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.

Acknowledgment.—This investigation was supported by Public Health Service Research Grant No. CA-04536-06 from the National Cancer Institute.

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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

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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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[1] Part XXVIII: *J. Org. Chem.*, **27**, 2667 (1962).

[2] O. Salomon, *J. prakt. Chem.*, [2] **7**, 252 (1873); R. Riemschneider and O. Lorenz, *Monatsh. Chem.*, **84**, 518 (1953); M. H. Rivier, *Bull. soc. chim. France*, [4] **1**, 733 (1907); M. H. Rivier and P. Richard, *Helv. Chim. Acta*, **8**, 490 (1925); F. Arndt, *Ber.*, **56**, 1983 (1923); H. Bretschneider and H. Haas, *Monatsh. Chem.*, **81**, 939 (1950); H. Tilles, *J. Am. Chem. Soc.*, **81**, 714 (1959); V. A. Rudenko, *et al.*, *J. Gen. Chem. USSR*, **17**, 2256 (1947).

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

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

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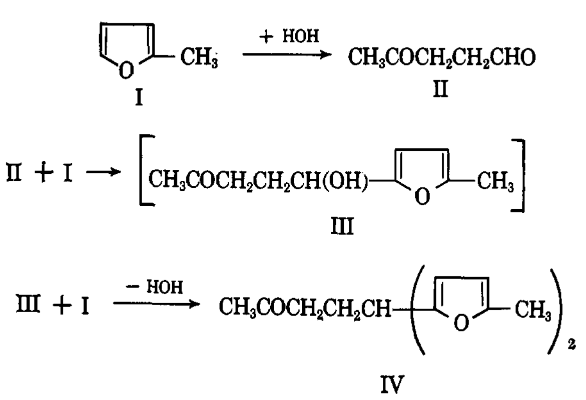
[1] For a general review, see A. P. Dunlop and F. N. Peters, "The Furans," American Chemical Society Monograph 119, Reinhold Publishing Corp., New York, N. Y., 1953, Chapter 14.

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



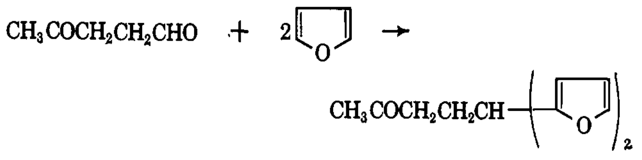
pentanal (II), which condenses with I to give IV, presumably by way of the intermediate carbinol III. The great facility with which the secondary condensation reaction goes forward explains the failure[3] to isolate II in more than taken yield. However, when the starting furan compound is blocked in both α-positions, no such secondary reaction can take place and the simple hydrolysis product may be obtained in high yield (*e.g.*, 2,5-dimethylfuran → 2,5-hexanedione[4]).

Obviously, if it were possible to effect immediate separation of II from the medium of its formation, high yields of this simple cleavage product should be obtainable from methylfuran. Wilson[5] reported 23% yield of the bis-2,4-dinitrophenylhydrazone of II when the reaction was carried out in 2 *N* HCl in the presence of the reagent. We were able to achieve even more effective interception of the secondary condensation reaction by a modification of Wilson conditions which produced the indicated derivative of II in 67% yield,

Other means of interception were attempted. In one of these, it was our objective to attempt the direct formation of 5,5-bis(hydroxyphenyl)pentan-2-one (compare IV) by hydrolytic cleavage of methylfuran in the presence of an excess of phenol. Essentially all of the latter was recovered unchanged, together with IV in *ca.* 50% yield based on the initial methylfuran. This is an interesting result. It indicates that, in aqueous acidic medium, the open α-position of methylfuran is more reactive toward aldehydes than are the *ortho* and *para* positions of phenol. In basic medium, of course, methylfuran is inert to aldehydes.

While no actual kinetic data were obtained, it is clear that the secondary reaction, condensation of an aldehyde with methylfuran, proceeds with much greater facility than does the cleavage reaction. In fact, by deliberately providing an aldehyde initially, condensation can go forward essentially to the exclusion of cleavage. Thus, acetaldehyde and methylfuran in cold aqueous sulfuric acid give rise to 1,1-bis(5-methyl-2-furyl)ethane in 90% yield.[6]

While this investigation was concerned mainly with methylfuran, it is indicated that furan behaves similarly. Thus, reaction of 4-oxopentanal with furan gave rise to 5,5-bis(2-furyl)pentan-2-one (V). In an attempt to prepare V directly by reaction of methylfuran with excess furan in aqueous acidic medium, we obtained a mixture of IV and V, and probably the related 5-(2-furyl)-5-(5-methyl-2-furyl)pentan-2-one.



