starting material was recovered, and 0.42 g. of thiophenol was identified by titration with iodine. Thus one mole of ethylene was formed for each two of thiophenol.

Acknowledgments.—Combustion microanalyses for C, H or N were performed by Margaret Ledyard, Patricia Craig, Margaret Hines and Jean Gibbs. Assistance given by Lawrence Buckles of the Chemical Corps eased many of the difficulties.

Summary

The reaction of chloroalkyl sulfides with sodium in inert solvents has been shown to be a general reaction. Examples were studied where *n* in the formula $RS(CH_2)_nCl$ represented 1, 2, 3 and 4. Ethylene is evolved when $n = 2$, cyclopropane when $n = 3$, and *n*-butane together with ethylene and butene when $n = 4$. Mixed gases were formed also when $n = 1$. Mercaptans and bis-(alkylthio)-alkanes, $RS(CH_2)_nSR$ were formed but practically none of the products which would have been predicted by the Wurtz reaction. 2-Chloroethyl ether also evolves ethylene in reaction with sodium.

Polymers were important products from the reactions involving 2-chloroethyl sulfide and 3-chloropropyl sulfide. The statements in the literature regarding the non-reactivity of mustard gas towards sodium need revision.

Zinc and zinc amalgam also cause liberation of ethylene from the 2-chloroalkyl sulfides.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

Dimercaptols of Acetonylacetone. II[1]

BY EDWARD G. RIETZ, JAMES B. FERNANDEZ, LLOYD T. SNIDER AND THOMAS K. TODSEN

With four exceptions, the normal dimercaptols of acetonylacetone, methyl through *n*-dodecyl, have been recorded.[2,3] The present paper describes the properties of the remaining four: *n*-amyl, *n*-heptyl, *n*-nonyl, and *n*-undecyl, as well as the preparation and properties of the sulfone and the mercuric chloride addition product derived from each member of the series.

The four dimercaptols were prepared in approximately 75% yield by the interaction of acetonylacetone and the mercaptan under the influence of hydrogen chloride according to the directions previously described.[3] The properties and analyses of the products are shown in Table I, and the melting points of the series are plotted in Fig. 1. Two observations should be made with regard to the series: Lengthening of four chains has the same effect as the lengthening of one chain in an ordinary homologous series, and a reversal of alternation of melting point occurs at the nonyl dimercaptol.

TABLE I

MELTING POINTS AND ANALYSES OF THE DIMERCAPTOLS, $CH_3C(SR)_2CH_2CH_2C(SR)_2CH_3$

Mercaptol	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Amyl[a]	6.5	$C_{26}H_{54}S_4$	63.09	62.90	11.00	11.00
n-Heptyl	31	$C_{34}H_{70}S_4$	67.26	67.26	11.62	11.64
n-Nonyl	50	$C_{42}H_{86}S_4$	69.16	69.05	11.88	11.56
n-Undecyl	61	$C_{50}H_{102}S_4$	72.20	71.83	12.37	12.27

[a] $d^{25}{}_4$ 0.9572. $n^{25}{}_D$ 1.5098. Calcd. M_D, 154.2. Found: M_D 154.6.

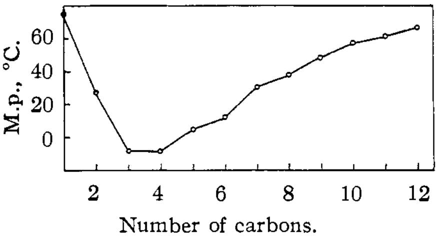

Fig. 1.—Melting points of the mercaptols plotted against the number of carbons in the alkyls.

Early attempts at the preparation of the sulfones were directed at the preparation of the sulfoxides as intermediates, but bromine oxidation failed to yield crystalline products. Hence the sulfones were prepared directly by use of permanganate or by acetic anhydride-catalyzed perhydrol oxidation. Yields of the sulfones were uniform and approximated 30%. The melting points and analyses of the sulfones are shown in Table II; the graph of the melting points in Fig. 2.

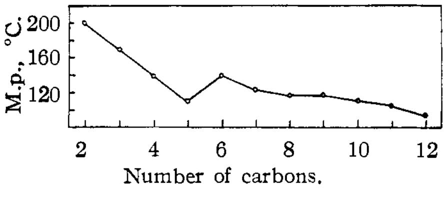

Fig. 2.—Melting points of the sulfones plotted against the number of carbons in the alkyls.

