The successive substitution of phenyl groups in ethane materially lowers the stability of the linkage of the ethane carbon atoms so that when three phenyl groups are in the molecule the ethane may be cleaved at 200° over a copper–chromium oxide catalyst. Pentaphenylethane may be cleaved over nickel at temperatures as low as 125°. The labilizing effect (if any) of cyclohexyl groups on the ethane carbon atoms is so small that pentacyclohexylethane was perfectly stable at 200° over nickel or copper–chromium oxide catalysts.

Four cyclohexylethanes and three ethers have been prepared and described for the first time. Further evidence of the activity of the copper–chromium oxide catalyst for the hydrogenation of alkene linkages has been presented.

MADISON, WISCONSIN

THE PREPARATION AND PROPERTIES OF A DOUBLE SERIES OF ALIPHATIC MERCAPTANS[1,2,3]

BY L. M. ELLIS, JR.,[4] AND E. EMMET REID[5]

Though aliphatic mercaptans have been known for nearly a century, our knowledge concerning any of them except a few of the lower ones is not extensive. The purpose of the present investigation was to prepare the normal and alpha secondary mercaptans up to nonyl in high purity for accurate determinations of their physical properties and to provide materials for studies of their reactions, some of which have been published. It seemed desirable to have these series complete for the comparisons of properties within the series and with the corresponding series of alcohols.

The literature on the mercaptans through butyl is too extensive to quote. n-Amyl mercaptan was prepared by Pexters,[6] n-hexyl by Pelouze and

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Cahours,[7] hexane-thiol-2 by Erlenmeyer and Wanklyn,[8] n-heptyl by Wissinger,[9] heptane-thiol-2 by Henry,[10] n-octyl by Kahn,[11] and octane-thiol-2 by Levene and Mikeska,[12] but none of these has been thoroughly studied.

Discussion

For brevity, such details of the experimental work as quantities and yields, along with the values found for the various properties determined, have been arranged in tabular form, Tables I, II, III, IV and V being concerned with various properties, and VI, VII and VIII chiefly with preparation. Included in the former are the mean coefficients of thermal expansion as calculated from the density data, the molal heats of vaporization of the higher mercaptans as calculated from the boiling point data
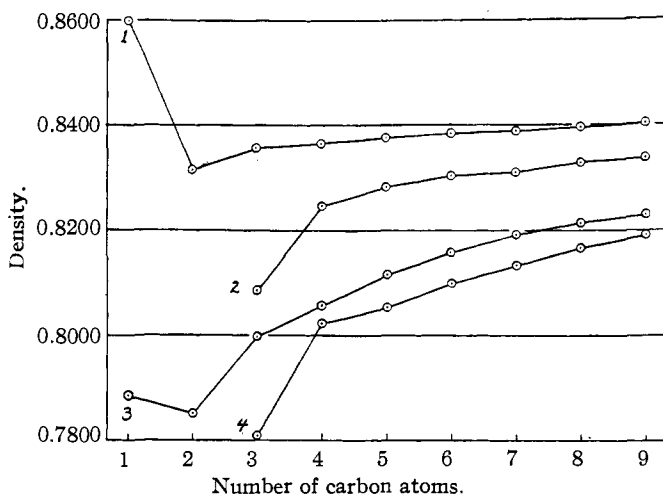
Fig. 1.—Densities of mercaptans and alcohols at 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

by use of the Clausius–Clapeyron equation, and the values for molecular refraction calculated by use of the Lorentz–Lorenz equation. For comparison with the last, values for molecular refraction as computed from atomic refraction data also are given, the two sets of values being headed respectively "found" and "calculated." Values for the atomic refraction of carbon, hydrogen, bromine and hydroxyl oxygen were taken from the

[7] Pelouze and Cahours, Jahresber., 526 (1863).

[8] Erlenmeyer and Wanklyn, Ann., 135, 138 (1865).

[9] Wissinger, Jahresber., 1280 (1887).

[10] Henry, Rec. trav. chim., 28, 444 (1909).

[11] Kahn, Bull. soc. chem. Roumania, 5, 70 (1923).

[12] Levene and Mikeska, J. Biol. Chem., 59, 475 (1924).

work of Eisenlohr,[13] while that for the atomic refraction of sulfur was taken from the work of Price and Twiss.[14] Agreement between the "found" and "calculated" values is very close.

The values determined for the densities and refractive indices at 25° of the mercaptans and higher alcohols are illustrated by Figs. 1 and 3. · To complete the curves, values from the work of Brunel[15] for the densities and refractive indices of the lower alcohols except the density of methyl alcohol, where the value given by Fischler[16] was used, are included in the plot. Resemblances between the curves for the corresponding mercaptans and alcohols are obvious. The point for the density of secondary heptyl mercaptan is apparently low. This may indicate the presence of a slight impurity, although none is shown by the analysis.