V

Experimental[7]

4-Oxopentanal Dimethylal.—As prepared initially by, Harries method,[3] this compound was obtained in 10% crude yield together with about 50% high-boiling compounds and tars. A better yield was obtained by refluxing a solution of 62 g. of 2-methylfuran in 350 g. of methanol for 24 hr. over 8 g. of Rohm and Haas XE-100 moist cation-exchange resin. The resin was held in a porous cup above the mixture. At the end of the reaction period the mixture was concentrated at 35° (25 mm.) and the residue was distilled up to *ca.* 110° (10 mm.) to give 21% of crude 4-oxopentanal dimethylal. Higher boiling material and tars accounted for 30% of the residue. A purified sample of the acetal, $n^{25}\text{D}$ 1.4218, boiled at 85–87° (15 mm.). Hydrolysis of the acetal to 4-oxopentanal (II), b.p. 73–78° (15 mm.), was accomplished in practically quantitative yield by refluxing in methanol in the presence of about 8% of sulfonic-type cation-exchange resins.

Ethylidene Bis(5-methyl-2-furan).—To a solution of 164 g. (2 moles) of 2-methylfuran and 55 g. (1.25 moles) of acetaldehyde at 0°, was added a solution of 65 g. of water and 8.5 ml. of concentrated sulfuric acid. The mixture was stirred for 15 hr. at 0–1°. The reaction mixture was then worked up according to a known procedure[6] to give 171.5 g. (90% yield) of the title compound, b.p. 107–109° (11 mm.).

Bis-2,4-dinitrophenylhydrazone of 4-Oxopentanal.—Incremental addition from a microburet of 0.9 g. (0.11 mole) of 2-methylfuran over a period of 13 min. to a solution maintained at 50–55° containing 5 g. of 2,4-dinitrophenylhydrazine, 450 ml. of water, and 45 ml. of concentrated sulfuric acid resulted, after washing of the precipitate, in 3.4 g. (67% crude yield) of the derivative, m.p. 222–225° dec. Wilson[5] reported m.p. 231° dec. for the purified derivative.

A compound having the composition of 1(2,4-dinitrophenyl)-6-methyl-1,4-dihydropyridazine was obtained by addition over 6 hr. of a solution of 0.9 g. (0.11 mole) of 2-methylfuran in 30 ml. of methanol to a solution maintained at reflux containing 5 g. of 2,4-dinitrophenylhydrazine, 30 ml. of water, 30 ml. of concentrated hydrochloric acid, and 170 ml. of methanol. On cooling, 1.6 g. of brown material resulted. After three recrystallizations from 95% ethanol, the brown crystals melted at 153.5–154.5°. About 2 g. of 2,4-dinitrophenylhydrazine was recovered.

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.84; N, 21.37. Found: C, 50.45; H, 3.85; N, 21.20.

Attempted Preparation of 5,5-Bis(*p*-hydroxyphenyl)pentan-2-one.—Two runs were made using 41 g. of 2-methylfuran (0.5 mole), 110 g. of phenol (1.17 moles), and a solution of 45 ml. of

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(3) C. Harries, *Ber.*, **31**, 37 (1898).

(4) D. M. Young and C. F. Allen, "Organic Synthesis," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 219.

(5) C. L. Wilson, *J. Am. Chem. Soc.*, **70**, 1313 (1948).

(6) K. Tsuboyama and M. Yanagita, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **53**, 318 (1959); see also L. L. J. Fauqué, U. S. Patent 2,681,917 (June 22, 1954); R. G. Ackman, W. H. Brown, and G. F. Wright, *J. Org. Chem.*, **20**, 1147 (1955); W. H. Brown and H. Sawatzky, *Can. J. Chem.*, **34**, 1147 (1956); Yu. K. Yur'ev, *et al.*, *Zh. Obshch. Khim.*, **30**, 3214 (1960); *Chem. Abstr.*, **55**, 19890*d* (1961).

