Warning is given of the possibility of reactions taking place with explosive violence.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ORGANIC COMPOUNDS OF SELENIUM. II. THE ACTION OF SELENIUM OXYCHLORIDE UPON ETHERS[1]

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Selenium oxychloride is a very reactive compound and, therefore, lends itself readily to the synthesis of organic compounds. The action on ketones was reported[2] in the first paper of this series. In this investigation selenium oxychloride was allowed to act on the following ethers: anisole, phenetole, propyl phenyl ether, butyl phenyl ether, diphenyl ether, *o*-methyl cresyl ether, *o*-bromoanisole, *p*-bromoanisole, *o*-nitroanisole and *p*-nitroanisole.

Kunckell has reported the action of selenium oxychloride upon anisole and phenetole.[3] Kunckell stated that two products were formed in the action of selenium oxychloride on anisole in ethereal solution. He reports bis-(*p*-methoxyphenyl)-selenium dichloride and bis-(*p*-methoxyphenyl) selenide. Kunckell used water in the purification of his products, which leads to the hydrolysis of the chlorine attached to the selenium. The second product could have been formed by the reduction of the first product during the purification. In our experiments we did not find the selenides among the primary products of the selenium dichlorides.

The first seven ethers, upon reacting with selenium oxychloride in anhydrous ether at room temperature, form the selenium dichlorides according to the following equation in which anisole is used as a typical example

$$C_6H_5OCH_3 + SeOCl_2 \longrightarrow (C_6H_4OCH_3)SeCl_2 + H_2O$$

The last three ethers listed did not react under these conditions and could be quantitatively recovered unchanged after hydrolysis of the selenium oxychloride. By raising the temperature, and without a solvent, the *p*-bromoanisole formed a 2-chloro-4-bromoanisole, just as has been reported for the action of thionyl chloride on the same compound.

The selenium dichlorides are light yellow solids and react readily with cold water. These compounds are soluble in chloroform, hot glacial acetic

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[1] Based upon a thesis submitted by F. N. Alquist to the Faculty of the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

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

[3] Kunckell, *Ber.*, **28**, 609 (1895).

acid, *slightly soluble in carbon tetrachloride, absolute alcohol,* benzene and ether. Chloroform is the best solvent for purification.

The selenium dichlorides reacted with boiling aqueous sodium bicarbonate, or dilute sodium hydroxide to form a series of white crystalline selenium dihydroxides.

Chloroform solutions of the selenium dichlorides boiled with zinc dust gave yellow reduction products, which could be purified by the use of norite and alcohol recrystallization. The same reduction products could also be obtained by the use of alcohol and zinc dust. The products obtained in this way were white crystalline selenides.

The selenides in a solution of chloroform add bromine, producing selenium dibromides. The selenium dibromides, formed from selenides of propyl phenyl ether, butyl phenyl ether and *o*-cresyl methyl ether, decomposed within three to six days forming oils. The other bromides are unchanged after a period of five months.

In all reactions it is assumed that selenium oxychloride condenses with the para position of the benzene ring. If the para position is blocked by either nitro or bromine, no reaction takes place at room temperature in ethereal solution. A nitro group in the ortho position on the benzene ring also prevents the action. Bromine or methyl groups, in the ortho position, do not prevent the condensation. If the action is carried out in the absence of a solvent and at a higher temperature, the selenium oxychloride causes chlorination, as was found in the case of *p*-bromoanisole.

Experimental

All ethers used in the experiments were obtained from the Eastman Kodak Company except the propyl phenyl ether, which was prepared in this Laboratory. The selenium oxychloride was obtained from the J. T. Baker Chemical Company and was not further purified.

In each case the reagents were added in a ratio of 0.4 mole of ether to 0.4 mole of selenium oxychloride in 200 ml. of anhydrous ether, which was found to be the most satisfactory solvent in which to carry out the reaction. The reaction mixture was stirred and allowed to react for a period of five days at room temperature. The solvent was removed and the crystalline mush pressed out on a porous plate. The product was recrystallized repeatedly from chloroform.

The products were identified by analysis for selenium and chlorine; also by comparison with the literature in case of known compounds.

Analysis for selenium[4] was carried out by fusion with sodium peroxide in a Parr bomb. The fused mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by addition of sulfur dioxide. Analysis for chlorine was carried out in a similar way, except that nitric

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[4] Shaw and Reid, This Journal, 49, 2330 (1927).

acid was used for acidifying and silver chloride was precipitated by addition of silver nitrate.

Table I summarizes the work carried out with the various ethers.

