benzene in 61% yield with Tf_2O and $AlCl_3$ at room temperature, it is clear that TFMT is less effective as a sulfonylating agent than is Tf_2O.

Conclusion

We have found that TFMT is conveniently and economically prepared in high yield by the reaction of Tf_2O with strong Lewis acids such as $TfOSbF_4$, which is formed in the reaction of Tf_2O with SbF_5. Although TFMT is readily accessible as a result of this reaction, we have found no examples of trifluoromethylation by this reagent, contrary to published reports.[4b] Initial reaction with a wide range of nucleophiles occurs at sulfur to displace trifluoromethoxide to give trifluoromethanesulfonylation of the nucleophile. The synthetic utility of TFMT as a trifluoromethanesulfonylating reagent is severely limited, however, because the reagent is rapidly destroyed by a fluoride ion chain reaction in the presence of other nucleophiles. Fluorophosgene, a product of the decomposition, reacts with many of the added nucleophiles to make them less accessible for reaction with TFMT.

Although we suggest that CF_3^+ may be an intermediate in the formation of TFMT, the strongly electrophilic nature of the reaction medium makes trapping of the CF_3^+ with added nucleophiles difficult. We have not been able to devise a suitable system to carry out trifluoromethylations by trapping the CF_3^+.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (NSF CHE 81-13142). Mass spectra were obtained from facilities provided under grants from the National Institutes of Health (CA 11388 and GM 16864).

Registry No. 1, 109084-87-9; 5, 420-56-4; 6, 28920-31-2; 8, 88035-99-8; TFMT, 3582-05-6; Tf_2O, 358-23-6; HMDS, 999-97-3; THF, 109-99-9; SbF_5, 7783-70-2; $TiCl_4$, 7550-45-0; AsF_5, 7784-36-3; $TiCl_2(OSO_2CF_3)_2$, 15001-53-3; Et_3N, 121-44-8; $PhSO_2CF_3$, 426-58-4; Ph_2CO, 119-61-9; $(n\text{-}C_7H_{15})_4N^+I^-$, 3535-83-9; Ph_2S, 139-66-2; Ph_3P, 603-35-0; pyridine, 110-86-1; cesium fluoride, 13400-13-0; phenyllithium, 591-51-5; diphenyl sulfone, 127-63-9; sodium naphthalenide, 3481-12-7; perfluorohexanesulfonic acid, 355-46-4; perfluorohexanesulfonic anhydride, 109065-55-6.

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Reactions of the Readily Accessible Electrophile, Trifluoroacetyl Triflate: A Very Reactive Agent for Trifluoroacetylations at Oxygen, Nitrogen, Carbon, or Halogen Centers

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Received March 26, 1987

Trifluoroacetyl triflate (TFAT) is readily prepared in 82% yield by the dehydration (phosphorus pentoxide) of a 2:1 mixture of trifluoroacetic acid and trifluoromethanesulfonic (triflic) acid. Reactions of this highly electrophilic trifluoroacetylating reagent with alcohols, ketones, ethers, amines, and pyridines give esters, enol esters, ether cleavage, amides, and acylpyridinium ions, respectively. Reactions with ionic or easily ionizable alkyl halides give the very volatile trifluoroacetyl halides and the ionic triflate. Triphenylmethyl chloride, for example, is quantitatively converted to triphenylcarbenium triflate in a very convenient synthetic procedure. Trifluoroacetyl triflate is used in the synthesis of the first member of a new class of pyrylium salts, 2,6-dimethoxypyrylium triflate.

Compounds that contain the trifluoromethanesulfonate (triflate) moiety[2] are potent electrophilic reagents because the triflate (OTf) group is one of the best electrofugal leaving groups known[3] and is a powerful electron-withdrawing group. This is illustrated by the marked electrophilicity observed for alkyl,[4] acyl,[5] and halogen[6] triflates. Of the many trifluoroacetylating reagents that have been reported, trifluoroacetyl triflate (TFAT) is probably the most powerful and useful, as evidenced here and in an earlier paper,[7a] by virtue of its reactivity toward several types of nucleophiles under mild conditions. Although evidence for salts of the trifluoroacetylium cation, which would be expected to be a more powerful trifluoroacetylating reagent, have been claimed,[8] further work[9] showed them to be covalent acyl fluoride complexes, not acylium salts. We here report the convenient synthesis of TFAT and survey its reaction with a variety of nu-

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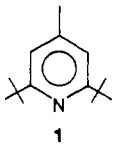
cleophiles, including the synthesis of the first member of a new class of pyrylium salts, 2,6-dimethoxypyrylium triflate.

