[CONTRIBUTION FROM THE CHEMICAL CORPS TECHNICAL COMMAND, EDGEWOOD ARSENAL, MD.]

bis-(2-Chloroethylmercapto)-alkanes[1]

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In connection with certain research projects in these Laboratories, a series of bis-(2-hydroxyethylmercapto)-alkanes were converted into the corresponding chloro derivatives employing thionyl chloride as the chlorinating agent. The glycols were furnished by C. S. Marvel,[3] Division B, N.D.R.C. The compounds chlorinated were of both the straight-chain and branched-chain type of substitution between the sulfur atoms and one contained an aryl residue between the sulfur atoms. They were all isolated in a state of purity and density, freezing point and vapor pressure determinations made.

Experimental

The bis-(2-chloroethylmercapto)-alkanes were prepared by the same general procedure as follows: A 10% excess over a 2 mole equivalent of thionyl chloride was placed in a 3-necked round-bottom flask of the proper capacity and diluted with 1 to 2 parts of ethyl ether. A mercury-sealed stirrer, thermometer, calcium chloride drying tube, and dropping funnel completed the set-up. The glycol, 1 mole equivalent, was added slowly to the thionyl chloride-ether solution with good stirring. The reaction temperature was maintained at 15–20°. At this temperature the chlorination proceeded smoothly. The reaction mixture was stirred for an additional half hour, after all of the glycol had been added, to complete the reaction. The reaction mixture was then transferred to a Claisen flask and the solvent, excess thionyl chloride, and volatile gases removed by distillation at 50–60°. The apparatus was then evacuated to about 2 mm. at 50–60° for two hours, which removed any remaining volatile material. No tarring occurred during chlorination and the crude yields were better than 96%. The chlorinated sulfides were liquids at room temperature except the 1,10-bis-(2-chloroethylmercapto)-decane and the α,α'-bis-(2-chloroethylmercapto)-*p*-xylene. The crude sulfides were remarkably pure, which was due to the absence of side reactions and the pure condition of the starting materials, the glycols. However, further purification was necessary in order to obtain the desired physical data. The solids were purified by crystallization from absolute ethyl alcohol. Due to the extreme low volatility of these compounds distillation under a vacuum of 0.02 mm. or lower was required. They were distilled from a small wide-necked flask which was immersed in an oil-bath up to the side arm. The flask contained a sealed-in thermometer well. For this reason, the boiling points may not be exact, but they do show the approximate boiling range of the compounds. The bis-(2-chloroethylmercapto)-alkanes isolated are recorded in the following table together with their analyses and some of their physical and chemical properties.

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TABLE I

CHEMICAL AND PHYSICAL DATA ON A SERIES OF BIS-(2-CHLOROETHYLMERCAPTO)-ALKANES, $ClC_2H_4—S—R—S—C_2H_4Cl$

R	Formula	B. p., °C. (uncor.)	Mm.	Analyses, % Cl Calcd.	Cl Found	S Calcd.	S Found	Density,[a] g./ml. 25°	30°	F. p., °C.[a]	Vapor pressure,[b] mm., at 25°	30°
$—CH_2—$	$C_5H_{10}Cl_2S_2$	85	0.035	34.56	34.37	31.25	31.11	1.316	1.312	25.5	.....	2.2×10^{-3}
$—CH(CH_3)CH_2—$	$C_7H_{14}Cl_2S_2$	101	.02	30.41	30.05	27.49	27.44	1.231	1.227	..	6.5×10^{-3}	.....
$—(CH_2)_3—$	$C_7H_{14}Cl_2S_2$	97	.055	30.41	30.02	27.49	27.82	1.233	1.229	10.6	.....	4.1×10^{-4}
$—CH(CH_3)CH_2CH_2—$	$C_8H_{16}Cl_2S_2$	108	.017	28.68	28.30	25.93	25.55	1.195	1.191	..	.....	1.7×10^{-4}
$—(CH_2)_4—$	$C_8H_{16}Cl_2S_2$	112–113	.05–.03	28.68	28.62	25.93	25.79	1.200	1.196	−0.9	.....	1.2×10^{-4}
$—(CH_2)_5—$	$C_9H_{18}Cl_2S_2$	128	.044	27.14	26.65	24.54	24.41	1.173	1.168	−3.0	.....	5.2×10^{-5}
$—C(CH_3)_2CH_2CH(CH_3)—$	$C_{10}H_{20}Cl_2S_2$	108–104	.02–.006	25.76	25.22	23.29	23.45	1.149	1.145	..	.....	1.4×10^{-4}
$—(CH_2)_6—$	$C_{10}H_{20}Cl_2S_2$	132	.055	25.76	25.54	23.29	23.14	1.159	1.155	14.4	.....	2.4×10^{-5}
$—CH_2CH(C_2H_5)CHC_3H_7$	$C_{12}H_{24}Cl_2S_2$	122	.014	23.38	22.78	21.14	21.14	1.11	1.11	..	.....	2.0×10^{-5}
$—(CH_2)_{10}—$	$C_{14}H_{28}Cl_2S_2$	33 (m. p.)	...	21.40	20.83	19.35	19.40	...	...	..	.....	.....
$—CH_2(C_6H_4)CH_2—$	$C_{12}H_{16}Cl_2S_2$	76–76.5 (m. p.)	...	24.02	23.74	21.71	21.81	...	...	..	.....	.....

[a] The densities of these compounds plotted against the number of carbon atoms gives a fairly smooth curve. The melting points plotted against the number of carbon atoms show some irregularity but no more than is usual for the early members of a series. [b] The vapor pressure measurements were made by the effusion method of Swan and Mack.[4] Except for the first two members of the series, methane and propane 1,2, the values obtained were well below the saturation concentration of 0.01 mg./liter, set as the lowest concentration for which vapor pressure data should be determined. The vapor pressures for the remaining members of the series were found to be in the region of 2×10^{-4} to 2×10^{-5} and should not be taken as precise vapor pressures, but rather as upper limits of the true vapor pressures.

Summary

A series of new bis-(2-chloroethylmercapto)-alkanes has been synthesized. They were all isolated in a state of purity and density, freezing point and vapor pressure determinations made.

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(2) Technical Command, Chemical Corps, Edgewood Arsenal, Md.

(3) N. D. R. C. Reports 30 and 80.

(4) Swan and Mack, THIS JOURNAL, **47**, 2112 (1925).