of (S)-1-phenylethyl isocyanate, and 7.80 g (77.2 mmol) of Et_3N were heated to reflux for ca. 60 h and then allowed to stir at room temperature for 24 h. Removal of the solvents under reduced pressure gave the mixed epimers of **17c** (~30 g) which were chromatographically separated on a 2 in. × 48 in. column of 58-μm silica gel (eluent CH_2Cl_2–hexane, 1:1) by using a previously described preparative chromatography system.[28] There was recovered 2.0 g of unreacted **2f**. Each of the epimeric allophanates was recrystallized from CH_2Cl_2–hexane (1:3, ~400 mL). High-R_f epimer: white needles; mp 145–146 °C; NMR ($CDCl_3$) δ 1.49 (d, CH_3), 4.92 (quintet, 1 H), 5.54 (AB d, NCH), 5.78 (AB d, OCH), 6.7–7.2 (m, 10 H), 7.34 (s, 5 H), 8.3 (br d, 1 H). Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.75; H, 5.67; N, 7.29. Low-R_f epimer: white needles; mp 151–152.5 °C; NMR ($CDCl_3$) δ 1.56 (d, CH_3), 4.98 (quintet, 1 H), 5.64 (AB d, NCH), 5.91 (AB d, OCH), 6.7–7.2 (m, 10 H), 7.32 (s, 5 H), 8.3 (br d, NH). Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.29; H, 5.76; N, 7.32.

The reaction afforded a slight excess of the low-R_f epimer (low R_f, 12.97 g; high R_f, 11.12 g).

Hydrolysis of the low-R_f epimer (12.30 g, 31.9 mmol) by using 2.0 g (36 mmol) of KOH, CH_3OH (175 mL), and H_2O (25 mL) at reflux affords in 4 h 11.0 g (96%) of the corresponding β-hydroxyurea: mp 186–187 °C (CH_3OH–H_2O, 7:1); NMR (acetone-d_6) δ 1.41 (d, CH_3), 3.1 (br s, 3 H), 5.02 (qt, 1 H), 5.22 (AB pattern, OCH and NCH), 7.2–7.6 (m, 15 H). Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.48; H, 6.75; N, 7.83.

Hydrolysis of the high-R_f epimer (9.66 g, 25.0 mmol) by using 1.50 g (28.0 mmol) of $NaOCH_3$ in anhydrous THF (ca. 300 mL) at room temperature for 3 h affords a 1:1 mixture of the parent heterocycle (5.95 g) and the methyl carbamate of 1-phenylethylamine (4.45 g) in quantitative yield. These two components could easily be separated by liquid chromatography (α = 6.0, 2% isopropyl alcohol–hexane, silica gel) or by fractional crystallization from EtOAc–EtOH–hexane (3:1:5). Chiroptic data: **2f** from high-R_f epimer (4R,5S), $[\alpha]^{23}_D$ +57.1 ± 3.0° (c 0.95, $CHCl_3$); **2f** from low-R_f epimer (4S,5R), $[\alpha]^{23}_D$ −58.1 ± 2.5° (c = 0.91, $CHCl_3$). The optical rotation of the recovered (S)-methyl (1-phenylethyl)carbamate was $[\alpha]^{23}_D$ −83.2 ± 0.5° (c = 7.25, $CHCl_3$) compared to $[\alpha]^{23}_D$ −83.7 ± 1.2° (c 4.2, $CHCl_3$) for optically pure carbamate.

