[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A Series of α,ω-Dimercaptans[1]

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Some time ago a study was made in this Laboratory of two series of mercaptans.[3] It seemed desirable to secure accurate comparable data on the α,ω-dimercaptans. Ethylene mercaptan is the only one of this class that is at all well known; several of the higher ones have been prepared,[4,5] but the information about them is scanty. All of the dimercaptans up to dodecamethylene have been prepared and their properties determined. To these octadecamethylene dimercaptan has been added. The hepta-, octa-, nona-, undeca-, dodeca- and octadecamethylene mercaptans are new. For comparisons it was necessary to determine the melting points of pentamethylene glycol −18°, and of hexa- hepta-, nona- and undeca-methylene bromides, −2.3, −41.7, −22.5 and −10.6°, respectively as they could not be found in the literature. Octadecamethylene mercaptan melts at 52°.

The properties and analyses of the dimercaptans are given in Table I. The boiling and melting points are plotted in Figs. 1 and 2 along with those of the corresponding glycols and dibromides. The curves for the boiling points of the dimercaptans and dibromides are similar and cross between the third and fourth members. The lower glycols boil much higher but the two curves cross near the octamethylene. The corresponding curves for the alcohols and the mercaptans cross at the heptyl. The melting point pattern of the dimercaptans resembles that of the dibromides much more closely than that of the glycols. The melting points of the alcohols, mono-bromides and mercaptans show similar relationships.

TABLE I

PROPERTIES AND ANALYSES OF α,ω-DIMERCAPTANS

No. C	M. p., °C.	B. points,[a] °C at 10 mm.	B. points,[a] °C at 100 mm.	B. points,[a] °C at 760	d^{0}_{4}	d^{25}_{4}	$n^{25}D$	Latent heat of evaporation	Sulfur, % Calcd.	Sulfur, % Found	
2	−41.2[b]	...	...	146[c]	1.1454	1.1192	1.5558[b]	....	...	...	...
3	−79[c]	...	104.6	172.9	1.1007	1.0775	1.5371	....	...	...	...
4	−53.9	74.5	127.7	195.6	1.0621	1.0395	1.5265	11,135	52.47	51.92	51.75
5	−72.5	90.1	147.2	217.3	1.0375	1.0158	1.5194	11,842	47.07	46.38	46.80
6	−21.0	106.0	163.8	237.1	1.0102	0.9886	1.5077	12,246	42.68	41.86	42.10
7	−38.1	119.5	178.0	252.2	0.9900	.9707	1.4950	12,845	39.02	38.64	38.72
8	0.9	132.0	192.4	269.3	0.9814	.9620	1.5009	13,217	35.97	35.32	35.40
9	−17.5[d]	145.0	206.5	284.0	0.9698	.9510	1.4940	13,897	33.35	32.42	32 81
10	17.8	161.0	219.5	297.1	....	.9432	1.4950	14,590	31.07	31.02	30.82
11	− 5.4	171.5	230.6	308.8[d]	....	.9368	1.4931	15,090	29.11	29.48	28.84
12	28.4	181.5	241.0	319.3[e]	....	.9270[f]	....	15,660	27.35	27.10	26.98

[a] The boiling points at 10 mm. are from distillations at that pressure, those at 100 and 760 mm. were taken with the Cottrell apparatus. [b] Tucker and Reid, THIS JOURNAL, 55, 775 (1933). [c] Meadow and Reid, *ibid.*, 56, 2177 (1934). [d] v. Braun, *Ber.*, 42, 4568 (1909). [e] Estimated from the curve. [f] At 30°.

The preparation and isolation of the dimercaptans are complicated by the appreciable solubility in water of the lower ones, by their less volatility, by the tendency to form sulfide-mercaptans $HS(CH_2)_nS(CH_2)_nCH$ and polymers. In alkaline solution they are quite susceptible to oxidation by air to linear disulfides. With sodium hydrosulfide tetra- and pentamethylene bromides give poor yields of the dimercaptans on account of the tendency to form five and six membered cyclic sulfides. The thiourea method gave good results with these, 80 to 85%. For the higher ones sodium hydrosulfide in absolute alcohol gave satisfactory yields, 70 to 85%. For comparison trimethylene bromide was treated with potassium xanthate and thiobenzoate and with sodium and ammonium phenyl-dithiourethans.[6] The yields were 40 to 50%. Efforts to isolate methylene mercaptan failed.

For making tetramethylene bromide, tetra-

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[1] Original manuscript received July 25, 1941.

[2] From dissertation, Johns Hopkins University, 1936.

[3] Ellis and Reid, THIS JOURNAL, **54**, 220 (1932).

[4] v. Braun, *Ber.*, **42**, 4568 (1909).

[5] Schwarzenbach and Epprecht, *Helv. Chim. Acta*, **19**, 169–178 (1936).

[6] v. Braun, *Ber.*, **42**, 4568 (1909).