Results and Discussion

The reactions of TFAT with anhydrous[10] alcohols and phenols rapidly give the trifluoroacetate esters in high yield. The hindered base 2,6-di-*tert*-butyl-4-methylpyridine[11] (1) may be used to scavenge the triflic acid produced in the reactions, since it does not react with TFAT under conditions.[12] Alcohols **2a,b** and phenols **2c,d**



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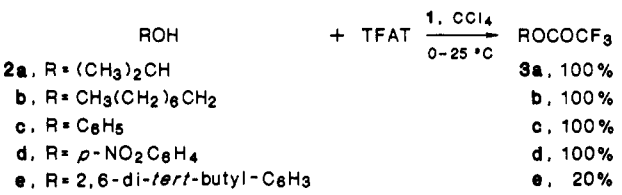
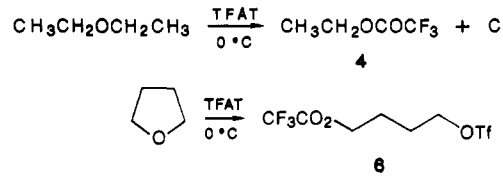


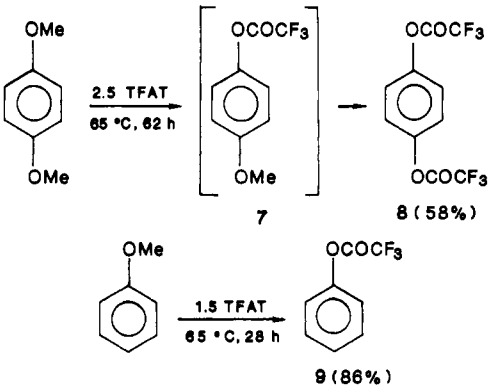
are rapidly and quantitatively (by ^1H NMR) derivatized by TFAT. Only 20% of the sterically encumbered phenol **2e** is trifluoroacetylated after 18 h. Boiling the reaction mixture did not increase the yield of **3e** but converted **2e** to 4-*tert*-butylphenol by dealkylation, probably a result of the presence of small amounts of triflic acid.[13]

Unlike other trifluoroacetylating reagents, TFAT reacts readily with alkyl ethers. Both tetrahydrofuran (THF) and diethyl ether react quantitatively with TFAT at 0 °C to cleave the ether linkage. Both undergo a similar reaction

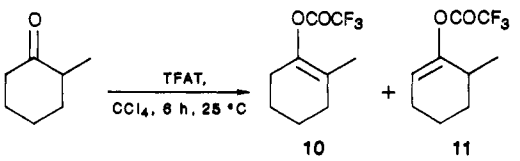


with triflic anhydride[14] but fail to react with trifluoroacetic anhydride. Phenyl alkyl ethers are slowly cleaved by TFAT. The reaction of TFAT with 1,4-dimethoxybenzene give a 1.4/1.0 mixture of **7** and **8** after 17 h at 65 °C. The other reaction product is methyl triflate. The remainder of **7** is converted to **8** (58%) after 62 h at 65 °C. The reaction of TFAT with anisole gives **9** (86%) and methyl triflate after 26 h at 65 °C.

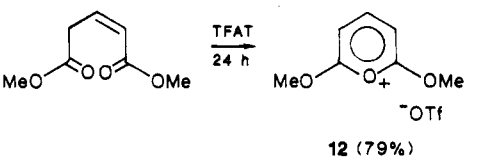
Ketones are trifluoroacetylated by TFAT at oxygen to give enol trifluoroacetates. Reaction of TFAT, in the presence of hindered base **1**, with cyclohexanone and acetophenone gives the corresponding enol trifluoroacetates in 72%[7a] and 85% yield. The acetophenone enol



trifluoroacetate has previously been synthesized in 50–69% yield.[15,16] Reaction with 2-methylcyclohexone gives enol trifluoroacetates **10** and **11** in a 9 to 1 ratio. It has recently been reported[17] that TFAT reacts with a thioketone at 25 °C to give a stable cation. We found no evidence for reaction with carbon disulfide, however, even after 24 days at 80 °C.