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Registry No. (±)-**2a**, 60426-44-0; (±)-**2b**, 86217-38-1; (±)-**2c**, 86217-39-2; (±)-**2d**, 86217-40-5; (±)-**2e**, 86217-41-6; (±)-**2f**, 86286-49-9; (+)-**2f**, 86286-50-2; (−)-**2f**, 23204-70-8; (±)-**5b**, 71006-16-1; (±)-**5d**, 86217-42-7; (±)-**5f**, 23412-95-5; (±)-**6b**, 86217-43-8; (±)-**6d**, 86217-44-9; (±)-**6f**, 86217-45-0; **12a**, 100-52-7; **12b**, 66-77-3; (±)-**13a**, 86286-51-3; (±)-**13b**, 86217-46-1; (±)-**14a**, 86217-47-2; (±)-**14b**, 86217-48-3; **15a** (isomer 1), 86217-49-4; **15a** (isomer 2), 86238-44-0; **15b** (isomer 1), 86217-50-7; **15b** (isomer 2), 86217-51-8; **15c** (isomer 1), 86217-52-9; **15c** (isomer 2), 86217-53-0; **15d** (isomer 1), 86217-54-1; **15d** (isomer 2), 86217-55-2; **15e** (isomer 1), 86217-56-3; **15e** (isomer 2), 86286-52-4; **15f** (isomer 1), 86217-57-4; **15f** (isomer 2), 86217-58-5; **16f**, 86217-59-6; **17a** (isomer 1), 86217-60-9; **17a** (isomer 2), 86217-61-0; **17b** (isomer 1), 86238-45-1; **17b** (isomer 2), 86217-62-1; **17c** (isomer 1), 86217-63-2; **17c** (isomer 2), 86217-64-3; **17d** (isomer 1), 86217-65-4; **17d** (isomer 2), 86217-66-5; **17e** (isomer 1), 86217-67-6; **17e** (isomer 2), 86217-68-7; **17f** (isomer 1), 86217-69-8; **17f** (isomer 2), 86217-70-1; **17g** (isomer 1), 86217-71-2; **17g** (isomer 2), 86217-72-3; **17h** (isomer 1), 86217-73-4; **17h** (isomer 2), 86217-74-5; 4-acetylbiphenyl, 92-91-1; 4-(bromoacetyl)biphenyl, 135-73-9; α-bromoacetophenone, 70-11-1; α-hydroxyacetophenone, 582-24-1; α-hydroxy-4-phenylacetophenone, 37166-61-3; 2-phenyl-2-isonitrosoethanol, 25070-24-0; 2-(4-biphenylyl)-2-isonitrosoethanol, 86217-75-6; (±)-α-amino-1-naphthaleneacetonitrile, 86217-76-7; methyl (±)-1-(1-naphthyl)aminoacetate hydrochloride, 86217-77-8; benzoin oxime, 441-38-3; methyl chloroformate, 79-22-1; ethyl bromoacetate, 105-36-2; ethyl (1-hydroxyacenaphthen-2-yl)carbamate, 86217-78-9; ethyl sodiochlorocarbamate, 17510-52-0; acenaphthylene, 208-96-8; (R)-(−)-1-(1-naphthyl)ethyl isocyanate, 42340-98-7; (±)-2-butyl isocyanate, 86217-79-0; (±)-2-heptyl isocyanate, 86217-80-3; (±)-4-methyl-2-pentyl isocyanate, 86217-81-4; (±)-2-butanamine, 33966-50-6; (±)-2-octanamine, 44855-57-4; (±)-1-phenylethylamine, 618-36-0; (±)-1,2-diphenylethylamine, 35373-59-2; (±)-1-(4-biphenylyl)ethylamine, 86217-82-5; (±)-5-aminodecane, 86217-83-6; (±)-2-amino-3,3-dimethylbutane, 59367-75-8; (±)-N-methyl-1-phenylethylamine, 42882-26-8; (S)-1-phenylethyl isocyanate, 14649-03-7; methyl (S)-(1-phenylethyl)carbamate, 14185-42-3.

Methyl-Transfer Reactions. 6. Arenesulfonates as Nucleophiles and Leaving Groups. Methyl Trinitrobenzenesulfonate

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The methyl-transfer reactions from several substituted methyl arenesulfonates to potassium benzenesulfonate in sulfolane have been studied with respect to both rates and equilibria. Because the reactions were followed by proton NMR of the methoxy group, only cases of methyl arenesulfonates with quite distinct methoxy chemical shifts from the unsubstituted ester could be studied, and this, in fact, required the use of ortho substituents. Hammett plots for these data were thus impossible, but a plot of log k_+ vs. log K, although somewhat scattered, did allow an estimation of the rate of the identity reaction for the unsubstituted compound. These methyl arenesulfonates, as well as methyl iodide, were placed roughly on the scale of equilibrium methylating agents studied earlier in the same solvent. Methyl 2,4,6-trinitrobenzenesulfonate is a very reactive substance not compatible with sulfolane. It is soluble and stable only in thionyl chloride among a large number of solvents attempted and methylates a few weak nucleophiles more extensively than methyl trifluoromethanesulfonate.

