[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

Organic Compounds of Selenium. III. The Action of Selenium Oxychloride upon Esters of Salicylic Acid[1]

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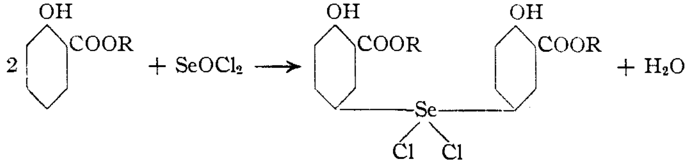
The first paper[2] of this series discussed the action of selenium oxychloride upon ketones and the second paper[3] dealt with the action of selenium oxychloride upon ethers. In this investigation selenium oxychloride has been allowed to act upon methyl, ethyl, propyl, isopropyl, butyl, amyl and phenyl salicylates. The reaction takes place according to the equation



Their structure will be discussed in a later paper.

The resulting dialkyl 5,5′-seleno-disalicylate Se-dichlorides are converted to the dialkyl 5,5′-seleno-disalicylates by reduction with zinc

$$R_2SeCl_2 + Zn \longrightarrow R_2Se + ZnCl_2$$

The dialkyl 5,5′-seleno-disalicylate Se-dihydroxides have been prepared by treating the respective dichloro derivatives with sodium bicarbonate in aqueous solution

$$R_2SeCl_2 + 2HOH \longrightarrow R_2Se(OH)_2 + 2HCl$$

The dialkyl 5,5′-seleno-disalicylate Se-dibromides and the corresponding iodo derivatives were prepared by the addition of bromine or iodine to seleno-salicylate derivatives in chloroform.[4]

The dichlorides, diiodides and disalicylates were yellow, the dibromides orange-red and the dihydroxides were white.

Experimental

The selenium oxychloride for these experiments was obtained from the J. T. Baker Company and used without further purification. The methyl salicylate and phenyl salicylate (salol) were obtained from the Mallinckrodt Chemical Works. The other esters were prepared in this Laboratory by the usual methods of synthesis.

The products were identified by analysis for selenium and halogen. Analysis for selenium[5] was carried out by fusion with sodium peroxide in a Parr bomb. The fused

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(1) R. R. LaMotte prepared a number of these compounds in this Laboratory but the work was not published.

(2) Nelson and Jones, THIS JOURNAL, **52**, 1588 (1930).

(3) Alquist and Nelson, *ibid.*, **53**, 4033 (1931).

(4) Kunckell prepared the iodo derivative by treating the dichloro derivative of a similar compound with potassium iodide in alcoholic solution [Kunckell, *Ber.*, **28**, 609 (1895)]. The reaction was tried in this Laboratory but good results were not obtained. Some of the iodo derivative was formed but the major portion was reduced to the selenodisalicylate and free iodine was formed. This effect was greatly increased by the presence of small amounts of water.

(5) Shaw and Reid, THIS JOURNAL, **49**, 2330 (1927).

mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by addition of sulfur dioxide. Analysis for halogen was carried out in a similar way, except that nitric acid was used for acidifying and silver halide was precipitated by addition of silver nitrate. In some cases the Volhard volumetric method was used.

The melting points of these compounds are rather difficult to obtain, due to decomposition. The melting points were taken by raising the temperature rapidly until the compound melted. A second sample was then placed in the bath and heated slowly until it melted.

The preparation of the methyl salicylate derivatives, which is typical of all the preparations, was as follows.

Dimethyl 5,5′-Seleno-disalicylate Se-dihalide.—Seventy-five grams of methyl salicylate was treated with an equivalent amount of the selenium oxychloride, plus a 10% excess (45 g.). The two were shaken together and warmed only enough to start the reaction. The solution darkens and some hydrogen chloride is evolved. On cooling the mass solidifies. This is broken up, washed several times with ether and recrystallized from benzene. It is soluble in alcohol, ether and glacial acetic acid and is slightly soluble in benzene. The solubility in benzene increases with the higher homologs.

