Anal. Calcd. for $C_{18}H_6F_6O_2S_2$: C, 50.00; H, 1.38. Found: C, 49.62; H, 1.41.

o-Trifluoromethylthiobenzoic Acid-S-Phenyl Ester. Benzoyl chloride (1.6 grams) was added at room temperature to a solution of 1.8 grams of *o*-trifluoromethylthiophenol in 5 ml. of dry pyridine. After standing 1 hour, the mixture was diluted with water and acidified with hydrochloric acid. An oily product was separated, which after cooling was solidified and recrystallized in dilute alcohol.

Acetonyl o-Trifluoromethylphenyl Sulfide. A solution of 10 grams of *o*-trifluoromethylthiophenol in 30 ml. of ethanol an hour with 1.5 grams of chloroacetone. The mixture was diluted with water and extracted with chloroform.

The quinolinecarboxylic acid derivatives (Table I) were prepared by refluxing this ketone for 20 hours with isatin or bromoisatin and alcoholic potassium hydroxide.

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Some Organic Tetrafluoroborates

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The preparation of several new organic tetrafluoroborates by treatment of the corresponding methiodides with boron trifluoride etherate is reported. The preparation of trimethyl sulfonium tetrafluoroborate S-oxide is also discussed.

THE PREPARATION of tetrafluoroborates most frequently requires the use of tetrafluoroboric acid (*3, 12, 17*), metal salts of this acid such as silver and copper tetrafluoroborates (*4, 11*), boron trifluoride etherate (*13, 16*), or such reagents as triethyloxonium tetrafluoroborate (*1, 5, 10*). As part of a program to synthesize organic compounds for testing as herbicides and fungicides, and for other biological applications, a series of organic tetrafluoroborates have been prepared, presumably according to the following stoichiometry (*16*):

$$4(C_2H_5)_2O \cdot BF_3 + 3[R_4\overset{+}{N}]\,I^- \rightarrow 3[R_4\overset{+}{N}]\,BF_4^- + 3C_2H_5I + B(OC_2H_5)_3 + (C_2H_5)_2O$$

Pyridinium, picolinium, quinolinium, sulfonium, and pyrylium tetrafluoroborates have been prepared readily, by treating the corresponding methiodides with boron trifluoride etherate. The results of this work are summarized in Table I.

This paper also describes the preparation of trimethylsulfonium tetrafluoroborate *S*-oxide (*14, 18*) from the cor-

Table I. Organic Tetrafluoroborates, $[R]^+[BF_4]^-$

[R]	M.P., °C.	Recrystg. Solvent	Yield, %	Formula	Calcd., % C	H	B	F	N	Found % C	H	B	F	N
	10–11.5[a]	MeOH	49	$C_6H_8BF_4N$	39.8	4.5	6.0	42.0	7.7	40.1	4.1	6.4	42.4	8.0
	70–71.5	MeOH–Et_2O	61	$C_7H_{10}BF_4N$	43.1	5.2	5.5	39.0	...	43.2	4.9	5.8	38.8	...
	75–76.5	EtOH	82	$C_{10}H_{10}BF_4N$	52.0	4.4	4.7	32.9	6.0	52.2	4.4	4.7	33.0	6.1
	62–64	MeOH–Et_2O	59	$C_7H_{17}BF_4S$	38.2	7.8	4.9	34.5	S 14.6	38.1	8.0	4.6	34.5	S 14.4
	127–128[b]	MeOH	59	$C_8H_{11}BF_4OS$	39.7	4.6	4.5	31.4	13.2	39.5	4.7	4.3	31.2	13.1
	273–275[c]	CH_3CN	57	$C_3H_9BF_4OS$	20.0	5.0	6.0	42.3	17.8	20.1	5.2	6.2	41.9	17.6

[a] *1-Methylpyridinium tetrafluoroborate* is a liquid at room temperature. With the exception of trimethylsulfonium tetrafluoroborate *S*-oxide [corresponding iodide melts 200° C. (*7*)] the tetrafluoroborates listed in Table I have significantly lower melting points than their corresponding iodides. [b] This compound appeared to be considerably more stable on storage than did the known related 4-ethoxy-2,6-dimethylpyrylium tetrafluoroborate (*11*), a sample of which was prepared at the same time. None of the tetrafluoroborates listed in this table appeared hygroscopic; all remained unchanged in appearance after two months storage. [c] Decomposition.