Introduction

Methyl-transfer reactions have been recently of interest both experimentally, including studies of rates and equilibria,[1-4] and isotope effects,[5,6] and theoretically[7-9] as an apparently simple model for the S_N2 reaction.

The majority of the theoretical work, as well as a little

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Table I. Rate Constants for Reaction 1 in Sulfolane-2,2-5,5-d_4 Solution

Ar	T, °C	k, M^{-1} s^{-1}	E_a, kcal/mol
C_6F_5	77.2	1.7×10^{-1}	
	65.5	8.1×10^{-2}	
	55.0	3.5×10^{-2}	
	45.0	1.7×10^{-2}	
	34.5	7.4×10^{-3}	15.8
2-$O_2NC_6H_4$	77.2	5.7×10^{-2}	
	65.5	1.9×10^{-2}	
	56.0	8.4×10^{-3}	
	41.0	1.6×10^{-3}	
	34.5	9.0×10^{-4}	20.4
2,5-$Cl_2C_6H_3$	100.0	1.3×10^{-1}	
	77.2	4.0×10^{-2}	
	65.5	2.4×10^{-2}	
	55.0	6.1×10^{-3}	
	45.0	1.7×10^{-3}	
	34.5	6.3×10^{-4}	22.0

experimental work,[3,4] have been devoted to the gas phase, whereas most of the experimental work has been limited to work in solution. Unlike the proton transfer there appears to be a real barrier to the S_N2 reaction even in the gas phase, although electrostatic effects conceal this barrier beneath the stabilization of ion–molecule complexes. In solution there are remarkable solvent effects on rates (and presumably equilibria) that give rise to the great differences between protic and aprotic solvents, first explored by Parker.[10] In our work we have believed that special solvent effects due to hydrogen bonding may be irrelevant to the more fundamental problems of the nature of the barrier and its variation with structure of the nucleophile and the leaving group. Thus, by using dipolar aprotic solvents we hope to simulate the nonexistent high dielectric constant gas phase.

Results

We have measured reaction 1 with various Ar groups,

$$ArSO_3Me + {}^-O_3SPh \rightarrow ArSO_3^- + MeO_3SPh \quad (1)$$

with respect to both rates and equilibrium in solution in sulfolane. The extent of reaction was measured by proton NMR of the reaction solutions, using a Varian EM390 spectrometer. Sulfolane has peaks that often have not reached the baseline at the chemical shift of the methoxy group, so much of the work was done in sulfolane deuterated in the positions α to the sulfone grouping (by base-catalyzed exchange with D_2O). Sulfolane is also a poor solvent for tetramethylsilane, especially when nearly saturated with electrolytes, thus we could not get a reliable lock on the Me_4Si signal, which is not far from the major solvent peaks. For this reason, the spectra were run unlocked, and thus the chemical shifts of the methoxy signals are not as precise as with the instrument locked.

Because of the interest rates of identity reactions, we had hoped to apply the Hammett equation to different substituents in the Ar group of reaction 1, but our analytical method did not allow this approach, for in these unlocked NMR spectra, most methyl groups of $ArSO_3Me$ had sufficiently similar chemical shifts that the analysis of a mixture was impractical. Enough difference in chemical shift between substituted and unsubstituted cases for a satisfactory analysis was found only with ortho substituents, thus preventing the Hammett treatment. The results are presented in Table I, which shows rate constants for reaction 1.

