Experimental

The higher alcohols, alkyl bromides, and mercaptans were prepared by standard methods and fractionated through precision stills,[3] cuts taken of 1° or less. Ethyl mercaptan was purchased and methyl mercaptan was prepared according to Klason.[4]

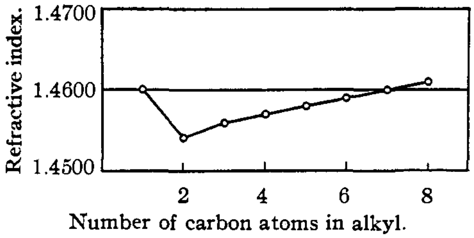

Fig. 3.—Refractive indices of normal thiolacetates.

Preparation of the Esters. Method (a).—To the mercaptan in a flask packed in ice the calculated amount of acetyl chloride was added slowly from a dropping funnel through a reflux condenser. The flask was allowed to come to room temperature at which it was kept for three days and then emptied into water. The ester was washed, dried over calcium chloride, and distilled. Four hundred and ten grams of ethyl thiolacetate, b. p. 115.5–116.5°, was prepared by this method with yields from 60–70%; also 55 g. of *n*-propyl, b. p. 138–140°, yield 70%, and 67 g. of *n*-butyl, b. p. 162–164°, yield 91%.

Method (b).—A mixture of 1 mole of mercaptan and 1.2 moles of acetanhydride and one-fifth of its weight of anhydrous sodium acetate was refluxed for an hour by the use of an oil-bath which was raised from 130° at the start to 150° at the end of this time. The reaction usually became so vigorous, after short heating, that the flask had to be removed from the oil-bath for a time. The cooled mixture was poured into water, the ester separated, washed free of acid, dried, and distilled. Thirty-three grams of ethyl thiolacetate, b. p. 115.5–116.5°, yield 78.5%, was prepared by this method; also 35 g. of *n*-butyl, b. p. 162–164°, yield 95%; 68 g. of *n*-amyl, b. p. 182.5–185°, yield 92.5%; 64 g. of *n*-hexyl, b. p. 204–206°, yield 94%; 108 g. of *n*-heptyl, b. p. 145.5–146° at 70 mm., yield 91%; and 48 g. of *n*-octyl, b. p. 146.5–147° at 38 mm., yield 93%. Seventy grams of the methyl thiolacetate, b. p. 98–99°, was prepared by passing methyl mercaptan directly into the boiling anhydride–sodium acetate mixture.

Method (c).—A mixture of 40 g. of sodium hydroxide, 75 cc. of water, and 1.2 mole of mercaptan was poured over 500 g. of shaved ice in a flask and 1.25 mole of acetanhydride was added rapidly with vigorous stirring which was continued for five minutes. The ester was separated immediately and worked up as in method (b): 100 g. of ethyl thiolacetate, b. p. 115.5–116.5°, yield 79.3%, was prepared by this method.

Conclusion

A series of normal alkyl thiolacetates have been prepared by various methods and their physical properties determined.

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[3] Ellis and Reid, THIS JOURNAL, **54**, 1685 (1932).

[4] Klason, *Ber.*, **20**, 3049 (1887).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

Some Monothioformals

BY F. W. WENZEL, JR., AND E. EMMET REID

Formals are well known, and a few dithioformals have been prepared, but the intermediate monothioformals, $ROCH_2SR$, have been neglected.[1] The purpose of this investigation was to prepare and study several of these, so as to compare them with the formals and the dithio compounds.

They are obtained readily from a chloromethyl alkyl ether and a mercaptan in alkaline solution

$$RSNa + ClCH_2OR = RSCH_2OR + NaCl$$

They can be made also from lead mercaptides in benzene solution. On account of side reactions the yields are only fair, about 50%. Care must be taken to get rid of any remaining chloromethyl ether, otherwise hydrochloric acid will be generated and the product decomposed.

The compounds chosen for study were the ethyl, *n*-propyl, and *n*-butyl. The data obtained are given in Table I.

The monothioformals are stable; the diethyl compound was refluxed for eight hours without any sensible change. However, if 1% of hydrogen chloride is added, rearrangement takes place and a formal and a dithioformal are obtained, the equilibrium being readjusted as the most volatile constituent is removed. On account of this instability in the presence of acid, care must be taken in the preparation of a monothioformal not to leave any of the chloroether in the crude product.

It is known that a Grignard reagent does not react with formals below 100°.[2] We have found this to be true with a monothioformal. Heating

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[1] Since our work was completed Böhme has made the diethyl derivative. *Ber.*, **69**, 1610 (1936).

[2] Späth, *Monatsh.*, **35**, 319 (1914).