Under the heading "expansion" in Tables I, II and V are given the mean coefficients of thermal expansion of the compounds over the range 0–25°. Figure 2 illustrates these for the mercaptans and alcohols. Here again there are obvious similarities between the curves for the corresponding alcohols and mercaptans. In order to obtain values for this property of the lower alcohols, densities obtained from the literature were plotted against temperature and the points for 0 and 25° read from the curves. In all cases only the values given by the same author for a compound were used in making these plots. Coefficients of expansion were calculated from the densities thus obtained using the values given for methyl alcohol by Klason and Norlin,[17] for ethyl alcohol by Winkler,[18] for propanol-1

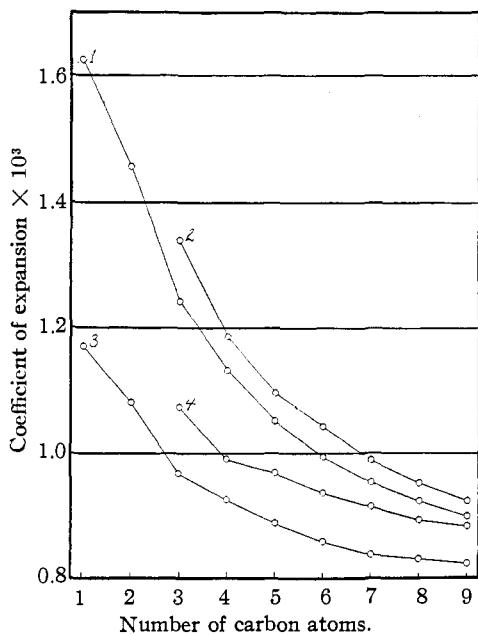Fig. 2.—Mean coefficients of thermal expansion of mercaptans and alcohols from 0 to 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

[13] Eisenlohr, Z. physik. Chem., 75, 605 (1911).

[14] Price and Twiss, J. Chem. Soc., 101, 1263 (1912).

[15] Brunel, Crenshaw and Tobin, THIS JOURNAL, 43, 574 (1921); Brunel, ibid., 45, 1338 (1923).

[16] Fischler, Z. Electrochem., 19, 128 (1913).

[17] Klason and Norlin, Chem. Centr., II, 1480 (1906).

[18] Winkler, Ber., 38, 3614 (1905).

and propanol-2 by Atkins and Wallace,[19] and for butanol-2 by Timmermans and Martin.[20] All the values for the density of butanol-1 thus obtained from the literature resulted in a value for the coefficient of expansion badly off the curve, hence the density of a sample of boiling point 117.3 at 759 mm. was determined, the values being d_4^0 0.82431; d_4^{25} 0.80563. From these, the coefficient of expansion $\times$ 10 was calculated to be 0.9265.

TABLE I

PROPERTIES OF THE MERCAPTANS

Instead of giving the name of each compound in this and the subsequent tables the following system has been used: the Roman numeral gives the number of carbon atoms in the compound and the Arabic numeral indicates the number of the carbon atom to which the characteristic group is attached. Thus IV-1 designates normal butyl mercaptan, alcohol or bromide, according to the table heading, while IV-2 is butane-thiol-2, butanol-2 or 2-bromobutane.

Mer-captan	Melting point, °C.	d_4^0	d_4^{25}	Expansion $1°\times 10^3$	Latent heat of vapori-zation, g. cal.	n_D^{25}	MR_D, found	MR_D, calcd.
I	−123.1	0.89482	0.85991	1.6239				
II	−147.3	.86174	.83147	1.4562		1.4270	19.19	19.13
III-1	−113.3	.86169	.83572	1.2430		1.4351	23.77	23.74
III-2	−130.7	.83559	.80851	1.3397		1.4223	23.97	23.74
IV-1	−115.9	.86006	.83651	1.1261		1.4401	28.41	28.36
IV-2	−165.0	.84906	.82459	1.1870		1.4338	28.46	28.36
V-1	− 75.7	.85952	.83750	1.0517	8,847	1.4440	33.04	32.98
V-2	−169.0	.85086	.82815	1.0969	8,662	1.4386	33.06	32.98
VI-1	− 81.0	.85911	.83826	0.9949	9,836	1.4473	37.68	37.60
VI-2	−147.0	.85217[a]	.83050	1.0437	9,146	1.4426	37.69	37.60
VII-1	− 43.4	.85894	.83891	0.9551	10,363	1.4498	42.33	42.22
VII-2	−141.0	.85171	.83114	.9900	9,786	1.4452	42.35	42.22
VIII-1	− 49.2	.85898	.83956	.9252	10,842	1.4519	46.97	46.83
VIII-2	− 79.0	.85281	.83293	.9542	10,372	1.4481	47.00	46.83
IX-1	− 20.1	.85907	.84015	.9008	11,522	1.4537	51.62	51.45
IX-2	− 69.0	.85313	.83384	.9254	11,039	1.4500	51.64	51.45

[a] Erlenmeyer and Wanklyn[8] gave d_0^0 0.8856, corresponding to d_4^0 0.8854, for secondary hexyl mercaptan.

The melting points of the mercaptans given in Table I are illustrated by Fig. 4. These melting points were determined in this Laboratory by Dr. D. H. Andrews and Mr. Donald Teats, who have kindly permitted them to be included here. The normal mercaptans gave excellent melting points, but the secondary butyl, amyl, hexyl and heptyl compounds formed glasses, so that the melting points of these can be regarded only as approximate. For comparison, the melting points of the normal alcohols and hydrocarbons have been included in Fig. 4. In selecting values for these from the literature there was often considerable latitude of choice. The melting points used for methyl, ethyl and butyl alcohols were those

[19] Atkins and Wallace, J. Chem. Soc., 103, 1471 (1913).

