Anal. Calcd. for $C_{19}H_{16}O_2S_2$: C, 67.05; H, 4.71; S, 18.82; mol. wt., 340. Found: C, 66.99; H, 4.72; S, 18.54; mol. wt.,[10] 339.

p-Phenylsulfonylphenyl *p*-tolyl sulfide was oxidized by hydrogen peroxide in acetic acid to *p*-phenylsulfonylphenyl *p*-tolyl sulfone, m.p. 219–220°, in 73% yield.

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(10) Molecular weight was determined on a Mecrolab vapor pressure osmometer in chloroform solution.

Organic Fluorine Compounds. XXIX.[1] Thiol Fluoroformates

GEORGE A. OLAH, STEPHEN J. KUHN,
AND ROBERT E. A. DEAR

*The Dow Chemical Company, Eastern Research Laboratory,
Wayland, Massachusetts 01778*

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Although thiol chloroformates[2] are well known, the corresponding thiol fluoroformates, RSC(O)F, have not yet been reported in the literature. It was therefore of interest to investigate the preparation of this new class of fluoro-organic compounds.

Two simple preparations of alkyl- and arylthiol fluoroformates were developed starting either from the corresponding thiol chloroformates or thiols (thiophenols).

A.—Thiol fluoroformates can be considered as acyl fluorides. The Colson–Fredenhagen method of preparation using anhydrous hydrogen fluoride as a fluorinating agent under our previously described conditions[1] was successfully applied.

$$\mathrm{RSC(O)Cl + HF \longrightarrow RSC(O)F + HCl}$$

Table I summarizes the data obtained for the thiol fluoroformates prepared.

TABLE I
RSC(O)F

R	B.p., °C. (mm.)	Yield, %	% S Calcd.	% S Found	% F Calcd.	% F Found
Methyl	65	89	34.04	33.92	20.20	20.11
Ethyl	82–83	91	29.69	29.60	17.59	17.50
n-Propyl	50–51 (38)	90	26.22	26.17	15.57	15.48
i-Propyl	80–82	86	26.22	26.13	15.57	15.43
Butyl	135–137	93	23.53	23.41	13.97	14.06
Phenyl	65 (7)	94	20.51	20.50	12.17	12.16
p-Chlorophenyl	93–95 (10)	90	16.79	16.71	9.97	9.81
p-Fluorophenyl	66–68 (7)	93	18.38	18.32	21.83	21.76

B.— Thiol fluoroformates were also obtained directly from the corresponding thiols and thiophenols without the intermediate preparation of the thiol chloroformates. The reaction was carried out in accordance with previously reported method of Olah and Kuhn[3] for the preparation of alkyl fluoroformates. The corresponding thiols or thiophenols were treated with carbonyl chloride fluoride (or carbonyl bromide fluoride) in the presence of a tertiary amine in an inert solvent such as heptane. A 75–85% yield of thiol fluoroformate was

$$\mathrm{RSH + ClC(O)F \longrightarrow RSC(O)F + HCl}$$

achieved, with practically no chloroformate (bromoformate) formed as by-product in the reaction.

The thiol fluoroformates are stable liquids with a characteristic odor. When pure they do not possess lacrimatory activity. Their infrared spectra show a strong C–F stretching vibration at about 1050 cm.$^{-1}$ and a strong C=O stretching vibration at about 1800 cm.$^{-1}$ (consisting of a close doublet).

Experimental

A.—The thiol chloroformate (0.5 mole) was cooled to about −20° and 2.5 moles of anhydrous hydrogen fluoride was condensed into the system with stirring (Teflon-coated magnetic stirrer). The reaction was carried out in a plastic or fused-silica reaction vessel protected in the usual way from atmospheric moisture. Upon completion of the addition of hydrogen fluoride, the reaction mixture was continuously stirred and permitted to warm slowly to room temperature, over a period of 1 hr. During this time the major part of the unreacted hydrogen fluoride and the hydrogen chloride produced distilled off. The reaction mixture was then washed with ice–water; the organic layer which formed was separated, dried with anhydrous sodium sulfate, and fractionally distilled. Table I gives the observed boiling points and yields obtained.

B.—To a stirred and cooled solution of 54 g. (0.65 mole) of carbonyl chloride fluoride (COClF) in 500 ml. of heptane was added a mixture of 0.5 mole of the appropriate mercaptan (thiophenol) and 0.5 mole of a tertiary amine (triethylamine, pyridine, or dimethylaniline). Stirring was then continued for 45 min. After the reaction was completed the separated amine salt was filtered, the reaction mixture was washed with ice–water, and the organic layer was separated and dried with anhydrous sodium sulfate. The heptane and excess of carbonyl halide were removed by distillation and the product was fractionated as in A. Yields obtained varied from 75–85%.

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(3) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **21**, 1319 (1956).

Hydrolysis of Simple Furans.[1] Products of Secondary Condensation[2]

D. S. P. EFTAX AND A. P. DUNLOP

*The Quaker Oats Company, John Stuart Research Laboratories,
Barrington, Illinois*

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In connection with studies relating to the acid-catalyzed polymerization of 2-methylfuran, our attention was drawn to a specific compound invariably formed whenever even a small amount of water was present in the reaction mixture. This compound proved to be 5,5-bis(5-methyl-2-furyl)pentan-2-one (IV).

In aqueous acidic medium at reflux, methylfuran (I) undergoes the expected cleavage to form 4-oxo-

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(1) For a general review, see A. P. Dunlop and F. N. Peters, "The Furans," American Chemical Society Monograph 119, Reinhold Publishing Corp., New York, N. Y., 1953, Chapter 14.

(2) Presented by A. P. Dunlop at the 16th Annual Kansas City Chemistry Conference, Nov. 1964.