[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Preparation and Properties of a Series of Alkyl Thiolacetates[1]

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

This is a continuation of the comparison of sulfur compounds with their oxygen analogs.[2] The task undertaken was the preparation of the thiolacetates of the normal alcohols, or rather the acetyl derivatives of the mercaptans, from methyl to octyl, and the determination of their physical properties.

Thiol esters usually have been prepared by the action of an acid chloride on a mercaptan or mercaptide. The esters here described were made from the mercaptans (a) by treating them with acetyl chloride, (b) by refluxing them with acetanhydride and sodium acetate, and (c) by dissolving them in strong caustic soda and adding acetanhydride. Method (c) is preferred for the lower mercaptans which are too volatile for (b) and which dissolve readily in aqueous alkali, while (b) is best for the higher members. The properties of these esters are given in Table I and some are plotted in Figs. 1 and 2 along with the corresponding data for the oxygen esters.

TABLE I

Normal alkyl	B. p., °C. 760 mm.	d^0_4	d^{25}_4	n^{25}_D	Mol. refraction Calcd.	Mol. refraction Found	Sulfur, % Calcd.	Sulfur, % Found	
Methyl	98.0[a]	1.0461	1.0170	1.4600	24.03	24.27	35.58	34.89	35.41
Ethyl	116.4[b]	1.0006	0.9739	1.4540	28.65	29.05	30.79	30.93	30.64
Propyl	139.8[c]	0.9789	.9537	1.4558	33.27	33.65	27.14	26.83	26.80
Butyl	163.4	.9628	.9390	1.4570	37.89	38.33	24.26	24.36	24.22
Amyl	185.1	.9511	.9285	1.4579	42.51	42.94	21.93	21.87	21.77
Hexyl	205.8	.9408	.9192	1.4591	47.13	47.66	20.01	19.92	20.18
Heptyl	227.4	.9334	.9128	1.4600	51.74	52.29	18.40	18.40	18.36
Octyl	247.0	.9259	.9058	1.4609	56.36	57.04	17.03	17.15	17.25

[a] Ralston and Wilkinson, THIS JOURNAL, **50,** 2160 (1928) reported 95–96°.

[b] Hepworth and Clapham, *J. Chem. Soc.*, **119,** 1188 (1921), give 116–117°; Baker and Reid, THIS JOURNAL, **51,** 1567 (1929), found 116–117°, d^0_4 1.0008, d^{25}_4 0.9755, r^{28}_D 1.4503.

[c] According to Ralston and Wilkinson, 135–137°.

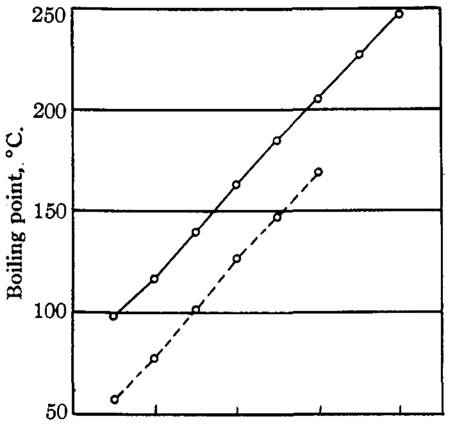

Fig. 1.—Boiling points: normal thiolacetates ———; normal acetates - - - - -.

The amount by which the boiling point of an acetate is raised by the substitution of —S— for —O— is 40° for the methyl and decreases slightly as the series is ascended. Methyl thiolacetate has the same molecular weight as butyl mercaptan and both boil at 98°, but the higher members of the series boil somewhat lower than the mercaptans of the same molecular weight.

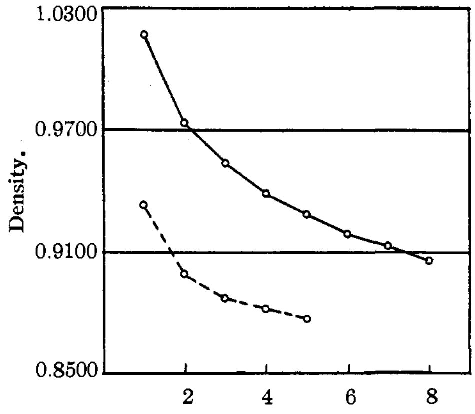

Fig. 2.—Densities: normal thiolacetates at 25° ———; normal acetates at 20° - - - - -.

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[1] Read at the Cincinnati meeting of the American Chemical Society, 1930.

[2] THIS JOURNAL, **37,** 1934 (1915); **38,** 2757 (1916); **39,** 1930 (1917); **54,** 1685 (1932).

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]

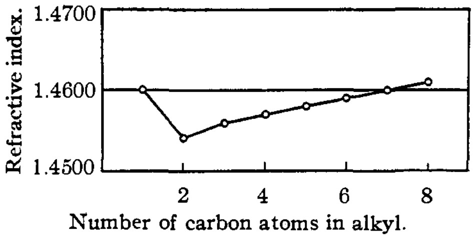

Fig. 3.—Refractive indices of normal thiolacetates.

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.

BALTIMORE, MD.

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

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

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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).