[20] Timmermans and Martin, J. chim. phys., 25, 431 (1928).

TABLE II

PROPERTIES OF THE HIGHER ALCOHOLS

Alcohol	d_4^0	d_4^{25}	Expansion per degree $\times 10^3$	n_D^{25}	MR_D, found	MR_D, calcd.
V-1	0.82963[a]	0.811589[b]	0.8896	1.4077	26.76	26.82
V-2	.82481[c]	.80528	.9701	1.4041[c]	26.76	26.82
VI-1	.83336[d]	.81581	.8605	1.4161	31.42	31.43
VI-2	.82876[e]	.80977	.9380	1.4126	31.42	31.43
VII-1	.83634[d]	.81915	.8394	1.4222	36.04	36.05
VII-2	.83203	.81340	.9162	1.4190	36.05	36.05
VIII-1	.83848[d]	.82137	.8332	1.4274	40.71	40.67
VIII-2	.83505	.81678	.8947	1.4244	40.69	40.67
IX-1	.84002[f]	.82303	.8257	1.4320	45.43	45.29
IX-2	.83723	.81910	.8854	1.4290	45.37	45.29

[a] Lieben and Rossi[21] gave d_0^0 0.8296, corresponding to d_4^0 0.8294 for pentanol-1. [b] Holmes[22] gave d_{25}^{25} 0.80915, corresponding to d_4^{25} 0.80675, for pentanol-1. [c] Brunel[23] found d_4^{25} 0.80483 and n_D^{25} 1.4043 for pentanol-2. [d] Lieben and Janek[24] reported d_0^0 0.8333, corresponding to d_4^0 0.8331, for hexanol-1. [e] Zander[25] determined for this compound d_0^0 0.8327, corresponding to d_4^0 0.8325, d_0^0 0.8342, corresponding to d_4^0 0.8340, for heptanol-1, and d_0^0 0.8361, corresponding to d_4^0 0.8359 for octanol-1. For heptanol-1, Cross[26] reported d_0^0 0.838, corresponding to d_4^0 0.8379. [f] Zelinsky and Przewalsky[27] found d_4^0 0.8287 for hexanol-2. Kraft[28] gave d_4^0 0.8415 for nonanol-1.

given by Parks,[29] for propyl alcohol that given by Parks and Huffman,[30] for amyl alcohol by Simon,[31] for hexyl alcohol by Kelley,[32] for heptyl alcohol by Timmermans and Mattaar,[33] and for nonyl alcohol by "International Critical Tables." The melting point of octyl alcohol also was determined by Dr. Andrews and Mr. Teats. The melting point of methane was that given by "International Critical Tables." For ethane, propane and butane the melting points reported by Coffin and Maass[34] were used, for pentane that given by Timmerman,[35] for hexane and octane those given by Timmermans and Martin,[36] and for heptane and nonane the constants

[21] Lieben and Rossi, Ann., 157, 71 (1871).

[22] Holmes, J. Chem. Soc., 103, 2162 (1913).

[23] Brunel, THIS JOURNAL, 45, 1334 (1923).

[24] Lieben and Janek, Ann., 187, 137 (1877).

[25] Zander, ibid., 224, 84 (1884).

[26] Cross, ibid., 189, 3 (1877).

[27] Zelinsky and Przewalsky, Chem. Centr., II, 1185 (1908).

[28] Kraft, Ber., 19, 2221 (1886).

[29] Parks, THIS JOURNAL, 47, 342 (1925).

[30] Parks and Huffman, ibid., 48, 2788 (1926).

[31] Simon, Bull. soc. chim. Belg., 38, 47 (1929).

[32] Kelley, THIS JOURNAL, 51, 783 (1929).

[33] Timmermans and Mattaar, Bull. soc. chim. Belg., 31, 389 (1922).

[34] Coffin and Maass, THIS JOURNAL, 50, 1433 (1928).

[35] Timmermans, Bull. soc. chim. Belg., 25, 300 (1916).

[36] Timmermans and Martin, J. chim. phys., 25, 411 (1928).

given in recent work by Midgley, Henne and Shepard.[37] The melting points of the normal mercaptans furnish a striking case of alternation with the high points coming where the compounds have an odd number of carbon atoms, whereas these points occur in the alcohols and hydrocarbons having even numbers of carbon atoms.