TABLE I

PREPARATIONAL DATA, PHYSICAL CONSTANTS AND ANALYSES OF SELENIUM DICHLORIDES

	Ethers	Product, selenium dichloride	M. p., °C.	Yield, %
1	Anisole	Bis-(*p*-methoxyphenyl)-	163	75
2	Phenetole	Bis-(*p*-ethoxyphenyl)-	139	71
3	Propyl phenyl	Bis-(*p*-propoxyphenyl)-	91	40
4	Butyl phenyl	Bis-(*p*-butoxyphenyl)-	93	42
5	Diphenyl	Bis-(*p*-phenoxyphenyl)-	135–140	87
6	*o*-Bromoanisole	Bis-(3-bromo-4-methoxyphenyl)-	180	29
7	*o*-Methyl cresyl	Bis-(3-methyl-4-methoxyphenyl)-	155–158	67

	Formulas	Selenium, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found
1	$(CH_3OC_6H_4)_2SeCl_2$	21.7	21.5	19.3	19.2
2	$(C_2H_5OC_6H_4)_2SeCl_2$	20.2	19.8	18.1	17.7
3	$(C_3H_7OC_6H_4)_2SeCl_2$	18.8	18.4	16.9	16.6
4	$(C_4H_9OC_6H_4)_2SeCl_2$	17.8	17.5	15.8	16.0
5	$(C_6H_5OC_6H_4)_2SeCl_2$	16.2	15.5	14.5	15.0
6	$(CH_3OC_6H_3Br)_2SeCl_2$	15.3	15.2	..	..
7	$(CH_3OC_6H_3CH_3)_2SeCl_2$	20.2	19.9	18.1	17.9

One-tenth mole of the selenium dichloride was boiled either with 0.1 mole excess of the calculated quantity of sodium bicarbonate or sodium hydroxide dissolved in 300 ml. of water. On cooling a white solid or a colorless oil was obtained which was boiled repeatedly with distilled

TABLE II

PREPARATONAL DATA, PHYSICAL CONSTANTS AND ANALYSES OF SELENIUM DIHYDROXIDES

	Ethers	Product, selenium dihydroxide	M. p., °C.	Yield, %
1	Anisole	Bis-(*p*-methoxyphenyl)-	134	90
2	Phenetole	Bis-(*p*-ethoxyphenyl)-	146–148	80
3	Propylphenyl	Bis-(*p*-propoxyphenyl)-	51–54	60
4	Butylphenyl	Bis-(*p*-butoxyphenyl)-	58–60	65
5	Diphenyl	Bis-(*p*-phenoxyphenyl)-	122–125	84
6	*o*-Bromoanisole	Bis-(3-bromo-4-methoxyphenyl)-	150	80
7	*o*-Methyl cresyl	Bis-(3-methyl-4-methoxyphenyl)-	91	65

	Formulas	Selenium, %		Bromine, %	
		Calcd.	Found	Calcd.	Found
1	$(CH_3OC_6H_4)_2Se(OH)_2$	24.2	24.4	..	..
2	$(C_2H_5OC_6H_4)_2Se(OH)_2$	22.3	22.3	..	..
3	$(C_3H_7OC_6H_4)_2Se(OH)_2$	20.7	21.1	..	..
4	$(C_4H_9OC_6H_4)_2Se(OH)_2$	19.2	18.8	..	..
5	$(C_6H_5OC_6H_4)_2Se(OH)_2$	17.5	14.5	..	..
6	$(CH_3OC_6H_3Br)_2Se(OH)_2$	16.3	16.0	32.9	33.3
7	$(CH_3OC_6H_3CH_3)_2Se(OH)_2$	22.3	22.3	..	..

water until the decanted layer gave no test for chloride ions. The crude selenium dihydroxides were recrystallized from alcohol.

The product of hydrolysis of the selenium dichloride of diphenyl ether always melted over a range of three degrees and contained 3% lower selenium content than the theoretical for the pure selenium dihydroxide. It contained no chlorine. Repeated purification did not yield a more satisfactory product.

Chloroform solutions containing 0.1 mole of selenium dichloride in 250 ml. were prepared. The zinc dust was added, using a half mole above the calculated quantity, and refluxed for a half hour. The chloroform solution was filtered while hot. The product obtained in this manner was yellow. By the use of alcohol as a solvent the products obtained were white. The selenides prepared in this way are identical in the case of anisole and phenetole derivatives with those which Kunckell stated were formed in the reaction between selenium oxychloride and the above-named ethers. The selenides are soluble in chloroform, alcohol, ether and glacial acetic acid.