(7) Analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer; samples were in the liquid phase (0.025-mm. cell). Melting points (open capillaries) and boiling points are not corrected. Yields have been calculated, generally, on the furan charged and do not necessarily indicate optimum conditions.

concentrated sulfuric acid in 250 ml. of water. In the first, the above-named components were refluxed for 1 hr. at 60°; in the second, 2-methylfuran was added over a period of 2.5 hr. to the aqueous phenolic acidic solution which was maintained at 60°. In both instances, on work-up, compound IV (confirmed by derivative preparation and also by boiling point) was obtained in *ca.* 50% yield based on the 2-methylfuran charged. Pure phenol recovery was *ca.* 80 and 87%, respectively, the remaining phenol probably being in the aqueous phase and washings. Higher boiling material and tars amounted to *ca.* 13 g. in each case.

5,5-Bis(5-methyl-2-furyl)pentan-2-one (IV).—To a stirred solution of 160 g. (1.65 moles) of concentrated sulfuric acid and 500 g. (28 moles) of water was added 82 g. (1 mole) of 2-methylfuran. The mixture was refluxed for 1 hr. at 60°, cooled, and then transferred to a separatory funnel. The top organic layer (77 g.) was neutralized and then distilled *in vacuo*; 2-methylfuran (10 g., 0.12 mole) was first recovered and then 54 g. (66%) of pale yellow liquid, b.p. 125–128° (1.25 mm.), $n^{25}\text{D}$ 1.5045, leaving a residue of 7 g. On subsequent reuses of the bottom aqueous acidic layer, the yield of the title compound improved and the percentage of 2-methylfuran accounted for approached 100%. Analyses and preparation of derivatives were conducted using a purified sample: b.p. 108° (0.25 mm.); $n^{25}\text{D}$ 1.5050; ν 1715 (vs, carbonyl), 1563 (s)*, 1450 (m), 1362 (s), 1215 (vs), 1156 (m), 1018 (vs, ether), 998 (m), 960 (m), 944 (m), 932 (m), and 782 (vs)* cm.$^{-1}$. The asterisk marks absorbancies reported to be characteristic of 2,5-disubstituted furans,[8,9] the others are consistent with the furan structure.[10–12]

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.36. Found: C, 72.89; H, 7.41.

The bright orange 2,4-dinitrophenylhydrazone,[13] recrystallized from 95% ethanol, melted at 115–116°.

Anal. Calcd. for $C_{21}H_{22}N_4O_6$: C, 59.14; H, 5.20; N, 13.14. Found: C, 59.08; H, 5.13; N, 12.83.

The white semicarbazone,[13] m.p. 162–163°, was recrystallized from 50% ethanol.

Anal. Calcd. for $C_{16}H_{21}N_3O_3$: C, 63.34; H, 6.98; N, 13.85. Found: C, 63.35; H, 6.96; N, 13.67.

The hydantoin[14] was obtained as a white powder after recrystallization from 50% ethanol and melted at 131.5–132.5°.

Anal. Calcd. for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.38; H, 6.46; N, 8.82.

5,5-Bis(2-furyl)pentan-2-one (V).—This compound was prepared by refluxing 25 g. (0.17 mole) of 4-oxopentanal dimethylal, 102 g. (1.5 moles) of furan, and 30 g. of 85% phosphoric acid dissolved in 6.5 ml. of water in 300 ml. of benzene for about 6 hr. Neutralization of the reaction mixture, followed by distillation *in vacuo* of the benzene layer, gave the crude material: b.p. 90–96° (0.23 mm.); ν 1720 (vs, carbonyl), 1595 (m), 1505 (vs), 1415 (m), 1362 (vs), 1231 (s), 1150 (vs), 1074 (m)*, 1008 (vs, ether), 942 (s), 922 (m), 909 (m), 883 (s)*, 805 (s)*, and 735 (vs)* cm.$^{-1}$. The asterisk marks absorbancies reported to be characteristic of 2-substituted furans[8–10]; the others are consistent with the furan structure.[11,12]

The orange 2,4-dinitrophenylhydrazone[13] was recrystallized from 95% ethanol and melted at 104–106°.