The mercuric chloride addition products were readily obtained by mixing diethylcarbitol solutions of the mercaptol and of mercuric chloride in molecular proportions 1:8, respectively.

The constitution of the mercuric chloride addition product is a function of the chain length. Maximum addition of eight mercuric chloride molecules per molecule of dimercaptol occurs with the

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Oak Ridge, Tenn., June 11, 1949.

[2] Posner, *Ber.*, **33**, 2983–2993 (1900).

[3] Rietz, Chapman and Fernandez, THIS JOURNAL, **70**, 3486 (1948).

TABLE II

MELTING POINTS AND ANALYSES OF THE SULFONES, $CH_3C(SO_2R)_2CH_2CH_2(SO_2R)_2CH_3$, AND OF THE MERCURIC CHLORIDE ADDITION PRODUCTS OF THE DIMERCAPTOLS, $CH_3C(SR)_2CH_2CH_2C(SR)_2CH_3$

	Sulfones						Addition products						
			% Carbon		% Hydrogen					Carbon, %		Hydrogen, %	
R	M. p., °C.	Formula	Calcd.	Found	Calcd.	Found	M. p., °C., dec.	X	Formula	Calcd.	Found	Calcd.	Found
Methyl	230[a]	$C_{10}H_{224}O_8$	30.14	30.13	5.56	5.54	dec.	8.0	$C_{10}H_{22}S_4·8HgCl_2$	4.91	5.06	0.91	1.27
Ethyl	...	....	...	...	...	...	dec.	6.0	$C_{14}H_{30}S_4·6HgCl_2$	8.59	8.25	1.54	1.91
n-Propyl	169	$C_{18}H_{38}S_4O_8$	42.32	42.47	7.50	7.56	182–183	5.0	$C_{18}H_{38}S_4·5HgCl_2$	12.42	12.48	2.20	2.73
n-Butyl	140	$C_{22}H_{46}S_4O_8$	46.61	46.22	8.13	8.09	180–181	4.5[b]	$C_{22}H_{46}S_4·4.5HgCl_2$	15.91	16.14	2.79	3.16
n-Amyl	114	$C_{26}H_{54}S_4O_8$	49.33	49.21	8.60	8.21	184–185	5.0	$C_{26}H_{54}S_4·5HgCl_2$	16.86	17.11	2.93	3.36
n-Hexyl	140	$C_{30}H_{62}S_4O_8$	53.07	53.34	9.26	9.19	173–175	4.5[c]	$C_{30}H_{62}S_4·4.5HgCl_2$	20.32	20.29	3.53	3.91
n-Heptyl	125	$C_{34}H_{70}S_4O_8$	55.54	55.71	9.60	9.33	161–163	4.0	$C_{34}H_{70}S_4·4HgCl_2$	22.77	23.07	3.93	3.93
n-Octyl	118	$C_{38}H_{78}S_4O_8$	57.68	57.64	9.93	10.09	159–160	4.0	$C_{38}H_{78}S_4·4HgCl_2$	26.09	25.76	4.49	4.49
n-Nonyl	110	$C_{42}H_{86}S_4O_8$	59.53	60.09	10.23	10.43	157–158	4.0	$C_{42}H_{86}S_4·4HgCl_2$	27.94	27.72	4.80	5.15
n-Decyl	110	$C_{46}H_{94}S_4O_8$	61.15	60.85	10.49	10.40	155–156	4.0	$C_{46}H_{94}S_4·4HgCl_2$	29.67	29.55	5.08	5.30
n-Undecyl	105	$C_{50}H_{102}S_4O_6$	62.58	62.57	10.71	10.92	154–155	4.0	$C_{50}H_{102}S_4·4HgCl_2$	31.31	31.35	5.36	5.52
n-Dodecyl	93	$C_{54}H_{110}S_4O_8$	63.85	63.81	10.91	10.73	153–154	4.0	$C_{54}H_{110}S_4·4HgCl_2$	32.85	32.36	5.61	5.76

[a] Dec. [b] After washing with alcoholic HCl: C, 16.59; H, 3.34. [c] After washing with alcoholic HCl: C, 20.95; H, 4.00.

methyl dimercaptol. This value decreases until it reaches the limiting value of four for the heptyl and subsequent dimercaptols.