This paper also describes the preparation of trimethylsulfonium tetrafluoroborate *S*-oxide (*14, 18*) from the corresponding iodide (*7*). Treatment of trimethylsulfonium iodide *S*-oxide with boron trifluoride etherate failed to produce the desired *S*-alkylated tetrafluoroborate, probably because of lack of solubility of the iodide in the reaction medium. Reaction of dimethyl sulfoxide with silver tetrafluoroborate, followed by treatment with methyl iodide, produces the known *O*-alkylated tetrafluoroborate (*11*). The reaction of the preformed trimethylsulfonium iodide *S*-oxide with silver tetrafluoroborate leads to the formation of the *S*-alkylated isomer:

$$(CH_3)_2S{=}O + AgBF_4 \xrightarrow{ClCH_2CH_2Cl} [(CH_3)_2\overset{+}{S}{-}O{-}Ag]BF_4^-$$

$$\xrightarrow{CH_3I} \underset{I}{[(CH_3)_2\overset{+}{S}{-}O{-}CH_3]BF_4^-}$$

$$[(CH_3)_3\overset{+}{S}{=}O]I^- + AgBF_4 \xrightarrow{ClCH_2CH_2Cl} \underset{II}{[(CH_3)_3\overset{+}{S}{=}O]BF_4^-} + AgI$$

The known *O*-alkylated derivatives of dimethyl sulfoxide have relatively low melting points and undergo rapid hydrolysis (*15*). In accord with these findings, Meerwein, Hedreich, and Wunderlich (*11*) observed that the *O*-alkylated tetrafluoroborate (I) had a relatively low melting point (108° C.) and was rapidly hydrolyzed, regenerating dimethyl sulfoxide. The *S*-alkylated isomer (II) has a high melting point (275° C.,) and can be recrystallized from water without change.

EXPERIMENTAL

Materials. Boron trifluoride ether complex, 47%, practical grade, was obtained from Matheson, Coleman, and Bell, division of the Matheson Co., Inc. The requisite methiodides were prepared by standard literature methods: 1-methylpyridinium iodide (*9*), 1-methyl-4-picolinium iodide (*9*) 1-methylquinolinium iodide (*8*), *n*-amyldimethylsulfonium iodide (*2*), 2,6-dimethyl-4-methylthiopyrylium iodide (*6*), and trimethylsulfonium iodide *S*-oxide (*7*).

General Method for Preparing Tetrafluoroborates Using Boron Trifluoride Etherate. The appropriate methiodide was combined with a 2.5 molar excess of boron trifluoride etherate under a dry nitrogen atmosphere. The mixture was stirred and heated at 50° C. for 2.5 hours. An additional 2.5 molar excess of boron trifluoride etherate was added, and heating at 50° C. continued another 2.5 hours. The red-brown solution was cooled to room temperature, and a large volume of ether was added to precipitate the product. Some products were obtained as dark colored oils; these were separated and washed repeatedly with ether, then crystallized and recrystallized from the appropriate solvent (Table I).

Trimethylsulfonium Tetrafluoroborate S-Oxide. Trimethylsulfonium iodide *S*-oxide (28.6 grams, 0.13 mole) was added to a solution of anhydrous silver tetrafluoroborate (25.4 grams, 0.13 mole) in 500 ml. of 1,2-dichloroethane. The mixture was stirred at room temperature for 24 hours under a dry nitrogen atmosphere. Filtration of the reaction mixture provided 53 grams of a yellow solid (either a loose addition complex or an intimate mixture of silver iodide with the desired tetrafluoroborate). This solid was subjected to continuous extraction with methanol (Soxhlet) for 3 days. The desired tetrafluoroborate readily crystallized from the methanol extract on cooling to room temperature. Meerwein, Hedreich, and Wunderlich (*11*) had extracted their crude reaction product with acetonitrile to isolate the *O*-alkylated tetrafluoroborate. The *S*-alkylated product could be recrystallized without change form water or from acetonitrile.

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