The reaction of TFAT with the methyl ester of glutaconic acid gives 2,6-dimethoxypyrylium triflate (**12**), the first example of pyrylium salt with alkoxy groups at positions 2 and 6.[18] While the cyclodehydration of 1,5-di-



oxopent-3-enes to give pyrylium salts is generally carried out by heating in the presence of a strong acid,[19] an attempted cyclodehydration of dimethyl glutaconate in triflic acid was unsuccessful. Cyclodehydrations of sulfoxide alcohols[20] and one example of a phosphine oxide alcohol[21] to produce sulfonium or phosphonium triflates have been effected by using TFAT.

Primary or secondary amines are readily trifluoroacetylated with TFAT, as with other reagents. Either a second equivalent of amine or added **1** can be used to scavenge the triflic acid produced. Excess TFAT converts primary amine **13a** to the imide.

Under conditions at which pyridine does not react with trifluoroacetic anhydride[22] it does react with TFAT to give

(10) Water reacts vigorously with TFAT at 25 °C to give trifluoroacetic and triflic acid. Trifluoroacetic acid reacts reversibly with TFAT to give trifluoroacetic anhydride and triflic acid. Since the equilibrium is shifted far to the right, 1 equiv of water consumes nearly 2 equiv of TFAT. The K_{eq} for a 1.2/1 mixture of trifluoroacetic acid and TFAT is ca. 11.

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(18) Reaction of **12** with aniline does not give *N*-phenyl-2,6-dimethoxypyridinium triflate. The ^1H NMR spectra suggest that the methoxy groups are displaced by the aniline.

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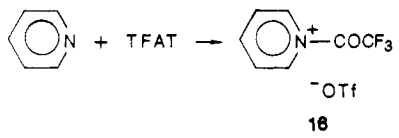
(22) Although we observed no reaction between trifluoroacetic anhydride and pyridine in $CDCl_3$ at 25 °C as determined by ^1H and ^{19}F NMR, its reaction at −78 °C in ether has been reported to give a solid pyridinium trifluoroacetate that decomposes upon melting (38.5–40 °C) and is soluble in dimethyl sulfoxide, trimethyl phosphate, hexamethylphosphoramide, and water: Moore, J. A.; Goldstein, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2103.

$$RR'NH + TFAT \xrightarrow[0\text{-}25\ ^\circ C]{1.\ CCl_4} RR'NCOCF_3$$

13a, R = $CH_2{=}CHCH_2$, R′ = H — **14a**, 100%
b, R = C_6H_5, R′ = H — **b**, 100%
c, R = CH_3CH_2, R′ = CH_3CH_2 — **c**, 100%
d, R = C_6H_5, R′ = CH_3 — **d**, 100%

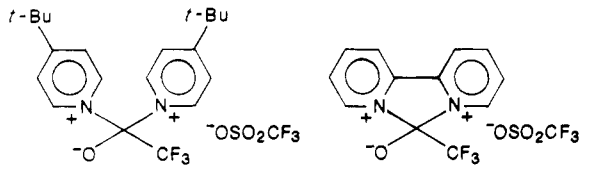
$$\mathbf{13a} \xrightarrow[CCl_4,\ 1,\ 25\ ^\circ C]{TFAT\ (excess)} CH_2{=}CHCH_2N(COCF_3)_2$$

a pyridinium species. A 1:1 reaction gives pyridinium triflate **16**, itself a potent trifluoroacetylating reagent. The



16

addition of 1 equiv of ethanol to **16** gives ethyl trifluoroacetate (**4**). The addition of 2 equiv of 4-*tert*-butylpyridine to TFAT gives pyridinium salt **17**, and the addition of 1 equiv of 2,2′-bipyridyl gives pyridinium salt **18**.[23]