TABLE III

BOILING POINTS (°C.) OF HIGHER MERCAPTANS UNDER VARIOUS PRESSURES

Mercaptan	30 mm.	50 mm.	70 mm.	90 mm.	110 mm.	150 mm.	300 mm.	760 mm.
V-1			57.7		68.7	76.7	95.9	126.5
V-2					55.9	63.9	83.6	112.9
VI-1		72.4		86.4		99.7	120.1	151.5[a]
VI-2		60.6		74.2		87.5	107.3	138.9[b]
VII-1	81.2		101.2			121.6	142.9	176.2[c]
VII-2	69.6		89.2			109.5	130.4	163.6[d]
VIII-1	99.8		120.6			142.1	164.0	199.1[e]
VIII-2	88.9		109.1			130.1	151.7	186.4
IX-1	117.4		138.7			160.8	184.1	220.2
IX-2	106.8		128.1			149.9	172.4	208.2

[a] Pelouze and Cahours[7] gave 145–148° at atmospheric pressure as the boiling point of n-hexyl mercaptan. [b] Erlenmeyer and Wanklyn[8] reported 142° for this boiling point. [c] Wissinger[9] described n-heptyl mercaptan as boiling at 174–175° at 760 mm. Adams, Bramlett and Tendick[38] obtained a small amount of this compound, b. p. 174–176°, by the action of ethylmagnesium bromide on n-heptyl thiocyanate. [d] Henry[10] found 164–165° at 765 mm. for the boiling point of this compound. [e] Kahn[11] gave 198–200° for the boiling point of his n-octyl mercaptan.

TABLE IV

BOILING POINTS OF HIGHER ALCOHOLS AT 760 MM.

Alcohol	Boiling point, °C.	Alcohol	Boiling point, °C.
V-1	137.8	VII-2	158.7
V-2	119.5	VIII-1	194.7
VI-1	156.5	VIII-2	179.0
VI-2	139.8	IX-1	213.5
VII-1	176.3	IX-2	198.3

In acquiring the technique of the Cottrell apparatus used in determining the boiling points of the higher mercaptans under various pressures, given in Table III, similar determinations of the boiling points of the higher alcohols were carried out. The values thus obtained for the atmospheric boiling points of these alcohols are given in Table IV, and plotted in Fig. 5 along with the corresponding values for the mercaptans and those for the lower alcohols as given by Brunel and his co-workers.[15] Figure 6, based on the data of Table III, shows the shape of the vapor pressure–

[37] Presented at the Cincinnati meeting of the American Chemical Society, September, 1930, under the title "The Preparation and Physical Properties of Pure Normal Paraffins."

[38] Adams, Bramlett and Tendick, THIS JOURNAL, 42, 2369 (1920).

temperature curve for each of the higher mercaptans. In Fig. 5 it will be observed that while the lower alcohols boil much higher than the corresponding mercaptans, this is reversed higher in the series, and in Fig. 6 it will be observed that the curves for the secondary mercaptans show more resemblance to those for the next lower normal compounds than to the normal compounds containing the same number of carbon atoms. In their work on the association and molecular constitution of the isomeric octanols and of a number of mercaptans, Bingham and his co-workers[39] show that of these the iso (or secondary) compounds are less associated than the corresponding normal ones, and that the degree of association decreases with increasing molecular weight. It appears possible, then, to explain
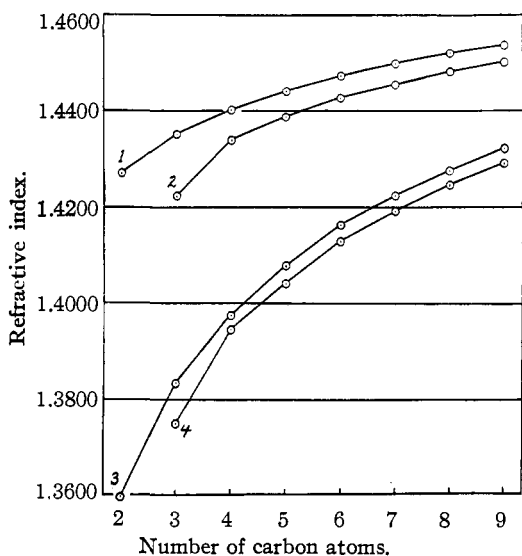

Fig. 3.—Refractive indices of alcohols and mercaptans at 25°: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols; 4, α-secondary alcohols.

TABLE V

PROPERTIES OF THE HIGHER BROMIDES

Alcohol	d_4^0	d_4^{25}	Expansion per degree $\times 10^3$	n_D^{25}	MR_D, found	MR_D, calcd.
V-1	1.24313	1.21135	1.0494	1.4417	32.97	33.06
V-2	1.23257[a]	1.20056	1.0662	1.4394	33.12	33.06
VI-1	1.19807[a]	1.16899	0.9957	1.4452	33.59	37.67
VI-2	1.18913	1.15979	1.0119	1.4432	37.74	37.67
VII-1	1.16191	1.13484	0.9541	1.4480	42.24	42.39
VII-2	1.14363	1.11634	.9778	1.4450	42.70	42.39
VIII-1	1.13337	1.10788	.9203	1.4503	46.87	46.91
VIII-2	1.12246	1.09681	.9354	1.4482	47.15	46.91
IX-1	1.10925	1.08490	.8978	1.4523	51.53	51.63
IX-2	1.10266	1.07806	.9127	1.4507	51.69	51.63

[a] Karvonen[40] reported d_4^0 1.2428 for normal amyl bromide, and d_4^0 1.1992 for normal hexyl bromide. For the latter, Lieben and Janek[24] found d_0^0 1.1935, corresponding to d_4^0 1.1933.

[39] Bingham and Darrall, *J. Rheol.*, **1**, 174 (1930); Bingham and Fornwalt, *ibid.*, **1**, 372 (1930).