TABLE I

YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF DIALKYL 5,5′-SELENO-DISALICYLATE AND DERIVATIVES

						Analytical data, %			
						Selenium		Halogen	
	Dialkyl	Acidic radical	M. p., °C.	Yields, %	Formula	Calcd.	Found	Calcd.	Found
1	Dimethyl	Dichloride	176	25	$C_{16}H_{14}Cl_2O_6Se$	17.5	17.8	15.7	15.6
2	Diethyl	Dichloride	165	20	$C_{18}H_{15}Cl_2O_6Se$	16.5	16.6	14.8	15.7
3	Dipropyl	Dichloride	130	20	$C_{20}H_{22}Cl_2O_6Se$	15.6	15.5	13.9	14.0
4	Diisopropyl	Dichloride	173	46	$C_{20}H_{22}Cl_2O_6Se$	15.6	15.8	13.9	13.9
5	Dibutyl	Dichloride	133	20	$C_{22}H_{26}Cl_2O_6Se$	14.8	14.9	13.2	13.1
6	Diamyl	Dichloride	138	25	$C_{21}H_{30}Cl_2O_6Se$	14.0	13.3	12.5	12.6
7	Diphenyl	Dichloride	185	47	$C_{26}H_{18}Cl_2O_6Se$	13.7	14.0	12.3	12.3
8	Dimethyl		158	60	$C_{16}H_{14}O_6Se$	20.8	20.6		
9	Diethyl		88	58	$C_{18}H_{18}O_8Se$	19.3	19.3		
10	Dipropyl	Yellow viscous unstable liquid		34	$C_{20}H_{22}O_6Se$	18.1	17.8		
11	Diisopropyl		81	70	$C_{20}H_{22}O_6Se$	18.1	18.4		
12	Dibutyl	Yellow viscous unstable liquid		31	$C_{22}H_{28}O_6Se$	17.0	17.4		
13	Diamyl	Yellow viscous unstable liquid			$C_{24}H_{30}O_6Se$	No analysis made			
14	Diphenyl		138		$C_{26}H_{18}O_6Se$	15.7	15.1		
15	Dimethyl	Dibromide	143	41	$C_{16}H_{14}Br_2O_6Se$	14.6	14.6	29.5	29.5
16	Diethyl	Dibromide	147	39	$C_{18}H_{18}Br_2O_8Se$	13.9	13.8	28.1	28.3
17	Dipropyl	Dibromide	110	23	$C_{20}H_{22}Br_2O_6Se$	13.3	13.1	26.8	26.5
18	Diisopropyl	Dibromide	159	94	$C_{20}H_{22}Br_2O_6Se$	13.3	13.0	26.8	27.1
19	Dibutyl	Dibromide	95	19	$C_{22}H_{26}Br_2O_6Se$	12.7	12.5	25.6	25.3
20	Diamyl	Dibromide	121		$C_{24}H_{30}Br_2O_6Se$	12.1	11.9	24.5	25.0
21	Diphenyl	Dibromide	160		$C_{26}H_{18}Br_2O_6Se$	11.9	12.1	24.0	24.8
22	Dimethyl	Diiodide	150	24	$C_{16}H_{11}I_2O_6Se$	12.5	12.6	40.0	39.9
23	Diethyl	Diiodide	140	21	$C_{18}H_{18}I_2O_6Se$	11.9	11.6	38.3	38.4
24	Dipropyl	Diiodide	78	17	$C_{20}H_{22}I_2O_6Se$	11.5	11.6	36.7	36.3
25	Diisopropyl	Diiodide	96	95	$C_{20}H_{22}I_2O_6Se$	11.5	11.9		
26	Dibutyl	Diiodide	65	15	$C_{22}H_{26}I_2O_6Se$	11.0	11.3	35.3	35.0
27	Diamyl	Diiodide	Dark brown viscous liquid		$C_{24}H_{30}I_2O_6Se$				
28	Diphenyl	Diiodide	120		$C_{26}H_{18}I_2O_6Se$	10.4	11.1		
29	Dimethyl	Dihydroxide	137	37	$C_{16}H_{16}O_8Se$	19.1	18.2		
30	Diethyl	Dihydroxide	107	39	$C_{18}H_{20}O_8Se$	17.9	17.0		
31	Dipropyl	Dihydroxide	63	33	$C_{20}H_{24}O_8Se$	16.8	15.5		
32	Diisopropyl	Dihydroxide	83	83	$C_{20}H_{24}O_8Se$	16.8	17.2		
33	Dibutyl	Dihydroxide	57	31	$C_{22}H_{28}O_8Se$	15.9	15.4		
34	Diamyl	Dihydroxide	97	80	$C_{24}H_{32}O_8Se$	15.0	15.5		
35	Diphenyl	Dihydroxide	122	75	$C_{26}H_{20}O_8Se$	14.7	15.2		

The disalicylate was prepared from the above by treating with 10% excess of zinc dust in a 0.1 *N* chloroform solution of the derivative. This was refluxed for ten minutes after the solution became clear. The solution was filtered and the chloroform allowed to evaporate. The product was washed with alcohol. It is soluble in chloroform, ether and alcohol and is rather unstable.

The bromides and iodides were prepared by adding 10% excess of halogen in chloroform solution to a chloroform solution of the corresponding disalicylate derivative. The chloroform was allowed to evaporate. The bromide was recrystallized from alcohol.

The iodide was washed with a solution of potassium iodide to remove the excess of iodine. It was then washed thoroughly with water and dried in a vacuum desiccator over calcium chloride. The crystals were soluble in alcohol, ether and chloroform.

The dihydroxide was prepared by treating the dichloride with warm distilled water containing 10% excess of sodium bicarbonate and allowed to stand for twenty-four hours at 40–50°. The original yellow compound changed to a practically white compound. After filtering the product was recrystallized from hot alcohol. It was soluble in chloroform, ether, alcohol and very slightly soluble in water.

The corresponding derivatives of the other esters of salicylic acid were prepared in an analogous way and the yields, physical constants and analyses are summarized in the table.

Summary

1. The reaction between selenium oxychloride and certain esters of salicylic acid has been studied in which two molecules of the ester condensed with one molecule of selenium oxychloride.
2. The resulting selenium dichlorides can be hydrolyzed to produce selenium dihydroxides.
3. The reduction of the selenium dichlorides by zinc gives selenides.
4. The selenides readily add bromine or iodine, forming selenium dibromides and selenium diiodides.

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