Equilibrium constants for some of these processes are given in Table II. It can be seen that (at 35 °C) the range of equilibrium constants is quite large, even though extreme electron-withdrawing substituents are absent. In this connection the reported stability of trimethyloxonium 2,4,6-trinitrobenzenesulfonate[11] was of interest, since the stability implies that methyl 2,4,6-trinitrobenzenesulfonate is a more powerful methylating agent than the trimethyloxonium ion, otherwise the oxonium ion would methylate the sulfonate anion extensively. We have therefore prepared this ester (by the vacuum sublimation of the trimethyloxonium salts. This demonstrates that the equilibrium methyl transfer is not so one-sided that it cannot be shifted by heat and removal of dimethyl ether), in order to place it on our equilibrium scale of methylating agents.[1] Sulfolane solutions of methyl trinitrobenzenesulfonate, prepared in this way, gave a complex NMR spectrum, and it became obvious that there was a rapid reaction with sulfolane, and that the first products are not stable. A search for a solvent to study the NMR spectrum eventually led to thionyl chloride as the only practical solvent. Others were either too reactive or did not give a solution concentrated enough for the proton NMR spectrum. In thionyl chloride, methyl 2,4,6-trinitrobenzenesulfonate gave only two singlets in the ratio 3:2 for the methyl group and the two aromatic protons in the 3- and 5-positions. This ester is a powerful methylating agent but also shows irreversible reactions leading to products we have not characterized. In addition to the sulfonate anion, there seem to be products with nonequivalent aromatic hydrogens, leading to two peaks of equal intensity with about the same chemical shift as that of the ester, suggesting an attack that destroys the symmetry of the aromatic system. We have not succeeded in a quantitative measurement of the ester as a methylating agent, but Table III shows a comparison of methyl trifluoromethanesulfonate (methyl triflate) with methyl 2,4,6-trinitrobenzenesulfonate. In this table all reactions were detected by proton NMR. It is clear that this ester reacts more rapidly than methyl triflate and is a more powerful methylating agent in an equilibrium sense, confirming the initial conclusion based on the stability of trimethyloxonium 2,4,6-trinitrobenzenesulfonate.

Discussion

The rates in Table I are some of the first of this nature available and are of interest in this connection. Kevill[12] has observed rather faster rates for reaction of some very powerful methylating agents [$CH_3O_3SCF_3$, CH_3O_3SF, CH_3OClO_3, $(CH_3)_3O^+$] with tetramethylammonium benzenesulfonate in acetonitrile and also has studied the reactions of various substituted benzenesulfonates with methyl triflate in acetonitrile, showing a value of the Hammett ρ of about −1.1. The substituent effects in Table I are more difficult to interpret because σ constants cannot be applied, but a substantial positive ρ, compatible with Kevill's, since the substituent is on the other reagent, is suggested by the results.

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Table II. Equilibrium Constants for $Nu_j^- + MeNu_i \rightleftarrows Nu_i + MeVu_j$ of Various Charge Types in Sulfolane-2,2,5,5-d_4

Nu_j^-	$MeNu_i$	T, °C	K_{ij}	ΔH, kcal/mol
$C_6H_5SO_3^-$	$2,5\text{-}Cl_2C_6H_3SO_3CH_3$	100	299	−2.3
		62	426	
		35	(576)[a]	
$C_6H_5SO_3^-$	$2\text{-}O_2NC_6H_4SO_3CH_3$	100	144	−3.1
		77.2	220	
		62	230	
		35	(344)[a]	
$C_6H_5SO_3^-$	$C_6F_5SO_3CH_3$	35	(6.1×10^5)[b]	
$2,5\text{-}Cl_2C_6H_3SO_3^-$	$C_6F_5SO_3CH_3$	77.2	979	
		65	1001	
		55	1014	−0.4
		35	(1060)[a]	
I^-	$PhSMe_2^+$	35	45.3[d]	
I^-	$PhSMe_2^+$	35	200[c]	
I^-	$2\text{-}O_2NC_6H_4SO_3CH_3$		$>10^3$[e]	
I^-	MeO_3SOMe	35	[420][f]	

[a] Extrapolated equilibrium constants from the higher temperature measurements, using the value of ΔH given. [b] Calculated as the product 576 × 1060 from elsewhere in the table. [c] Measured by adding methyl iodide to thioanisole. [d] Measured by adding dimethylphenylsulfonium triflate to potassium iodide. [e] A lower limit, the reaction is essentially complete. [f] One measurement of low reliability, the number is probably much larger.