TABLE III

PREPARATIONAL DATA, PHYSICAL CONSTANTS AND ANALYSES OF SELENIDES

	Ethers used	Product, selenide	M. p., °C.	Yield, %
1	Anisole	Bis-(*p*-methoxyphenyl)-	54	88
2	Phenetole	Bis-(*p*-ethoxyphenyl)-	60–62	92
3	Propylphenyl	Bis-(*p*-propoxyphenyl)-	46–48	70
4	Butylphenyl	Bis-(*p*-butoxyphenyl)-	(Unable to solidify or purify oily product)	
5	Diphenyl	Bis-(*p*-phenoxyphenyl)-	83–85	85
6	*o*-Bromoanisole	Bis-(3-bromo-4-methoxyphenyl)-	95	80
7	*o*-Methyl cresyl	Bis-(3-methyl-4-methoxyphenyl)-	36	75

	Formulas	Selenium, % Calcd.	Selenium, % Found
1	$(CH_3OC_6H_4)_2Se$	27.0	26.0
2	$(C_2H_5OC_6H_4)_2Se$	24.6	24.0
3	$(C_3H_7OC_6H_4)_2Se$	22.7	22.0
4	$(C_4H_9OC_6H_4)_2Se$	(Unable to solidify or purify oily product)	
5	$(C_6H_5OC_6H_4)_2Se$	19.0	18.5
6	$(CH_3OC_6H_3Br)_2Se$	17.6	17.8
7	$(CH_3OC_6H_3CH_3)_2Se$	24.6	23.9

One-tenth mole of the selenide was dissolved in chloroform and allowed to react with a solution containing a 0.1 mole excess of bromine in chloroform. The selenium dibromides which were obtained were crystallized repeatedly from chloroform. The dibromides are brown, crystalline solids when pure. Decomposition of three of the dibromides on standing has been observed. They are soluble in chloroform and slightly soluble in ether and absolute alcohol.

Table IV

Preparational Data, Physical Constants and Analyses of Selenium Dibromides

	Ethers used	Product, selenium dibromide	M. p., °C.	Yield, %
1	Anisole	Bis-(*p*-methoxyphenyl)-	125	76
2	Phenetole	Bis-(*p*-ethoxyphenyl)-	117	80
3	Propylphenyl	Bis-(*p*-propoxyphenyl)-	69	77
4	Butylphenyl	Bis-(*p*-butoxyphenyl)-	65	60
5	Diphenyl	Bis-(*p*-phenoxyphenyl)-	113	85
6	*o*-Bromoanisole	Bis-(3-bromo-4-methoxyphenyl)-	87	80
7	*o*-Methyl cresyl	Bis-(3-methyl-4-methoxyphenyl)-	136	63

		Bromine, %	
	Formulas	Calcd.	Found
1	$(CH_3OC_6H_4)_2SeBr_2$	35.3	35.8
2	$(C_2H_5OC_6H_4)_2SeBr_2$	33.2	32.4
3	$(C_3H_7OC_6H_4)_2SeBr_2$	31.4	31.8
4	$(C_4H_9OC_6H_4)_2SeBr_2$	29.8	29.7
5	$(C_6H_5OC_6H_4)_2SeBr_2$	27.7	27.3
6	$(CH_3OC_6H_3Br)_2SeBr_2$	52.2	51.9
7	$(CH_3OC_6H_3CH_3)_2SeBr_2$	33.2	33.5

Summary

1. The reaction between selenium oxychloride and certain ethers has been studied in which two molecules of the ether condensed with one molecule of selenium oxychloride.
2. The action of alkali on the resulting selenium dichlorides produces selenium dihydroxides.
3. The reduction of the selenium dichlorides by zinc gives selenides.
4. The selenides readily add bromine, forming selenium dibromides.

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REACTIONS OF CARBON DISULFIDE. II.[1] REACTION WITH ACETONE

By E. Wertheim

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The reaction of carbon disulfide with ketones has been a subject of investigation since the discovery of the desaurins by Victor Meyer.[2] During 1904 and later years Apitzsch[3] studied the reaction between various aromatic and aliphatic ketones of the type $RCH_2(C{=}O)CH_2R$ with carbon disulfide in the presence of solid potassium hydroxide. In this way he secured derivatives of 1,4-thiopyrone, which were supposed to be formed as indicated in the following series of equations

[1] Paper No. 245, Journal Series, University of Arkansas.

[2] Meyer, *Ber.*, **21**, 353 (1888); **23**, 1571 (1890); **24**, 3535 (1891); **25**, 1727, 2239 (1892).

[3] Apitzsch, *ibid.*, **37**, 1599 (1904); **38**, 2888 (1905); **41**, 4028 (1908).