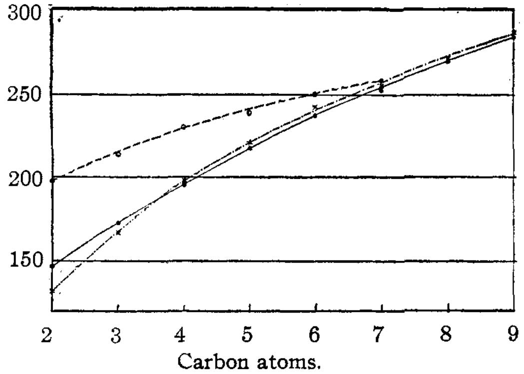

Fig. 1.—Boiling points of the dimercaptans, -●——●-; dibromides, *-·-·-*; glycols, -⊖------⊖-.

hydrofuran[7] was treated with hydrogen bromide. The higher bromides were made from glycols obtained by Bouveault and Blanc reduction of esters of the dibasic acids. The ethyl esters of suberic and azelaic acids were obtained by fractionating the ethyl esters of the crude acids from the nitric acid oxidation of ricinoleic acid. The oxidation of hydrogenated ricinoleic acid gave a mixture of the C_{11} and C_{12} dibasic acids, the ethyl esters of which were separated by fractionation.

Experimental

Suberic and Azelaic Acids.—Crude ricinoleic acid was oxidized, 1 kg. at a time, by running it slowly into 4 l. of boiling nitric acid containing 1 g. ammonium vanadate stirred by a current of air, continuing the heating and stirring for twelve hours after all was in. The hot aqueous layer was separated and yielded 300–390 g. of crude dibasic acid mixture which was converted to the ethyl esters and fractionated. The mono-basic acids, chiefly caproic and heptoic, were recovered from the oily layer by steam distillation.

Glutaric acid was made by nitric acid oxidation of cyclopentanone and pimelic acid from the sodium–alcohol reduction of salicylic acid.[8]

The Bouveault–Blanc reduction of the esters was done in anhydrous *n*-butanol. Sodium was added to the butanol and when the reaction became vigorous the ester mixed with butanol was added through the condenser. Water was added and the butanol steam-distilled off. The lower glycols were separated by ether extraction; the higher appeared as solids on chilling. Except when the pure glycols were wanted for study, the crude glycols were converted directly by hydrogen bromide into the dibromides which are easy to isolate and purify by distillation.

A special case was tetramethylene bromide from tetrahydrofuran which resulted from the catalytic reduction of ethyl succinate. Hydrogen bromide was passed into it under efficient reflux. Much heat was evolved. The product separated into two layers. The dibromide was separated from the upper layer and the residue united with the first lower layer for retreatment. The yield was 78%. The other dibromides were made from the glycols by hydrogen bromide.

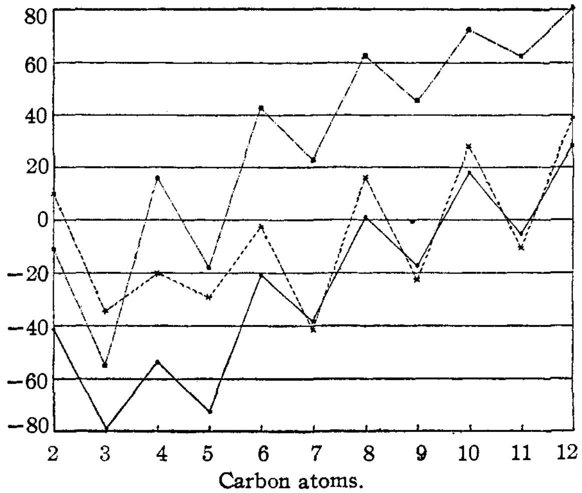

Fig. 2.—Melting points of the dimercaptans, ●——●; dibromides, *------*; glycols, -■-·-·-·-■-.

The preparation of pentamethylene mercaptan from thiourea is given as an example. To 85 g. (1.12 mole) of thiourea and 60 cc. of water in a three-necked flask, fitted with stirrer and reflux, 86 g. (0.37 mole) of pentamethylene bromide was added and the flask heated for six hours on a sand-bath. The stirrer was started and 112 g. (2 moles) of potassium hydroxide in 200 cc. of water was added and the heating continued for six hours. On cooling the mercaptan separates as an oily layer; an additional amount can be obtained by acidifying and extracting the aqueous layer, yield 83%.