Table III. Qualitative Comparison of Methyl 2,4,6-Trinitrobenzenesulfonate with Methyl Triflate

solvent	added species	$MeO_3SC_6H_2(NO_2)_3$	MeO_3SCF_3
sulfolane	none	destroyed rapidly at room temperature	stable at room temperature, destroyed in hours at 80 °C
$SOCl_2$	none	stable[a]	stable[a]
$SOCl_2$	sulfolane	ester destroyed	no reaction
$ClSO_2CH_3$	none	methylation of solvent[b] extensive, δ 5.48 $(MeO)_2S^+Cl$	methylation just detectable
$MeOS(=O)OMe$	none	rapid decomposition giving as detected products Me_2O, SO_2, Me_3O^+, $O_3SC_6H_2(NO_2)_3^-$	slow reaction, solvent decomposed in days
	none	perceptible methylation, then irreversible decomposition yielding SO_2	no fast reaction detected

[a] The chemical shifts of the methyl group of the two reagents were indistinguishable at δ 4.4, which suggested that both reagents quantitatively methylate the solvent. However, methyl triflate in $SOCl_2$ solution preserved the small fluorine splitting ($J_{HF} \sim 0.9$ Hz) also observed in other solvents. [b] The starting methyl chlorosulfite had δ 3.93. After adding the methyl trinitrobenzenesulfonate (δ CH_3 4.40), this peak disappeared and a new peak at δ 5.48 (6 H), together with the aromatic H peak at δ 8.89 (2 H), showed the formation of product, presumably cationic because of the high δ, with two equivalent methyl groups. The same peak, δ 5.48, was barely detectable in the $CH_3OSOCl + CH_3O_3SCF_3$ mixture. The coincidence of the aromatic peak chemical shifts between the trinitrobenzenesulfonate ester and the anion is not significant because the solvent is different and the external reference does not correct for this well.

Even though the Hammett equation is not applicable to these ortho-substituted systems, we hoped that the steric influences might be in the same direction and proportioned between the transition state and the product, so that a plot of log k_{ij} vs. log K_{ij} might be linear and might be extrapolated back to give a value of k_{ii}, the identity reaction rate for methyl benzenesulfonate itself. This hope was mostly justified as seen by the fit to the straight line in Figure 1. The points for the reverse reaction are included and shown in Figure 1. This forces the slope 0.5 for the line, as pointed out earlier,[1] but it does show that the slope 0.5 is an adequate if less than perfect fit to the three points in the table. In this plot the intercept at $K = 1$ gives $k_{ii} \simeq 2 \times 10^5$ M^{-1} s^{-1} at 35 °C. The actual measurement of this rate by a ^{35}S tracer technique is underway.

Table II also contains some further entries to establish the position of methyl iodide and these arenesulfonates in the list of equilibria established earlier by the combination of our work[1] with that of Jackman.[13] In this we have been qualitatively successful in showing methyl iodide to be less potent than dimethylphenylsulfonium ion, dimethyl sulfate, and methyl *o*-nitrobenzenesulfonate. The first is in agreement with the qualitative knowledge that

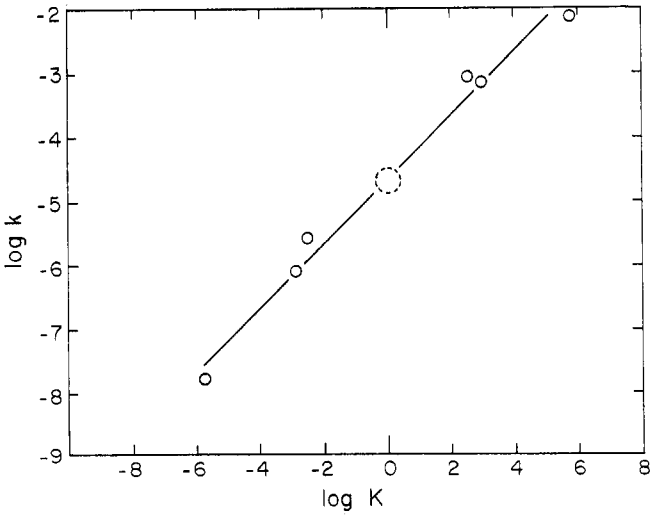

Figure 1. A plot of log k_+ *vs.* log K_+ for $ArSO_3Me + PhSO_3^-$ and for the reverse reaction rates and equilibria with $k_- = k^+/K_+$ and $K_- = 1/K_+$, showing estimation of log $k = -4.7$ for the $PhSO_3Me + PhSO_3^-$ identity reaction by the intercept at log $K_+ = 0$.