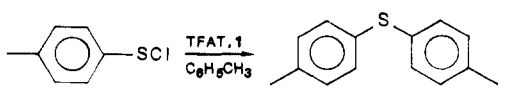


17 **18**

The reaction of TFAT with ionic halides provides a convenient and easy method for replacing a halide ion by triflate ion in aprotic media. Some covalent chlorides and fluorides are trifluoroacetylated at the halogen to produce trifluoroacetyl halides and the corresponding triflates. One of the driving forces for these reactions is the high volatility of the trifluoroacetyl halides. The ease of removal of the low-boiling CF_3COX products (X = F,[24a] bp −50 °C; Cl,[24b] −27 °C; Br,[24b] −5 °C; I,[24c] 23 °C) also greatly simplifies the workup procedure. An alternative reagent, silver triflate, is more expensive and less convenient to use.

Fluorine attached to iodine is replaced with triflate by reaction with TFAT to convert a 12-I-5[25] periodinane to a 10-I-4 periodonium triflate salt.[26] Exchange of phosphorus hexafluoride anion by triflate has been accomplished with loss of a fluoride ion by reaction with TFAT.[27] The reaction of TFAT with *p*-toluenesulfenyl chloride in the presence of toluene to form *p*-tolyl sulfide[7a] may proceed through a sulfenyl triflate intermediate. Trityl triflate is quantitatively produced by reaction of trityl chloride with TFAT. TFAT does not react at 65 °C with phosgene over 48 h or with benzoyl chloride over 12 h.

$$PF_6^- \xrightarrow{TFAT} PF_5 + CF_3COF + {}^-OTf$$



Although titanium tetrachloride reacts with TFAT at 25 °C to give some replacement of chloride with triflate, tin(IV) chloride does not react at 65 °C over 4 h. It appears that for the preparation of metal triflates of this type, triflic acid/triflic acid anhydride is a superior reagent.[28]

Trifluoroacetylation at carbon in anthracene occurs under milder conditions and gives a higher yield of product when TFAT is used instead of trifluoroacetic anhydride.[7a] Toluene is not trifluoroacetylated by TFAT at 110 °C over 3 h. Cyclohexene, in the presence of hindered base **1**, is not trifluoroacetylated by TFAT at 100 °C over 40 h.

The high reactivity of TFAT limits the number of solvents that can be used for its reactions. We have found that TFAT is unreactive toward saturated hydrocarbons, benzene, and common halogenated solvents. It reacts only very slowly with nitromethane, but reacts relatively rapidly with ethers, ethyl acetate, and acetonitrile.

Experimental Section

General. Triflic and trifluoroacetic acids were used without purification. Alcohols were distilled from CaO and amines from KOH and CaH_2. Pyridine **1**[11] was sublimed prior to use. The ^1H and ^{19}F NMR chemical shifts are reported downfield from tetramethylsilane (internal standard) and $CFCl_3$ (internal standard), respectively, unless otherwise indicated. Elemental analyses were within 0.4% of theoretical values for the indicated amounts.

Preparation of Trifluoroacetyl Triflate (TFAT). With conditions similar to those published earlier[7] a larger scale synthesis was effected. A mixture of triflic acid (113 g, 0.750 mol) and trifluoroacetic acid (171 g, 1.50 mol) was added to a mixture (1:1 by volume) of powdered P_2O_5 (320 g, 2.25 mol) and dried fine sand at −20 °C, and the slurry was thoroughly shaken. After 2.5 h at room temperature, a simple distillation (bath temperature raised ultimately to 240 °C) gave a mixture of TFAT, trifluoroacetic acid and its anhydride, triflic acid and its anhydride, and trace amounts of trifluoromethyl triflate.[29] Fractional distillation from 10 g of P_2O_5 gave 151 g (82%) of TFAT (bp 62.5 °C)[7a] of 99% purity as determined by ^{19}F NMR.

