether and ether eluents and then distilled under reduced pressure (0.2 mm) to yield clear liquid products: *n*-dodecanoyl chloride, bp 84 °C (0.2 mm); NMR ($CDCl_3$) δ 7.12 (t, J = 7 Hz, 2 H), 8.73 (m, 21 H); *n*-octyl-*n*-dodecanoate, distilled on molecular still at 0.2 mm; NMR ($CDCl_3$) δ 5.96 (t, J = 6.5 Hz, 2 H), 7.72 (t, J = 6.5 Hz, 2 H), 8.73 (m, 36 H); 2-octyl-*n*-dodecanoate, bp 120 °C (0.18 mm); NMR ($CDCl_3$) δ 5.12 (m, 1 H), 7.72 (6, J = 7 Hz, 2 H), 8.75 (m, 37 H).

Sodium Monoalkyl Sulfates XI and XV. This procedure is based on that of Dreger et al.[41] **XI.** A 50-ml round-bottom flask cooled to 0 °C and equipped with an addition funnel topped by a drying tube was charged with 9.6 ml of glacial acetic acid and 3.3 ml of chlorosulfonic acid. While stirring this mixture with a magnetic stir bar, 12 ml of neat 2-tridecanol (K and K) was added dropwise over approximately 5 min. When the addition was complete the reaction was allowed to stir at 0 °C for 1 h and then quenched by pouring onto 30 g of ice. *n*-Butanol (30 ml) was then added, followed by sufficient saturated aqueous Na_2CO_3 to neutralize the entire solution. The mixture was saturated with solid $NaHCO_3$ and extracted five times with 50-ml portions of *n*-butanol. The combined organic extracts were washed once with saturated aqueous NaCl solution and briefly dried over solid anhydrous Na_2SO_4. The solution was filtered and all of the solvent was removed under reduced pressure to yield 13 g of white solid. This material was recrystallized twice from water and once from ethanol to yield 7.9 g of pure material (55% yield). A repeat of this procedure using 7.3 ml of alcohol yielded, after five recrystallizations, 5 g of material (81% yield); mp 158–161 °C; NMR (D_2O) δ 5.5 (m, 1 H), 8.68 (m, 26 H).

XV. A 10-ml round-bottom flask was charged with 3 ml of glacial acetic acid and 0.7 ml of chlorosulfonic acid and allowed to stir under N_2 at 0 °C. Alcohol **X** (2.47 g, 73% pure by VPC, mixture of diastereomers) was added in one portion and the reaction was allowed to stir at 0–4 °C for 45 min. The reaction was warmed to 17 °C over 30 min and then quenched with ice and worked up as above to yield 2.35 g of crude white solid (100% yield = 2.71 g), which by NMR showed a significant NaOAc impurity. Attempts to purify this material by recrystallization from H_2O failed and a partial purification was achieved by oiling the product out of ≤2 ml of H_2O, redissolving the oil in 5 ml of H_2O, and lyophilizing it to dryness. This powder shows ≤10% OAc^- impurity and was used as the "known" for purposes of characterizing XV: ^1H NMR (D_2O) δ 4.95 (m, 1 H), 7.24 (m, 1 H), 8.6 (m, 14 H). The ^{19}F NMR chemical shift values for the mixture of diastereomeric sulfates was very solvent dependent and very concentration dependent. Each diastereomer appeared as a doublet (J = 10 Hz), but the chemical shift difference between them varied between 15 and 30 Hz. Typically these peaks were approximately 1160 Hz downfield from an external standard of CF_3SO_3H in D_2O.

C. Correlation of Configurations of Ii Diastereomers. During the course of the solvolyses of Ii it was observed that each diastereomer gave only one of the two possible trisubstituted olefinic products. Since we had previously assigned structures to the *E* and *Z* isomers of 3-trifluoromethyl-2-octene based on their NMR chemical shifts (vide supra), we were able to use the identity of these olefins to correlate

the diastereomers of Ii. The major diastereomer of Ii gave only the *E* olefin, and was therefore assigned the *R,S/S,R* configuration (assuming that the elimination process prefers a trans elimination of proton and leaving group). Similarly, the minor diastereomer of Ii gave only the *Z* isomer and was assigned *R,R/S,S*.