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this sulfonium salt cannot be prepared by methyl iodide methylation of thioanisole, although methyl iodide–$AgClO_4$ or methyl triflate both work well. Quantitatively we see a further problem. When methyl iodide and thioanisole are mixed, there is substantially less salt produced than that remaining when corresponding concentrations of dimethylphenylsulfonium triflate and potassium iodide are mixed. These two experiments give the two equilibrium constants in the table. The discrepancy is almost certainly a salt effect, since the latter experiment is done with a much higher ionic strength. The discrepancy is in the direction expected and is not unreasonable, for even the Debye–Hückel limiting law predicts at 0.1 M ionic strength in a solvent of this dielectric a factor of 4 in K, greater than the infinitely dilute value. These salt effects are serious when the two sides of reaction 1 have a different net charge but are not as serious in the cases when the charge on Nu_j and Nu_i are the same, as in the other entries in the table.

The comparisons of methyl iodide with the other two are qualitatively plausible, but the comparison with methyl *o*-nitrobenzenesulfonate is only a limit; the observation is that this ester reacts quantitatively with iodide ion within the sensitivity of the NMR analysis. The comparison with dimethyl sulfate is qualitatively correct, but the number appears far too small. With use of the lower value for the sulfonium salt from Table II and the equilibrium constant[1] (believed to be of low precision) for the methylation of thioanisole by dimethyl sulfate of 5.4×10^4, the value in Table II of 420 appears far below the calculated value of 2.4×10^6. Since the apparently very low number was not reproduced, and corresponds to a measurement of reduced precision at very unequal concentrations, we were tempted to reject it. We leave it here tentatively, since the value of 5.4×10^4 was also based on a single measurement and is less firm than the others.

It appears that a really firm thermodynamic scale of methylating power in sulfolane will require the use of far more dilute solutions, perhaps possible by Fourier transform NMR, but not yet attempted, in part because of solvent problems. Nevertheless, we are continuing to accumulate the high-concentration data, which is rough but still useful.

The powerful methylating agent methyl 2,4,6-trinitrobenzenesulfonate appears from Table III to be substantially more powerful than methyl triflate by a qualitatively significant amount, but we have no basis for a quantitative comparison. This ester is, however, not a very practical reagent. Our synthesis required diazomethane or trimethyloxonium salts to prepare the precursor. (We have not succeeded in reproducing the reported synthesis by way of methyl iodide and silver trinitrobenzenesulfonate.[14] Although we would not expect the ester to survive the solvents used, the low solubility of the ester might possibly have allowed its isolation under these circumstances.) It is soluble in very few inert solvents, and thionyl chloride, which is a satisfactory solvent, is reactive toward many nucleophiles itself. The major unidentified side reactions in the reaction with nucleophiles by methyl transfer also reduce the utility of this reagent. Possible side reactions include nucleophilic attack on sulfur and on the highly activated aromatic carbon.

The details of the reaction with the sulfites and chloro sulfites are contained in the accompanying paper;[15] the essence of the reactions is a prior reversible methylation, accompanied by the irreversible decomposition occurring by way of the intermediate CH_3OS^+O, itself a very powerful methylating agent.

Experimental Section

Materials. The arenesulfonyl chlorides were commercial materials and were converted to the methyl esters by treatment with sodium methoxide in methanol. A typical procedure used for all the esters is that used for the methyl *p*-bromobenzenesulfonate.

Anhydrous methanol (20 mL) was stirred at room temperature for 1 day with 0.01 g of magnesium methoxide. A sample of 1.41 g (61 mmol) of metallic sodium, rinsed with petroleum ether, was placed in a flask and warmed in a stream of nitrogen to remove residual petroleum ether. The flask was then covered and the dried methanol was added; the sodium dissolved in about 1 h. *p*-Bromobenzenesulfonyl chloride (16.75 g, 66 mmol) was dissolved in dry toluene (90 mL) and cooled to about −15 °C. The sodium methoxide solution was added dropwise with a syringe, and the solution was then allowed to come to room temperature and then filtered. The precipitated salts were washed with some more toluene, and the toluene solution was then concentrated on the rotary evaporator to a total volume of about 45 mL. On cooling and adding petroleum ether, the ester precipitated, yielding 13.9 g (90%) of the methyl ester, mp 57.7–60.5 °C.