[40] Karvonen, *Chem. Centr.*, II, 1271 (1912).

the "crossing over" of the curves for the atmospheric boiling points by assuming a greatly decreased association in the higher alcohols, and to explain the appearance of the vapor pressure curves of the secondary mercaptans by the lesser association of these compounds as compared to the corresponding normal ones.

Figure 7, plotted from data kindly furnished the authors by Dr. E. C. Bingham of Lafayette College, illustrates the greater fluidity of the secondary as compared to the normal mercaptans, and the greater fluidity of the mercaptans as compared to the alcohols. Because the curve for the secondary alcohols fell so close to that for the primary compounds, values for the former were not included in this figure. A more complete discussion of these fluidities will be found in the previously mentioned work of Bingham.[39]

In considering the yields of the mercaptans and bromides as given in Tables VI and VIII it must be remembered that purity of final product rather than high percentage yield was the desired object. In particular, the method of purification employed for the lower mercaptans resulted in heavy losses, while the close fractionation given the alkyl bromides caused low yields in several cases.
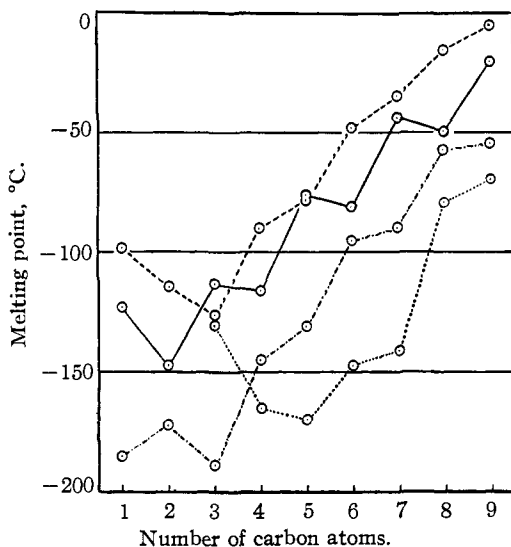

Fig. 4.—Melting points of mercaptans, normal alcohols and normal hydrocarbons: ————, normal mercaptans; ...., α-secondary mercaptans; – – – –, normal alcohols; — · — · —, normal hydrocarbons.

Experimental Part

Fractionation of the intermediate bromides and of the samples of alcohols on which the physical constants were determined was accomplished by use of 112-cm. packed column stills of the general type described by Peters and Baker.[41] These stills had lagged columns and controlled reflux. A smaller still of the same type was used for fractionating the mercaptans. Except in the cases of methyl and ethyl mercaptans, density determinations were carried out by use of carefully calibrated pycnometers of about 8 cc.

[41] Peters and Baker. *Ind. Eng. Chem.*, **18**, 69 (1926).

volume, and were made either in duplicate or triplicate. The maximum deviation between any two accepted values on a compound was 0.00007.
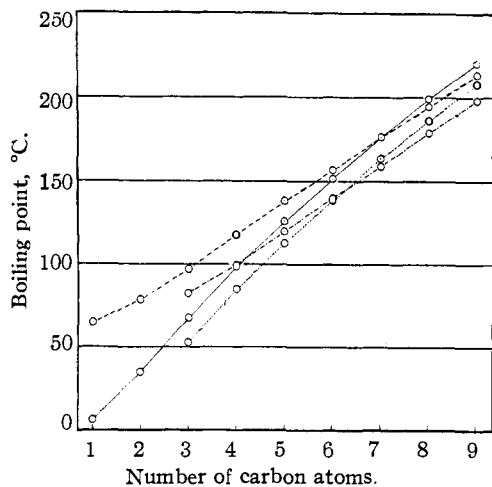

Fig. 5.—Atmospheric boiling points of alcohols and mercaptans: ———, normal mercaptans; ·····, α-secondary mercaptans; – – – –, normal alcohols; ·—·—·—, α-secondary alcohols.

The densities of methyl and ethyl mercaptans were determined by use of dilatometers of similar volume calibrated with distilled water and read with a cathetometer. Refractive indices were determined by use of an Abbé type refractometer with water-jacketed prisms maintained at 25° by circulating water from a thermostat. The boiling points of the higher mercaptans under various pressures were obtained by use of a Cottrell boiling point apparatus which required a sample of about 8 cc. Pressure control here and in the various vacuum distillations was accomplished by means of an apparatus to be described elsewhere. The temperature values given were determined by use of thermometers for which Reichsanstalt or Bureau of Standards certificates were available.
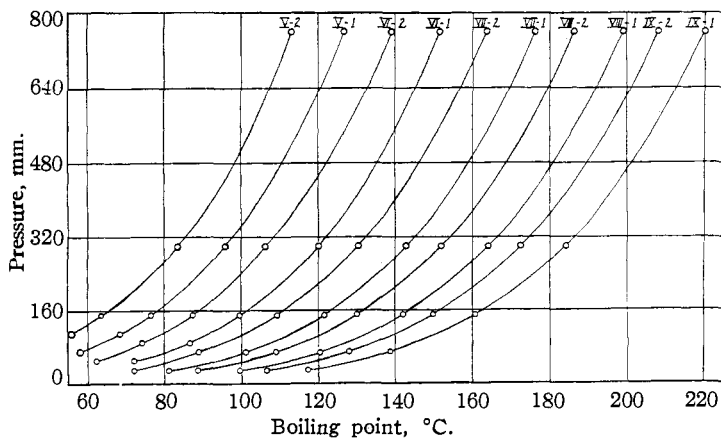

Fig. 6.—Boiling points of mercaptans under various pressures.