D. Procedure for Analytical Solvolysis Reactions. The appropriate substrate (5–20 mg) was transferred into a 10-ml vial with a teflon-lined cap. (Note: Secondary and allyl substrates were handled only in an N_2 atmosphere in a glove bag.) A known amount of solvent (either water or a freshly prepared stock solution of a surfactant) was added and the vial was capped and placed on a Burrell wrist action shaker for the duration of the reaction. The organic products were then extracted two to four times with 1-ml portions of pentane. The problem of separating the organic solution from the aqueous surfactant solution was aggravated by the formation of emulsions. This was usually solved by centrifuging the vial in a desk top centrifuge and then pipetting off the organic layer. If sulfate surfactants were being used, they could be precipitated by saturating the aqueous layer with barium chloride during the first extraction (barium sulfates are insoluble in water).

The products were analyzed by injecting the combined pentane solution directly onto the analytical VPC and integrating the resulting chromatogram. The problem of simultaneously separating isomeric olefins as well as isomeric and diastereomeric alcohols was solved most efficiently by the use of temperature programming and relatively long, heavily loaded, and tightly packed columns. The following two columns gave the best results: column 1: 27 ft × ⅛ in., 15% Carbowax 20M on Chromosorb W-DMCS 100/120; column 2: 20 ft × ⅛ in., 25% STAP on Chromosorb W-DMCS 100/120. For less demanding analyses or when analyzing for alcohols with 12 or 13 carbons a 12 or 15 ft version of column 1 was used. All products (except those of Ii, which were independently synthesized) were identified by comparison with commercially available authentic samples.

E. Kinetic Measurements. (1) By NMR. These runs were generally carried out using the Varian XL-100-15 spectrometer operating in the FT mode. This was particularly crucial for those reactions where the concentration of I was 5×10^{-3} M or less. The rate of the reaction was measured by monitoring the appearance of either the $^{+}N(CH_3)_3$ peak (a very sharp singlet) or the peak attributable to the aromatic ring of the zwitterion being produced. These peaks were well resolved from those of the starting material and thus could be easily followed. Plots of ln $(P_\infty - P_t)$ vs. time were linear for over 80% reaction and the average deviation from the least squares "best line" was <6%.

(2) By Autotitration. These experiments were done using a Radiometer autoburet and titrator with a jacketed cell that was thermostated using a Precision Scientific constant temperature circulating system. The automatic buret was filled with a 0.01 N NaOH solution and was set to maintain a pH stat of 6.5. The rate of consumption of base was automatically recorded and was a direct measure of the rate of the reaction. Rate constants were obtained from plots of ln $(V_\infty - V_t)$ vs. time, where V_∞ is the infinity titer of the reaction. In these cases the plots were linear for >90% reaction.

F. Stereochemistry Determinations. Resolved (+)-2-octanol was obtained (Norse) and used as is. The optical purity of the 2-octanol used in these studies as well as the 2-octanol obtained as a reaction product was determined by two independent means. The alcohol was purified by preparative VPC (22 ft × ⅜ in., 20% Carbowax 20M on Chromosorb W). It was then weighed (5–20 mg) by pipetting directly into a 1-ml volumetric test tube. The sample was diluted to 1 ml with spectral quality chloroform and the observed rotation measured. The value used for the optical purity of a given sample is the average of its purity compared to starting alcohol at all five wavelengths (three readings at each wavelength). This same sample was then subjected to esterification with (+)-methoxyphenyltrifluoromethylacetyl chloride using the procedure of Dale, Dull, and Mosher,[42] with one simplification. The acid chloride (1 drop acid chloride per 5 mg of alcohol) and pyridine were added directly to the 1-ml $CHCl_3$ polarimeter sample and this mixture was stored at room temperature for 1 day. After workup the resulting esters were dissolved in an 80% $CDCl_3$–20% TFA solvent and were subjected to analysis by ^{19}F NMR. Broad band proton decoupling was very helpful in improving the signal resolution. The two singlets from the CF_3 groups of the diastereomeric 2-octyl esters were cleanly resolved and separated by 20–45 Hz, depending on small changes in solvent. Peak areas were determined by both machine integration and cutting and weighing three Xerox copies of the peaks.