Similarly methyl *o*-nitrobenzenesulfonate, mp 58.3–59 °C, 83%, methyl 2,5-dichlorobenzenesulfonate, mp 44 °C, 76%, methyl pentafluorobenzenesulfonate, mp 56.9–59 °C, 36%, methyl benzenesulfonate, bp 106–110 °C (0.9 torr), 91%, were prepared.

Methyl 2,4,6-trinitrobenzenesulfonate was made by vacuum sublimation of trimethyloxonium 2,4,6-trinitrobenzenesulfonate.[11] The oxonium salt is made either by the organic syntheses preparation via diazomethane[11] or by the reaction of commercial trimethyloxonium tetrafluoroborate with anhydrous 2,4,6-trinitrobenzenesulfonic acid in acetonitrile. It dissolves in many solvents with rapid reaction; these include acetonitrile, acetone, sulfolane, and others. It is not perceptibly soluble in carbon tetrachloride, chloroform, dichloromethane, or sulfuryl chloride. It does, however, dissolve unchanged in thionyl chloride, giving a simple NMR spectrum (δ 8.89, 2 H; 4.40, 3 H), referred to tetramethylsilane in a capillary.

Potassium Arenesulfonates. These were mostly made by neutralizing commercial sulfonic acids with an equivalent of potassium hydroxide, evaporating to dryness, and recrystallizing the product from ethanol.

Sulfolane-d_4. Commercial sulfolane was distilled several times from sodium hydroxide and then from calcium hydride; 60 g was exchanged in about a day at about 120 °C with D_2O (30 g), using potassium *tert*-butoxide (1 g). After each exchange, water is removed by distillation, more D_2O added, and further exchange accomplished, yielding after three exchanges product deuterated in the 2- and 5-positions to greater than 98.5%. Exchange with Na_2CO_3, NaOH, or KOH in dioxane with D_2O was ineffective; exchange with NaOD in sulfolane and D_2O was very slow. The 90-MHz proton NMR now consists of only a singlet, broad because of deuterium coupling, δ 2.6. Sulfolane-d_8 can be made by the sequence hexachlorobutadiene → butadiene-d_6 → sulfolene-d_6 → sulfolane-d_8, but the purification problems of the product made this route impractical. Thionyl chloride was purified following the procedure of Cason described by Fieser and Fieser.[16]

Rate Measurements. Rates were measured by following the concentrations of the two methyl esters from their resolved methoxy peaks in the proton NMR. Potassium benzenesulfonate is soluble in sulfolane to a level of up to 0.02 M at 30 °C. The sodium, lithium, and tetramethylammonium salts were somewhat less soluble. Sulfolane-d_4 solutions of potassium benzenesulfonate and the substituted methyl benzenesulfonates in equivalent concentrations were made up and put in a thermostat. Proton NMR spectra (Varian EM390) taken at intervals gave the relative concentrations of starting ester and methyl benzenesulfonate. Since the reactions were not sensibly reversible under these conditions, the rate constants were determined by the method

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of least squares from the slope of a plot of $1/[ArSO_3Me]$ vs. time. The precision of this method is limited by the rather low solubility of the potassium benzenesulfonate (since doing this work we have been able to increase these concentrations by using 18-crown-6) and with some aryl groups by the poor resolution of the two methoxy groups. The problem of resolution is compounded by the fact that the spectra were taken unlocked, because tetramethylsilane is not soluble enough in sulfolane, and the sulfolane-d_4 peak is too broad to give a good lock.

Equilibrium Measurements. Equivalent concentrations of potassium benzenesulfonate and the substituted methyl benzenesulfonates with the substituents used (*o*-NO_2, 2,5-dichloro, pentafluoro) did not give any measurable amount of starting ester. Thus to measure the equilibria, a substantial measured excess of unsubstituted methyl benzenesulfonate was added to an NMR tube containing potassium benzenesulfonate and the substituted methylbenzenesulfonate. The tube was sealed and put in the thermostat until there was no further change, the concentrations of the two methyl esters were measured, and the equilibrium constant was calculated. This was successful for the first two substituents mentioned above but not for the pentafluoro-substituted compound. Hence equilibrium between the pentafluoro ester and potassium 2,5-dichlorobenzenesulfonate was measured as a relay to get the desired equilibrium constant for the pentafluoro and unsubstituted esters.