Reaction of TFAT: (a) With Alcohols and Phenols. A typical reaction is illustrated by the treatment of a solution of 0.190 g (2.02 mmol) of phenol (**2c**) and 0.412 g (1.01 mmol) of hindered base **1** in 5 mL of CCl_4 with 0.320 mL (2.10 mmol) of TFAT at 0 °C and then warming to room temperature for 5 min. After removal of the pyridinium triflate salt by filtration, the only compound observed in the filtrate by ^1H and ^{19}F NMR was phenyl trifluoroacetate, by comparison with an authentic sample.[30]

Sterically encumbered phenol **2e** gave only 20% of **3e** (by ^1H and ^{19}F NMR) after 18 h at 25 °C. When the reaction was run under more forcing conditions (reflux), 20% conversion to **3e** was observed after 2 h, but longer reaction times converted **2e** to *tert*-butylphenol.[13]

(b) With Diethyl Ether. The slow addition of 2.95 mL (19.4 mmol) of TFAT to 2.00 mL (19.3 mmol) of diethyl ether at 0 °C gave ethyl trifluoroacetate (**4**) and ethyl triflate (**5**) in equal amounts (determined by ^1H and ^{19}F NMR). Distillation gave **4**: bp 53–54 °C (lit.[31] bp 61 °C); ^1H NMR (CCl_4) δ 1.39 (t, CH_3, J = 7 Hz), 4.33 (q, CH_2, J = 7 Hz); ^{19}F NMR (CCl_4) δ −75.92 (s). Anal. ($C_4H_5F_3O$) C, H. Ethyl triflate (**5**) was collected as a second fraction (lit.[32] bp 42 °C (40 torr)): ^1H NMR (CCl_4) δ 1.50 (t, CH_3, J = 7 Hz), 4.54 (q, CH_2, J = 7 Hz); ^{19}F NMR (CCl_4) δ −76.03 (s).

(c) With Tetrahydrofuran (THF). The addition of 0.300 mL (1.97 mmol) of TFAT to 0.155 mL (1.91 mmol) of THF at

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0 °C gave a light brown solution, whose NMR spectra are consistent with **6**: ^{1}H NMR (neat) δ 1.94 (m, 4), 4.37 (m, 2), 4.57 (m, 2); ^{19}F NMR (neat) δ −75.43 (s, 3), −75.57 (s, 3).

(d) With 1,4-Dimethoxybenzene. A mixture of TFAT (1.1 mL, 7.2 mmol) and 1,4-dimethoxybenzene (0.40 g, 2.9 mmol) was sealed in an NMR tube and heated at 65 °C. After 17 h, the only aromatic compounds observed by ^{1}H and ^{19}F NMR were a 1.4/1.0 mixture of **7** [^{1}H NMR δ 3.90 (s, 3, CH_3), 7.05 (d, 2, J = 9 Hz) 7.20 (d, 2, J = 9 Hz); ^{19}F NMR δ −75.25 (s)] and **8**. Heating at 65 °C for another 45 h gave **8** in 58% yield (by integration of NMR spectra using $PhCF_3$ as an internal standard). Kugelrohr distillation at 85 °C (190 torr) gave 0.45 g (2.7 mmol) of methyl triflate (lit.[33a] bp 97 °C): ^{1}H NMR ($CDCl_3$) δ 4.20 s) (lit.[33b] δ 4.22); ^{19}F NMR ($CDCl_3$) δ −74.70. Distillation at 140 °C (150 torr) and recrystallization from hexane gave 0.45 g (51%) of **8**: mp 76–77 °C (lit.[34] mp 78–79 °C); ^{1}H NMR ($CDCl_3$) δ 7.30 (s); ^{19}F NMR ($CDCl_3$) δ −75.20 (s). Anal. ($C_{10}H_4F_6O_4$) C, H, F.

(e) With Anisole. A mixture of TFAT (0.64 mL, 4.2 mmol) and anisole (0.30 g, 2.8 mmol) was sealed in an NMR tube and heated at 65 °C. After 28 h, the ^{1}H NMR showed that no anisole remained. Integration of the ^{1}H and ^{19}F NMR spectra with $PhCF_3$ as an internal standard showed methyl triflate (2.55 mmol) and phenyl trifluoroacetate (**9**) (2.4 mmol, 86%). The spectra of **9** were identical with those of an authentic sample prepared by the trifluoroacetylation of phenol.