In the preparations, the alkyl bromide was prepared from the alcohol corresponding to the desired mercaptan, and the mercaptan prepared

in the usual manner by the action of an alkali hydrosulfide on the bromide. With the exception of heptanol-1, all the alcohols higher than butyl were made by the Grignard reaction. The preparation of the Grignard reagent and the addition of the various reactants, ethylene oxide, formaldehyde or other aldehydes, to this reagent was carried out in accordance with well-known procedure except in the preparation of octanol-1, where liquid formaldehyde was added to *n*-heptylmagnesium bromide in general accordance with a method developed by Glass and Reid.[42] Heptanol-1 was prepared by reducing heptaldehyde according to the method of "Organic Syntheses."[43] In order to obtain any reduction in this process it was found necessary to use degreased filings from cast iron instead of the grade specified. The alcohols were given a rough distillation and the major fraction boiling over a range of a few degrees collected. A portion of this crude product was then carefully distilled through one of the column stills to obtain the sample on which determinations of physical constants were carried out. The crude alcohol was then converted to the bromide, and this carefully fractionated in one of the column stills. Preparation of the two propyl, two butyl and *n*-amyl bromides was carried out according to the method of "Organic Syntheses,"[44] using portions of the corresponding commercial alcohols. The other alkyl bromides were prepared by a slight

Fig. 7.—Fluidities of mercaptans and normal alcohols: 1, normal mercaptans; 2, α-secondary mercaptans; 3, normal alcohols.

modification of that procedure. The alcohol was placed in a balloon flask equipped with a stirrer and reflux condenser, and for each mol of alcohol present 200 cc. of the more concentrated hydrobromic acid solution described in "Organic Syntheses" was added. The reaction mixture was stirred and heated in a water-bath kept at 80° if the alcohol was primary, or 60° if it was secondary. At the end of two hours another like portion of hydrobromic acid solution was added, and the treatment continued for another two hours. The stirring compensated for the slight solubility of the higher alcohols, while the relatively mild treatment prevented
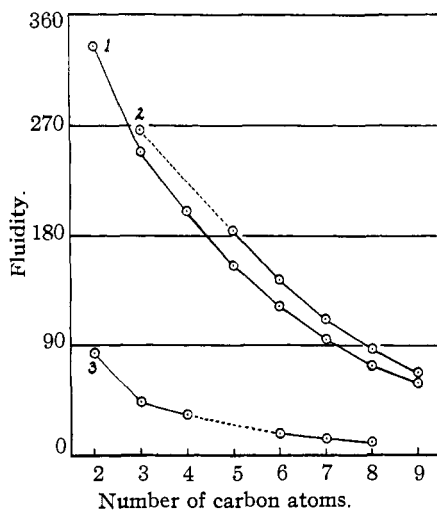
[42] H. B. Glass, Dissertation, The Johns Hopkins University, 1929.
[43] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 62.
[44] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 5.

TABLE VI

PREPARATION OF MERCAPTANS AND MELTING POINTS OF ANTHRAQUINONE DERIVATIVES

Mer-captan	Alkyl bromide used, g.	Mercaptan obtained, g.	Yield, %	Boiling range, °C.	Press., mm.	Purity titration	M. p. of an-thraquinone thio ether, °C.
I				5.8– 6.2[b]	756	100.1	
II				34.4– 34.6[b]	752	100.1	
III-1	565	187	49.2	67.4– 67.6[c]	763	99.5	
III-2	565	140	36	52.3– 52.5[d]	753	99.9	
IV-1	685	241	53.5	98.6– 99.0[e]	768	100.3	
IV-2	...	...	..	84.4– 84.6[f]	754	99.7	
V-1	302	145	69	126.3–126.5[g]	759.5	99.9	128.8
V-2	302	135	60	112.5–112.6	753	100.1	
VI-1	330	158	67	86.0– 86.2	90	100.2	113.9
VI-2	330	100	42	73.8– 74	90	99.8	
VII-1	358	192	72	96.3– 96.5	59.5	100.2	95.9
VII-2	358	102	38	85.0– 85.2	60	100.2	
VIII-1	193	62	42.5	94.4– 94.6	25	99.6	95.2
VIII-2	193	97	66	91.2– 91.5	35	99.9	
IX-1	207	119	74	91.9– 92.4	10	99.7	117.5
IX-2	207	118	73.7	89.7– 90	15	99.9	

[a] The anthraquinone derivatives of the lower mercaptans have been prepared by Reid, Mackall and Miller.[45]   [b] Klason[46] gave 5.8° at 742 mm. as the boiling point of methyl mercaptan. Berthoud and Brun[47] reported it as 6.1–6.2° at 727 mm., and for ethyl mercaptan 33.4° at 724 mm. For the latter, Vespignani[48] and Ferretto[49] found 37° at 759.2 and 760.15 mm., and Naisini[50] gave 36.2–36.8° at 761 mm.   [c] Roemer[51] records 67–68° as the boiling point of this compound.   [d] Claus[52] reported 57–60° for this boiling point.   [e] Saizew and Grabowsky[53] found 97–98° for the boiling point of n-butyl mercaptan.   [f] Reymann[54] recorded 84–85° for the boiling point of secondary butyl mercaptan.   [g] Pexters[55] gave 126° for the boiling point of n-amyl alcohol.[55]

charring or bad discoloration. The bromides were recovered by steam distillation, washed with water, with small portions of cold concentrated sulfuric acid, then with water and finally dried over anhydrous potassium carbonate.