TABLE I

PHYSICAL PROPERTIES AND ANALYSIS OF THE MONOTHIOFORMALS

	B. p., °C. 760 mm.	d^0_4	d^{25}_4	n^{25}_D	Mol. refraction Calcd.	Mol. refraction Found	Sulfur, % Calcd.	Sulfur, % Found	
Diethyl	135.8[3]	0.9363	0.9122	1.4432	34.90	34.94	26.68	26.13	26.20
Di-*n*-propyl	179.2	.9185	.8960	1.4473	44.14	44.23	21.51	21.76	21.11
Di-*n*-butyl	220.0	.9061	.8853	1.4500	53.38	53.51	18.10	18.04	18.27

Ethylal boils 47.8° below and the diethyl methylene mercaptal 48° above the diethyl monothioformal.

the diethyl compound with ethylmagnesium bromide at 100° for five hours decomposed less than one-third of it. Ethyl mercaptan and ethyl propyl ether were identified as the reaction products, which shows that the —SR is replaced more readily than the —OR.

Oxidation of a monothioformal takes place readily, but we have been unable to isolate a sulfone.

Experimental

In the preparation of the monothioformals the mercaptan was dissolved in about five volumes of alcohol and the equivalent amount of sodium hydroxide added. This solution was cooled to 0° and an equivalent of the chloroether added dropwise with stirring. Sodium chloride precipitated at once. The mixture stood overnight and was diluted with an equal volume of water. The top layer was separated, washed with water, dried over potassium carbonate, and fractionated at 100 mm., a 1° cut being taken. There was always a considerable amount of a low boiling fraction, apparently the formal. The boiling points of the best fractions were determined with a Cottrell apparatus with a calibrated thermometer and analysis for sulfur made by a Parr bomb.

A sample of the diethyl monothioformal was refluxed for eight hours and distilled. The boiling point and other properties were unchanged. Into a 90-g. sample (0.75 mole) about 1% of hydrogen chloride was passed. It was refluxed for eight hours, moisture being excluded. Fractionation separated it into two main fractions: (1) 30 g. (0.29 mole) boiling at 85–89° at 760 mm., d^{25}_4 0.8301, n^{25}_D 1.3715; and (2) 48.5 g. (0.36 mole) boiling at 186° and containing 45.87% sulfur, yielded a sulfone, m. p. 103°. Ethylal has b. p. 88° and d^{20}_4 0.8318 and diethyl methylene mercaptal has b. p. 184°, 47.07% sulfur, and gives a sulfone, m. p. 104°.[4]

To 148 g. of the dipropyl monothioformal the Grignard reagent from 137 g. of butyl bromide in ether was added and the mixture refluxed for four hours. By working this up in the usual way 86% of the monothioformal was recovered with unchanged properties and tests for mercaptan were negative. In a second experiment 120 g. of the diethyl derivative was treated with ethylmagnesium bromide, the ether distilled off, and the residue heated to 100° for five hours. The product was worked up as usual and fractionated. The first fraction was ethyl mercaptan, identified by the α-anthraquinone thio ether.[5] The second fraction had b. p. 63.5°, d^{25}_4 0.7360, n^{25}_D 1.3745 which identified it as ethyl *n*-propyl ether, b. p. 61.4, d^{20}_4 0.732, n^{20}_D 1.3695. The third fraction, 71–78° at 100 mm. was the unreacted thioformal and accounted for 70% of that taken.

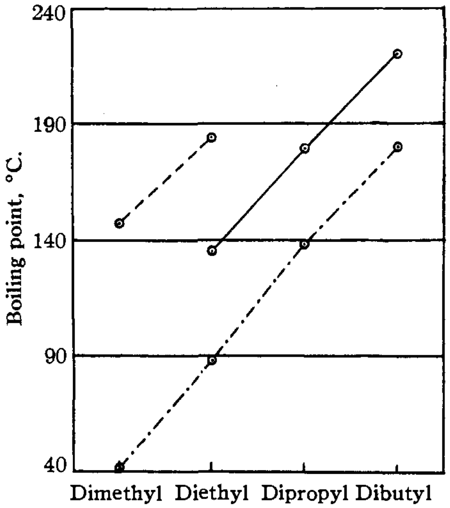

Fig. 1.—Boiling points: monothioformals ———; dithioformals - - - - -; formals -·-·-·-.

Summary

1. Diethyl, di-*n*-propyl and di-*n*-butyl monothioformals were prepared by treating the sodium mercaptide with the chloromethyl alkyl ether, and their physical properties were determined.

2. A monothioformal, heated with hydrogen chloride, rearranges into a formal and a dithioformal.

3. They react, but not readily, with ethylmagnesium bromide.

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(3) Böhme gives 134–136° at 755 mm.

(4) Claesson, *J. prakt. Chem.*, [2] **15**, 176 (1877).

(5) Reid, Mackall and Miller, THIS JOURNAL, **43**, 1199 (1921).