The products derived from the butyl and hexyl dimercaptols were anomalous. Analysis of the compounds after washing with diethylcarbitol indicated an apparent coördination of 4.5 molecules of mercuric chloride per molecule, but treatment with alcoholic hydrochloric acid caused this value to become intermediate between 4.0 and 4.5. In view of the indefiniteness of the data, the authors can offer only a provisional statement regarding the constitution of these compounds The analyses and melting points of the addition compounds are collected in Table II.

Acknowledgment.—The authors are indebted to Dr. E. Emmet Reid for his advice and to Mr. Max Gergel of the Columbia Organic Chemicals Co., Columbia, S. C., for mercaptans used in the preparation of the dimercaptols.

Experimental

Tetrasulfones.—All tetrasulfones of this article may be prepared in approximately 30% yield by permanganate oxidation or by the use of acetic anhydride-catalyzed perhydrol. If the latter method is to be used, the directions described below should be followed rigorously. Simple addition of the reactants results in a violent reaction after an induction period of about thirty minutes.

2,2,5,5-Tetra-decylsulfonyl Hexane.—A 2.0-g. sample of *n*-decyl dimercaptol was mixed in a separatory funnel with 200 ml. of 4% $KMnO_4$, 3 ml. of 9 *M* H_2SO_4 and 5 ml. of glacial acetic acid. After heating to 60° on a water-bath the mixture was shaken vigorously for five minutes. On cooling, solid sodium bisulfite was added until the solution became clear. The product was extracted with three 50-ml. portions of chloroform and the solvent evaporated on the steam-bath. A repetition of the oxidation, extraction and evaporation followed by crystallization of the residue from ethanol yielded 0.6 g. of the tetrasulfone, m. p. 109–110°, yield, 26%.

2,2,5,5-Tetra-octylsulfonyl Hexane.—A mixture of 15 ml. of 30% perhydrol and 5 ml. of acetic anhydride was allowed to react until the temperature returned to 30°. A 1.8-g. sample of *n*-octyl dimercaptol was added under stirring whereupon the temperature rose gradually to 40°. This temperature was maintained by cooling until the initial reaction was completed. The solution was then warmed to 45° for ten minutes. On cooling, the solid was removed by filtration and crystallized from a 1:1 acetone–methanol solution; yield of product 0.6 g., or 28%; m. p. 117–118°.

This general procedure was modified for the members following the octyl dimercaptol. After the initial reaction had been completed, the mixture was warmed to 55° for completion of the reaction. At ten-minute intervals, the mixture was warmed to melt the products and reactants and was then permitted to cool to 55°. When successive heatings produced no change in melting point, the reaction was complete.

Mercuric Chloride Addition Compounds.—All dimercaptol mercuric chloride salts were prepared by the general method described below.

A 1.5-g. sample of *n*-octyl dimercaptol in 25 ml. of diethylcarbitol was mixed with a solution of 5 g. of mercuric chloride in 20 ml. of diethylcarbitol at 50°. The mixture was heated to effect solution of the initial precipitate and cooled. Filtration, followed by washing with two 5-ml. portions each of diethylcarbitol and ethanol resulted in 2.0 g. of product, m. p. 159–160°. Recrystallization from diethylcarbitol did not alter the melting point.

Great difficulty was encountered in attempts to crystallize the first six dimercaptol salts of the series. In these instances, the elevated temperatures necessary for solution resulted in decomposition. Hence occluded mercuric chloride was removed by washing with 30 ml. of 0.05 *M* hydrochloric acid in ethanol. Such treatment resulted in compounds of composition corresponding to integral numbers of mercuric chloride molecules per molecule of dimercaptol except for the butyl and hexyl dimercaptols.

Summary

1. The acetonylacetone dimercaptols of *n*-amyl, *n*-heptyl, *n*-nonyl and *n*-undecyl mercaptans have been prepared and characterized. These are new to the literature.

2. The tetrasulfones of the normal acetonylacetone dimercaptols, methyl through dodecyl, have been prepared and characterized. With the exception of the ethyl derivative, these are new to the literature.

3. Mercuric chloride forms coördination compounds with acetonylacetone dimercaptols. The extent of such addition is a function of the chain length.

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