Acknowledgment.—The author is grateful to the Humble Oil and Refining Company for permission to publish these results.

A New Selective Desulfurization Method[1]

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Received November 2, 1964

The catalysis exhibited by nickel salts on the hydrolysis of sodium borohydride was described by Schlesinger and co-workers[2] in 1953. The black material resulting from the reaction of nickel salts with sodium borohydride is believed to be nickel boride, Ni_2B,[2,3] and has been reported[3,4] to be a selective hydrogenation catalyst nearly as active as Raney nickel.

The first use of nickel boride as a desulfurization reagent was reported[5] in 1963 when it was found possible, by varying the amount of nickel boride, to replace one or both sulfur atoms of a mercaptole by hydrogen. With this apparent selectivity a further study of nickel boride as a desulfurization reagent was in order.

The use of nickel boride for desulfurization has now been extended and it has been shown to be an effective reagent for desulfurization of mercaptans, sulfides, and sulfoxides in yields nearly comparable to Raney nickel (Table I). The utility of nickel boride as a desulfurization reagent for disulfides is diminished by the formation of the corresponding sulfide as a by-product. Furthermore, the lack of desulfurization activity toward sulfones by nickel boride indicates a high degree of selectivity when compared with Raney nickel, which is known to cleave many simple sulfones in high yield.[6] To determine the extent of this selectivity, *p*-phenylsulfonylphenyl *p*-tolyl sulfide was treated with both nickel boride and Raney nickel. As expected, the Raney nickel treatment produced high yields of both benzene and toluene, whereas the nickel boride treatment produced high yields of toluene and phenyl sulfone.

TABLE I

DESULFURIZATION WITH RANEY NICKEL AND NICKEL BORIDE

	% yield of toluene[a]	
Compd.	Nickel boride	Raney nickel
p-Toluenethiol	60	91
p-Tolyl disulfide	37[b]	85
p-Tolyl sulfide	72	86
p-Tolyl sulfoxide	80	100
p-Tolyl sulfone	0	88
p-Phenylsulfonylphenyl *p*-tolyl sulfide	84[c,d]	91[e]

[a] Percentages were determined by vapor phase chromatographic analysis on a 12-ft. column packed with di-*n*-decyl phthalate on Chromasorb W. [b] *p*-Tolyl sulfide (5.7% of theoretical) was isolated and identified by melting point. [c] Phenyl sulfone (91% of theoretical) was isolated and identified by melting point and mixture melting point with an authentic sample. [d] There was no detectible amount of benzene by vapor phase chromatographic analysis. [e] Benzene (100% of theoretical) was observed by vapor phase chromatographic analysis.

Despite the fact that the yields of desulfurization products are lower when nickel boride is used than when Raney nickel is used, nickel boride does have significant advantages over Raney nickel as a desulfurization reagent. First of all, nickel boride can be used to remove selectively only a single sulfur atom of a mercaptole or to remove selectively mercapto, sulfide, and sulfoxide groups without disturbing sulfone groups which may be present. Second, since nickel boride is more easily prepared, the necessity for a tedious preparation of Raney nickel is eliminated. Third, nickel boride is completely nonpyrophoric[3] and is less hazardous than Raney nickel. Fourth, since the nickel boride is generated from easily handled materials, the exact amounts can be determined, in contrast to Raney nickel which cannot be weighed accurately because the pyrophoric solid must be kept wet.

In summary, a selective new desulfurization method using nickel boride has been developed, which is safer and in many instances more convenient than desulfurization with Raney nickel.

Experimental[7]

A Generalized Procedure for Desulfurization Using Nickel Boride.—In a flask fitted with an addition funnel, a stirrer, and a condenser was placed the organic sulfur compound, 10 mole equiv. of nickelous chloride hexahydrate, and ethanol solvent. After the system had been swept with a stream of nitrogen for 15 min., an aqueous solution of 30 mole equiv. of sodium borohydride was added dropwise, while the reaction mixture was being cooled in an ice bath. The evolved hydrogen was passed through a vapor trap cooled in a Dry Ice bath. After addition was complete, the reaction mixture was refluxed for 7 hr. and distilled until the distillate showed no trace of toluene by vapor phase chromatographic analysis. The distillation residue was filtered and washed with acetone to remove any remaining organic material. The acetone solution was evaporated and the residual organic material was identified.

A Generalized Procedure for Desulfurization Using Raney Nickel.—In a flask, fitted with a stirrer and reflux condenser, was placed the organic sulfur compound (2.0 g.), W2 Raney nickel[8] (7 level teaspoons or approximately 21 g. of nickel), and ethanol (100 ml.). This mixture was refluxed 7 hr. and then water (50 ml.) was added. The mixture was distilled until the distillate failed to show the presence of toluene by vapor phase chromatographic analysis.

Preparation of *p*-Phenylsulfonylphenyl *p*-Tolyl Sulfide.[9]—A mixture of *p*-bromophenyl phenyl sulfone (29.7 g., 0.1 mole), cuprous *p*-tolylmercaptide (18.65 g., 0.1 mole), quinoline (84 ml.), and dry pyridine (2 ml.) was refluxed 36 hr. with stirring. The reaction mixture was poured slowly into a mixture of cracked ice and concentrated hydrochloric acid and allowed to stand for 2 hr. This mixture was filtered and both residue and filtrate were washed several times with chloroform. The chloroform washings were combined and treated twice with charcoal. After evaporation of the chloroform, the residue was recrystallized from absolute ethanol to give *p*-phenylsulfonylphenyl *p*-tolyl sulfide (50% yield), m.p. 107–110°.

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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.

[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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Received November 3, 1964

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		% F	
			Calcd.	Found	Calcd.	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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Hydrolysis of Simple Furans.[1]
Products of Secondary Condensation[2]

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Received November 23, 1964

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.