stretch); nmr (dimethyl sulfoxide-d_6, TMS internal standard) δ 0.85 (t, 3, J = 7 Hz, CH_3CH_2), 2.95 (q, 2, J = 7 Hz, CH_2CH_3), and 7.0–8.0 ppm (m, 13, aromatic).

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6-Methyl-2-naphthalenesulfonate (Menasylate). A New and Useful Leaving Group for Trifluoroacetolysis

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Recently, trifluoroacetic acid has become an important solvolyzing solvent because of its very low nucleophilicity and relatively high ionizing power. Its strong acidity, however, restricts the method for measurement of solvolysis rates so that only the ultraviolet spectroscopic method has been the one for general use.[1] This method, developed originally by Swain and Morgan for following the reactions of arenesulfonates,[2] takes advantage of the differences in the absorptions of alkyl tosylates and tosylate anion at 261 or 272 nm; at 261 nm methyl tosylate has ε 671 and tosylate anion has ε 344 both in water. For the reactions of aralkyl arenesulfonates, whose aralkyl groups absorb in the same region as arenesulfonate groups do, extraction techniques were recommended by the original authors.[2] Although this technique has been successfully utilized by Bentley and Dewar[3] and by us[4,5] for trifluoroacetolysis of 2-arylethyl tosylates and nosylates, the experimental procedure is tedious and the accuracy of the results is limited. We report now that 6-methyl-2-naphthalenesulfonate, abbreviated as "menasylate (OMns)," is a useful leaving group for following the reactions in trifluoroacetic acid without extraction techniques.

Although menasyl chloride is commercially unavailable, it can be prepared easily from 2-methylnaphthalene.[6,7] Any indication of the presence of an isomer could not be observed for the chloride and all the menasylates prepared from it. The ultraviolet spectrum of ethyl menasylate in 95% ethanol showed maxima at 282 nm (ε 5650), 311 (1240), 318 (782), and 326 (936). On the other hand, the spectrum of menasylic acid in the same solvent showed maxima at 278 nm (ε 5470), 308 (393), and 318 (194); ε was only 56 at 326 nm and no maximum was observed around there. Addition of trifluoroacetic acid and sodium trifluoroacetate to the solutions did not cause any change in the spectra at all. This remarkable difference in the absorptions at 326 nm (*ca.* 20-fold) facilitated the measurement of the trifluoroacetolysis rates of several menasylates whose alkyl groups have absorptions at a longer wavelength region. Thus, the trifluoroacetolysis rates of 2-phenylethyl and 2-(*p*-methoxyphenyl)ethyl menasylate (**1** and **2**) were determined (Table I). In a typical run, the absorbance at 326 nm changed from 0.733 (at zero point) to 0.060 (at "infinity" after more than 10 half-lives). This large variation in the absorbance resulted in much improved accuracy and reproducibility without a great deal of skill such as necessary for extraction techniques. Correlation coefficients were better than 0.9999 in most cases. The presence of even a nitrophenyl group in the substrate (**3**) did not interfere with the measurement, although the background absorbance was relatively high in this case; the absorbance changed from 0.582 to 0.339 in one run. Application of a high temperature (>130°) caused desulfonation from the leaving group, and a small amount of 2-methylnaphthalene was detected in the products of trifluoroacetolysis of **3**.

It is apparent that menasylates can be used conveniently in any solvent other than trifluoroacetic acid; their reactions can be followed accurately and their melting points are usually high. Comparison of the present data with those reported by Nordlander and Deadman[8] revealed that the reactivity of a menasylate was almost the same as that of a tosylate.

Experimental Section

Menasylic Acid. A mixture of 71 g of 2-methylnaphthalene and 71 g of *concentrated* sulfuric acid (*d* 1.84) was stirred for 6 hr at 90–100°. At the end of this period the hot reaction solution was poured into 250 ml of water while stirring. The unreacted 2-methylnaphthalene and the sulfone produced as a by-product were extracted twice with 50 ml each of benzene. To the water layer was added 400 ml of aqueous solution saturated with sodium chloride. After stirring for several hours the sodium salt thus precipitated was filtered and dried at 120–150° *in vacuo*. The crystals were suspended in acetone and warmed under reflux for 2 hr. After filtration sodium menasylate recrystallized twice from water. The yield was 25–40%.