Methyl mercaptan was prepared from dimethyl sulfate and potassium hydrosulfide according to the method of Klason.[56] Ethyl mercaptan was obtained from the Eastman Kodak Co. and purified as described below,

[45] Reid, Mackall and Miller, THIS JOURNAL, **43**, 1199 (1921).

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

[47] Berthoud and Brun, *J. chim. phys.*, **21**, 159 (1924).

[48] Vespignani, *Gazz. chim. ital.*, **33**, I, 76 (1903).

[49] Ferretto, *ibid.*, **30**, I, 297 (1900).

[50] Naisini, *Ber.*, **15**, 2881 (1882).

[51] Roemer, *ibid.*, **6**, 784 (1873).

[52] Claus, *Ber.*, **5**, 659 (1872).

[53] Saizew and Grabowsky, *Ann.*, **171**, 251 (1874); **175**, 351 (1875).

[54] Reymann, *Ber.*, **7**, 1287 (1874).

[55] Pexters, *Bull. sci. acad. roy. Belg.* 801 (1906).

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

TABLE VII

PREPARATION OF HIGHER ALCOHOLS[a]

Alcohol	Prepared from	B. p. crude products, °C.	Pressure	Yield G.	%	Final boiling range, °C.	Pressure, mm.
V-1	n-C$_4$H$_9$Br + HCHO	132–142	Atm.	1910	56.4	137.5[b]	754
V-2	n-C$_3$H$_7$Br + CH$_3$CHO	118–119.5	Atm.	735	61.9	119.4[b]	754
VI-1	n-C$_4$H$_9$Br + (CH$_2$)$_2$O	152–158	Atm.	1109	40	100.5–101	90
VI-2	n-C$_4$H$_9$Br + CH$_3$CHO	76– 79	65 mm.	910	74.3	85.2– 85.5	90
VII-1	n-C$_7$H$_{14}$O + H	171–176	Atm.	3603	69.8	99.3– 99.5	40
VII-2	n-C$_5$H$_{11}$Br + CH$_3$CHO	92– 97	70 mm.	870	83.3	95.8– 96	70
VIII-1	n-C$_7$H$_{15}$Br + HCHO	110–117	50 mm.	459	70.6	104.3–104.4	25
VIII-2	CH$_3$I + n-C$_7$H$_{14}$O	102–105	52.5 mm.	505	77.6	102.4–102.7	50
IX-1	n-C$_7$H$_{15}$Br + (CH$_2$)$_2$O	98–102.5	10 mm.	575	49.9	100.2–100.4	10
IX-2	n-C$_7$H$_{15}$Br + CH$_3$CHO	100–103	12.5 mm.	754	65.4	89.5– 89.8	10

[a] Commercial samples of the propyl and butyl alcohols were used after careful fractionation. [b] A number of boiling points are given in the literature for these compounds. The values given by "International Critical Tables" are 137.9° for normal, and 119.5° for secondary amyl alcohol. Such boiling points as are given in the literature for the other alcohols are at atmospheric pressure.

For the other mercaptans except secondary octyl and nonyl, 90 g. potassium hydroxide for each mol of bromide to be used was dissolved in alcohol (500 cc. 95% for the bromides below amyl, 400 cc., absolute for those above) and the solution saturated with hydrogen sulfide. This solution was then transferred to a flask of suitable size equipped with a reflux condenser and hydrogen sulfide inlet tube reaching nearly to the bottom of the flask. Hydrogen sulfide was passed slowly into the solution during all phases of the reaction to provide stirring and to keep the equilibrium as far as possible on the hydrosulfide side. The alkyl bromide was added slowly through the dropping funnel, after which the reaction mixture was allowed to stand for some time and heated either at 50–60° for two hours or at reflux for one hour. The reaction mixture was then diluted with a large volume of water and the mercaptan separated.