Reactions with Methylating Agents. The reactions of Table III were all done in NMR tubes, with a capillary containing tetramethylsilane as external reference. As an example, methyl 2,4,6-trinitrobenzenesulfonate (ca. 50 mg) was dissolved in methyl chlorosulfite[17] (1 mL) in an NMR tube. When solution was complete, the NMR spectrum (Varian EM390) was taken; none of the methyl group of the sulfonate ester remained; the other peaks are described in footnote *b* of Table II.

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Registry No. Methyl pentafluorobenzenesulfonate, 4434-87-1; methyl 2-nitrobenzenesulfonate, 30384-53-3; methyl 2,5-dichlorobenzenesulfonate, 78150-04-6; potassium benzenesulfonate, 934-55-4; potassium 2,5-dichlorobenzenesulfonate, 46019-98-1; dimethylphenylsulfonium triflate, 85980-21-8; dimethyl sulfate, 77-78-1; potassium iodide, 7681-11-0; methyl 2,4,6-trinitrobenzenesulfonate, 53541-31-4; methyl triflate, 333-27-7.

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Methyl-Transfer Reactions. 7. System with CH_3OSO^+ Intermediate

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Methyl chlorosulfite with antimony pentachloride in thionyl chloride initially at dry ice temperature is a very powerful methylating system. It methylates sulfones, methyl chloride, and even to some extent dimethyl sulfate. The active methylating species is apparently the cation CH_3OSO^+. Dimethyl sulfite is decomposed catalytically by methyl trifluoromethanesulfonate to dimethyl ether and sulfur dioxide, and the same cation appears to be intermediate. The mechanism includes an exchange of the methyl groups between the two esters, allowing a practical synthesis of methyl-d_3 triflate. Dimethyl sulfite does not methylate detectably on sulfur.

Introduction

Powerful methylating agents are in principle compounds or ions with methyl attached to good leaving groups. Anionic leaving groups of exceptional stability are ClO_4^-, FSO_3^-, $F_3CSO_3^-$, 2,4,6-$(NO_2)_3C_6H_2SO_3^-$, listed in order of apparent increasing methylating power.[1-3] However, still more powerful cationic methylating agents may be designed with neutral leaving groups; thus trimethyloxonium ion is more powerful than methyl triflate, although less so than methyl 2,4,6-trinitrobenzenesulfonate.[3] Dimethylhalonium ions are presumably more powerful than trimethyloxonium ion, but even less nucleophilic leaving groups than methyl halides are known, notably N_2 from $CH_3N_2^+$, the leaving group in the system diazomethane + acid, as well as in perceptibly stable diazonium salts. The system $CH_3F + SbF_5$ is perhaps as powerful as any well-characterized system, but one can conceive of other stable neutral molecule leaving groups, some of which may show reactions other than methylation, such as the known mass spectrometric species $CH_3^+H_2(CH_5^+)$ and CH_3Ar^+, and in the gas-phase limit, CH_3^+. In solution, however, the solvent will always be attached to methyl if there is not a better nucleophile in solution. Thus in the solvent S, no better methylating agent than CH_3S^+ will exist at equilibrium, although (in contrast to the leveling effect of solvents on proton acidity) more powerful methylating agents than CH_3S^+ may have transient stability, since the methyl-transfer reactions are often perceptibly slow. Thus it is possible to do alkylations in aqueous solution with cyclic halonium salts[4] or with methyl triflate.[5] In this paper we shall be concerned with the species CH_3OS^+O (*1*), which is formally the ultimate methylating agent in liquid SO_2 and can be made from SO_2 and a more powerful methylating agent. This has been realized, by the mixture of $CH_3F + SbF_5 + SO_2$, and the ion CH_3OS^+O has been well identified in solution[6] and as a crystalline salt with the counter ion $Sb_2F_{11}^-$.[7] The use of CH_3F, SbF_5, or CH_2N_2 + acid are possible but expensive, inconvenient, and hazardous methods. Our approach has been to use the

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