Sodium menasylate was dissolved in 3 *N* hydrochloric acid at 60°. Upon cooling to room temperature colorless crystals precipitated. Menasylic acid was obtained as a monohydrate after recrystallization from 3 *N* hydrochloric acid and then from ethyl acetate, mp 118–121°.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03; S, 13.34. Found: C, 55.22; H, 4.83; S, 13.23.

Menasyl Chloride. To a stirred suspension of 20 g of sodium

Table I
Trifluoroacetolysis Rates of 2-Arylethyl Arenesulfonates

Substrate	Temp, °C	$10^5 k_t$, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
$PhCH_2CH_2OMns$ (**1**)[a,b]	50	8.08 ± 0.01	19.9	−15.9
	60	21.1 ± 0.1		
p-$MeOPhCH_2CH_2OMns$ (**2**)[a,b]	24	6.38 ± 0.03		
p-$NO_2PhCH_2CH_2OMns$ (**3**)[b,c]	130	2.64 ± 0.00	25	−19
	150	11.9		
$PhCH_2CH_2OTs$[b,d]	50	7.75	20.8	−13.1
$PhCH_2CH_2ONs$[e]	50	26.0	19.5	−14.7

[a] 0.05 *M* in menasylate. [b] With 0.125 *M* sodium trifluoroacetate. [c] 0.025 *M* in menasylate. [d] Interpolated from data in ref 8. 0.05 *M* in tosylate. [e] Reference 5; 0.02 *M* in nosylate.

menasylate in 80 ml of dimethylformamide was added dropwise over a 15-min period 9 ml of thionyl chloride at room temperature. After stirring for an additional 5 min, the reaction solution was poured into ice-water. Precipitates were filtered and dried. Recrystallization from ligroin gave 15.7 g of the pure chloride, mp 98.0–99.0° (lit.[6] mp 97–98°).

Preparation of Menasylates. Menasylates were prepared by standard procedures from menasyl chloride and alcohols at 0° in pyridine as a solvent.

2-Phenylethyl menasylate (**1**) had mp 101.9–102.5° (from ligroin).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56; S, 9.82. Found: C, 69.98; H, 5.29; S, 9.71.

2-(*p*-Methoxyphenyl)ethyl menasylate (**2**) had mp 112.8–113.3° (from ligroin-benzene).

Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66; S, 9.00. Found: C, 67.30; H, 5.46; S, 8.80.

2-(*p*-Nitrophenyl)ethyl menasylate (**3**) had mp 135.0–135.8° (from carbon tetrachloride-chloroform).

Anal. Calcd for $C_{19}H_{17}NO_5S$: C, 61.44; H, 4.61; N, 3.77; S, 8.63. Found: C, 61.31; H, 4.47; N, 3.58; S, 8.78.

Trifluoroacetolysis Media. Trifluoroacetic acid and its 2 vol % of trifluoroacetic anhydride were refluxed for 2 hr. The solution was then distilled through a 85-cm vacuum-jacketed column packed with glass helices. The middle cut (bp 71.5–72.0°) was redistilled through the same column. To this middle cut (bp 71.5–72.0°) was added 1 wt % of freshly distilled trifluoroacetic anhydride. Sodium trifluoroacetate (17.0 g, 0.125 mol) was dissolved with the previous solution in a 1000-ml volumetric flask to prepare buffered medium.

Kinetic Procedure. The required amount of menasylate for making a 0.05 *M* solution was weighed in a volumetric flask and diluted with the trifluoroacetolysis media prepared as above. For the reactions above 50°, 1.5-ml portions of this solution were sealed in 5-ml glass ampoules, which were placed together in a thermostatic bath at the desired temperature (±0.02°). At the appropriate intervals, the tubes were quenched in ice-water successively. Each was warmed to room temperature and opened, and 1.00 ml of the solution was pipetted into *ca.* 48 ml of 95% ethanol in a 50-ml volumetric flask, followed by 95% ethanol up to the mark. The absorbance of the resulting solution was measured at the maximum of 326 nm, using a Hitachi Perkin-Elmer 139 uv-visible spectrophotometer. A Beer's law for the concentration of ethyl menasylate was shown to be linear over the range used for the kinetics.