(f) With Acetophenone. A solution of acetophenone (3.15 mL, 27.0 mmol) and **1** (5.59 g, 27.2 mmol) in 50 mL of CCl_4 was treated with 4.31 mL (28.0 mmol) of TFAT for 6 h at 25 °C. The pyridinium triflate salt was filtered and the filtrate distilled to give 4.98 g (85%)[16] of the enol trifluoroacetate: bp 31 °C (0.5 torr) (lit.[15] bp 75 °C (13.5 torr)); ^{1}H NMR (CCl_4) δ 5.20 (d, 1, J = 29 Hz), 5.55 (d, 1, J = 29 Hz), 7.35 (m, 5); ^{19}F NMR (CCl_4) δ −75.50. Anal. ($C_{10}H_7F_3O_2$) C, H, F.

(g) With 2-Methylcyclohexanone. A solution of 2-methylcyclohexanone (0.135 mL, 1.11 mmol) and hindered base (0.240 g, 1.17 mmol) in 3 mL of pentane was treated with TFAT (0.180 mL, 1.17 mmol) at 25 °C. No TFAT remained after 45 min. The reaction mixture was filtered and washed with pentane, and pentane was removed from the filtrate. The residue was distilled (Kugelrohr) to give 0.20 g (87%) of a 9:1 mixture of compounds: **10** [^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3, CH_3), 1.72 (m, 4, methylene), 2.13 (m, 4, methylene); ^{19}F NMR ($CDCl_3$) δ −75.55] and **11** [^{1}H NMR ($CDCl_3$) δ 1.00 (d, 3, Me), 5.52 (m, 1, vinyl H); ^{19}F NMR ($CDCl_3$) δ −75.62]; mass spectrum m/e 208 (M^+). The methylene protons of **11** in the ^{1}H NMR spectrum were obscured by the methylene protons of **10**.

(h) With Dimethyl Glutaconate. A mixture of 5.67 g (36 mmol) of dimethyl glutaconate and 18.5 g (75 mmol) of TFAT was stirred together at 25 °C for 24 h. The addition of cold ether to the resulting red oil gave a dark red solid. The solid was washed with more ether, and residual ether was removed in vacuum to give 7.9 g (76%) of a moisture-sensitive, dark red solid, **12**: ^{1}H NMR (acetone-d_6) δ 4.47 (s, 6, OMe), 7.10 (d, 2 H-3,5, J = 8 Hz), 8.78 (t, 1, H-4, J = 8 Hz); ^{19}F NMR (CD_3CN) δ −78.05 (s). Anal. ($C_8H_9F_3O_6S$) C, H, F, S.

(i) With Amines. A typical reaction is illustrated by the treatment of a solution of allyl amine **13a** (0.119 g, 2.08 mmol) and hindered base **1** (0.412 g, 2.01 mmol) in 3 mL of CCl_4 with 0.320 mL (2.10 mmol) of TFAT. After 5 min, the pyridinium triflate was removed by filtration to give amide **14**:[35] ^{1}H NMR (CCl_4) δ 3.90 (t, 2, CH_2N, J = 6 Hz), 5.07 and 5.23 (m, 2, CH=CH_2), 5.80 (m, 1, CH=CH_2), 6.5 (br s, 1 NH); ^{19}F NMR (CCl_4) δ −76.55 (s). Because a small excess of TFAT was used, small peaks were also observed for imide **15** (R = CH_2=$CHCH_2$): ^{1}H NMR (CCl_4) δ 4.37 (d, 2, CH_2N, J = 6 Hz), 5.07 and 5.26 (m, 2, CH=CH_2), 5.80 (m, 1, CH=CH_2), ^{19}F NMR (CCl_4) δ −71.30. The addition of a drop of amine **13a** causes the imide to disappear. The addition of 1.1 equiv of TFAT and **1** to amide **14a** converts it quantitatively (by ^{1}H and ^{19}F NMR) to the imide over 4 h.

(j) With Pyridine. A solution of pyridine (0.53 mL, 0.65 mmol) in 1.5 mL of $CHCl_3$ was treated with 0.10 mL (0.65 mmol) of TFAT. Removal of solvent gave 0.19 g (95%) of a 5:1 mixture of acylpyridinium triflate **16** and its hydrolysis product, pyridinium triflate: ^{1}H NMR (CH_3NO_2) δ 8.50 (br m, 2), 9.15 (br m, 1), 9.40 (br m, 2); ^{19}F NMR (CH_3NO_2) δ −66.7 (br s, 3.0, $COCF_3$), −78.3 (s, 3.6, OTf). An acceptable elemental analysis was found (C, H, N, S) for a calculated 5:1 mixture of the pyridinium triflates.