Anal. Calcd. for $C_{19}H_{18}N_4O_6$: C, 57.28; H, 4.55; N, 14.07. Found: C, 57.42; H, 4.68; N, 14.04.

The colorless semicarbazone,[13] after recrystallization from 50% ethanol, melted at 166–167°.

Anal. Calcd. for $C_{14}H_{17}N_3O_3$: C, 61.07; H, 6.23; N, 15.26. Found: C, 61.13; H, 6.13; N, 15.21.

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[8] M. Fetizon and J. Guy, *Compt. rend.*, **247**, 1182 (1958); *Chem. Abstr.*, **54**, 70*d* (1960).

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[11] A. H. J. Cross, S. G. E. Stevens, and T. H. E. Watts, *J. Appl. Chem.* (London), **7**, 562 (1957); *Chem. Abstr.*, **52**, 4323*b* (1958).

[12] L. Daasch, *Chem. Ind.* (London), 1113 (1958); *Chem. Abstr.*, **53**, 3882*a* (1959).

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 170–171.

[14] H. R. Henze and R. J. Speer, *J. Am. Chem. Soc.*, **64**, 522 (1942).

Hydrogenation in the Pyridine Series. III. Formation of a By-product in the Nickel-Catalyzed Reduction of 2-(2-Hydroxyethyl)pyridine

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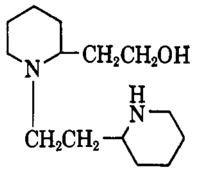
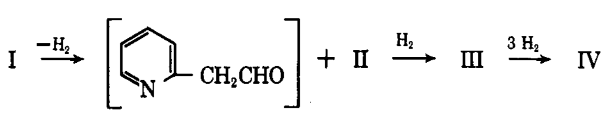
Prior to the investigation of the use of rhodium and ruthenium catalysts in the hydrogenation of pyridines,[1] 2-(2-hydroxyethyl)pyridine (I) was reduced in the presence of Raney nickel at 150° and 130 atm. for 8–15 hr. In addition to 2-(2-hydroxyethyl)piperidine (II), a much higher boiling material was obtained. From elemental analysis a formula of $C_{14}H_{28}N_2O$ was derived. Near-infrared and infrared examinations showed the presence of NH and OH and the absence of the pyridine ring. Structure IV seemed to fit the data on hand.



IV

The structure was corroborated by treating 2-vinylpyridine with II to give 1-[2-(2-pyridyl)ethyl]-2-(2-hydroxyethyl)piperidine (III), which was subsequently hydrogenated at low pressure in the presence of rhodium on a carrier. The resultant product compared in all respects with IV obtained from the high-pressure nickel reduction of I.

The formation of IV from II may have taken place in the following manner.[2] We have been able to obtain 5–10% yields of IV by treating I and II under high-pressure hydrogenation conditions with Raney nickel. In the reaction of II alone, under similar conditions, over 60% of it was recovered unchanged. In addition, about 25% of 2-methylpiperidine was obtained.[3]



Compound IV could also form by dehydration of I to 2-vinylpyridine which, in turn, would follow the series of reactions which was used to corroborate the

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[1] M. Freifelder, R. M. Robinson, and G. R. Stone, *J. Org. Chem.*, **27**, 284 (1962); M. Freifelder and G. R. Stone, *ibid.*, **26**, 3805 (1961).

[2] The phenomenon of catalytic dehydrogenation of alcohols and subsequent reductive alkylation of amines with the resultant aldehyde has been pointed out by R. G. Rice and E. J. Kohn [*J. Am. Chem. Soc.*, **77**, 4052 (1955)]. The formation of carbonyl compound resulting from such dehydrogenation has been reported by B. B. Corson and H. Dressler [*J. Org. Chem.*, **21**, 474 (1956)].

[3] M. G. Reinecke and L. R. Kray [*ibid.*, **29**, 1737 (1964)] point out that dehydroxymethylation is the primary process occurring during attempted cyclization of II; E. R. Lavagnino, R. R. Chauvette, W. N. Cannon, and E. C. Kornfeld [*J. Am. Chem. Soc.*, **82**, 2609 (1960)] report dehydroxymethylation to 2-methylpiperidine on heating II in water with a large amount of Raney nickel.