The preparation of heptamethylene mercaptan from sodium hydrosulfide is given as an example. A solution of 9.2 g. (0.4 atom) sodium in abs. alcohol was saturated by passing hydrogen sulfide for seventy-two hours. This and 24.5 g. (0.096 mole) of heptamethylene bromide diluted with 50 cc. of alcohol and 50 cc. of ether were added slowly and simultaneously with constant stirring to 50 cc. of alcohol through which hydrogen, sulfide was passing. After standing for sixteen hours the mixture was heated for two hours. The precipitated sodium bromide was filtered off and dissolved in acidified water, and was extracted with ether, which was added to the alcoholic filtrate. This was distilled through a tall column until about 100 cc. remained. This residue was dissolved in 600 cc. of water containing 75 g. of potassium hydroxide which was extracted once with ether. The aqueous layer was acidified and extracted with ether, yield 88%.

The octadecamethylene dimercaptan was obtained as a solid mixed with considerable polymeric material. It was taken up in 50% alcoholic potash, precipitated and recrystallized from hot acetone. The dimercaptans were distilled at 10 mm. under a heated jacket, the middle cuts over 0.5° range being taken for the determination of properties. The boiling points at 100 mm. and at atmospheric

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(7) Kindly made for us by the du Pont Company by hydrogenating ethyl succinate.

(8) "Organic Syntheses," Vol. XI, p. 42, John Wiley and Sons, Inc., New York, N. Y.

pressure were taken in a Cottrell apparatus specially designed for a small quantity of liquid, about 2 cc. The vertical portion of this had a sealed on vacuum jacket surrounding the Anschütz thermometer.

For taking a melting point, a portion of the liquid sufficient to cover the bulb of the thermometer was put in a test-tube. By alternately freezing and melting the melting temperature was obtained. Then the same amount of a substance of known melting point near that determined, was frozen and melted under the same conditions to calibrate the thermometer in that particular region.

Summary

The α,ω-dimercaptans up to dodecamethylene have been prepared. Their properties have been determined and compared with those of the corresponding glycols and dibromide.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Preparation of Nonane and Decane α,ω-Dicarboxylic Acids[1]

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These acids, though known for a long time, have not been readily available. We have found that a mixture of the two is easily obtained by the nitric acid oxidation of μ-hydroxystearic acid from hydrogenated castor oil. According to whether the chain breaks at the one side or at the other of the hydroxyl group, heptoic acid and a C_{11} dibasic acid or hexoic and a C_{12} dibasic acid are obtained. Actually all four of these acids and some sebacic are produced. The monobasic acids are largely eliminated by steam distillation and the remaining mixture of acids is converted into the ethyl esters which are then separated by fractionation. The 175–178° and the 184–186° fractions at 8 mm. of the esters were 20 and 13%, respectively, of the weight of the starting material, or about 40% of the calculated which is satisfactory considering the low cost of the starting materials. That they were the desired materials was shown by their saponification numbers. The fact that the properties, particularly the melting points, of the glycols, dibromides and dimercaptans made from them fit into the respective series is even more convincing. The yields might well be pushed higher by further experimentation but our aim was to find a practicable method of preparation of the esters from which the acids may be obtained by saponification. Asalima and Takimoto[3] oxidized five grams of hydroxystearic acid and obtained a solid acid of average mol. wt. 221, which is between 216 and 230, the molecular weights of the C_{11} and C_{12} dibasic acids. We found fractionation of the esters of suberic and azelaic acids obtained by the oxidation of ricinoleic acids according to Vogel[4] and Baker and Ingold[5] to be a satisfactory method of separation of the esters of these acids.

Experimental

The oxidation was carried on in a 12-liter balloon flask fitted with an efficient mechanical stirrer. To 4 liters of concd. nitric acid, containing 1 g. of ammonium vanadate and heated nearly to boiling, 1 kilo of the hydroxystearic acid was added in small portions at such a rate that the reaction could be kept under control. After this addition the stirring and heating were continued until the heavy fumes died down, which took about eight hours. The slow evolution of red fumes never ceased. The mixture was steam distilled to remove the most of the monobasic acids. The mass was then cooled and the solid acid filtered off and washed on the filter. The air-dry weight of the dibasic acids was always high owing to retained monobasic acids and unoxidized starting material. The solid dibasic acid mixture was esterified and the purified ethyl esters fractionated at 8 mm., taking cuts at 175–178° and 184–186° which corresponded to plateaus in the distillation curve. These boiled at 120–122° and 130–132° at 0.5 mm. and gave saponification numbers of 408.9 and 389.9 compared with the calculated 412.0 and 391.8 of the desired esters.

Summary

Nitric acid oxidation of μ-hydroxystearic acid gives a mixture of mono- and di-basic acids. From this by esterification and fractionation the ethyl esters of the C_{11} and C_{12} dibasic acids may be obtained in satisfactory yields.

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(1) Original manuscript received July 25, 1941.

(2) From part of dissertation, Johns Hopkins University, 1936.

(3) Asahina and Takimoto, *J. Pharm. Soc. Japan*, **49**, 1017 (1929); *C. A.*, **24**, 1346 (1930).

(4) Vogel, *J. Chem. Soc.*, **123**, 2023 (1923).

(5) Baker and Ingold, *ibid.*, **123**, 122 (1923).