The addition of 6.4 μL (0.11 mmol) of absolute ethanol to 0.040 g (0.11 mmol of **16**) of the solid mixture at 0 °C gave 56% conversion to ethyl trifluoroacetate (by ^{1}H NMR).

(k) With *p*-Toluenesulfenyl Chloride. A solution of 0.43 g (2.72 mmol) of *p*-toluenesulfenyl chloride and 0.60 g (2.92 mmol) of pyridine **1** in 2.5 mL of toluene was treated with 0.7 g (2.82 mmol) of TFAT at 0 °C for 30 min. The reaction was quenched with water, and the products were extracted into ether, dried ($MgSO_4$), and filtered. Removal of the ether in vacuum gave 0.21 g (36%) of pure *p*-tolyl sulfide: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6), 7.04 (d, 4), 7.20 (d, 4). Purity was determined by GLPC comparison with an authentic sample.

(l) With Trityl Chloride. A solution of 10.1 g (36.1 mmol) of trityl chloride in 30 mL of CCl_4 was treated with 6.0 mL (39.0 mmol) of TFAT at 25 °C. After 3 h the volatile components were removed in vacuum to give 14.2 g (100%) of a very hygroscopic yellow solid, trityl triflate:[36] ^{1}H NMR (CH_3NO_2) δ 7.87 (m, 12), 8.33 (m, 3); ^{19}F NMR (CH_3NO_2) δ −78.1 (s). Anal. ($C_{20}H_{15}F_3O_3S$) F, S.

(m) With Anthracene. A solution of 0.045 g (0.25 mmol) of anthracene and 0.056 g (0.27 mmol) of pyridine **1** in 0.5 mL of benzene was treated with 0.069 g (0.28 mmol) of TFAT, sealed in an NMR tube, and heated at 80 °C for 44 h. Integration of aromatic absorptions showed 81% of 9-(trifluoroacetyl)-anthracene:[37] ^{19}F NMR ($CDCl_3$) δ −74.4 (s).

Acknowledgment. This research was supported in part by a grant from the National Institute of Health (GM 33064). The NMR spectra were provided by the University of Illinois Midwest NSF Regional NMR Facility (CHE 79-16100). Mass spectra were obtained from facilities provided under grants from the National Institutes of Health (CA 11388 and GM 16864).

Registry No. **1**, 38222-83-2; **2a**, 67-63-0; **2b**, 111-87-5; **2c**, 108-95-2; **2d**, 100-02-7; **2e**, 128-39-2; **3a**, 400-38-4; **3b**, 2561-21-9; **3d**, 658-78-6; **3e**, 109244-15-7; **4**, 383-63-1; **5**, 425-75-2; **6**, 109244-09-9; **8**, 34065-73-1; **9**, 500-73-2; **10**, 109244-10-2; **11**, 109244-11-3; **12**, 109244-13-5; **13a**, 107-11-9; **13b**, 62-53-3; **13c**, 109-89-7; **13d**, 100-61-8; **14a**, 383-65-3; **14b**, 404-24-0; **14c**, 360-92-9; **14d**, 345-81-3; **15** (R = CH_2=$CHCH_2$), 109244-16-8; **16**, 109244-14-6; TFAT, 68602-57-3; THF, 109-99-9; CF_3CO_2H, 76-05-1; $MeCH_2OCH_2Me$, 60-29-7; 4-$MeOC_6H_4OMe$, 150-78-7; C_6H_5OMe, 100-66-3; C_6H_5COMe, 98-86-2; MeO_2CCH_2CH=$CHCO_2Me$, 5164-76-1; 4-$MeC_6H_4SO_2Cl$, 933-00-6; $(C_6H_5)_3CCl$, 76-83-5; $(C_6H_5)_3CTf$, 64821-69-8; $(4\text{-}MeC_6H_4)_2S$, 620-94-0; CF_3SO_3H, 1493-13-6; 2-methylcyclohexanone, 583-60-8; pyridine, 110-86-1; anthracene, 120-12-7; 9-(trifluoroacetyl)anthracene, 53531-31-0.

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