Among the impurities possibly present in mercaptans prepared in this manner are (1) unchanged bromide, (2) ethyl alcohol and (3) alkyl sulfide. Because of the wide divergence of their boiling points from those of the mercaptans, (3) and in the case of the higher mercaptans (2) would presumably be removed by distillation. The presence of (1) was suspected only in the cases of one or two of the lower mercaptans were the reaction did not appear to go to completion readily. The ethyl, the two propyl and the two butyl mercaptans were purified by dissolving them in 20% sodium hydroxide solution, extracting with a small portion of benzene, and steam distilling the alkaline solution until clear. Only a small amount of distillate had come over when this stage was reached. After cooling, the solution was faintly acidified with 15% sulfuric acid, and the mercaptan distilled out. The two amyl, two hexyl and two heptyl mercaptans were

TABLE VIII

PREPARATION OF ALKYL BROMIDES

Bromide	Alcohol used, g.	Bromide obtained, g.	Yield, %	Boiling point, °C.	Pressure, mm.
III-1			Approx. 50[a]	70.7– 70.9[b]	755
III-2			Approx. 40[a]	59.4– 59.7[b]	754
IV-1			Approx. 70[a]	100.5–101.5[b]	760
IV-2			Approx. 60[a]	90.5– 91[b]	756
V-1	2040	1990	47.7	129.6–129.8[c]	761
V-2	645	760	67.6	118.6–118.9[d]	761
VI-1	992	867	54.1	87.8– 88 2	90
VI-2	475	575	74.2	77.8– 78.1	90
VII-1	3509	4485	82.8	94.0– 94.5	50
VII-2	620	665	69.7	84.4– 84.6	50
VIII-1	430[e]	425	65.3	92.0– 92.5	10
VIII-2	745[e]	541	48.3	87.4– 87.9	25
IX-1	490	410	58.2	94.3– 94.8	10
IX-2	664	485	49.7	85.7– 86.2	10

[a] The propyl and butyl bromides were made in quantity for various preparations and no exact record of the yields was kept. [b] The boiling points given in "International Critical Tables" for the lower bromides are: n-propyl, 70.9°; isopropyl, 59.6°; n-butyl, 101.6°; sec.-butyl, 91.3°. The literature is too extensive to quote here. [c] The first portions of this bromide were distilled from 127.5–128.7° at 756 mm.; 1208 g. of this material was used in the preparation of heptanol-2. It was later found that a faint odor of formaldehyde in the bromide was removed by stirring for one hour with 5% sodium hydroxide solution. The balance of the bromide after this treatment gave the boiling point in the table. Although this is higher than the numerous values to be found in the literature, that given by "International Critical Tables" being 127.9°, it has been duplicated by other work[57] in this Laboratory. [d] Lucas, Simpson and Carter[58] reported 117–118° at 745 mm. as the boiling point of this bromide. [e] Portions of these alcohols were obtained from the Eastman Kodak Co.

similarly treated except that ether was substituted for the benzene, and the steam distillation omitted (the ease with which the mercaptans are distilled from alkaline solution increases with the molecular weight); the mercaptans were recovered by separating them from the acidified solution. No preliminary purification was given the other higher mercaptans; from the analyses, none was needed.

In the attempted preparation of secondary octyl and nonyl mercaptans by the previously outlined procedure, products were obtained which, from their boiling points, were almost entirely the sulfides. Rule[59] has shown that quite pure sodium hydrosulfide can be prepared by the action of hydrogen sulfide on sodium ethoxide, so the procedure for the preparation of these mercaptans was altered to take advantage of this. For each mol of the alkyl bromide to be used, 40 g. of sodium was dissolved in 500 cc. of ab-

[57] F. C. Wagner, Dissertation, The Johns Hopkins University, 1929.

[58] Lucas, Simpson and Carter, THIS JOURNAL, 47, 1467 (1925).

[59] Rule, J. Chem. Soc., 99, 560 (1911).

solute ethyl alcohol, and this saturated with hydrogen sulfide. Since a large amount of the sodium hydrosulfide came out of the solution, mechanical stirring was used during the addition of the alkyl halide. The other procedure was as previously described.

Preparation of the anthraquinone α-alkyl thio-ethers was carried out according to the method of Reid, Mackall and Miller,[60] except that the time of refluxing was doubled. The compounds were recrystallized from alcohol, benzene, methanol or mixtures of these. It was not found possible to obtain satisfactory melting points for the derivatives of the higher secondary mercaptans.

The mercaptans were analyzed for total hydrosulfide content by oxidation to the disulfide with excess standard iodine solution according to the method of Kimball, Kramer and Reid.[61]   The results were calculated to percentage purity, the values given in Table VI representing the mean of several determinations. The widest deviation between any of the individual determinations on a mercaptan was approximately 1%.

The authors wish to express their thanks to Dr. R. F. Deese, Jr., whose assistance in this work included the determination of the densities of the higher bromides which are included in Table V.

Summary

1. Normal and alpha secondary mercaptans from methyl through nonyl, and a number of intermediate alcohols and bromides, have been prepared. The mercaptans have been analyzed.

2. The densities at 0 and 25°, and the refractive indices at 25° have been determined for the mercaptans and the higher alcohols and bromides. The mean coefficients of thermal expansion over this range and the values for molecular refraction have been calculated for these compounds.

3. The melting points of the mercaptans have been given.

4. The boiling points at various pressures have been determined for the higher mercaptans.

5. The anthraquinone α-alkyl thio-ethers have been prepared from the higher normal mercaptans and their melting points determined.

6. Curves illustrating certain relationships between these mercaptans and alcohols have been given.

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[60] Reid, Mackall and Miller, THIS JOURNAL, **43**, 2104 (1921).

[61] Kimball, Kramer and Reid, ibid., **43**, 1199 (1921).