References and Notes

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(14) (a) The critical micelle concentrations for Ia and Ib have been determined at 25 °C by a plot of surface tension vs. concentration. Ia = 1.2×10^{-2}, Ib = 9×10^{-3} M. The value for Ib is approximate because its cmc is very close to the maximum additive concentration for this surfactant. (b) We have not carried out extensive studies of the pH dependence of these rates. However, the rates seem to be identical when measured by pH stat titration (no pH change during reaction) and by NMR (1 mol of strong acid generated during reaction). In addition, we observed similar inhibitions using NaDd and SLS, which during the solvolysis reactions should generate very different pH's. These observations, combined with the large body of work which demonstrates that solvolytic displacement reactions of organic sulfonates are uncatalyzed (see ref 15a), indicates that the reactions discussed here are pH independent as well.
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(22) (a) The large substituent effect exerted by this CF_3 group in the β position is consistent with our contention that an alkyl amsylate ionizes via a transition state with significant carbonium ion character. (b) Rate and stereochemical experiments were carried out on each of the pure diastereomers of compound Ii.
(23) (a) Cmc[23b] of SLS at 25 °C = 8.3×10^{-3}, at 70 °C = 11.4×10^{-3} M; (b) P. Mukerjee and K. J. Mysels, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 38 (1971); (c) The temperature dependence of micellar catalyses has been repeatedly demonstrated (catalysis decreases with increased temperature): see ref 4.
(24) Lit.[23b] cmc of XI at 40 °C = 6.5×10^{-3} M. We measured the cmc at 25 °C = 4.5×10^{-3} M.
(25) (a) Since the simple decomposition of monoalkyl sulfates is a well precedented process,[25b] we carried out the following controls to show that we were not just observing simple surfactant decomposition. The rate of 2-tridecyl species production in our solvolysis was $\gg 10^2$ faster than that observed in water, 0.1 N HCl, and 1 N HCl. Mixing a solution of XI with a completed SLS–Ic reaction mixture resulted in no detectable decomposition of XI. Only when XI was present during an ongoing solvolysis of Ic could its decomposition be noted. Lastly, the ratio of alcohol to olefin products of XI we obtained resemble typical solvolysis products (Ij) and do not resemble the mixtures obtained from monoalkyl sulfate decomposition;[25b] (b) see: J. Kurz, *J. Phys. Chem.*, **66,** 2239 (1962); V. A. Motsavage and H. B. Kostenbauder, *J. Colloid Sci.*, **18,** 603 (1963); R. L. Burwell, *J. Am. Chem. Soc.*, **74,** 1462 (1952).
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Molecular Stereochemistry of a Nitrogen-Bridged Metalloporphyrin: μ-Nitrido-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron]

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Abstract: The molecular stereochemistry of a nitrogen-bridged iron porphyrin, μ-nitrido-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron] has been determined. The structures of two crystalline solvates have been studied, a xylene solvate and a chloroform solvate. Both crystallize in the orthorhombic system, space group *Fddd*, with the unit cell containing eight oligomeric molecules and sixteen solvent molecules. Unit cell constants for the xylene solvate are $a = 22.427$ (2), $b = 32.446$ (5), and $c = 21.942$ (3) Å; the calculated and experimental densities (20 ± 1 °C) are 1.300 and 1.27 g/cm^3, respectively. The unit cell constants for the chloroform solvate are $a = 22.150$ (6), $b = 30.976$ (14), and $c = 22.109$ (6) Å; calculated and experimental densities are 1.390 and 1.35 g/cm^3, respectively. The complex in both solvates has required D_2–222 molecular symmetry. Measurement of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex four-circle diffractometer. All independent data for $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} were measured; 3663 (xylene) and 2908 (chloroform) reflections were retained as observed. The structures were determined using the heavy-atom method and full-matrix least-squares refinement. Final discrepancy indices are 0.076 (xylene) and 0.064 (chloroform solvate). The binuclear $N_4FeNFeN_4$ coordination group approximates D_{4d}–$\bar{8}2m$ symmetry with a bridging Fe–N distance of 1.6605 (7) Å, an averaged Fe–N_p distance of 1.991 (3) Å, and a linear FeNFe bridge bond. The iron atom in the square-pyramidal coordination group is displaced 0.32 Å from the mean plane of the four porphinato nitrogen atoms towards the axial nitrido ligand. The porphine skeleton departs significantly from planarity.

The thermal decomposition of azido-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) has been investigated recently by Summerville and Cohen.[2] The product of the reaction was found to be a nitrogen-bridged species, μ-nitrido-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron], hereinafter written as $(FeTPP)_2N$. The compound is apparently the first example of a nitrogen-bridged complex with a first row transition element, although a few examples with second and third row transition metal ions are known.[3]

We report herein the molecular stereochemistry of $(FeTPP)_2N$, determined by x-ray diffraction methods from two different solvated derivatives. The structure of $(FeTPP)_2N$ might be expected to be closely similar to those of the bridged μ-oxo-bis[porphinatoiron(III)] derivatives;[4-6] however, comparison of structure reveals some substantial differences. The stereochemistry of this interesting iron porphyrin derivative is compared with other iron and manganese porphyrin derivatives as well.

Experimental Section

Attempts to obtain crystals of $(FeTPP)_2N$ from chloroform, methylene chloride, or benzene initially yielded crystals too small for