The reaction of **3** was followed using a 0.025 *M* solution. For the reaction of **2** at 24°, 1-ml aliquots were pipetted out from a reaction flask placed in a thermostatic bath.

Registry No.—1, 51751-79-2; **2,** 51751-80-5; **3,** 51751-81-6; menasylic acid, 29181-96-2; 2-methylnaphthalene, 91-57-6; menasyl chloride, 1875-72-5; sodium menasylate, 13035-04-6; 2-phenylethanol, 60-12-8; 2-(*p*-methoxyphenyl)ethanol, 702-23-8; 2-(*p*-nitrophenyl)ethanol, 100-27-6; trifluoroacetic acid, 76-05-1.

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Friedel-Crafts Alkylations with Aromatic Aldehydes

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Friedel-Crafts reactions of benzaldehyde with aromatic substrates have been reported to produce either triarylmethanes or anthracene derivatives depending on the catalyst, substrate, and reaction conditions.[1] In the reaction of substituted benzaldehydes with benzene in the presence of aluminum chloride to produce anthracenes it was found that the aldehyde served only to supply the meso carbon atoms in the anthracene molecule[2] *via* decarbonylation to carbon monoxide. Benzoic acid[3] and "traces" of diphenylmethane[4] have also been reported as products of the reaction of benzaldehyde with benzene in the presence of aluminum chloride.

During the course of a study of Tishchenko reactions catalyzed by boron compounds[5] a new modification of the Friedel-Crafts reaction of benzaldehydes with aromatics has been found. When boron trifluoride etherate is used as catalyst at elevated temperatures the major products are diphenylmethane derivatives along with low yields of the corresponding benzoic acids. If the assumption is correct that the initial reaction step is disproportionation of the aldehyde to benzyl benzoate, the following reaction stoichiometry would be expected.

$$2\mathrm{ArCHO} \xrightarrow{\mathrm{BF_3}} \mathrm{ArCO_2CH_2Ar} \xrightarrow[\mathrm{BF_3}]{\mathrm{Ar'H}} \mathrm{ArCH_2Ar'} + \mathrm{Ar'CO_2H}$$

Table I summarizes the results observed under typical conditions using excess aromatic hydrocarbon as solvent.

Although good yields of diphenylmethane derivatives were usually obtained, the corresponding carboxylic acid was generally found in only 10–15% yield by basic extraction. In addition to the products isolated there were rather substantial quantities of heavy tars produced. Dibenzylated materials were found in some cases but there was no indication of incorporation of the bulk of the benzoic acid in the form of volatile carbonyl-containing compounds; however, minor quantities of ethyl benzoate were detected (control experiments showed that benzoic acid in benzene solution reacted with boron fluoride etherate to give ethyl benzoate at 150°). Benzylation of benzene and toluene with benzyl benzoate in the presence of catalytic quantities of boron fluoride etherate was found to give high yields of both diphenylmethane and benzoic acid. Treatment of benzaldehyde with boron fluoride etherate in cyclohexane gave no reaction at reflux and tars under more forcing conditions. Pure benzyl benzoate when refluxed with boron fluoride in cyclohexane was converted to polymer (polybenzyl) and benzoic acid. Benzene did not react with carbon monoxide at 200° and 1800 psig in the presence of boron fluoride. Stannic chloride was completely ineffective as a catalyst for the reaction using method B; the starting materials were recovered unchanged. Because of the differences in reaction products between benzaldehyde and benzyl benzoate cited the equation above undoubtedly represents an oversimplification. Although mechanisms can be written which would account for the observed products, they would be speculative at this time; a competition between other routes and a Tishchenko disproportionation, followed by alkylation, may also be occurring.

Isomer distributions of the benzyltoluenes from the reaction of benzaldehyde with toluene were determined by capillary glc and found to be substantially the same for all three methods of preparation: 49–51% para, 7–8% meta, and 41–43% ortho. Reaction of *p*-tolualdehyde with benzene gave *p*-benzyltoluene of >99.5% purity and *p*-chlorobenzaldehyde with benzene gave 4-chlorodiphenylmethane, also in very high purity. Where the requisite aldehydes are available this method may provide a useful synthetic procedure for the preparation of substituted diphenylmethanes,[6] since the experimental procedure, par-